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Adsorption Mechanism of Wet Strength Agents in Lignocellulosic Fibers and Their Regulatory Effect on Paper Wettability

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Abstract: This study focuses on the adsorption mechanism of wet strength agents in lignocellulosic fibers and their regulatory effect on paper wettability. Through experimental analysis and theoretical discussion, the adsorption process and mode of action of wet strength agents on the surface of lignocellulosic fibers are clarified, and the inherent mechanism by which they affect paper wettability is revealed. The research results have important theoretical and practical guiding significance for optimizing paper production processes and improving paper performance.

Keywords: Lignocellulosic fibers; Wet strength agents; Adsorption mechanism; Paper wettability; Regulatory effect

1. Introduction

In the paper industry, lignocellulosic fibers are one of the most commonly used raw materials. The performance of paper is influenced by various factors, among which wettability is a key indicator that directly relates to the printability, writing performance, and packaging applications of paper [1]. Wet strength agents, as chemical additives that can significantly affect paper wettability, have attracted much attention regarding their adsorption mechanism in lignocellulosic fiber raw materials and their regulatory effect on paper wettability. Deep research in this field is conducive to developing more efficient and environmentally friendly paper production technologies to meet the growing market demand.

2. Types and adsorption mechanisms of wet strength agents for lignocellulosic materials

2.1. Types and characteristics of wet strength agents

2.1.1. Common types of wet strength agents

Currently, the wet strength agents commonly used in lignocellulosic materials mainly include polyamide polyamine epichlorohydrin resin (PAE), polyethyleneimine (PEI), and cationic polyacrylamide (PAM). PAE is a water-soluble cationic thermosetting resin that offers advantages such as good wet strengthening effects, low usage amounts, ease of use, easy recovery of damaged paper, and non-toxicity. It is currently the most widely used wet strength agent. PEI is a polymer with high cationic density that can form strong bonds with cellulose in pulp, thereby improving the wet strength of paper. It is often used for special-purpose papers such as filter paper and industrial paper. By introducing cationic groups, cationic PAM can interact with negatively charged lignocellulose, improving the wet strength of paper. It is commonly used for packaging paper and decorative paper, etc. [2].

2.1.2. Characteristics of wet strength agents

Wet strength agents are generally non-toxic, odorless, and can be used under various conditions, including neutral, slightly alkaline, and acidic environments. Additionally, these agents have the functions of aiding retention and filtration, which can improve the retention rate of pulp fibers, clarify white water, and reduce pulp flocculation and wet web breaks [3]. Different types of wet strength agents vary in terms of molecular structure, charge density, and reactivity, and these differences determine their adsorption behavior on lignocellulosic materials and their effects on regulating paper wettability.

2.2. Adsorption mechanism of wet strength agents in lignocellulosic materials

2.2.1. Electrostatic adsorption

The surface of lignocellulose is typically negatively charged, which is due to the ionization of groups such as carboxyl groups on the molecular chains of cellulose and hemicellulose in aqueous solutions. Most wet strength agents are cationic polymers with a large number of cationic groups, such as amino and quaternary ammonium groups, on their molecular chains. Therefore, there is a strong electrostatic attraction between the wet strength agent and lignocellulose, which is one of the main driving forces for the adsorption of wet strength agents on the surface of lignocellulose [4]. For example, the cationic groups in PAE molecules can attract the negative charges on the surface of lignocellulose, enabling PAE molecules to rapidly adsorb onto the lignocellulose surface. The presence of this electrostatic adsorption can be verified through Zeta potential analysis. When PAE is added to a lignocellulose suspension, the Zeta potential of the system changes significantly, shifting from a negative value to a positive value, indicating that PAE molecules have adsorbed onto the lignocellulose surface, changing its surface charge properties.

2.2.2. Hydrogen bonding

Besides electrostatic adsorption, hydrogen bonding also exists between wet strength agents and lignocellulose. As mentioned earlier, lignocellulose molecular chains contain a large number of hydroxyl groups, while wet strength agent molecules may also contain groups capable of forming hydrogen bonds with hydroxyl groups, such as amino and hydroxyl groups. These groups interact through hydrogen bonding, further enhancing the adsorption stability of the wet strength agent on the lignocellulose surface. Taking PEI as an example, the amino groups on its molecular chain can form hydrogen bonds with the hydroxyl groups on the lignocellulose surface, allowing PEI molecules to be firmly adsorbed onto the lignocellulose surface. The formation of hydrogen bonds can be detected through infrared spectroscopy. Before and after adding the wet strength agent, infrared spectroscopy tests on lignocellulose reveal shifts or intensity changes in absorption peaks related to hydrogen bonding, indicating the formation of hydrogen bonds between the wet strength agent and lignocellulose.

2.2.3. Chemical reaction

Some wet-strength agents can chemically react with lignocellulosic fibers to form chemical bonds, achieving a stronger bond. For example, under certain conditions, the epoxy groups in PAE molecules can undergo ring-opening reactions with hydroxyl groups in lignocellulosic fibers, forming ether bonds. The formation of these chemical bonds stabilizes the bond between PAE and lignocellulosic fibers, making it difficult to detach. The occurrence of chemical reactions can be confirmed through X-ray photoelectron spectroscopy (XPS) analysis. XPS can detect changes in the elemental composition and chemical state of the surface of lignocellulosic fibers. When PAE reacts with lignocellulosic fibers, characteristic peaks related to ether bonds appear in the XPS spectrum, proving the existence of chemical reactions. The adsorption of wet-strength agents in lignocellulosic raw materials is a complex process, and electrostatic adsorption, hydrogen bonding, and chemical reactions often coexist and synergize, jointly determining the adsorption effect of wet-strength agents.

2.3. Regulatory effect of wet-strength agents on paper wettability

2.3.1. Impact on paper surface tension

The adsorption of wet-strength agents alters the chemical composition and structure of the paper surface, thereby affecting its surface tension. When wet-strength agents adsorb onto the paper surface, the hydrophilic or hydrophobic groups on their molecular chains become exposed, changing the paper's wettability. If the wet-strength agent's molecular chain contains more hydrophilic groups, such as amino groups in PAE molecules, it enhances the paper surface's hydrophilicity, reducing surface tension. Conversely, if the molecular chain contains more hydrophobic groups, it increases the paper surface's hydrophobicity, raising surface tension. Contact angle measurements provide a direct indication of changes in paper surface tension. Adding PAE to the paper reduces the contact angle of water droplets on the paper surface, indicating enhanced hydrophilicity, decreased surface tension, and improved wettability.

2.3.2. Impact on the pore structure of paper

The pore structure of paper also has a significant impact on its wettability. The adsorption and crosslinking of wet strength agents between lignocellulosic fibers can alter the pore structure of paper. On one hand, the adsorption of wet strength agents may fill some pores in the paper, reducing pore size; on the other hand, crosslinking between wet strength agent molecules may form a network structure, increasing the compactness of the paper. Smaller pore sizes and a more compact structure can increase the resistance of liquids penetrating the paper, thereby affecting its wettability. Equipment such as mercury porosimeters can be used to analyze the pore structure of paper. Studies have found that as the amount of PAE increases, the average pore size of paper gradually decreases, and the porosity decreases, indicating that the addition of PAE alters the pore structure of paper and affects its wettability.

2.3.3. Impact on the bonding force between paper fibers

One of the main roles of wet strength agents is to enhance the bonding force between paper fibers, and changes in this bonding force can indirectly affect the wettability of paper. When wet strength agents undergo adsorption and crosslinking reactions with lignocellulosic fibers, more chemical bonds or hydrogen bonds are formed between the fibers, resulting in tighter bonding. This tight bonding can reduce fiber swelling and water absorption, protecting existing hydrogen bonds between fibers, thus reducing the water absorption of paper and improving its wettability. For example, the crosslinked network structure formed by PAE in paper can effectively restrict fiber movement, reduce water absorption and swelling of fibers, enabling the paper to maintain good strength and low water absorption in a wet state. Changes in the bonding force between paper fibers can be detected through methods such as tensile testing. As the amount of wet strength agent increases, both the dry and wet tensile strengths of paper improve, indicating enhanced bonding force between fibers, reduced water absorption, and controlled wettability of the paper.

3. Experimental section

3.1. Experimental materials

Bleached sulfate softwood pulp (produced by a certain paper mill, Kappa number 12.5, fiber length 1.8–2.2 mm) was selected as the lignocellulosic raw material. Its main chemical components are: cellulose 68.5%, hemicellulose 19.2%, lignin 2.3%, and ash content 0.5%. The wet strength agents used were commercially available polyamide polyamine epichlorohydrin resin (PAE, produced by a certain chemical company, solid content 12.5%, pH 3.0–6.0, viscosity 15–100 mPa·s), polyethyleneimine (PEI, molecular weight 10,000, solid content 30%, from a certain biotechnology company), and cationic polyacrylamide (CPAM, molecular weight 8 million, cationic degree 30%, from a certain material company) [6]. The experimental water was deionized water (conductivity ≤ 10μS/cm), and other reagents (NaOH, HCl, etc.) were analytically pure.

3.2. Experimental instruments

All instruments used in this experiment are listed in **Table 1**.

Table 1. Experimental instruments

Instrument name	Model	Manufacturer	Primary application
Dynamic Zeta Potential Analyzer	Nano-ZS90	Malvern Instruments, UK	Measures the zeta potential of fiber suspensions
Fourier Transform Infrared Spectrometer (FTIR)	Nicolet iS50	Thermo Fisher Scientific, USA	Analyzes hydrogen bonding and functional group changes
X-ray Photoelectron Spectrometer (XPS)	ESCALAB 250Xi	Thermo Fisher Scientific, USA	Detects surface elements and chemical states
Contact Angle Meter	OCA20	DataPhysics, Germany	Measures paper surface contact angles
Mercury Porosimeter	AutoPore IV 9500	Micromeritics, USA	Analyzes paper pore structure (pore size, porosity)
Universal Testing Machine	CMT6104	MTS Systems, China	Tests dry/wet tensile strength of paper
Standard Sheet Former	ZQJ1-B	Hangzhou Qingtong Boke Automation, China	Produces paper sheets with basis weight of 80 g/m²
Constant Climate Chamber	BPS-100CL	Yiheng Instruments, China	Paper conditioning (23°C, 50% RH)

3.3. Experimental methods

3.3.1. Paper sample preparation

(1) Pulp pretreatment: Soak the softwood pulp board in deionized water for 24 hours, then disintegrate it with a standard disintegrator (3000 r/min) for 10 minutes to prepare a 0.5% (mass concentration) fiber suspension. Adjust the pH to 7.0 ± 0.1 with 0.1mol/L NaOH or HCl [7].

(2) Wet strength agent addition: Add different amounts (0.2%, 0.4%, 0.6%, 0.8%, 1.0% based on the mass of the absolutely dry pulp) of PAE, PEI, and CPAM to the fiber suspension, and stir for 15 minutes on a

magnetic stirrer (300 r/min) to ensure uniform dispersion of the agents.

(3) Sheet formation and processing: Use a standard sheet former to create paper samples with a basis weight of 80g/m². After vacuum dewatering (-0.08 MPa, 2min), the samples are dewatered in a press (0.3 MPa, 3min) and finally dried in a dryer (105 °C, 5min). Place the paper samples in a constant temperature and humidity chamber (23 °C, 50%RH) for 24 hours to equilibrate before use. Repeat each experiment 3 times and take the average value [8].

3.3.2. Characterization of the adsorption mechanism

(1) Electrostatic adsorption test: Take 0.1% fiber suspension, add different amounts of wet strength agent, stir for 10 minutes, and measure the Zeta potential of the suspension using a Zeta potential meter at a test temperature of 25 °C. Measure each sample 5 times and take the average value.

(2) Hydrogen bonding analysis: Wash the fibers adsorbed with wet strength agent 3 times with deionized water (to remove unadsorbed agent), freeze-dry, mix with KBr, and press into tablets. Scan with FT-IR in the range of 4000–400cm^{-1}, with a resolution of 4cm^{-1} and 32 scans. Compare and analyze changes in characteristic peaks of hydroxyl (around 3400cm^{-1}) and amino groups (around 3300cm^{-1}) [9].

(3) Chemical reaction verification: Use XPS to analyze changes in fiber surface elements, with an Al target (1486.6eV), vacuum degree of 1×10^{-8}Pa, and an analysis area diameter of 500 μm. Perform peak fitting on C1s and N1s spectra, and calculate the proportion of ether bond (C-O-C) characteristic peak (binding energy 286.5eV) [10].

3.3.3. Wettability and related performance tests

(1) Contact angle measurement: Use a contact angle meter to perform the sessile drop method test. Drop 5 μL of deionized water onto the surface of the paper sample, record the contact angle at 0s, and measure 5 different positions for each sample to obtain an average value.

(2) Pore structure analysis: The pore distribution of the paper sample was measured using a mercury intrusion porosimeter with a test pressure range of 0.001–414 MPa (corresponding to pore diameters of 3.6 nm–1.1 mm). The average pore diameter and porosity were calculated.

(3) Strength performance testing: According to the GB/T12914-2018 standard, the dry tensile strength of the paper sample was tested using an electronic universal material testing machine. For the wet tensile strength test, the paper sample was soaked in deionized water for 30 minutes, removed, and the surface water was absorbed with filter paper before immediate testing. The stretching speed was 10 mm/min.

4. Discussion

4.1. Adsorption characteristics of wet strength agents

With the increase in PAE addition, the Zeta potential of the lignocellulosic fiber suspension gradually shifted from negative to positive, indicating that PAE molecules were gradually adsorbed onto the surface of the lignocellulosic fibers through electrostatic adsorption. FT-IR analysis showed significant shifts and intensity changes in absorption peaks related to hydrogen bonding after adding PAE, demonstrating the formation of hydrogen bonds between PAE and lignocellulosic fibers. XPS analysis revealed the emergence of characteristic peaks associated with ether bonds after the reaction between PAE and lignocellulosic fibers, confirming the occurrence of chemical reactions. These results suggest that the adsorption of PAE in lignocellulosic fiber raw materials is a combined effect of electrostatic adsorption, hydrogen bonding, and chemical reactions.

4.2. Effects on paper wettability

Contact angle measurement results indicated that as the amount of PAE increased, the contact angle of water droplets on the paper surface gradually decreased, indicating improved wettability of the paper. Mercury intrusion porosimeter test results showed that with increasing PAE usage, the average pore diameter of the paper gradually decreased, and the porosity decreased. This suggests that the addition of PAE altered the pore structure of the paper, thereby affecting its wettability. Tensile test results demonstrated that both the dry and wet tensile strengths of the paper significantly increased with increasing PAE usage, while the water absorption of the paper decreased. This indicates that PAE enhances the bonding force between paper fibers, thereby improving the wettability of the paper. Based on these combined results, it can be concluded that the wet strength agent PAE effectively regulates the wettability of paper by altering factors such as surface tension, pore structure, and inter-fiber bonding force.

5. Conclusion

This study deeply explored the adsorption mechanism of wet strength agents in lignocellulosic materials and their regulatory effects on paper wettability. The adsorption of wet strength agents on the surface of lignocellulose fibers is achieved through a combination of electrostatic adsorption, hydrogen bonding, and chemical reactions, which enable the wet strength agents to be strongly adsorbed onto the lignocellulose fibers. The regulation of paper wettability by wet strength agents is primarily achieved by influencing the surface tension of the paper, pore structure, and inter-fiber bonding force.

Disclosure statement

The author declares no conflict of interest.

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