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EFFECT OF VARIOUS CELLULOSE DERIVATIVES ON THE PROPERTIES OF PIGMENT COATINGS: A COMPARATIVE STUDY

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Due to the low-cost, earth-abundant availability and eco-friendly characteristics, cellulose derivatives (CDs) are being increasingly used as co-binders in the production of pigment coatings. In the present work, a comparative study on the effect of nanocrystalline cellulose (NCC) and sodium carboxymethyl cellulose (CMC) on the colloidal stability and rheological properties of pigment coatings was carried out. The sedimentation stability assessment results indicated that NCC replacing CMC significantly improved the colloidal stability of pigment coatings. In the presence of NCC, the resulting coatings showed no indication of sedimentation within a 48-hour storage period. Moreover, the rheological measurements revealed that all pigment coatings exhibited a strong shear-thinning behavior as the shear rate varied from 0 to 100 s^{-1}. When further increasing the shear rate, the pigment coatings containing NCC tended to experience a shear-thickening behavior. More importantly, NCC was found to impart lower viscosity to pigment coatings in comparison with CMC. The presence of NCC resulted in a marked decrease in average particle size of coatings, implying that NCC might act as an efficient dispersion agent in pigment coatings. In addition, it was observed that the incorporation of NCC in pigment coatings offered a relatively uniform coating layer and was effective in enhancing the hydrophobicility of coated paper.

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Keywords: Cellulose derivatives (CDs); Pigment coatings; Nanocrystalline cellulose; Colloidal stability; Microstructure

1. Introduction

Paper is a versatile material with many uses and it is mainly made of natural cellulosic fibers derived from renewable bio-resources including wood and non-wood lignocellulosic materials [1]. In the production of traditional printing papers, various kinds of coatings deposited onto the surface of base paper are very common practice.

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The paper industry in particular has widely recognized decades ago the importance of pigment coatings on the surface properties of coated paper [2]. In general, pigment coatings consist of three main components. There are mineral pigments, synthetic or natural binders and other functional additives [3]. Being the most important component of paper coatings, pigment can offer cost and energy savings and also improve the optical properties, dimensional stability as well as printability of the cellulosic paper [4]. Binder is an essential part in paper coatings. In addition to performing their basic desired role of binding pigment particles to each other and binding them to the substrate [5], binders also play an important role in enhancing the properties of the pigment coatings and coated paper.

Apart from pigment and binder, co-binder can be considered as another important ingredient. It is commonly used to modify the rheological behavior and water retention of paper coatings to satisfy the demands of specified coating processes. In recent years, the application of water-soluble CDs as co-binders in paper coatings has received great attention due to the increasing popularity for natural-based, environmentally friendly products [6-8]. Moreover, it is generally accepted that water-soluble CDs can be favorable for preventing the free water from flowing out from paper coatings, thus subsequently modifying the properties of coated paper. CDs can also be employed to advance the rheological behavior of the paper coatings, making them more viscous and suitable for coating process. It is well known that CMC is typically characteristic of water-soluble CDs, which can be easily used as co-binders in pigment coatings. Lately, NCC, an emerging renewable nanomaterial derived from naturally occurring cellulose, has been an eye-catching candidate in various application areas. There is a presence of references related to the application of NCC with the goal of improving the performance of traditional products. For instance, Huq et al. [9] developed a renewable and biodegradable alginate based nano-composite films by incorporating NCC for food-packaging applications and found that the mechanical and barrier properties of the alginate-based matrix were significantly increased. Azizi Samir et al. [10] dissolved polyolefin elastomer in water and mixed with NCC to obtain desired solid films by casting and evaporating the products. Besides, Lalia et al. [11] used NCC to reinforce electrospun poly (vinylidenefluoride-co-hexafluoropropylene) nano-composite separators. Kaboorani et al. [12] reported the utilization of NCC as a wood adhesive to improve the performance of polyvinyl acetate.

To our knowledge, however, there is still an absence of references associated with the potential utilization of NCC in pigment coatings, particularly in paper coatings. Here, the concept of using NCC to improve the properties of pigment coatings was proposed and implemented. The effects of NCC addition level on the sedimentation stability, rheological behavior of pigment coatings and the particle size distribution, as well as the surface properties of coated paper were investigated. Meanwhile, the role of CMC, one of the conventional water-soluble CDs, in pigment coatings was used as a reference to evaluate the application potential of NCC.

2. Experimental

2.1 Materials

Kaolin, used as primary pigments in this work, was received from a paper mill in Zhejiang Province, China. Ground calcium carbonate (GCC) and nano-sized precipitated calcium carbonate (PCC) were supplied by Ningbo Zhonghua Paper Co., Ltd. Nano-sized PCC can be used to modify the carboxylated styrene-butadiene (SB) latex, which was reported in our previous work [13]. Commercially available SB latex was obtained from BASF. CMC, representing one of the common CDs, was used as co-binders in pigment coatings. The molecular structural formula of CMC is presented in Fig. 1. Microcrystalline cellulose (MCC) powder used to produce NCC via acid hydrolysis process was received from Shanghai Tonnor Material Science Co., Ltd. Sodium hexametaphosphate (SHMP) was supplied by Zhejiang Dongsheng Chemical Reagent Co., Ltd. Tertiary butyl alcohol (TBA), obtained from Shanghai Luer trade Co., Ltd, served as a foam control agent. Optical brightening agent (OBA) was obtained from Zhejiang Yongtai Paper Group Co., Ltd. Sulfuric acid and dialysis bags were purchased from Hangzhou Mike Chemical Instrument Co., Ltd. The base paper for surface coating process was provided by Ningbo Zhonghua Paper Co., Ltd.

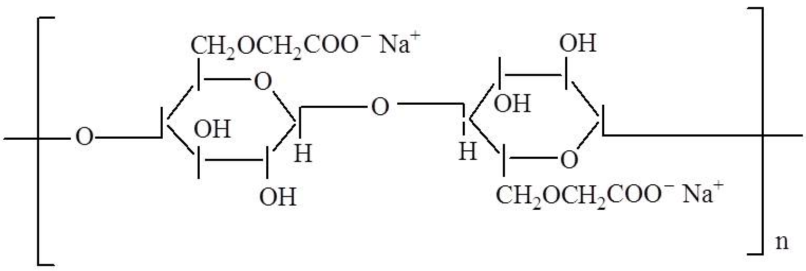

Fig.. 1. The molecular structure formula of CMC [14].

2.2 Preparation of NCC sample

NCC was prepared from MCC using a traditional acid hydrolysis method, which has been described in our recently published work [15]. A specified amount of MCC was poured into sulfuric acid aqueous solution, and then the suspension was reacted for a desired time under stirring condition. The resulting suspension was subsequently required to undergo centrifugation, neutralization and evaporation prior to the occurrence of NCC.

2.3 Preparation of pigment coatings

In this process, the pigment coatings with solid contents of about 55% were made. First, various kinds of pigments including kaolin (70% of total pigment weight), GCC (25%) and nano-sized PCC (5%) were added into the water in presence of 0.5 pph of SHMP. After continuous stirring for 20 min at 2600 rpm, a well dispersed pigment suspension was obtained. Second, 0.5 pph of TBA was added into the above suspension followed by 15 pph of SB latex addition, and then the suspension was stirred for 10 min at 3000 rpm. Third, various amounts of CDs such as NCC and CMC, as well as 0.5 pph of OBA were dispersed into the coatings. Last, the pH of the resulting pigment coatings was regulated at 7.5.

2.4 Preparation of coated paper

Commercially available paper was used as the substrates for paper coating process. The coating process was performed using a laboratory scale ZAA 2300 multi-coater (Zehntner, Switzerland). A specified amount of coating suspension was automatically spread over the base paper with a round steel bar. The coated paper was then dried in an electric heating oven.

2.5 Characterization method

The rheological behavior of paper coatings was measured on a cylinder rotary rheometer (Physica MCR301, Anton Paar, Austria). The particle size distribution of the paper coatings was tested by dynamic light scattering particle size analyzer (LB-550). The morphology of the base paper and coated paper was observed on a ULTRA-55 field emission scanning electron microscope (JEOL, Japan). The hydrophobic properties of coated paper were obtained using a surface and sizing tester (Emtec, EST 12, Germany).

3. Results and discussion

3.1 Effect of various CDs on the sedimentation stability of pigment coatings

Various amounts of CDs were added into the pigment coatings to improve the sedimentation stability. The sedimentation stability of the pigment coatings as a function of various CDs and different storage time was investigated, and the results are listed in Table 1.

Table 1 Effect of various CDs on the sedimentation stability of pigment coatings

CDs addition Level (pph)		***Storage time (h)***		
		12	***24***	***48***
CMC	0.6	extremely slight sedimentation	slight sedimentation	serious sedimentation
	0.7	no sedimentation	extremely slight sedimentation	slight sedimentation
	0.8	no sedimentation	no sedimentation	extremely slight sedimentation
	0.9	no sedimentation	no sedimentation	no sedimentation
	1.0	no sedimentation	no sedimentation	no sedimentation
NCC	0.6	no sedimentation	no sedimentation	no sedimentation
	0.7	no sedimentation	no sedimentation	no sedimentation
	0.8	no sedimentation	no sedimentation	no sedimentation
	0.9	no sedimentation	no sedimentation	no sedimentation
	1.0	no sedimentation	no sedimentation	no sedimentation

As can be seen, the sedimentation stability of the pigment coatings was largely dependent upon the CD variation and the added amount, particularly when extending the storage time up to 48 hrs. When CMC was used as co-binder in pigment coatings, at a lower amount of 0.6 pph, the pigment coatings would exhibit serious sedimentation behavior once the storage time exceeded 48 hrs. A stable suspension could be obtained provided that the amount of CMC was over 0.9 pph. As expected, in the presence of NCC, there was no indication of sedimentation in all of the pigment coatings within 48 h storage time period, greatly satisfying the demands of industrial coating process. As a result, NCC offered significant advantage in improving the sedimentation stability of pigment coatings over CMC. The significant enhancement in sedimentation stability can be probably due to the increased electrostatic repulsion derived from the highly charged NCC particles [16].

3.2 Effect of various CDs on the rheological behavior of pigment coatings

Rheological measurement provides an indirect method to study the interparticle forces of paper coatings, which is particularly important in industrial coating processes [17]. In order to investigate the influence of various CDs on the flow state of pigment coatings, the steady-shear rheological behavior was performed over a wide shear rate ranging from 1 to 1000 s^{-1}, and the rheological curves are presented in Fig. 2- 3. As can be seen, different coating samples appeared to exhibit similar non-linear flow curves, signifying that these coatings represented typical non-Newtonian fluids. Furthermore, it can be observed that the shear viscosity of pigment coatings decreased with the increased shear rate, showing an obvious shear-thinning behavior. It may be due to the fact that a better orientation of the pigment particles would be obtained under strong shear rate [18], thus resulting in the decrease in coating viscosity.

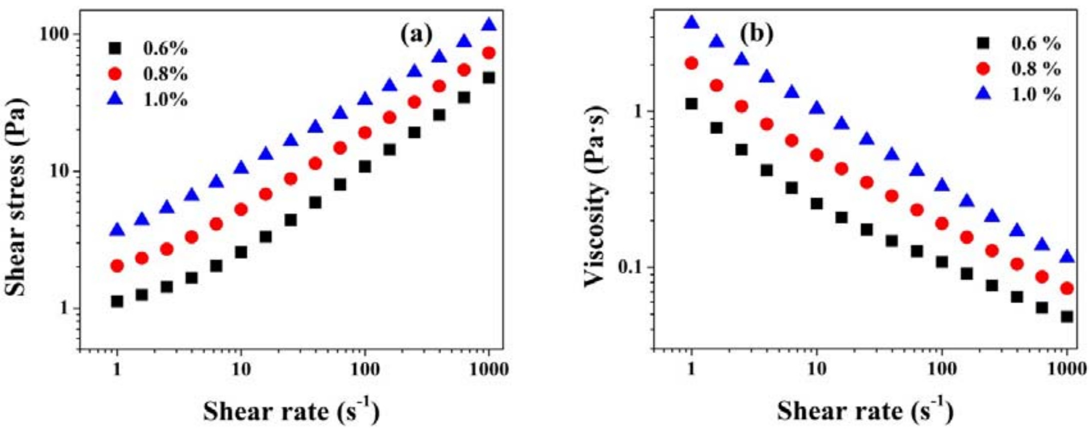

Fig. 2. (a) shear stress and (b) viscosity as a function of shear rate for pigment coatings containing various amounts of CMC

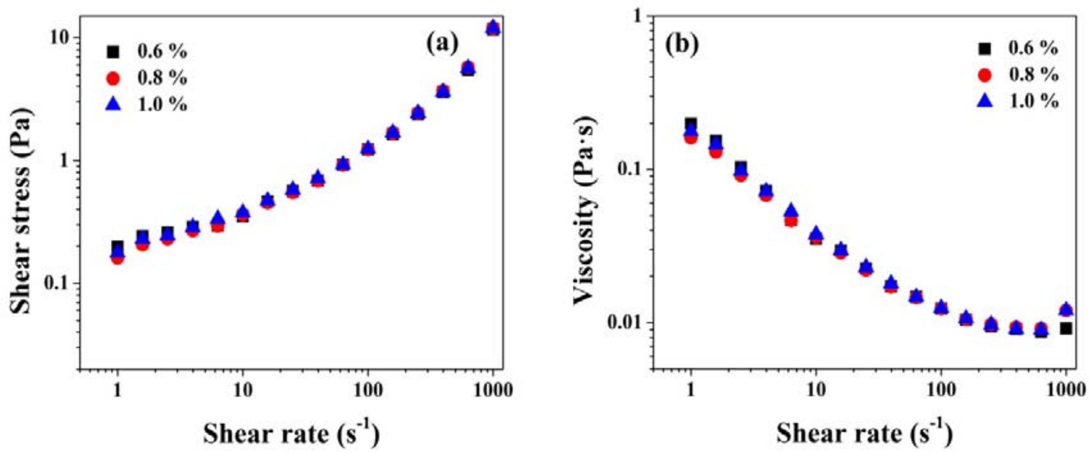

Fig. 3. (a) shear stress and (b) viscosity as a function of shear rate for pigment coatings containing various amounts of NCC

Moreover, apparently, increasing the added amount of CMC was found to lead to the increased viscosity of pigment coatings, greatly exhibiting the shear-thickening effect, which is associated with the increased colloidal forces induced by CMC adsorbing on clay pigment [19]. Alternatively, it was interestingly found that the coating viscosity remained almost unchanged regardless of the added NCC variation. This result is probably attributed to the higher charge density of NCC that resulted in a strong electrostatic repulsion, thereby facilitating the formation of stable coating network structures. Furthermore, it was evident that the paper coatings with NCC addition possessed a lower viscosity in comparison with that with CMC, essentially due to the strong electrostatic repulsion of the highly charged NCC. On another aspect, this result implied that NCC can contribute to the compatibility between pigments and other components, thus promoting the re-dispersion of pigment particles and preventing the agglomeration driven by hydrogen bonding [20, 21]. In this light, NCC can be presumed to act as a good dispersing agent in paper coatings in addition to its co-binder effect, which is particularly vital in the production of high solid content coatings. Meanwhile, another phenomenon should be noted. In the Fig. 3(b), the viscosity curves of NCC experienced two distinct regions as the shear rate increased from 0 to 1000 s^{-1}. Firstly, the viscosity showed a visible decrease with the increase of shear rate, suggesting a shear-thinning behavior. Then, the viscosity tended to ascend with further increasing the shear rate, indicating a shear-thickening behavior. This result did not occur in the rheological curves of the coating samples with CMC. The differences in viscosity curves can be partially ascribed to the structure features of various CDs. It should be pointed out that NCC possesses nano-scale particle structures with huge specific surface area and abundant hydroxyl group, which would make the coating sample more sensitive to shear rate. It can be generally accepted that the network structures of coating suspensions constructed by strong hydrogen or ionic bonding interactions among nanocrystals is easy to be destroyed under the strong shear at the first stage. After that, the network structure is re-built by the nanocrystals again, thus resulting in the increase of viscosity at the second stage [22].

In order to better understand the nature of the rheological behavior of pigment coatings, Herschel-Bulkley (H-B) model was employed to simulate the rheological curves of all coating samples. HB model is a well-established model that can satisfactorily describe the non-Newtonian tested suspensions, which has been introduced and implemented practically in our recent work [23]. The simulated results associated with the experimental data of coating samples using H-B model are listed in Table 2. As can be seen, for the coating samples including CMC, τ_0 and K values tended to go on rising with the increased amount of CMC. As the CMC amount varied from 0.6 to 0.8 pph, the τ_0 value increased from 0.6233 to 0.8612 Pa, which value reached 1.7940 Pa when further increasing the CMC amount to 1.0 pph. On the other hand, the pigment coatings showed similar variation trend in K value with increasing the CMC amount. Apparently, the higher amount of the added CMC, the stronger shear stress required to make the coatings flow [24]. Moreover, the n value of the pigment coatings containing various amounts of CMC was far less than 1.0, which further supported the shear-thinning behavior. More importantly, Table 1 revealed that the incorporation of NCC exerted a significant effect on the flow behavior of coatings. The coatings containing NCC showed a smaller K value than those containing CMC, predicting that the former was easier to flow than the latter. In addition, it should be noted that the coatings showed no clear indication of the change in K and n values in spite of the NCC amount variation from 0.6 to 1.0 pph, which was in good agreement with the shear rheological curves. Last but not least, it can be derived that, as to the pigment coatings containing NCC, all standard errors were more than 20, implying that the rheological behavior of the coating samples with NCC can not be well simulated by H-B model [13].

Table 2 Rheological parameters simulated from the rheological curves of the paper coating samples containing various CDs

CDs level (pph)		τ_0 ***(Pa)***	***K (Pa·s)***	***H-B model***	***Standard error***
	0.6	0.6233	0.4316	τ=0.6233+0.4316$\gamma^{0.6799}$	4.966
CMC	0.8	0.8612	1.1270	τ=0.8612+1.1270$\gamma^{0.6016}$	3.364
	1.0	1.7940	2.3230	τ=1.7940+2.3230$\gamma^{0.5612}$	5.543
	0.6	0.4355	0.0008	τ=0.4355+0.0008$\gamma^{1.380}$	25.78
NCC	0.8	0.4096	0.0010	τ=0.4096+0.0010$\gamma^{1.355}$	23.82
	1.0	0.4437	0.0008	τ=0.4437+0.0008$\gamma^{1.389}$	25.18

3.3 Effect of various CDs on the particle size distribution of pigment coatings

It is generally accepted that the particle size distribution of pigment, binder and even co-binder indeed exerts an important effect on the coating structure, flow state and also the coating processes [25, 26]. As an outcome, the effect of various CDs on the particle size distribution of the paper coatings was investigated, and the results are given in Fig. 4.

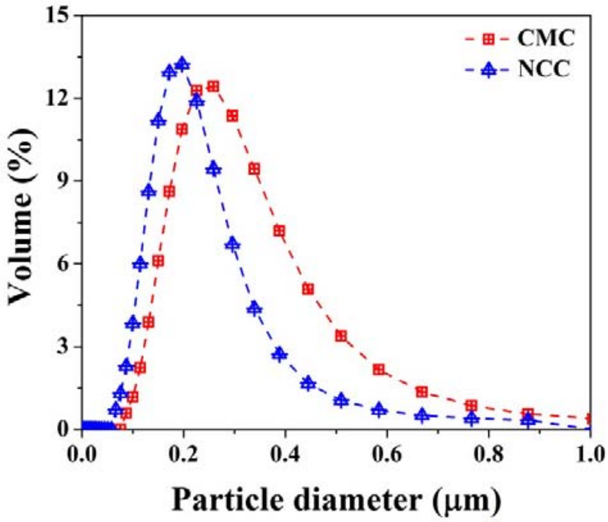

Fig. 4. Particle size distribution of paper coating samples containing 0.8 pph of CMC and NCC

It turned out that the pigment coatings containing NCC or CMC generally exhibited a wide particle size range from 0.1 to 1.0 μm. By contrast, the mean particle size of the coating sample with NCC addition was smaller than that of the coating sample with CMC addition. The intense distribution peak of the coating sample containing CMC was found to locate at about 266 nm; while the sample with NCC generated an intense distribution peak at 200 nm. Consequently, the presence of NCC can lead to the improvement in particle size distribution of pigment coatings, in good agreement with the sedimentation stability assessment and rheological behavior, as discussed above. It further supported the conclusion that NCC could be used as an efficient dispersing agent and lubricant in the production of pigmented coatings, thus subsequently contributing to the formation of coating layers and the properties of the coated paper.

3.4. Effect of various CDs on the hydrophobic properties of coated paper

Hydrophobic properties reflect an important characteristic index of coated paper, signifying the water repellent ability of the surface of coated paper [27]. It mainly depends on the coating layer structure and coating components. In this work, an advanced surface and sizing tester was employed to evaluate the hydrophobic property of all coated paper. The influence of various CDs addition level in the pigment coatings on the hydrophobic property of coated paper was compared, and the results are presented in Fig. 5.

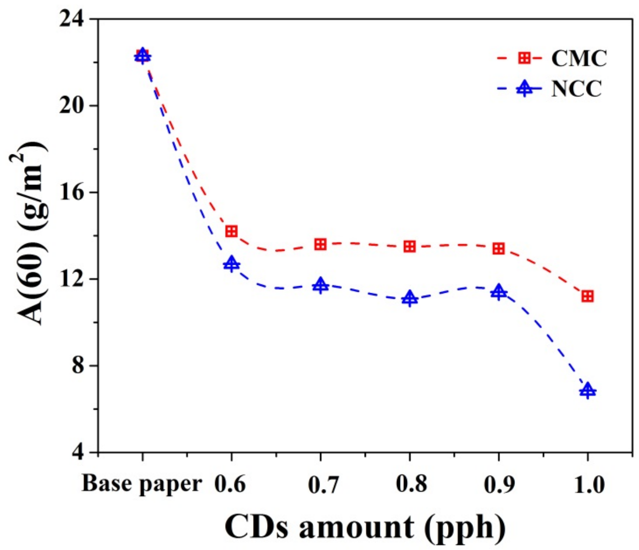

Fig. 5. Hydrophobic properties of the coated paper as a function of the various CDs of CMC and NCC addition in paper coatings

As shown in Fig. 5, A (60), representing the absorbance degree of water into a paper within 60 s. The lower values of A (60), the better hydrophobic properties of the coated paper. It was evident that the A (60) value of coated paper was significantly lower than that of base paper, implying that the hydrophobic properties of paper were greatly improved after coating process. Moreover, with the increase of CD amount, the hydrophobic properties of coated paper can be persistently enhanced. As expected, the coated paper with 1.0 pph NCC was found to possess the lowest A (60), probably attributed to the large specific surface area and high aspect ratio of NCC. The incorporation of NCC can contribute to the formation of a compact coating layer structure, hence reducing the transfer rate of the continuous phase to improve the hydrophobic properties [28].

3.5. Effect of various CDs on the microstructure of coated paper

To better understand the microstructure of coating layer, SEM was employed to observe the surface of coated paper, and the results are illustrated in Fig. 6.

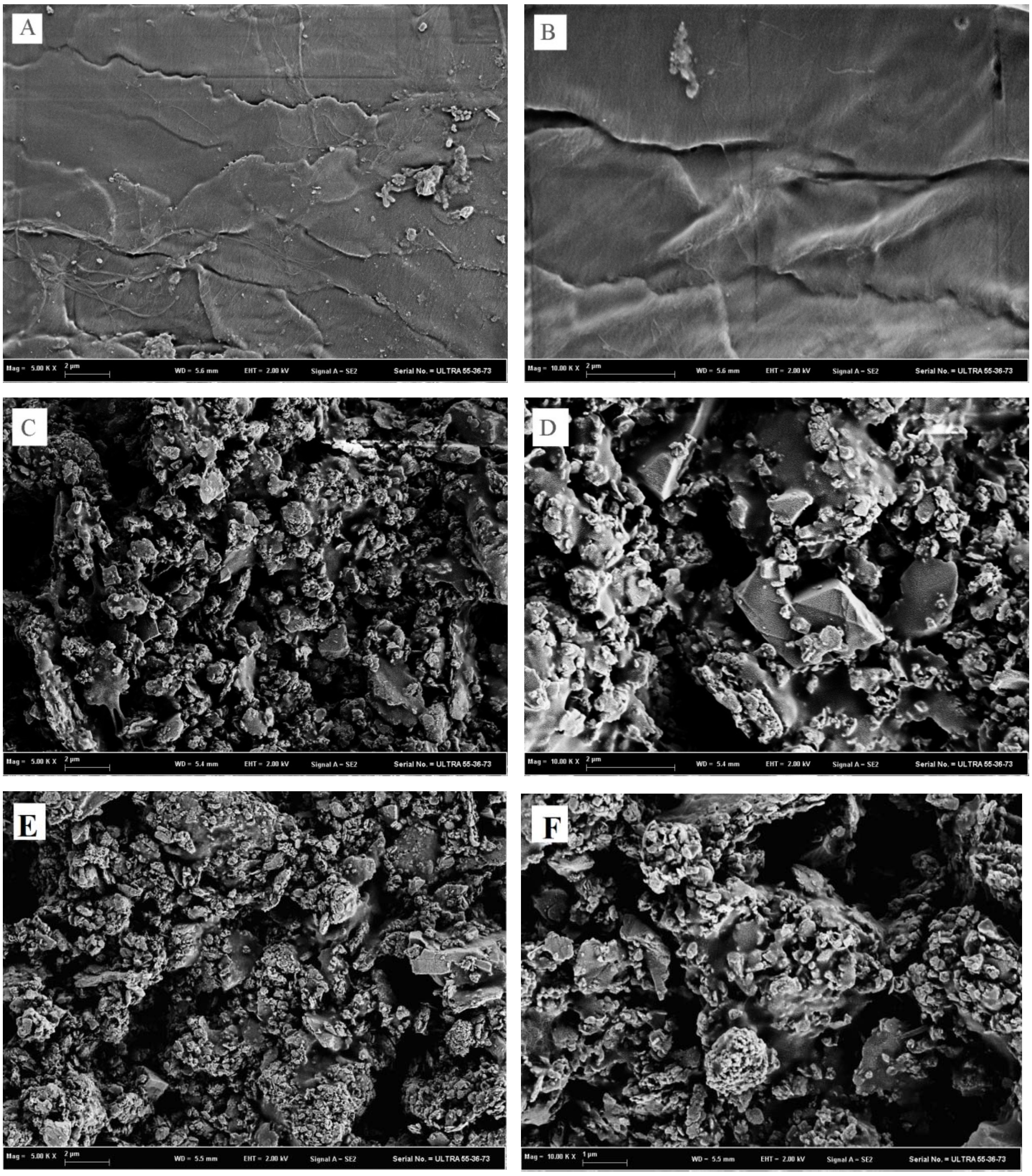

Fig. 6. SEM images of (A,B) base paper, paper coated with coating sample containing 0.8 pph of (C,D) CMC, and (E,F) NCC.

It can be observed that the base paper (Fig. 6A-B) contained extensive interwoven cellulosic fibrils, while the complete absence of visible cellulose fibrils in the SEM images of coated paper (Fig. 6 C-F) gave a significant indication of the coverage of pigments and binders in the coating layer. As can be seen, the coating layer structure appeared to be not homogeneous or uniform, similar to the observation in previously reported work [29, 30]. As a matter of fact, for the paper coated by pigment coatings, the coating network structure was constructed by the binding of pigments and binders, naturally exhibiting rough and full of high porosity on the surface structure. However, in general, NCC was found to render relatively more uniform to the coating layer of coated paper in comparison with the MCC, which would contribute to the optical properties and printability of coated paper.

4. Conclusions

The concept of using nanocrystalline cellulose to modify the sedimentation stability and rheological behavior of pigment coatings was proposed and implemented. The results showed that, in comparison with the conventional cellulose derivatives such as CMC, NCC was found to impart better sedimentation stability and lower viscosity to the pigment coatings. Moreover, the presence of NCC was found to be effective in the improvement in particle size distribution of pigment coatings. All of these results supported the conclusion that nanocrystalline cellulose can serve as an efficient dispersing agent or lubricant in addition to exhibiting its inherent co-binder effect in paper coatings. More importantly, NCC was also proved to exert a positive effect on the enhancement in the uniform structure of coating layer as well as the hydrophobic properties of coated paper.

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