FABRICATION AND PROPERTIES OF PAPER COATINGS WITH THE INCORPORATION OF NANOPARTICLE PIGMENTS: MICROSTRUCTURE AND PRINTABILITY OF COATED PAPER

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Nanoparticle pigments hold great promise for paper coating application targeting to improve the physical and optical properties of coated paper. In our previous work, the incorporation of TiO_2 and $CaCO_3$ nanoparticles was found to exert an important and significant effect on the rheological behavior of paper coatings. The objective of the current work was to investigate the influence of adding TiO_2 and $CaCO_3$ nanoparticles into conventional paper coatings on the properties and surface structure of coated paper. Results revealed that the addition of TiO_2 and $CaCO_3$ nanoparticles had a significantly positive effect on the overall properties of coated paper. The surface strength, opacity and smoothness of coated paper basically increased with the increased addition of nanoparticle pigments. It appeared that the optimum addition level of nanoparticle pigments was 12% with respect to the paper properties. SEM images provide further evidence that the addition of nanoparticle pigments conferred a relatively regular surface structure to the coated paper. This work might be a solid step forward towards the development of advanced paper coatings and high-value added coated paper.

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1. Introduction

The paper industry is constantly looking for new ideas for enhancing paper products due to ever-increasing cost pressures and competitive challenges. In this sense, surface coating technology offers a cost-effective and low-risk way to improve the optical properties and printability of cellulosic paper [1, 2]. Paper coating, a fairly well mixed colloidal suspension, generally consists of inorganic pigments such as kaolin and calcium carbonate, binder and thickener as well as additives for control of pH, friction, brightness and pigment dispersion [3]. In general, pigment is the most abundant component in paper coatings, and therefore is the most

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essential factor controlling the overall properties of paper coatings and even coated paper [4]. There may be only one kind of pigment in a coating formulation, or there more commonly may be several. Pigments were required to be well dispersed in paper coatings as very small particles; in practice, the size of almost all coating pigment particles is less than 10 μm [5]. As a matter of fact, particle shape, size and size distribution play an important role in governing the coating rheological behavior and the final properties of coated paper [6]. Specifically, pigment particle shape is advantageous for improving the coating structure through physical hindrance. Furthermore, particle size distribution and shape of the pigments also play a vital role in controlling the pore size and pore volume of the coating as a result of the change in packing characteristics of the pigment. These further have a direct influence on the paper properties, e.g., smoothness, gloss and printability [7].

In order to meet the production demands of high-quality coated paper, various kinds of pigments were increasingly employed to modify and/or upgrade the properties of conventional paper coatings. In particular, this creates attention towards the development of novel raw materials for paper coating application. Typically, nanoparticle pigments have attracted considerable attention both in academic and industrial sectors in recent years due to their unique optical, electrical, and catalytic properties that differ from that of bulk materials. All these unique properties make them available for use as functional pigments which would be expected to enhance the overall properties of coated paper [8]. In our previous work [9], we focused on the influence of TiO_2 and $CaCO_3$ nanoparticles on the rheological and colloidal properties of paper coatings, and the role of several major factors including solid content, binder, thickener and dispersant amount was systematically discussed. Furthermore, the classical rheological model was employed to fit the as-obtained data derived from rheological experiment. In the current work, the influence of adding TiO_2 and $CaCO_3$ nanoparticles into conventional paper coatings on the properties of coated paper was investigated, and the surface structure of coated paper was characterized by SEM. This work would be a solid step forward towards the development of advanced paper coatings and high-value added coated paper.

2. Experimental

2.1 Materials

The main components of paper coatings were previously described in an earlier work [9]. In brief, kaolin, representing the main pigment, was purchased from China International Medicine Co. Ltd. Nano-scale TiO_2 and $CaCO_3$ particles were received from Asia Pulp & Paper Co. Ltd. Commercially available cationic starch, used as a binder, was supported by Hangzhou Paper Technology Co., Ltd., China. Hydroxyethyl cellulose (HEC) was obtained from Aladdin and served as a co-binder. Additionally, sodium hexametaphosphate, tert-butyl alcohol and sodium hydroxide used as dispersant, foam control agent and pH control agent, respectively, were appropriately added into the tailored paper coatings. Cellulosic paper was received from a paper mill in eastern China and then used as substrates for surface coating process.

2.2 Preparation of paper coatings

In a typical preparation process, initially, the required pigments (i.e., kaolin and nanoparticle pigments) were well dispersed (GFJ-0.4, IKA RW 20) in water with the aid of dispersing agent. Afterward, the binder and co-binder were added into the above suspensions. To achieve the best possible coating quality, some other chemicals, e.g., foam control agent, pH control agent were also used. Subsequently, the pH value of paper coatings was adjusted to 8.5 with sodium hydroxide. Eventually, the targeted paper coatings passed through a 100-mesh screen for impurity removal. In order to evaluate the influence of nanoparticle pigment addition on the physical and optical properties of coated paper, various amounts of nanoparticle pigments (based on dry weight of total pigment) at 4, 8, 12, 16 and 20 % were added into the above coating suspensions.

2.3 Preparation of coated paper

The well-dispersed paper coatings were coated on the surface of base paper using a laboratory scale multi-coater (ZAA 2300, Zehntner, Switzerland) at a constant coating speed of 10 m/min. The coated paper was then oven dried at 105 °C for 60 s. The dry coat weight was controlled at about 10 g/m^2. To deepen the understanding within the present project, the surface application configuration of paper coatings on the surface of cellulosic paper was demonstrated in Fig. 1.

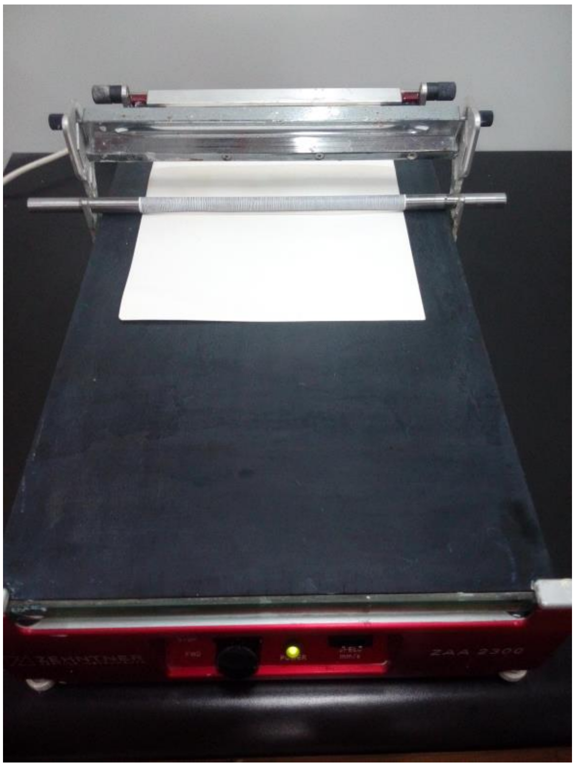

Fig. 1. Surface application configuration of paper coatings onto cellulosic paper

2.4 Characterization and analysis

The microstructure of TiO_2 nanoparticles and coated paper was observed using a field emission scanning electron microscopy (FE-SEM) (ULTRA-55, JEOL, Japan) with an accelerating voltage of 1.00 kV. All samples were coated with gold to avoid charging prior to determination. The morphology of $CaCO_3$ nanoparticles was characterized by transmission electron microscopy (TEM) (JSM-2100, JEOL, Japan), using an accelerating voltage of 80 kV. The measurement of surface strength, smoothness and opacity of coated paper followed the relevant TAPPI test methods.

3. Results and discussion

3.1 Characterization of kaolin and nanoparticle pigments

The microstructure of kaolin, TiO_2 and $CaCO_3$ nanoparticles was characterized by SEM and TEM, respectively, as shown in Fig. 2. It can be observed that kaolin sample exhibited a layered structure and tended to form large agglomerates (Fig. 2(a)). A typical SEM image in Fig. 2(b) shows the aggregated state of TiO_2 nanoparticles, which was much more serious in comparison to the observation reported in an earlier work [10]. In view of the results of TEM, the structure of calcium carbonate nanoparticles with a particle size of 100-200 nm was evident, although some agglomerated nanoparticles can be observed (Fig. 2(c, d)). To obtain maximum benefits from a pigment, especially from the view of industrial application, it should be noted that all agglomerated particles must be separated from each other and well-dispersed. Poor dispersion of pigment particles would inevitably cause problems when going through surface coating process, thereby resulting in undesirable paper properties, e.g., low gloss, low smoothness and poor surface strength. As a consequence, related factors should be considered involving proper equipment and appropriate use of chemicals with the purpose of obtaining satisfactory dispersion [11].

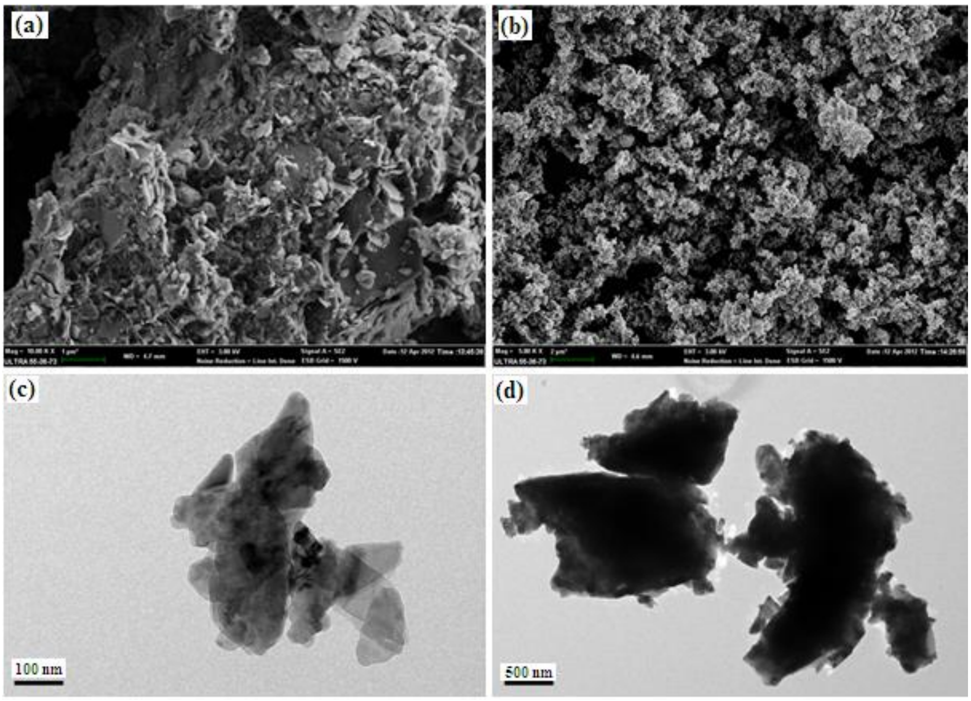

Fig. 2. SEM images of (a) kaolin, (b) TiO_2 nanoparticles; TEM images of (c) and (d) $CaCO_3$ nanoparticles with different magnification

3.2 Influence of nanoparticle pigment addition on particle size distribution of paper coatings

Fig. 3 shows the particle-size distribution of the paper coatings without and with different amount of nanoparticle pigments. As illustrated in Fig. 3, the particle size distribution of all paper coatings presented a uniform single-peak curve, implying that nanoparticles exhibited a desired dispersion into paper coatings in general. Specifically, the size distribution of the paper coatings without nanoparticles ranged from 296 to 1318 nm. In contrast, for those paper coatings with nanoparticle pigments, the volume ratio of small particles was obviously larger than the one without nanoparticle pigment, as can be observed in Fig. 3. Besides, the histograms of the particle size distribution of coatings exhibited peak value information. The peak value of paper coatings without nanoparticles was the same as that of the one with 4% nanoparticles. Whereas, the samples with 8, 12, 16 and 20% nanoparticles took on a histogram with a relatively low-level peak value, suggesting the contribution of nano-scale particles to the decreased average particle size of overall paper coatings.

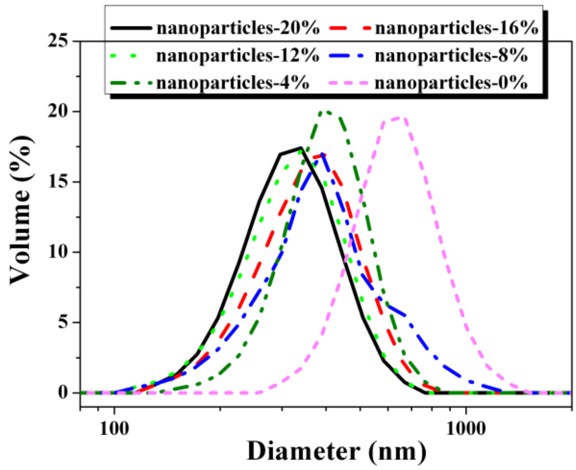

Fig. 3. Influence of nanoparticle amount on particle size distribution of paper coatings (Paper coating formulation: kaolin 80-96 %, the weight ratio (1:1) of TiO_2 to $CaCO_3$. Based on the total weight of pigment, cationic starch 12 pph, HEC 0.4 pph, dispersant 0.6 pph. Solid content of paper coatings 55 wt%）

3.3 Influence of nanoparticle pigment addition on surface strength of coated paper

Paper surface strength is an important property for modern multicolor printing using the offset process [12]. It is often used to describe the strength between the coated paper surface and inks, varnishes or films. The surface strength of coated paper was evaluated as a function of nanoparticle pigment addition dosage, and the results are shown in Fig. 4. It is evident that the incorporation of nanoparticle pigment had an important effect on the surface strength of coated paper. In the absence of nanoparticle pigment, the surface strength was only 91 cm/s; while, the surface strength was greatly improved with the increased addition dosage of TiO_2 and $CaCO_3$ nanoparticles. Specifically, when the addition level was 4, 8%, the surface strength increased to 106, 107 cm/s, respectively. It appeared that the optimum addition level was 12%, at which point the surface strength reached the highest value. When further increasing the addition dosage, the surface strength did not increase but decrease slightly. This unexpected observation may be largely attributed to the interaction between bio-latex and nanoparticle pigments. It is well known that the added latex is responsible for binding pigment particles to each other and bonding them to the surface of cellulosic paper. Based on this rule, it can be inferred, when the nanoparticle amount was below 12%, the incorporation of nanoparticles can promote the interaction among three or more components of coating suspensions, which essentially played an important role in establishing a multipoint bridging capability. However, excessive nanoparticle amount would possibly exert a negative influence on the surface strength. The above results might support the conclusion that the required binder amount should be increased when nanoparticle pigments were used in paper coatings mainly due to the higher specific surface area of nanoparticle pigments.

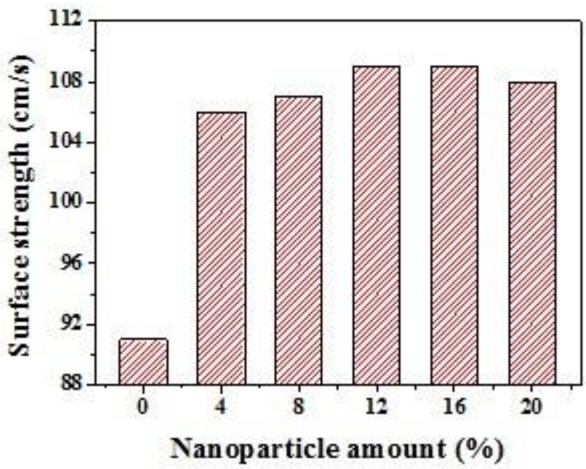

Fig. 4. Influence of nanoparticle amount on surface strength of coated paper (Paper coating formulation: kaolin 80-96 %, the weight ratio (1:1) of TiO_2 to $CaCO_3$. Based on the total weight of pigment, cationic starch 12 pph, HEC 0.4 pph, dispersant 0.6 pph. Solid content of paper coatings 55 wt%)

3.4 Influence of nanoparticle pigment addition on smoothness of coated paper

Surface smoothness is one of the key paper properties when it comes to printing application. For this purpose, a novel technology that combines hot press drying and curtain coating was proposed to produce high quality coated paper [13, 14]. It was considered that hot press drying decreased the coating penetration, resulting in improved surface smoothness. The role of pigment composition on the smoothness of single or double coated paper was also evident. Herein, the smoothness of coated paper was investigated by changing the nanoparticle addition amount, and the results are shown in Fig. 5. It can be observed that the coated paper basically exhibited an overall uptrend in surface smoothness with the increased addition amount of nanoparticle pigments.

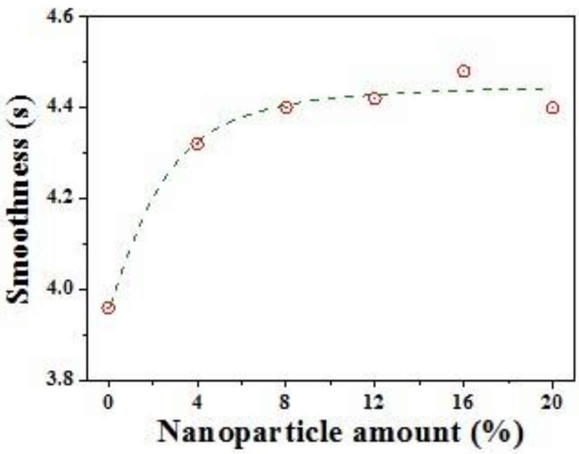

Fig. 5. Influence of nanoparticle amount on smoothness of coated paper

3.5 Influence of nanoparticle pigment addition on opacity of coated paper

Opacity is a diffuse reflectance from a single sheet with black background divided by the intrinsic reflectance factor [15]. It represents a desirable property of a paper to diminish the visibility of prints which are on the opposite of the viewing direction. Actually, it is feasible to achieve high-quality coated paper with desired opacity by tailored combination of related pigments [16]. Fig. 6 presents the opacity of coated paper as a function of various nanoparticle addition amounts. As can be seen, with the increase of nanoparticle amount from 0 to 20%, the coated paper exhibited a continuous and significant increase in opacity. This result is consistent with the results reported in the literature [17, 18]. The improvement in opacity of coated paper may be due to the following aspects: 1) higher inherent brightness of nanoparticle than that of conventional pigment is helpful to improve the percentage reflectance of light from a coated paper surface at a related wave length; and 2) small size effect and tremendously surface effect of nanoparticle can contribute to the reinforcement of wet coating structure, hence improving the coverage of base paper to produce a coating layer with good opacity.

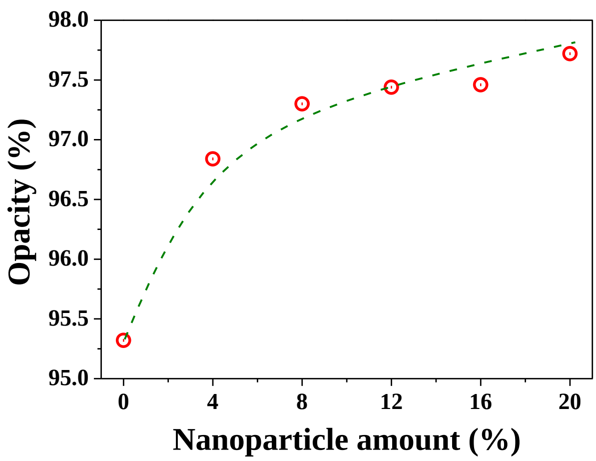

Fig. 6. Influence of nanoparticle amount on opacity of coated paper (Paper coating formulation: kaolin 80-96 %, the weight ratio (1:1) of TiO_2 to $CaCO_3$. Based on the total weight of pigment, cationic starch 12 pph, HEC 0.4 pph, dispersant 0.6 pph. Solid content of paper coatings 55 wt%)

3.6 Microstructure observation of coated paper

A SEM analysis has been performed to understand the interaction between coating components on the base paper under controlled laboratory conditions. In many cases, the base paper makes up the majority (50-80%) of the final product. The properties of base paper are very important for the final coated paper. Fig. 7(a) shows the SEM image of base paper surface. It can be seen that the base paper contains interlaced cellulose fibrils and some functional additives. During the course of the papermaking, a large number of inter- and intramolecular bonds of wood were broken. By applying different kinds of functional additives, additional new bonds were usually created to confer desired qualities to the paper. SEM image depicting the surface morphology of coated paper surface is shown in Fig. 7(b). The complete absence of visible cellulose fibrils in the SEM image of coated paper confirms the uniform distribution and coverage of pigments. The observance of the bulk shaped structure covering the entire surface of the base paper (as seen in Fig. 7(a)) can be due to the deposition of the kaolin phase during the drying process.

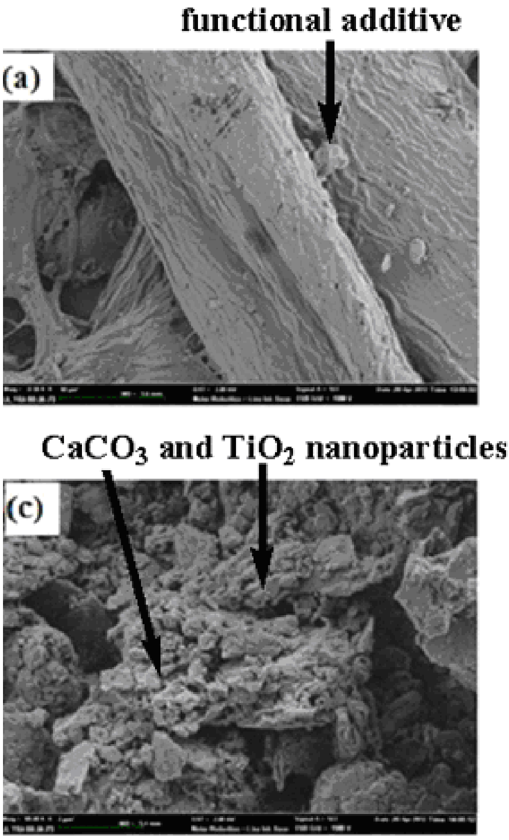

Fig. 7. SEM images of uncoated and coated paper surface: (a) uncoated paper; (b) coated paper formed from paper coatings without nanoparticles; (c) coated paper from paper coatings with 4% nanoparticle pigments.

However, it should be noted that the top coating layer appeared very rough and full of high porosity, as presented in Fig. 7(b). This unexpected result was similar to that derived from a SEM study regarding the surface structure of mineral pigments, latices and thickeners used for paper coating on non-absorbent substrates [19]. In the previous work, the presence of rough surface with a great number of surface pores was attributed to the incorporation of HEC in paper coating. HEC is a non-ionic polymer, known to flocculate kaolin particles and also to bind to calcium carbonate [20]. And so, paper coatings with HEC exhibited a greater number of surface pores. Similar phenomena are also shown in Fig. 7(c), in which nanoparticle pigments were coated on the surface of base paper which was expected to improve the smoothness, opacity and surface strength of coated paper. It should be pointed out that it is not possible to quantify the surface roughness or porosity using image analysis techniques and therefore these judgments are made by subjective evaluation of the images [21, 22].

SEM images of coated paper surface (Fig. 8) show that it is difficult to differentiate coating layer from paper, particularly when the two materials interpenetrate each other. For a better observation of paper coating layer interface, cross-sections of coated paper formed from paper coatings without and with 4% nanoparticles were visualized by SEM after specific treatment (Fig. 8). In Fig. 8(a), the coated layer without nanoparticles appeared irregular and was completely separated from the paper sheet. However，a continuous and regular structure of coated layer could be obtained and presented in Fig. 8(b). Except for its apparent homogeneity, SEM image of coated layer with nanoparticles reveals the presence of inclusion zones, suggesting the penetration of coating into cellulosic paper. In contrast, see Fig. 8(a), although the coated layer without nanoparticles appears irregular and rather disrupted, it exhibits no penetration into base paper.

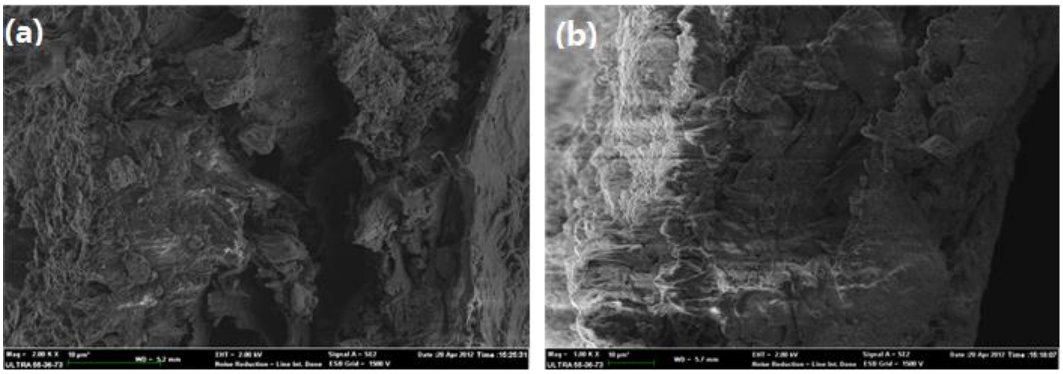

Fig. 8. SEM images of cross-sections of coated paper: (a) coated paper formed from paper coating without nanoparticles; (b) coated paper formed from paper coatings with 4% nanoparticle pigments.

4. Conclusions

To describe the role of adding nanoparticle pigments on the optical properties and surface properties of coated paper, the surface strength, smoothness and opacity of various coated paper samples were measured. A continuous increase in both smoothness and opacity can be expected with the increased nanoparticle pigment amount from 4% to 20%. The surface strength of coated paper increased first and then decreased as a function of the added nanoparticle pigments, and the optimum total nanoparticle amount was 12%. SEM images confirmed that a coating layer containing nanoparticle pigments was formed on the surface of base paper, which was probably responsible for the improved smoothness, opacity and surface strength of coated paper. From the SEM image of cross-sections of coated paper, the coated layer without nanoparticles appeared irregular and was completely separated from the base paper. Conversely, a continuous and uniform coating structure was observed on the surface of cellulosic paper when nanoparticle pigments were used.

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