Comparison of Nanofibrillated Cellulose and Hydroxyethyl Cellulose in Improving the Storage Stability of Waterborne Coatings

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Abstract: Waterborne coatings often delaminate and settle during long-term storage, requiring the addition of thickeners. The effects of nanofibrillated cellulose (NFC) and the commonly used thickener, hydroxyethyl cellulose (HEC), on the storage stability of waterborne coatings were compared in this study. The morphology of NFC was characterized using infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The rotational viscosity and rheological properties of the waterborne coatings with NFC and HEC were tested. Stationary settling experiments were also conducted at different temperatures to compare the difference of NFC and HEC on improving the storage stability of the waterborne coatings. The results showed that the waterborne coating with NFC exhibited pseudoplastic fluid characteristics; a small addition of NFC can achieve the same improvement effect on the storage stability of waterborne coatings as HEC. Further, the improvement effect of NFC was not affected by temperature. The waterborne coating with NFC still exhibited good storage stability at high temperatures, which was significantly superior to that of HEC. Therefore, NFC is a feasible agent for improving the prolonged storage stability and warming-induced delamination of waterborne coatings.

Keywords: waterborne coatings; nanofibrillated cellulose; hydroxyethyl cellulose; yield stress; storage stability

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1 Introduction

With the development of society and improvement of life quality, coatings not only need to meet the functional requirements of living and working, but also of aesthetics, comfort, artistry, energy conservation, and environmental friendliness [1]. Waterborne coatings have the advantages of good simulation effects, diverse decorative uses, simple construction, high-cost effectiveness, and environmental friendliness when used as building coatings [2]. Additionally, waterborne coatings have a lower volatile organic compounds (VOC) content than the traditional latex and elastomeric coatings in terms of composition and customization, allowing themselves to be configured according to customer requirements to obtain different patterns [3]. As multiphase suspension systems, waterborne coatings usually contain colored particles, protective adhesives with functional gels, film-forming emulsions, and other additives [4]; however, due to the poor stability of the coatings, caused by relatively high density of colored particles in the dispersion phase [5], waterborne coatings often exhibit delamination between the emulsion and colored particles under conditions of long-term storage and high temperature, which greatly limits their further development.

Currently, the rheological behavior of waterborne coatings is often altered by adding thickeners to improve their storage stability [6]. Hydroxyethyl cellulose (HEC), a nonionic cellulose ether, can coexist with water-soluble polymers and make aqueous solutions exhibit the characteristics of non-Newtonian fluids with shear-thinning properties [7]. The use of HEC and modified cellulose additives for improving the storage stability of waterborne coatings has garnered widespread attention [8]. Kastner [9] achieved a significant increase in the viscosity of waterborne coatings by adding hydrophobic HEC. Zeng et al [10] improved the storage stability of waterborne coatings by adding 1.6% HEC to the coating and compounding it with connective cellulose HE-10K; however, the viscosity of the coating only increased slightly. Mai [11] successfully enabled the long-term storage of waterborne coatings by building a ternary thickening system of HEC, xanthan gum, and magnesium aluminum silicate. However, the use of thickeners to improve the storage stability of waterborne coatings is not sufficient, as the viscosity of the liquid is highly affected by temperature [12]. When the temperature increases, the thickening effect of the HEC reduces, and delamination of waterborne coatings occurs.

Nanofibrillated cellulose (NFC) is commonly used as reinforcing agent [13–15] because of its nanoscale size, large aspect ratio, abundant surface hydroxyl groups, and high strength. To construct a fiber network structure through physical entanglement and hydrogen bonding in solution may improve storage stability without significantly increasing the viscosity of the waterborne coatings [16–18]. Furthermore, this may hinder the settling of colored particles. Here, the effects of NFC and HEC on the storage stability, viscosity, rheological behavior, and other properties of waterborne coatings were compared, and the feasibility and advantages of NFC as a suspension stabilizer for coatings was explored. The addition of NFC was expected to improve the storage stability of waterborne coatings and solve the temperature increase-induced delamination problem that currently waterborne coatings encounter, thereby broadening the application prospects of NFC.

2 Experimental

2.1 Materials

Pulp board was supplied by the National Engineering Lab for Pulp and Paper (Beijing, China). Quartz sand (200−300 mesh size) was supplied by the Dongguan Huaxin Composite Materials Co., Ltd., China. HEC was purchased from Shandong Heda Co., Ltd. (China). Waterborne acrylic resin (WPAA) was purchased from Guangdong Zuoli New Material Technology Co., Ltd., China. Waterborne aromatic polyurethane resin (WPU) was supplied by Guangzhou Lvbao New Materials Co., Ltd., China.

2.2 Preparation of NFC

The pulp board was shredded, diluted to 2% with water, and processed in a deflaker for 10 min. Then the fibrillation treatment of the slurry was performed by using a fine grinder (MKCA6-2J, Masuko Sangyo Co., Ltd., Japan) at a speed of 1500 r/min with a gap of about 100 μm. Finally, NFC was obtained through a high-pressure homogenizer (AH-PILOTN, Shanghai Duoning Biotechnology Co., Ltd.). The workflow for the preparation of the NFC is shown in Fig. 1.

2.3 Preparation of waterborne coatings

The waterborne coating was prepared using quartz sand, WPAA, WPU and deionized water in the ratio of 2:1:1:2 (*w*/*w*). The solution was magnetically stirred at 600 r/min for 30 min at 25 ℃, and then poured into a sample tube as a reference sample. Modified waterborne coatings were prepared in the same proportions with the additions of NFC and HEC separately. The NFC dosage was 1% (dry weight of NFC based on the total weight of the coating), and the addition of HEC were 1%, 2%, 3%, and 4% (dry weight of HEC based on the total weight of the coating). The waterborne coatings were magnetically stirred under room temperature at 600 r/min for 30 min, and then poured into the sample tubes and labeled as NFC0.2, HEC0.2, HEC0.4, HEC0.6, and HEC0.8, respectively.

2.4 Characteristics of NFC

2.4.1 Micromorphology

The NFC was observed using scanning electron microscope (SEM) (S-3400N, Hitachi, Japan) at a voltage of 10 kV. Before observation, the prepared NFC suspension was freeze-dried and crushed to obtain the NFC powder, and the sample surface was sprayed with gold using an ion sputtering instrument.

2.4.2 Chemical structure

The chemical structure of the NFC was determined using Fourier-transform infrared spectrometry (FT-IR) (Tensor 27, Bruker, Germany). After freeze-drying, the NFC sample was tested using the potassium bromide tableting method at wavelengths of 600−4000 cm^{-1}. A total of 32 scans were performed per sample at a resolution of 4 cm^{-1}.

2.5 Storage stability analysis of waterborne coatings

2.5.1 Stationary test

The waterborne coating samples (NFC0.2, HEC0.2, HEC0.4, HEC0.6, and HEC0.8) and the reference sample were stored at 25 ℃ for two months, and the delamination states of the coatings were recorded using a digital camera. Another set of the samples were stored at 45 ℃ for 24 h, after which the delamination states of the coatings were photographed and recorded.

2.5.2 Rheological behavior

Rheological measurements of the waterborne coating samples NFC0.2, HEC0.8, and the reference sample were performed using a rotational rheometer (Bohlin Gemini II, Malvern Instruments Co., Ltd., UK). The "viscometry" measurement mode was selected for the experiment. The shear rate was controlled and varied continuously. The sample was measured by sleeve rotor with a diameter of 40 mm, and the gap was set to 150 μm. For the shear rate, the measurement range was set to 0−400 s^{-1}, and the scanning time was 200 s.

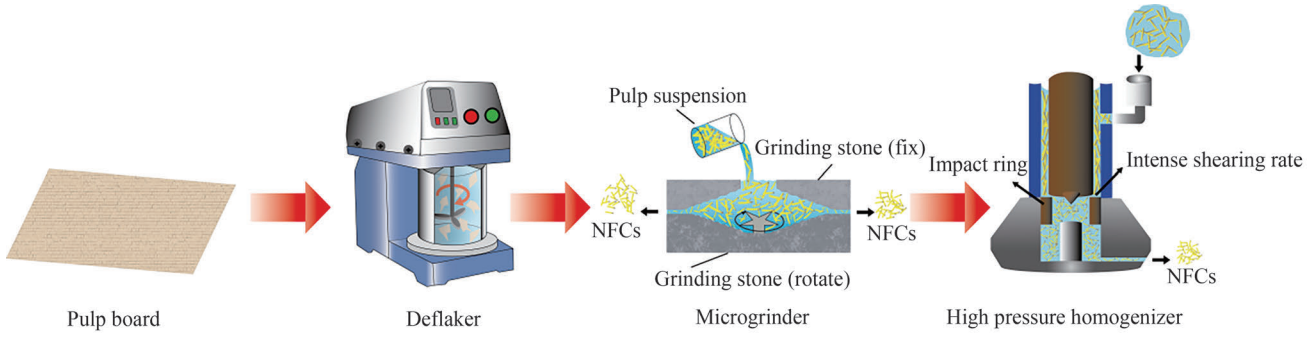


Fig. 1 Preparation process of NFC

2.5.3 Yield stress

The yield stress of the waterborne coating samples NFC0.2 was tested at both room temperature and 45 ℃ on the rotational rheometer. The experiment selected the "viscometry" measurement mode. The shear stress was tested with a sleeve rotor at a measurement spacing of 150 μm and the stress was controlled within a range of 0−5 Pa, and the scanning time was 100 s.

2.5.4 Viscosity

The viscosity of the waterborne coating samples NFC0.2, HEC0.8, and reference sample were measured using a rotational viscometer (NDJ-5S, Shanghai Balance Instrument Co., Ltd.) at 60 r/min under room temperature and 45 ℃.

3 Results and discussion

3.1 Chemical structure and microscopic morphology of NFC

Fig. 2 shows the FT-IR spectrum and SEM image of NFC. The strong and wide band at approximately 3400 cm^{-1} was attributed to the —OH stretching vibrations of the hydroxyl groups, while the absorption peak at 2908 cm^{-1} was likely associated with the —CH_2 stretching vibrations. The absorption peak at 1645 cm^{-1} is associated with the —OH bending of absorbed water. Moreover, the absorption peaks at 1436 cm^{-1} (—CH_2 scissoring), 1062 cm^{-1} (C—O stretching), and 896 cm^{-1} (β-glycosidic linkage of cellulose) were referred to the typical cellulose. In the SEM image, a portion of the dried NFC samples exhibited filamentous and interwoven fiber network structures, whereas the majority exhibited membrane-like structures, which is probably because of hydrogen bonding of the NFC during sample preparation. The NFCs obtained by Ji et al [19], using ultraparticle mills combined with a high-pressure homogenizer, also had similar network structure.

3.2 Analysis of stationary test for waterborne coatings

Fig. 3 shows the delamination of waterborne coatings with NFC or HEC added after standing at room temperature for two months and at 45 ℃ for 24 h. Compared with the reference sample, the coating sample NFC0.2 maintained a good suspension state without complete delamination after two months of standing at room temperature, while the sample with HEC addition couldn't reach the same stationary state as NFC until HEC0.8. In addition, when the waterborne coating was placed at 45 ℃ for 24 h, the suspension state of the waterborne coating sample NFC0.2 resembled that of NFC0.2 placed at room temperature for two months, while the waterborne coating sample HEC0.8 showed obvious delamination, indicating that HEC has poor temperature resistance when used as a suspension stabilizer for waterborne coatings. This phenomenon has also been observed with other inorganic thickeners. For example, Wang [20] improved the storage stability of waterborne coatings at room temperature by adding bentonite to increase their viscosity. However, the coatings exhibited delamination in the heating test, probably due to the sensitivity of liquid viscosity to temperature changes. As the temperature increased, the composite viscosity of the coatings gradually decreased [21]. Stationary experiments

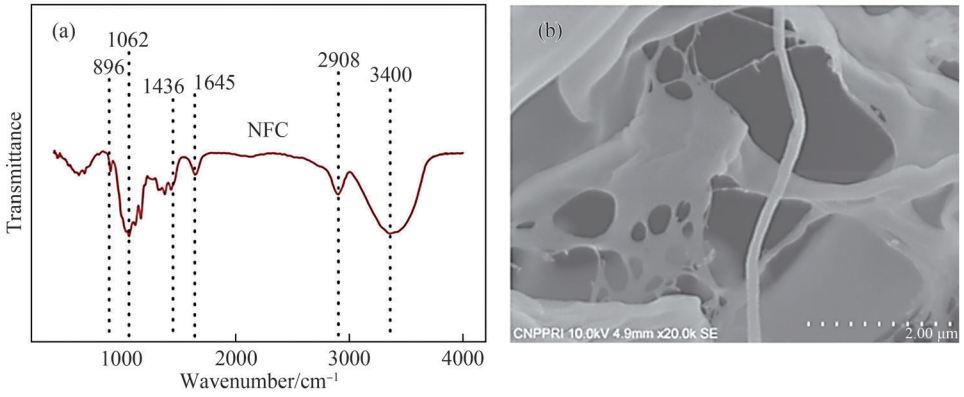
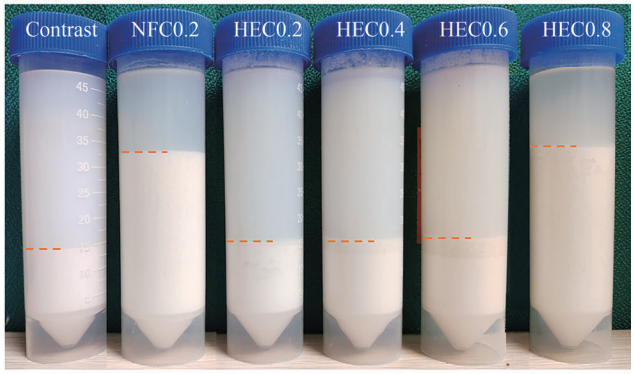
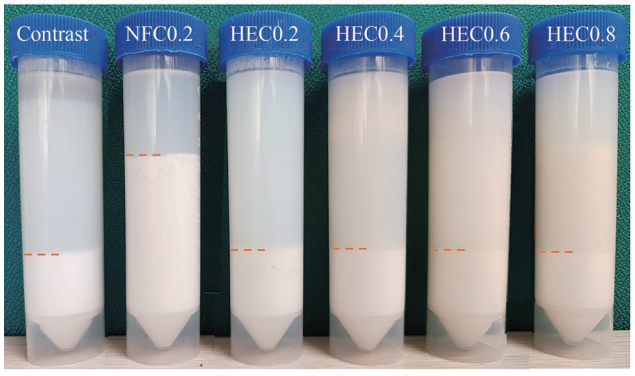


Fig. 2 (a) FT-IR spectrum and (b) SEM image of NFC

showed that both NFC and HEC could improve the suspension stability of the coatings; however, the amount of HEC required was much larger than that of NFC, and HEC was probably affected by temperature. Therefore, compared with HEC, NFC requires a lower dosage and exhibits better temperature resistance when used to improve the storage stability of waterborne coatings.



(a) Store at room temperature for 2 months



(b) Heat at 45 ℃ for 24 h

Fig. 3 Delamination of waterborne coatings with NFC or HEC added and reference samples after standing at room temperature for two months or at 45 ℃ for 24 h

3.3 Viscosity analysis for waterborne coatings

The viscosity tests of waterborne coatings NFC0.2, HEC0.8, and the reference sample were conducted under a low shear rate at room temperature and 45 ℃ using a rotational viscometer. The results summarized in Table 1 reveal that the viscosity of the coatings increased significantly with the addition of NFC or HEC. The increase in the coating viscosity induced by HEC was two orders of magnitude higher than that induced by NFC, indicating that HEC improved the storage stability of the coatings by substantially increasing their static viscosity. Some inorganic thickeners also increase the suspension of coatings via the same mechanism. For example, Jiryaei et al [22] added organic-modified clay to waterborne-acrylic-based coatings, resulting in a significant increase in the composite viscosity of the coatings and no delamination in the accelerated stability test. The results also suggest that, when the storage temperature was increased from room temperature to 45 ℃, the viscosity of the coating containing HEC decreased by nearly 50%, whereas the viscosity of the coating with NFC changed a little. This phenomenon of reduced thickening caused by heating has been observed in other experiments [23]. Studies have shown that the thickening effect of HEC can increase the static viscosity [24], thereby improving the storage stability of the coatings. However, under conditions of high temperature, the thickening effect of HEC reduces, rendering the coatings unable to maintain a high viscosity and leading to delamination of the coatings. The thickening effect of NFC on the coatings is less than that of HEC, indicating that NFC does not improve the suspension stability of the coatings by simply increasing their viscosity. Additionally, the thickening effect of NFC on waterborne coatings was less affected by temperature changes, which may suggest that the mechanism by which NFC improves the storage stability of waterborne coatings probably differs from that of HEC.

Table 1 Rotation viscosity of waterborne coatings

Sample	Rotation viscosity/(mPa·s)	
	Room temperature	45 ℃
Reference sample	2.31	2.28
NFC0.2	246.7	245.2
HEC0.8	28930	14089

3.4 Rheology analysis for waterborne coatings

Fig. 4 shows the shear stress-shear rate curves of the waterborne coatings NFC0.2, HEC0.8, and the reference sample. The rheological curves in Fig. 4 show that the shear stress of all waterborne coatings increased as shear rate increased, and the increase in shear stress was less than that in the shear rate, which is characterized by the

slope of the rheological curve *n* being less than 1, indicating obvious pseudoplastic fluid characteristics. Meanwhile, the rheological curve of the waterborne coating NFC0.2 did not pass through the origin of the coordinate axis, indicating that NFC0.2 is a pseudoplastic fluid with a yield value. Pseudoplastic fluids have a high viscosity at rest or at low shear rates though they exhibit shear thinning at high shear rates [25]. Coating NFC0.2, as a yield pseudoplastic fluid, has a certain yield value, which means that the fluid has a certain resistance to flow, such that the fluid only flows when the applied stress exceeds the yield value [26].

3.5 Yield stress analysis for waterborne coating with NFC

For fluids that have a yield stress, the viscosity peaks with an increase in shear stress, and the shear stress value corresponding to the peak is equivalent to the yield stress of the fluid. Before the yield point, even if the fluid underwent deformation under force, it would maintain its state [27]. The form of the fluid changed only when the applied stress exceeded the yield stress. Fig. 5 shows the viscosity shear stress curves of waterborne coating NFC0.2 at room temperature and 45 ℃. This result shows that the shear stress corresponding to the viscosity peak of coating NFC0.2 at both room temperature and 45 ℃ is the same, approximately 0.774 Pa, indicating that the yield stress of coating NFC0.2 is less affected by temperature. The yield stress of coating NFC0.2 may be provided by the fiber network structure constructed by NFC, wherein the yield stress value is the minimum stress required to break the fiber network. NFC can form a fiber network structure in coatings because of the fiber entanglement generated by the large-aspect-ratio branching chains and the hydrogen bonding effect generated by the abundant hydroxyl groups on the surface [28]. This structure can disperse

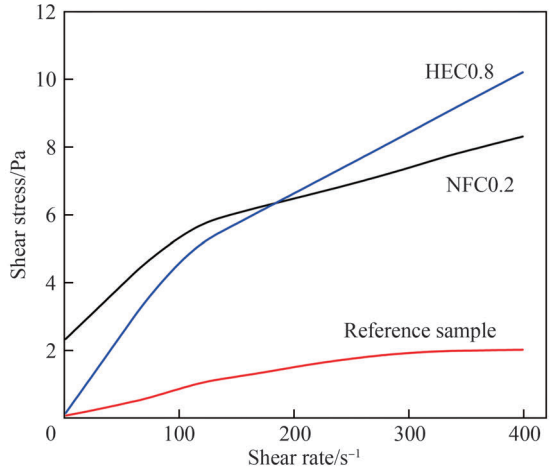


Fig. 4 Rheological curves of waterborne coatings NFC0.2, HEC0.8, and the reference sample

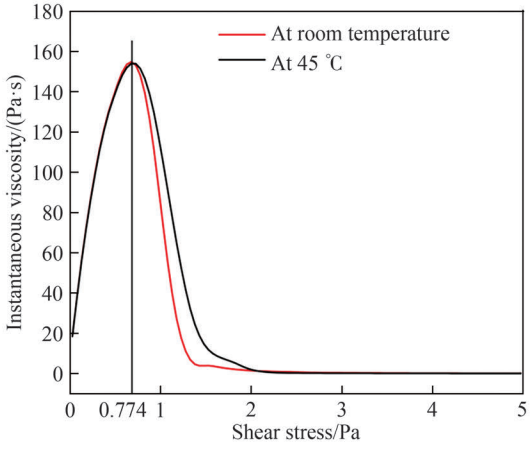


Fig. 5 Yield stress curve of NFC0.2

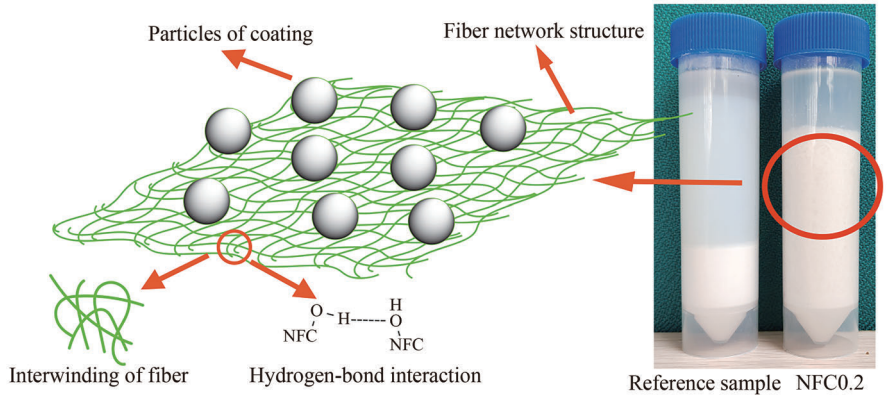


Fig. 6 Mechanism of NFC improving the suspension stability of waterborne coatings

high-density coatings or pigments in the network and prevent their gravity-induced sinking, thereby improving the suspension stability of the waterborne coatings.

4 Conclusion

In this study, the effects of nanofibrillated cellulose (NFC) and hydroxyethyl cellulose (HEC) on the storage stability of waterborne coatings were compared, and the mechanism of NFC improving the suspension stability of the coatings was explored. The results showed that the addition of either 0.8 g HEC or 0.2 g NFC can significantly improve the storage stability of waterborne coatings when placed at room temperature for at least two months. However, when the waterborne coatings were placed at 45 ℃ for 24 h, the improvement effect of HEC weakened on the storage stability of coatings, while the improvement effect of NFC was less affected with temperature changing. Rheological and viscosity analyses showed that HEC mainly achieves suspension stability by increasing the viscosity of the coating, which is significantly affected by temperature. In contrast, NFC improves the storage stability of the coatings probably by forming a fiber network to prevent the gravitational settling of the coating particles, which is relatively affected less by temperature. Therefore, adding a small amount of NFC in the waterborne coatings could help solve the delamination problem that occurs when the storage temperature increases. These findings will advance the application of NFC in coatings and broaden the application scopes of nanocellulose.

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