SURFACE SIZING APPLICATION OF WATERBORNE EPOXY RESIN ON LOW BASIS WEIGHT PAPER

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Reducing basis weight could lead to huge savings of forest resources as well as energy consumption and waste treatment in the papermaking process. However, low basis weight paper generally lacks normal strength and stiffness. The lower the basis weight of the paper, the more important is surface sizing. Highly cross-linked cured epoxy resin, due to its epoxy group and phenyl group, has gained such outstanding mechanical properties and dimensional stability that it could be utilized to enhance paper strength and stiffness through surface sizing when incorporated with oxidized starch. In this study, the impacts of sizing volume, fluid temperature, curing agent, and curing system dosage on sizing were investigated. Our results indicated that a rigid resin layer and interpenetrating polymer network formed on the surface and in the inner layer of the paper, respectively. The formed resin layers strongly support the paper and thus resulted in the improvement of strength and stiffness.

Keywords: Waterborne epoxy resin; Surface sizing; Tensile strength; Stiffness; Surface strength

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INTRODUCTION

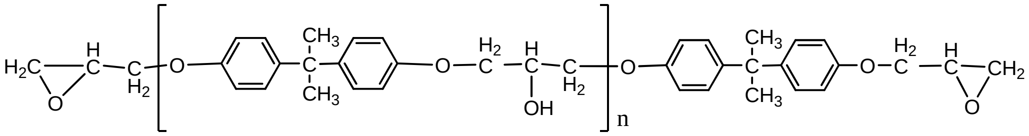
Reducing basis weight is gaining popularity and momentum as an effective way to save forest resources and energy consumption as well as "three wastes" (waste gas, waste water, and waste residues) treatment costs in the papermaking process. However, original production technology is facing new challenges due to its insufficient strength, opacity, and stiffness, as well as print-through in low-basis weight paper (Li et al. 2011).

Recent research efforts have been applied to improve paper strength, stiffness, and to modify the related mechanisms (Sun et al. 2010; Yan et al. 2009). It has been reported that bond strength between fibers is crucial in sheets with low density and strength (Page 1969). Cationic starch, being positively charged, is an important strength-enhancing agent. On one hand, it can enhance the bond interconnections between fibers. On the other hand, it can control process-water as well as enhance the paper strength by ameliorating the efficiency of process agents (Luo and Wang 2010). Chitosan and its derivatives as additives in paper formation have positive impact on strength and dielectric properties (Nada 2006); Incorporation of chitosan nanoparticles in hydroxypropyl methylcellulose (HPMC) films significantly improves their mechanical behavior, film barrier properties as well as thermal stability (de Mour and Aouada 2009). Nanocomposites made by molasses (a byproduct of the sugar industry), natural cellulose fibers and kaolin retain larger amounts of kaolin while exhibiting greater strength than that of molasses-free counterparts (Fahmy and Mobarak 2009). Both water-soluble polyurethane (Jiang et al. 2010) and styrol copolymer polyhydroxyalkanoate (Bourbonnais and Marchessault 2010) have been further investigated as surface sizing agents.

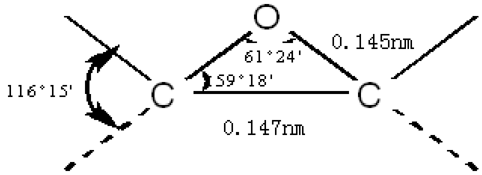
Bending stiffness depends on the macroscopic thickness of the paper or layers of board as well as the elastic modulus of the layered structure (Navaee-Ardeh 2008). Stiffness agents containing rigid groups are usually employed as internal additives or surface sizing agents to enhance stiffness. Such treatments strengthen the rigidity of single fiber as well as bonds between fibers. In addition, the three-dimensional network of paper is improved. Acetic acid lignin-toluene diisocyanate-polyethylene glycol (AAL-TDI-PEG) reacts with hydroxyl of cellulose in the paper to act as bridges between fibers by forming amino-formic ester structure. The connection between lignin and cellulose formed by the quaternary system polyurethane composite material of AAL-TDI-PEG-cellulose resulted in the enhancement of mechanical properties such as folding strength, stiffness, and wet strength (Deng et al. 2005; Yang 2010). For coated paper, the properties of coating layer affects the stiffness of the whole paper considerably, since the external layer undergoes a larger strain during bending than the internal layer (Okomori et al. 2001; Husband et al. 2009). When paper is coated with rigid film, its stiffness is enhanced greatly, so that paper itself is capable of being propped up (Zhou and Luo 2007). It is well known that higher bending stiffness increases the risk of folding cracks. With the aim of maximizing fold-crack resistance as well as bending stiffness, a combined modeling and experimental study has been designed and accomplished to assess the relationship between fold-crack resistance and bending stiffness in coated paper. The study showed that a stiff top coating contributes the most to the overall stiffness of the multilayered coated paper (Salminen et al. 2008a,b).

Although there are a variety of commonly used stiffness agents such as starch, polyacrylamide, and copolymer emulsion, they have both advantages and disadvantages in their gerneral applications. Some are commercially expensive, some have inadequate contribution to stiffness, while others are hostile to the environment. Epoxy resins are a class of highly cross-linked, hard, rigid, three-dimensional network thermosetting polymers containing epoxy groups that are produced when resins undergo a curing or cross-linking reaction. Epoxy resins are widely used in structural composites, adhesives, surface coatings, and electronic circuit board laminates (Lu 2009; Chatterjee and Islam 2008). In the papermaking industry, epoxy resins are employed as internal sizing agents or modifiers to synthesize surface sizing agents (Jiang et al. 2010; Ma 2009).

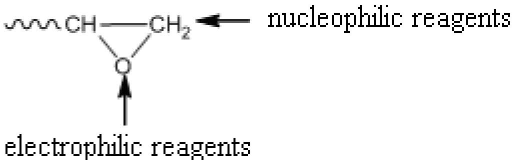
Bisphenol A waterborne epoxy resin contains epoxy, secondary hydroxyl, and other functional groups (Scheme 1). Two reactive sites exist in epoxy groups: oxygen atoms with higher electron density and carbon atoms with lower electron density due to its higher electron negativity on oxygen atoms (Scheme 2). When either nucleophilic or electrophilic reagents attack, C-O in epoxy groups begins to break and subsequently cross-linking reactions occur, forming three-dimensional polymers (Scheme 3). Reactions such as cross-linking, etherification, copolycondensation, esterfication, and addition occur respectively when secondary hydroxyl groups react with hydroxymethyl, carboxyl, isocyanate, and titanium or aluminium alkoxides (Guilin Li; 2003) (Scheme 4).



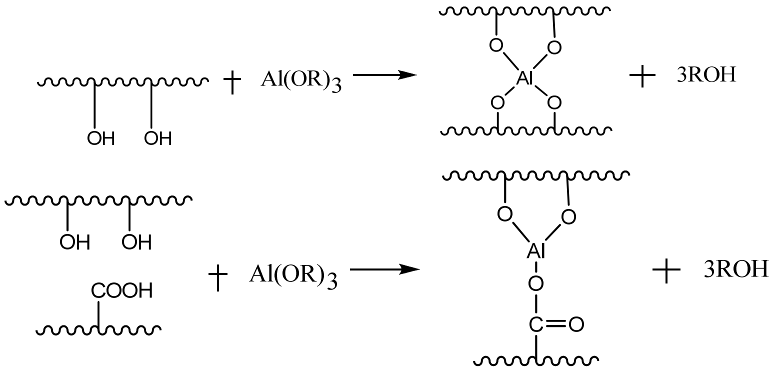
Scheme 1. Bisphenol A waterborne epoxy resin



Scheme 2. Ethylene oxide



Scheme 3. React mechanism of curing reaction



Scheme 4. Cross-linking reaction between epoxy resin and aluminum alkoxides

EXPERIMENTAL

Materials

In this paper, waterborne epoxy resin was deliberately chosen as a surface sizing agent coordinated with oxidized starch, and its sizing impact on paper was investigated. The waterborne epoxy resin (AB-EP-51) and curing agent (AB-HFG) were purchased from Zhejiang Anbang New Material Development Co., Lt. (Zhejiang China). The epoxy resin is a bisphenol A type epoxy resin, and it's epoxy value is 0.44 (100% solid), the curing agent is a modified amine, and it's amine value is 110 mgKOH/g. Oxidation starch was purchased from Gold Hongye Paper, China, and cationic starch was purchased from National Starch, USA. The base paper was a 47 g/m^2 newspaper purchased from Shanying Paper, Anhui, China.

Methods

Preparation and detection of epoxy resin film

Waterborne epoxy resin and curing agent were mixed uniformly with a mass ratio of 1:0.9, and then the mixtures were coated on polycarbonate film. After sitting at room temperature for 20 h, the curing reaction was performed at 80 ^{o}C±5 ^{o}C for 15 min. Dynamic mechanical analysis was conducted in a dynamic mechanical analyzer (Netzsch DMA242c) at 1 Hz using a compression operation. The samples were ramped from room temperature to 250 ^{o}C using a ramp rate of 5 ^{o}C /min. The storage modulus was measured. The loss factor peak was used for measuring the T_g of the resin. The epoxy resin samples were directly cut into square shapes 10 mm×10 mm for DMA analysis.

Thermo gravimetric analysis (DTG-60AH) was used to measure the thermo-stability of epoxy resin. The experimental parameters used for TG included a heating rate of 10 ^{o}C /min, room temperature to 500 ^{o}C, and a flow rate of nitrogen purging gas is 50 mL/min. Differential scanning caborimetry (DSC) was carried out by using a Netzsch DSC 204 device from -10 ^{o}C to 270 ^{o}C at a heating rate of 10 ^{o}C /min under nitrogen .

Water-resisting property was tested according to GB1733-93. Acid and alkali resistance were measured after samples (cut into square shapes 10 mm×10 mm) were insert in pH=4 H_2SO_4 solution and pH=12 NaOH solution, respectively, for 16h.

Starch gelatinization

The starch powder was mixed with deionized water by mechanical stirring, gelatinized at 90 ^{o}C for 30 min, and subsequently the mixtures were cooled to 50 ^{o}C to form a homogeneous solution with concentration of 4 wt%. Waterborne epoxy resin and curing agent were mixed uniformly with a mass ratio of 1:0.9, then added into paste starch in proportions of 1%, 3%, 5%, 7%, and 10% (EP/starch, wt) respectively to form sizing solutions. Solutions were applied with drawdown rods onto A4-size base paper. The coated paper were dried initially in an oven at 80 ^{o}C for 15min and subsequently in photo dryer with sizing surface sticking to dryer surface for 1min.

Detection of paper properties

The mechanical properties of paper sheets were tested by standard methods: TAPPI T451cm-84 (clark stiffness), TAPPI T494om-96 (tensile strength), and GB/T2679.15-1997 (picking speed). In this study, only machine direction (MD) tensile strength and machine direction (MD) stiffness were chosen for mechanical strength, since the machine directional strength was judged to be more important than that in the cross-machine direction.

RESULTS AND DISCUSSION

Fundamental Characteristics of Epoxy Resin

As shown in Table 1, epoxy resin is an excellent candidate to coat on paper for strengthening due to its overall outstanding properties such as mechanical properties, water, acid and alkali resistance, and its thermal stability. In addition, its optimum curing temperature is a good match with paper’s surface sizing temperature.

Table 1. Fundamental Characteristics of Epoxy Resin

	Cured Epoxy Resin
Storage modulus/MPa	1.57×10^3
Glass transition temperature/ ^{o}C	120
Optimum curing temperature/ ^{o}C	80
Decomposition temperature / ^{o}C	280
Water absorption soaked in water for 48h /%	3
Water absorption soaked in pH=4 H_2SO_4 solution for 16h /%	0
Water absorption soaked in pH=12 NaOH solution for 16h /%	3.1

Effects of Different Sizing Agents on Paper Performances

Compared with cationic starch, oxidized starch penetrates into paper more readily to enhance interactions between fibers and form interpenetrating polymer network. Stress can be transferred to the network through hydrogen bonds to protect paper from fracture (Kang and Shen 2008). More cationic starch resides on the surface to form film, which contributes more to surface strength and stiffness than that of oxidization starch (Fig. 1).

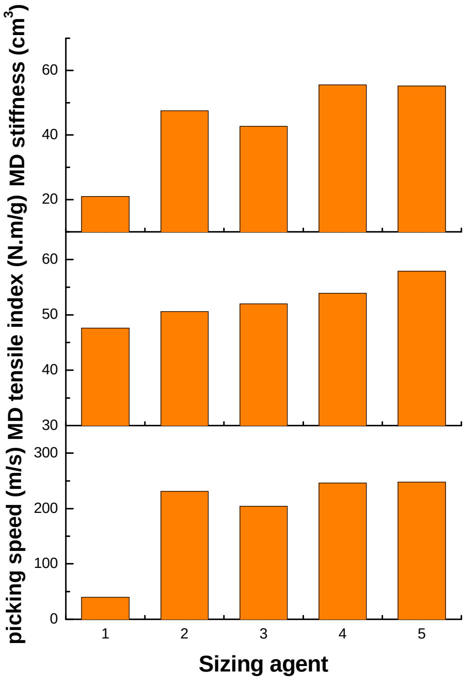


Fig. 1. Sizing effects of different sizing agents: (1) base paper, (2) cationic starch (CS), (3) oxidized starch, (4) CS + epoxy resin, (5) oxidized starch + epoxy resin

When epoxy resin was combined with either cationic starch or oxidized starch, mechanical performances of the paper were better than that of epoxy resin free sizing. Secondary hydroxyls in the resin reacted with hydroxyl, carboxyl, and aluminum alkoxide groups in fibers to create tight interconnections between resin and fibers. At the same time, the epoxy resin penetrated into paper and underwent a cross-linking reaction with curing agent to form hard, rigid, three-dimensional network structure, resulting in the enhancement of strength properties. The interaction between oxidized starch and epoxy resin is better than that of cationic starch and epoxy resin since charge neutralization occurs when electronegative epoxy resin encounters electropositive cationic starch, which weakens enhancement of cationic starch itself.

Effects of Sizing Level on Paper Performances

Figure 2 shows the sizing level's effect on paper performances. Epoxy resin coating enhanced paper strength. The reason was that sizing agent penetrated into paper was being transformed into interpenetrating polymer network. Higher sizing agent in paper leads to stronger network and better paper strength. When sizing volume was raised from 0.5 g/m^2 to 1.2 g/m^2, the picking speed, MD tensile, and MD stiffness index increased 28.7%, 9.4%, and 4.8% respectively.

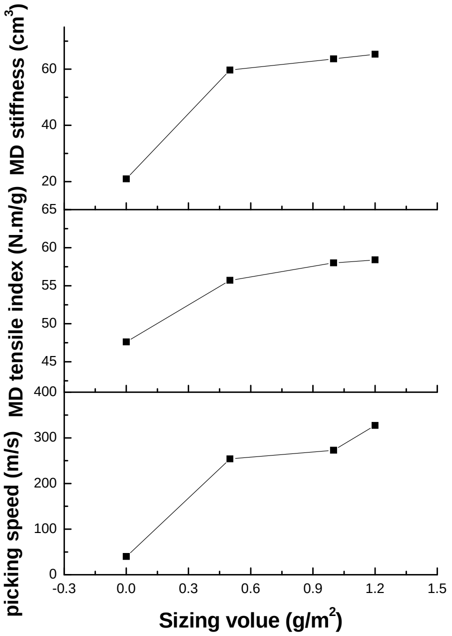


Fig. 2. Effects of sizing level vs. paper performances

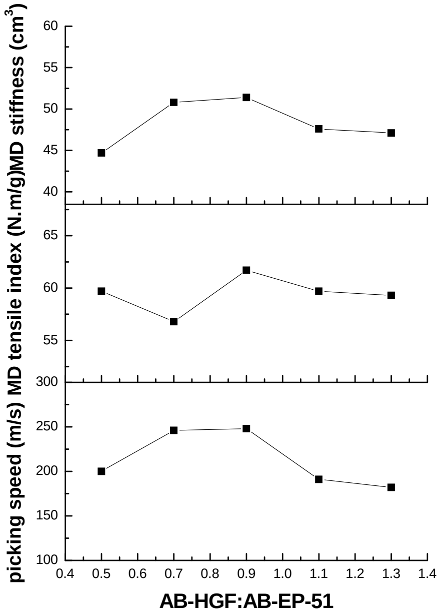


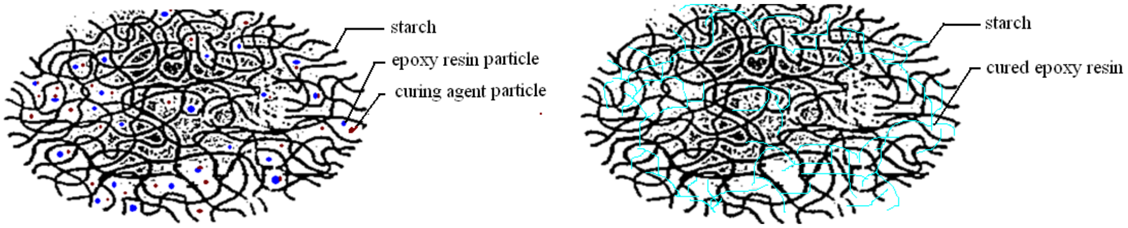
Fig. 3. Effects of curing agent dosage on paper performances

Effects of Curing Agent Dosage on Paper Performances

Cured resin properties vary significantly due to different curing agents and curing conditions. Optimum dosage for curing agent led to a greater network density and better performances, while an excessive or an insufficient amount reduced the cured resin performances noticeably. Paper properties tended to be optimal when the mass ratio of AB-HGF to AB-EP-51 was 0.9 (Fig. 3).

Effects of Curing System Dosage on Paper Performances

With higher curing system dosage, effects of epoxy resin were more dramatic, and thus higher paper strength was achieved. Colloidal particles in waterborne resin curing system should be coalesced during the film formation while kept stable during their shelf-life in water. In the mixed sizing agents, coalescence of colloidal particles was negatively affected by branched starch.



Scheme 5. Schematic representation of the combination between waterborne epoxy resin and starch. The left one shows the epoxy resin and curing agent particles dispersed in starch. The right one shows the combination between cured epoxy resin and starch.

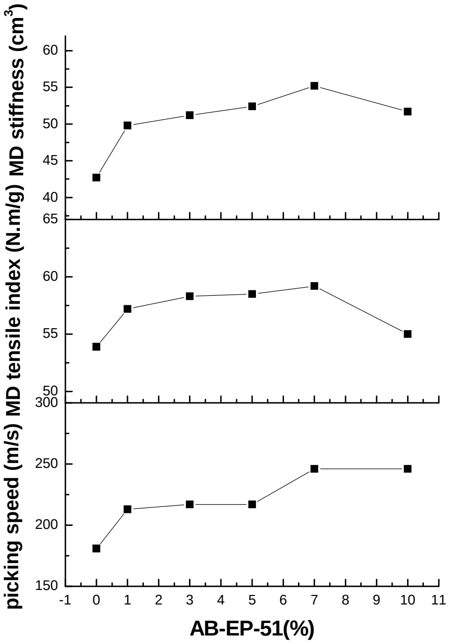


Fig. 4. Effects of curing system dosage on paper performances

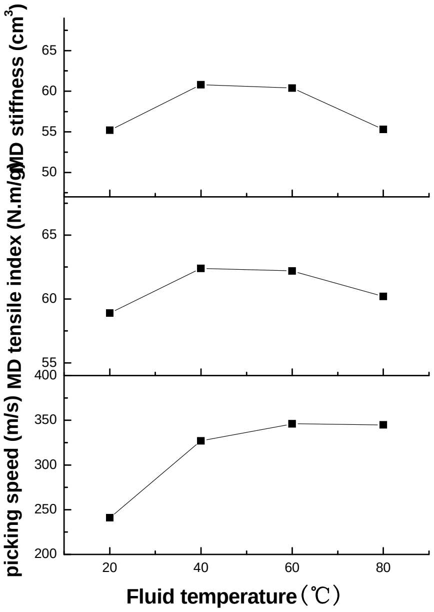


Fig. 5. Effects of fluid temperature on paper performances

At lower concentrations, more effective collision occurred with higher dosage of curing system added. However, effective collision was blocked noticeably when the dosage exceeded a certain amount and resulted in less efficient curing. As shown in Fig. 4, paper strength remained unchanged while tensile index and stiffness decreased dramatically when curing system dosage exceeded 7% (mass ratio of epoxy resin and starch).

Effects of Fluid Temperature on Paper Performances

Lower viscosity of mixed sizing agent was obtained and more effective curing reaction occurred at higher temperature. As a result, the picking speed was 327 m/s, MD tensile index was 62.4 N.m/g, and MD stiffness was 60.8 cm^3; these values represent increases of 35.7%, 5.9%, and 10.1%, respectively as fluid temperature was raised from 20 °C to 40 °C (Fig. 5).

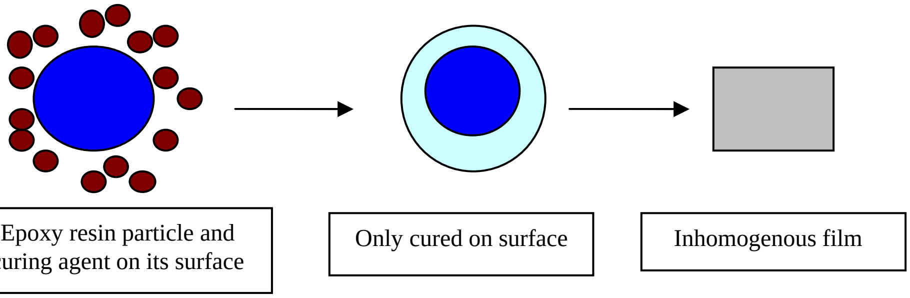


Fig. 6. Curing reaction at high temperature

The resin was cured rapidly on the surface and subsequently formed a layer of dense film as the temperature was raised. Consequently, this prevented curing agent from penetrating into the inner resin particle and resulted in an inhomogenous film (Fig 6). Meanwhile, curing before sizing made resin particles larger and therefore more difficult to penetrate into paper. All these effects led to more sizing agent residing on the surface of paper. As shown in Fig 5, surface strength still remained unchanged, while stiffness and tensile strength started to weaken. This finding was further confirmed by DSC curves of epoxy resin system.

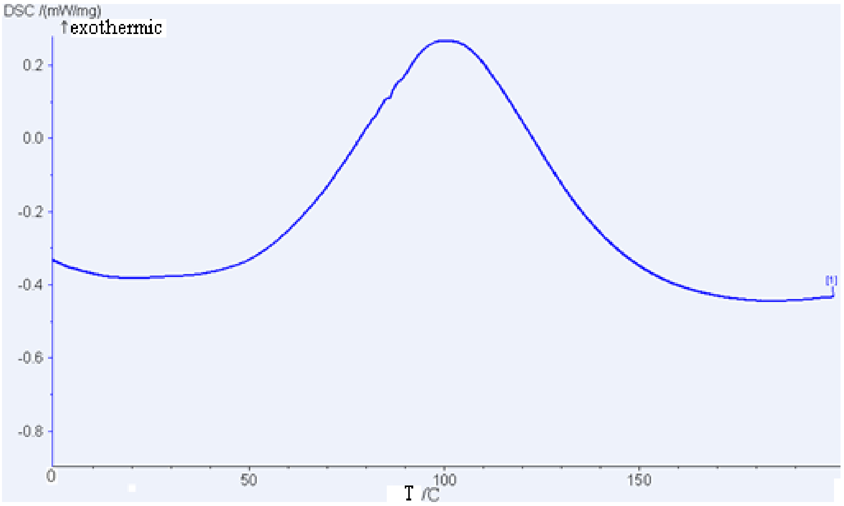


Fig. 7. DSC curve of epoxy resin system

A DSC curve of epoxy resin system showed a broad exotherm between 50 °C and 150 °C (Fig. 7). The curing reaction began slowly at 40 °C and proceeded exponentially when temperature exceeded 50 °C.

CONCLUSIONS

1. Cured epoxy resin is a kind of hard, rigid, three-dimensional network material. Epoxy resin penetrates into paper, enhances interconnections between resin and fibers, and forms an interpenetrating polymer network. As a result, the picking speed was 327 m/s, MD tensile index was 62.4 N.m/g, and MD stiffness was 60.8 cm^3; these values represent increases of 60.3%, 20.0%, and 42.4%, respectively, in comparison with sizing in the absence of epoxy resin. Results in this paper showed epoxy resin to be an effective surface sizing agent for improving paper strength properties such as stiffness, tensile strength, and surface strength.
2. Epoxy resin has great potential and could be a viable option among all the surface sizing agents widely used today. Therefore, further investigation on epoxy resin coating directly onto paper web with an in-line coating unit is deemed necessary.

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