Study on Characteristics of Six Polysaccharides and Cellulose Blends

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Abstract. In order to study the internal cross-linking mechanism between cellulose and polysaccharides as wet-end additives in papermaking reconstituted tobacco, crystalline cellulose (MCC) was used as the target in this paper, sodium alginate (SA), pullulan (Pul), κ-carrageenan (κ-C), carboxymethyl chitosan (CMCS), hydroxypropyl chitosan (HPCS) and tamarind polysaccharide (TSP) were selected, the structure and composition of the monomer polysaccharides were determined by dynamic light scattering and ion chromatography, at the same time, the characteristics of the above-mentioned polysaccharides and MCC blend were analyzed, the results showed that SA contained a lot of negative charge, which resulted in weak adhesion and poor adsorption ability in cellulose blend; Pul was the most compact chain conformation, effectively improve the adhesion of cellulose, can be quickly adsorbed on cellulose; κ-C increased the viscosity of MCC blend and could adhere the 30μm size fragments of cellulose CMCS had strong adhesion to cellulose edge; due to the introduction of carboxymethyl group, the hydrophilicity of HPCS and the apparent viscosity of MCC blend increased greatly; the complex branched-chain structure of TSP results in high storage modulus of TSP/cellulose blend, and the amount of TSP adsorbed on cellulose is large and lasts long. Pul, TSP, κ-c, CMCS and TSP could adsorb cellulose well.

1. Introduction

Polysaccharides are hydrophilic, high-molecular-weight polymers formed by polymerizing monosaccharide units such as glucose, fructose, galactose, and arabinose in certain proportions. Chemically, the structural diversity of polysaccharide polymers, arising from variations in sugar unit types, polymerization degrees, inter-sugar bonding and arrangement, degree of group substitution, and multi-level structures, gives rise to both common and specific properties such as viscosity, fluidity, gelation, film formation, among others.

As one of the crucial components in cigarette manufacturing, the paper-making process for reconstituted tobacco leaves has garnered increasing attention. This process transforms waste materials (such as tobacco dust, scraps, trimmings, ash rods, and low-grade tobacco leaves) into valuable resources and supports functions like reducing tar and harm, lowering consumption, and highlighting style in cigarette production. In the tobacco industry, food colloids, mainly wet-end retention aids, fiber dispersants, and adhesives, are applied to produce reconstituted tobacco leaves. In order to further explore the application of food colloids[1-2] in the reconstituted tobacco leaf industry, this study selected six typical food colloids, including tamarind polysaccharide, pullulan, sodium alginate, carboxymethyl chitosan, hydroxypropyl chitosan, and κ-carrageenan as additives for reconstituted tobacco leaves. These were blended with microcrystalline cellulose to investigate their interaction with cellulose and explain the internal crosslinking mechanism behind the macroscopic effects, providing a basis for applying food colloids in reconstituted tobacco leaves.

2. Materials and Methods

2.1 Materials and Instruments

Sodium alginate (SA) from MACKLIN; pullulan (Pul) from Usolf; κ-carrageenan (κ-C) from Usolf; carboxymethyl chitosan (CMCS) from Usolf; hydroxypropyl chitosan (HPCS) from Usolf; tamarind polysaccharide (TSP) with purity ≥97%, from Yunnan Maodouli Group Food Co., Ltd.; microcrystalline cellulose (MCC) with a length ≥30 μm.

Discovery HR-3 rotational rheometer from TA Instruments, USA; BC-R202 rotary evaporator from Shanghai Beikai Biological Chemical Equipment Co., Ltd.; HPSEC-MALLS multi-angle laser light scattering
appropriate amounts of polysaccharide samples and add
Clean chromatography bottles were used to weigh
Composition.
2.2.1 Analysis of Food Colloid Monosaccharide
2.2 Experimental Methods
Yiheng Scientific Instrument Co., Ltd.
BPZ-6933LC vacuum drying oven from Shanghai
balance from METTLER TOLEDO, USA;
microscope from JEOL, Japan; electronic analytical
FPLUS thermal field emission scanning electron
chromatography system from Thermo, USA; JSM 7610
high-performance liquid chromatography system
determined using a
The molecular weight and conformation of the six
and 60 min A/B/C (95:5:0, V/V)[4].
A/B/C (60:40:0, V/V), 52.1 min A/B/C (95:5:0, V/V),
0.2M NaAc), with a flow rate of 0.5 mL/min. The
column temperature was maintained at 30°C. The
of A (H2O), B (0.1M NaOH), and C (0.1 M NaOH,
monosaccharide components.
Dionex™ CarboPac™ PA20 (150*3.0 mm, 10 μm)
liquid chromatography column was used with an
injection volume of 5 μL. The mobile phases consisted
A (H2O), B (0.1M NaOH), and C (0.1 M NaOH,
0.2M NaAc), with a flow rate of 0.5 mL/min. The
column temperature was maintained at 30°C. The
equilution gradient was as follows: 0 min A/B/C (95:5:0,
V/V), 26 min A/B/C (85:5:10, V/V), 42 min A/B/C
(85:5:10, V/V), 42.1 min A/B/C (60:0:40, V/V), 52 min
A/B/C (60:40:0, V/V), 52.1 min A/B/C (95:5:0, V/V),
and 60 min A/B/C (95:5:0, V/V)[4].
2.2.2 Analysis of Food Colloid Molecular Weight
and Conformation.
The molecular weight and conformation of the six
polysaccharides were determined using a
high-performance liquid chromatography system
comprising a multi-angle laser light scattering detector
(MALLS, DAWN HELEOS-II), refractive index
(Optilab T-Rex, RI) detector, and differential pressure
viscometer (ViscoStar III, DP) (Wyatt Technology,
Santa Barbara, CA, USA). Following slight
modifications to the experimental method outlined by
Strydom et al. [5], 5 mg of the sample was dissolved in
5 mL of mobile phase (0.1 mol/L NaNO3) and hydrated
at room temperature with continuous stirring at 500 rpm
for 24 hours. Molecular weight analysis of prepared
samples was conducted using high-performance liquid
chromatography-multi-angle laser light scattering
detector-refractive index detector-viscometer analysis.
The analysis column comprised a guard column (OHpak
SB-G), Shodex OHpak 803 HQ, and 805 HQ, with a
flow rate of 0.6 mL/min and a column temperature of
40°C. Data analysis was performed using ASTRA7.1.3
software.
2.2.3 Preparation of Food Colloid-Cellulose Blend
Solutions.
2.0 g of cellulose was diluted with 10 mL of water,
stirred thoroughly until fully swollen, and mixed with 10
mL of polysaccharide solution (0.1%, w/v).
2.2.4 Adsorption Kinetics.
Adsorption kinetics of cellulose were determined by
adding 10 mg/mL cellulose and 1 mg/mL polysaccharide to deionized water under 25°C and 150
rpm shaking conditions. Samples were collected at 3, 6,
9, and 12 minutes, followed by centrifugation at 10000
rpm for 10 minutes. The supernatant was analyzed using
the phenol-sulfuric acid to determine the total sugar
content. The change in total sugar content before and
after adsorption onto cellulose was used to calculate the
amount of polysaccharide adsorbed onto the cellulose
sample.
Total sugar content was determined using the
phenol-sulfuric acid method. Specifically, 12.5 g of
anhydrous glucose was dissolved in distilled water and
made up to 50 mL, resulting in a 0.25 mg/mL glucose
standard solution. Varying volumes (0, 0.1, 0.2, 0.3, 0.4,
and 0.5 mL) of the glucose standard solution were
mixed with deionized water to 1.0 mL in test tubes,
followed by the addition of 0.5 mL of 3% phenol
solution and 5 mL of concentrated sulfuric acid (added
slowly). After mixing, the tubes were left to react for 0.5
hours at room temperature, and absorbance at 490 nm
was measured using a spectrophotometer. A standard
curve was plotted using the mass concentration of the
standard solution as the abscissa and A490 as the
ordinate. The experiment was performed in triplicate[6].
Accurately weigh 5.0 mg of the sample and dissolve
it in 10 mL of deionized water to obtain a solution with
a concentration of 0.5 mg/mL. Take 0.1 mL of the
solution and dilute it to 1.0 mL with water. Measure the
absorbance at 490 nm according to the procedure above.
Calculate the total sugar content based on the standard
curve. Perform triplicate measurements.
2.2.5 Rheological Property Measurement.
The steady flow characteristics and dynamic
viscoelasticity of the six polysaccharide blends were determined using a rotational rheometer. Steady-state
flow behavior was analyzed at shear rates of 0.1-100 s⁻¹,
while dynamic viscoelasticity, including storage modulus (G') and loss modulus (G''), was measured by
frequency scanning in the range of 0.1 to 100 rad/s. The
rheometer employed a plate-plate fixture (40mm) with
a gap set at 1.0 mm. All tests were performed within the
linear viscoelastic region, and strain scans (1Hz,0.01%~20%) were conducted to obtain all measurements, with
a strain value of 1%.
2.2.6 Viscosity Measurement.

1.36 g of cellulose was dissolved in 100 mL of DMSO, followed by the addition of 13.6 mg of polysaccharide. After thorough mixing and swelling, the viscosity of the resulting solution was measured using an Ubbelohde viscometer (constant temperature of 20°C with an error of ± 0.01°C). The solution's flow time (t) at each concentration was determined as the average of four parallel measurements.

In a polymer/solvent system, the relationship between the reduced viscosity of the polymer and its concentration follows the classical Huggins equation. By calculating $\eta_{sp} = (t - t_0)/t_0$, the specific viscosity $\eta_{sp}/c$ of the cellulose and polysaccharide solution and the specific viscosity $\eta_{sp}/c$ of the blend can be obtained. Plotting $\eta_{sp}/c$ and $\eta_{sp}/c$ against c allows for determining characteristic viscosity $[\eta]$. A series of data on the relative viscosity and specific viscosity of the blend were used to derive the viscosity average molecular weight ($\mu$). The calculation formula is as follows:

$$b_m = w_2 b_2 + w_3 b_3 + 2w_2 w_3 b_{23}$$

$$b_2 = [\eta]_2^2 k_2, b_3 = [\eta]_3^2 k_3$$

$$[\eta]_m = [\eta]_2 w_2 + [\eta]_3 w_3$$

$$VB = (b_m - b)/2(2w_2 w_3)$$

$$\mu = \frac{VB}{(l_3 - [\eta]_3)^2} = \frac{(b_m - b_2 + b_3 - b_{23})}{2([\eta]_3 - [\eta]_m)}$$

Among them, $w_i = C_i/C$, $i = 2,3$, where C is the total polymer concentration; $[\eta]_2$ and $[\eta]_3$ are the characteristic viscosities of each polymer. The compatibility of the blend was studied using the $\mu$ criterion. $\mu \geq 0$ indicates miscibility, while $\mu < 0$ indicates phase separation [7].

2.2.7 Microstructural Observation.

The polysaccharide blend solution was placed in a vacuum-drying oven at 55°C for 48 hours to remove moisture. The dried blend samples were adhered to conductive adhesive and sputter-coated. The dried blend samples' surface microstructure was analyzed using a field emission scanning electron microscope.

2.2.8 Thermal Gravimetric Analysis (DTG).

Thermogravimetric analysis was performed using a DTG-60H thermogravimetric analyzer with a sample loading of approximately 7 mg and nitrogen gas as the carrier with a 50 mL/min flow rate. The heating program was set to ramp at 20°C/min from 30°C to 800°C. The weight loss of the sample was calculated according to the following formula:

$$w(\%) = \frac{m_0 - m}{m_0} \times 100 \tag{6}$$

Where: w denotes the weight loss of the sample, % (mass fraction); $m_0$ denotes the initial mass of the sample, mg; and $m_t$ denotes the mass at temperature t, mg.

3. Results and Analysis

3.1 Monosaccharide Composition Analysis

Monosaccharide composition analysis is a necessary step in studying polysaccharides’ structural characteristics and structure-function relationships. Monosaccharide composition analysis was conducted on the six polysaccharides mentioned above, as detailed in Table 1.

Table 1. Monosaccharide composition of six polysaccharides.

<table>
<thead>
<tr>
<th>Monosaccharide</th>
<th>Ara</th>
<th>Gal</th>
<th>Glc</th>
<th>Xyl</th>
<th>Man</th>
<th>Gal-UA</th>
<th>Gul-UA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>0.35%</td>
<td>0.00%</td>
<td>96.72%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>1.09%</td>
<td>1.84%</td>
</tr>
<tr>
<td>Pul</td>
<td>0.00%</td>
<td>1.04%</td>
<td>96.84%</td>
<td>0.00%</td>
<td>2.12%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>κ-C</td>
<td>0.00%</td>
<td>75.41%</td>
<td>22.65%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>1.94%</td>
<td>0.00%</td>
</tr>
<tr>
<td>CMCS</td>
<td>0.00%</td>
<td>4.72%</td>
<td>91.24%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>HPCS</td>
<td>0.00%</td>
<td>0.46%</td>
<td>84.35%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
<td>0.00%</td>
</tr>
<tr>
<td>TSP</td>
<td>1.78%</td>
<td>21.34%</td>
<td>39.59%</td>
<td>35.17%</td>
<td>0.00%</td>
<td>2.13%</td>
<td>0.00%</td>
</tr>
</tbody>
</table>

It can be observed that Sodium Alginate (SA), Pullulan (Pul), Carboxymethyl Chitosan (CMCS), and Hydroxypropyl Chitosan (HPCS) are primarily composed of glucose. κ-Carrageenan (κ-C) predominantly comprises galactose and glucose, while Tamarind Seed Polysaccharide (TSP) consists mainly of glucose, xylose, and galactose.

According to literature reports [8-14], Sodium Alginate (SA) is a copolymer composed of β-D-mannuronic acid (M units) and α-L-guluronic acid (G units) connected by β-1,4-glycosidic bonds, forming different proportions of GM, MM, and GG segments. Sodium Alginate (SA) typically carries a negative charge over a wide pH range. Pullulan (Pul) is an α-glucan composed of repeating maltotriose units linked by α-1,4-glycosidic bonds and interconnected by α-1,6-bonds, resulting in short branch lengths, minimal steric hindrance, and high rigidity. Chitosan is a linear polysaccharide; in Carboxymethyl Chitosan (CMCS), the incorporation of carboxymethyl groups enhances the water solubility of chitosan, alters the secondary structure of chitosan molecules and reduces crystallinity, while Hydroxypropyl Chitosan (HPCS), a derivative of chitosan, exhibits improved water solubility due to the
introduction of hydroxypropyl groups. \(\kappa\)-Carrageenan (\(\kappa\)-C) is a linear polymer chain composed of galactose and glucose units, characterized by a large molecular weight and long chain length. Tamarind Seed Polysaccharide (TSP) comprises galactose, glucose, and xylose, featuring a relatively hydrophobic main chain. In TSP, d-glucopyranose (\(\beta\)-d-Glc \(p\)) is substituted at O-75 by pyranose xylose residues (\(\alpha\)-d-Xyl \(p\)) and further connected to pyranose galactose units (\(\beta\)-d-Gal \(p\)), resulting in a more complex branched structure compared to other polysaccharides.

### 3.2 Light Scattering Analysis

In polymer conformation, the structure parameter \(\rho\) (\(R_g/R_h\)) can be used to characterize the conformational features of polymer chains in solution:
- When \(\rho=0.77\), it indicates a spherical conformation.
- As \(\rho\) increases, the polymer chains become looser, more expanded, and more flexible.
- When \(\rho=1.5-1.8\), polymer chains are in a linear and flexible state.
- When \(\rho\) is around 2, the dispersion system becomes irregular aggregates or highly branched structures.
- When \(\rho\) is much larger than 2, the dispersion system turns into a rigid rod-like structure [15].

The Mark-Houwink-Kuhn-Sakurada equation (\([\eta]\ = kM^\alpha\)) with \(\alpha\) (M-H) values of 0.22, 0.5-0.8, and 1-2, respectively, reflects the conformation of spheres, flexible chains, and rigid rods [16].

<table>
<thead>
<tr>
<th>Name</th>
<th>(\text{Mw}/10^5) Da</th>
<th>(R_g/\text{nm})</th>
<th>(R_h/\text{nm})</th>
<th>(\alpha) (M-H)</th>
<th>(\rho)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>5.4</td>
<td>83.8</td>
<td>50.4</td>
<td>0.779</td>
<td>1.66</td>
</tr>
<tr>
<td>Pul</td>
<td>3.3</td>
<td>17.7</td>
<td>16.7</td>
<td>0.659</td>
<td>1.06</td>
</tr>
<tr>
<td>(\kappa)-C</td>
<td>7.4</td>
<td>83.0</td>
<td>52.4</td>
<td>0.747</td>
<td>1.58</td>
</tr>
<tr>
<td>CMCS</td>
<td>6.6</td>
<td>53.6</td>
<td>33.2</td>
<td>0.668</td>
<td>1.62</td>
</tr>
<tr>
<td>HPCS</td>
<td>7.4</td>
<td>61.3</td>
<td>42.1</td>
<td>0.696</td>
<td>1.45</td>
</tr>
<tr>
<td>TSP</td>
<td>8.1</td>
<td>63.1</td>
<td>43.3</td>
<td>0.687</td>
<td>1.46</td>
</tr>
</tbody>
</table>

Table 2 presents the results of light scattering for the six polysaccharides. From Table 2, it can be observed that the order of conformational looseness to compactness is as follows: Sodium Alginate (SA) > Carboxymethyl Chitosan (CMCS) > \(\kappa\)-Carrageenan (\(\kappa\)-C) > Tamarind Seed Polysaccharide (TSP) > Hydroxypropyl Chitosan (HPCS) > Pullulan (Pul). The polydispersity indices (\(\text{Mw/Mn}\)) of the six polysaccharides range from 1.0 to 2.0, indicating the broad distribution of molecular weights. Pullulan (Pul) exhibits high molecular weight, branched structure, and low viscosity, with a \(\rho\) value of 1.06, indicating a semi-rigid chain [17]. The extension of the molecular chains of Sodium Alginate (SA) is due to the ionization of its carboxyl groups into negative ions in solution, leading to electrostatic repulsion between chain segments. The molecular weights of these six polysaccharides are relatively large, with \(\alpha\) values ranging from 0.5 to 0.8, indicating that the conformation of the molecular chains is flexible and irregular.

### 3.3 Adsorption Kinetics Analysis

The adsorption of polymers onto cellulose is one mechanism by which polymers prevent pulp coagulation [18]. Therefore, analyzing the adsorption of food colloids on cellulose can elucidate their anti-coagulation effects in reconstituted tobacco pulp. Changes in the total sugar content of the supernatant can be used to evaluate the adsorption of food colloids on cellulose, as shown in Figure 1. From Figure 1, it can be observed that the adsorption concentration of Hydroxypropyl Chitosan (HPCS) and Carboxymethyl Chitosan (CMCS) on MCC surfaces showed minimal variations, indicating their stable adsorption on the MCC surface. Over the 3-12 minute period, the total sugar concentration of Tamarind Seed Polysaccharide (TSP) continuously decreased, indicating ongoing adsorption. The side-chain structure of TSP facilitates its cross-linking and entanglement with cellulose, although the adsorption process is relatively slow. Due to its high molecular weight, \(\kappa\)-Carrageenan (\(\kappa\)-C) becomes entwined with cellulose upon adsorption, significantly reducing the equilibrium concentration of \(\kappa\)-C. As the mixed system oscillates, the entangled \(\kappa\)-C molecules disentangle, leading to a subsequent increase in concentration.

### 3.4 Rheological Properties Analysis

The viscosity change of different groups of blend liquid.

**Figure 1.** Content of total sugar of supernatant time.
Figure 3. The modulus of different groups of blend liquid.
Note: Hollow symbols represent storage modulus\(G'\), while solid symbols represent loss modulus\(G''\).

Figures 2 and 3 depict the viscosity and modulus curves of MCC blends with added polysaccharides. Polymer solution viscosity analysis revealed that shear thinning occurred in all five blend solutions except for the κ-C group at low shear rates. The shear thinning behavior aligns with the trends observed in the frequency scan, indicating the loss of ordered structures. At low frequencies, all six blend systems' storage modulus (\(G'\)) exceeded the loss modulus (\(G''\)). Both storage and loss moduli increased with increasing frequency, with the storage modulus increasing more significantly than the loss modulus. At high frequencies, the storage moduli of all six polymer solutions exceeded the loss modulus. This is typical behavior of semi-dilute entangled polymer solutions, indicating the loss of ordered structures.

### 3.5 Viscosity Analysis

Tables 3 and 4 present polysaccharides' viscosity and blend compatibility test results with crystalline cellulose MCC. It can be observed that the addition of Tamarind Seed Polysaccharide (TSP) and Hydroxypropyl Chitosan (HPCS) groups resulted in a slight decrease in viscosity. In contrast, the addition of Pullulan (Pul), Sodium Alginate (SA), and Carboxymethyl Chitosan (CMCS) groups led to a slight increase in viscosity. The addition of the κ-Carrageenan (κ-C) group resulted in a significant increase in viscosity. All groups exhibited phase separation, forming microphase-separated blocks, indicating poor compatibility [21]. Due to the presence of numerous side chains in TSP and the influence of its molecular chain conformation by bonding modes, branching structures, intramolecular hydrogen bonds, and electrostatic repulsion, it formed larger aggregates after adhering to cellulose crystalline monomers, accelerating the settling of cellulose in the aqueous solution, consistent with the cellulose adsorption results.

Carboxymethyl Chitosan (CMCS) possesses viscosity and weakly increases viscosity through interaction with cellulose [22]. κ-Carrageenan (κ-C) solution exhibits high viscosity at low concentrations and significantly increases viscosity after blending with cellulose, forming a gel readily. Pululan is a linear macromolecule with low solution viscosity. Its hydrogen bonds with cellulose are weak, resulting in poor compatibility. However, blending with cellulose can increase viscosity.

### 3.6 SEM Analysis

Figure 4 illustrates the scanning electron microscopy (SEM) images of blends of six polysaccharides with crystalline cellulose. At a magnification of 500 times, Carboxymethyl Chitosan (CMCS) and Hydroxypropyl Chitosan (HPCS) groups exhibit similar structures. Cellulose forms a compact cluster as the main body, with the layered edges of cellulose folding and adhering to each other through the swelling caused by water absorption and the action of CMCS and HPCS in the blend state. Each cellulose fragment forms spherical shapes during the blending drying process. In the Tamarind Seed Polysaccharide (TSP) group, cellulose fragmentation is evident, but there is no significant change in size, with noticeable internal pores and no smooth outer surface. In the Sodium Alginate (SA) group, numerous small particles smaller than 100 μm appear, indicating that the adhesive ability of SA to high molecular weight and numerous branching structures, TSP exhibits stronger interactions among polymer chains [20], resulting in a higher storage modulus than the other five groups.

### Table 3. Viscosity of blend liquid.

<table>
<thead>
<tr>
<th>Number</th>
<th>System</th>
<th>(\mu) (mPa·s)</th>
<th>[(\eta)] (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MCC/SA</td>
<td>2.25±0.04</td>
<td>-0.196</td>
</tr>
<tr>
<td>2</td>
<td>MCC/Pul</td>
<td>2.3±0.01</td>
<td>-0.199</td>
</tr>
<tr>
<td>3</td>
<td>MCC/κ-C</td>
<td>4.68±0.07</td>
<td>-0.306</td>
</tr>
<tr>
<td>4</td>
<td>MCC/CMCS</td>
<td>2.27±0.07</td>
<td>-0.196</td>
</tr>
<tr>
<td>5</td>
<td>MCC/HPSC</td>
<td>1.86±0.01</td>
<td>-0.203</td>
</tr>
<tr>
<td>6</td>
<td>MCC/TSP</td>
<td>1.95±0.01</td>
<td>-0.199</td>
</tr>
<tr>
<td>7</td>
<td>MCC</td>
<td>2.12±0.03</td>
<td>-0.220</td>
</tr>
</tbody>
</table>

*Polysaccharide content by a mass fraction in the blend.
connect cellulose fragments is the weakest among the six groups, especially at a magnification of 500 times, where cellulose layers are peeled off individually. In the Pullulan (Pul) group, there is also a weak ability to bond individual large cellulose skeletons, but the internal interaction among cellulose is stronger, resulting in a higher proportion of filamentous entities than in other groups[23]. In the κ-Carrageenan (κ-C) group images, fewer cellulose fragments smaller than 30 μm are present, indicating that its electrostatic interaction can adsorb individual fragments effectively.
3.7 Research on the application of six polysaccharides in the papermaking practice of reconstituted tobacco sheet

In the practical application process, six kinds of polysaccharides, including sodium alginate (SA), pullulan (Pul), κ-carrageenan (κ-C), carboxymethyl chitosan (CMCS), hydroxypropyl chitosan (HPCS), and tamarind polysaccharide (TSP), were added to the reconstituted tobacco pulp as wet-end additives in papermaking reconstituted tobacco base sheet. The effects of polysaccharides on the retention rate of the reconstituted tobacco pulp and the physical properties of the leaf base are as follows:

<table>
<thead>
<tr>
<th>Table 5. Effects of polysaccharides on the retention rate of the pulp and the physical properties of the base sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysaccharide samples</td>
</tr>
<tr>
<td>--------------------------</td>
</tr>
<tr>
<td>Blank control</td>
</tr>
<tr>
<td>TSP 0.5%</td>
</tr>
<tr>
<td>Pul 0.5%</td>
</tr>
<tr>
<td>SA 0.5%</td>
</tr>
<tr>
<td>κ-carrageenan 0.5%</td>
</tr>
<tr>
<td>CMCS 0.5%</td>
</tr>
<tr>
<td>HPCS 0.5%</td>
</tr>
</tbody>
</table>

Note: Adding polysaccharide is 0.5% of the absolute dry weight of reconstituted tobacco sheet pulp.

Adding polysaccharide as a wet-end additive in the papermaking process, the six kinds of polysaccharides all contribute to the improvement of reconstituted tobacco sheet pulp retention rate, among which κ-carrageenan and TSP have better effects; the impact on the physical properties of reconstituted tobacco sheet base is as follows: the addition of polysaccharides will enhance the tensile strength of base sheet, which has a positive impact on improving the addictive properties of the product, but it will also reduce the bulk of sheet base to a certain extent, especially the permeability of the base will be significantly reduced. Therefore, the dosage of polysaccharides is worth further study.

4. Discussion

The discussion s are obtained as below:

(1) The total monosaccharide content of CMCS and HPCS is less than 100%, which may be related to the impurity of the samples.

(2) Generally, due to the structural similarity between polysaccharides and cellulose molecules, there is a high affinity between polysaccharides and the cellulose surface, leading polysaccharides to adsorb on the cellulose surface preferentially[24]. However, the negative charge of polymers hinders their adsorption to cellulose under conditions without electrolytes[25].

(3) CMCS itself has viscosity and weakly enhances the viscosity through interaction with cellulose.
κ-Carrageenan exhibits high viscosity at low concentrations in aqueous solution. After blending with cellulose, the viscosity increases significantly, and gel formation is easily induced[26]. As a linear macromolecule, Pullulan does not have high viscosity in aqueous solution. Its hydrogen bonding with cellulose is weak, leading to poor compatibility. However, blending with MCC can increase viscosity[27].

5. Conclusion

This study draws the following conclusions through analysis of monosaccharide composition, light scattering, adsorption kinetics, rheological properties, viscosity, and scanning electron microscopy:

1. The main monosaccharide components of SA, Pul, CMCS, and HPCS are glucose, while κ-Carrageenan consists mainly of galactose and glucose, and TSP consists mainly of glucose, xylose, and galactose. The degree of compactness from loose to compact is as follows: SA > CMCS > κ-C > TSP > HPCS > Pul.

2. When polysaccharides are blended with MCC, SA exhibits the weakest adhesion ability. Pul has a weak ability to bond individual large cellulose skeletons, but the internal interaction among cellulose is stronger. The adsorption of HPCS and CMCS on the MCC surface is stable. In the blend state, the layered edges of cellulose first swell by water absorption and then adhere to each other through the action of CMCS and HPCS, resulting in each cellulose fragment forming into spherical shapes during drying. The side chain structure of TSP is conducive to its cross-linking and entanglement with cellulose, but the adsorption process is relatively slow. The cellulose fragmentation of TSP is significant, with noticeable internal pores and no smooth outer surface. κ-Carrageenan adsorbs fragments through electrostatic interactions.

3. The storage modulus of TSP is higher than that of other polysaccharides, possibly due to its higher molecular weight and more abundant side chain structure, resulting in stronger interactions between polymer chains.

4. The viscosity of TSP and HPCS blended with MCC decreases slightly, while that of Pul, SA, and HPCS blended with MCC increases slightly. κ-Carrageenan blended with MCC significantly increases viscosity. All groups exhibit phase separation, forming microphase-separated blocks, indicating poor compatibility.

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References


