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DEVELOPMENT OF STARCH-NANOCELLULOSE COMPOSITES FOR USING IN SURFACE TREATMENT OF PAPER

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A Thesis Submitted in Partial Fulfillment of the Requirements
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Thesis Title	DEVELOPMENT OF STARCH-NANOCELLULOSE COMPOSITES FOR USING IN SURFACE TREATMENT OF PAPER
By	Mr. Phanthakan Ow
Field of Study	Chemical Engineering
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พันธกานต์ โอว : การพัฒนาสารประกอบแป้ง-นาโนเซลลูโลสเพื่อใช้ในการปรับปรุงผิวหน้าของกระดาษ (DEVELOPMENT OF STARCH-NANOCELLULOSE COMPOSITES FOR USING IN SURFACE TREATMENT OF PAPER) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร. เหมือนเดือน พิศาลพงศ์เหมือนเดือน พิศาลพงศ์, 67 หน้า.

หน้าที่หลักของกระบวนการฉาบผิวกระดาษคือ เพื่อเพิ่มความแข็งแรงให้ผิวหน้าของกระดาษ โดยทั่วไปแป้งถูกใช้เป็นสารฉาบผิวกระดาษ แต่การใช้งานแป้งยังคงมีข้อจำกัดอยู่มาก การศึกษาในงานวิจัยนี้เป็นการศึกษาการใช้งานนาโนแบคทีเรียเซลลูโลส (NBC) ที่ผลิตจาก *Acetobacto xylinum* เป็นสารเพิ่มความแข็งแรงในสารประกอบแป้ง โดยปริมาณ NBC ที่ใช้ในการเตรียมสารประกอบแป้ง-นาโนแบคทีเรียเซลลูโลสเพื่อใช้ในการฉาบผิวหน้ากระดาษอยู่ในช่วงร้อยละ 0.10-10.00 ของน้ำหนัก ฟิล์มสารประกอบแป้ง-นาโนแบคทีเรียเซลลูโลสถูกเตรียมและศึกษาคุณสมบัติโดยวิธี FTIR, XRD และ SEM ตลอดจนศึกษาคุณสมบัติเชิงกลและคุณสมบัติในการป้องกันของกระดาษที่ถูกฉาบผิวด้วยสารประกอบแป้ง-นาโนเซลลูโลส พบว่าการเติม NBC ที่ร้อยละ 1.00 ส่งผลให้คุณสมบัติเชิงกลในด้านของความต้านแรงดันทะลุ ความต้านแรงดึง และความต้านทานการหักพับเพิ่มขึ้นร้อยละ 10 ร้อยละ 10 และร้อยละ 40 ตามลำดับ นอกจากนี้ความต้านทานการซึมผ่านของอากาศเพิ่มขึ้นอย่างมีนัยสำคัญที่ร้อยละ 56 เมื่อเปรียบเทียบกับกระดาษที่ฉาบผิวหน้าด้วยน้ำแป้งโดยไม่เติม NBC จากผลการทดสอบคุณสมบัติเชิงกลและความต้านทานการซึมผ่านของอากาศแสดงให้เห็นว่าปริมาณการเติม NBC ในสารประกอบแป้งที่เหมาะสมที่สุดอยู่ที่ร้อยละ 1.00

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต .....

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก .....

ปีการศึกษา 2560

5970995121 : MAJOR CHEMICAL ENGINEERING
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PHANTHAKAN OW: DEVELOPMENT OF STARCH-NANOCELLULOSE COMPOSITES FOR USING IN SURFACE TREATMENT OF PAPER. ADVISOR: PROF. MUENDUEN PHISALAPHONG, Ph.D., 67 pp.

The main role of surface sizing is to increase the surface strength of paper. Starch is commonly used as surface sizing agents, but there are still some limitations. In this study, nano-bacterial cellulose (NBC) produced by *Acetobacto xylinum* was used as a reinforcing material in starch-based composites. The suspensions of NBC starch-based composites were prepared by the additions of 0.10-10.00% w/w NBC into starch solution and were used as surface sizing agents. The structures and properties of NBC starch-based composite films were characterized by FTIR, XRD, and SEM. The mechanical properties and barrier properties of cellulosic paper with surface sizing by the NBC reinforced starch-based composite suspensions were investigated. With the addition of NBC at 1.00%, the mechanical properties in terms of burst index, tensile index, and folding endurance were increased by 10%, 10%, and 44%, respectively. Furthermore, the air resistance of surface sized paper was significantly improved by 56%, as compared to the surface sized paper without NBC addition. According to the results of mechanical properties and air resistance, it was suggested that the optimal NBC dosage in starch-based composite was 1.00%.

Department:	Chemical Engineering	Student's Signature	.....
Field of Study:	Chemical Engineering	Advisor's Signature	.....
Academic Year:	2017		

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CHAPTER I
INTRODUCTION

1.1 Background and rationale

In recent years, recycled fibers are used increasingly in packaging paper which has poor mechanical and barrier properties [1, 2]. Physical properties such as high tear resistance and high impact strength are always required for packaging papers. Starch at approximately 5 million tons per year has been used by the world paper industry for strength improvement. The mostly used process is called “Surface sizing” [2].

More than 60% of total starch consumption in the paper industry is used for surface sizing. The main role of surface size is to strengthen the paper surface and to bind particles such as fiber and pigments to paper surface by applying starch solution onto the surface of the paper [2]. The starch solution for surface sizing process must have been treated to adjust viscosity prior to being used by means of thermochemical or enzyme process [3]. Although surface sizing can greatly improve paper strength, there are still limitations in the barrier properties and the high starch dosage cause of fold-cracking when the packaging paper was used in box making process. For improving barrier properties to air, moisture and water, paraffin wax or synthetic polymers, such as polyethylene, polyvinyl alcohol, and rubber latex can be used for this purpose [4, 5]. However, waxes and synthetic polymers are not perfectly safe for environment because of their non-degradable and difficult to recycle in papermaking process. To reduce these disadvantages, starch-based composites reinforced with nanocrystalline cellulose been developed [1].

There are many studies related to the reinforcing effect of nanocellulose on paper properties. Nanometer-scale cellulose fibers, commonly known as nano-fibrillated cellulose (NFC). Pure nanocellulose fibrils can be obtained from many resources with various treatments. Nanocellulose fibrils, known as bacterial cellulose (BC) or nano-bacterial cellulose (NBC), is produced by bacteria *Acetobacter xylinum*. BC structure has the same chemical structure as plant cellulose and about 100 times smaller than plant cellulose. It exhibits the unique properties such as nanofiber network structure, high mechanical strength and high crystallinity. BC is traditionally used in

food application to make Nata de coco in Philippines [6]. Moreover, BC has also been explored for many applications such as cosmetics application, medical application [7] and reinforcement material [8].

Nano-bacterial cellulose (NBC) possesses a potential as valuable reinforcement material. This study aims to develop nano-bacterial cellulose reinforced starch-based composite suspensions as surface sizing agents for improving the mechanical properties and the resistance to air permeability. The proper conditions for the treatment are determined.

1.2 Objectives

1. To investigate the use of NBC as reinforcing agent in NBC starch-based composite suspensions for surface treatment of cellulosic paper.
2. To determine the proper conditions for the use of NBC starch-based composite suspensions for surface treatment of cellulosic paper.

1.3 Research scope

1. To study the effects of conditions and parameters for the preparation and application of NBC starch-based composite suspensions in surface sizing process of cellulosic paper. In this study, the effect of various oxidized levels of starch (using starch; EXCELSIZE series from SMS Corporation Co., Ltd.) at starch concentration of 10 % wt.) and dosage of NBC (0.10-10.00 % wt. of dry starch) were investigated.
2. To characterize of NBC starch-based composite films by SEM, FTIR, and XRD, and examine important properties (i.e. mechanical properties; burst strength, internal bonding strength, tensile strength, and folding endurance followed TAPPI test methods, barrier properties; water resistance by Cobb's test, air resistance by Gurley method, and surface morphology by SEM) of cellulosic papers before and after surface treatment with NBC starch-based composite suspensions in surface sizing process and compare with the papers under the surface sizing method.

1.4 Benefits

To develop novel composite for using in surface sizing process of paper industry in order to improve the qualities of packaging papers such as improved mechanical properties with high air and water resistances.

CHAPTER II
THEORY

2.1 Bacterial cellulose

Bacterial cellulose (BC) is a biopolymer produced by some bacterial strains such as the genera *Acetobacter, Rhizibium, Agrobacterium, Aerobacter, Achromobacter, Azotobacter, Salmonella, Escherichia,* and *Sarcina*. BC exists as a basic structure of fibril that consists of linear β-1,4-glucan chains with molecular formula $(C_6H_{10}O_5)_n$ same as chemical structure of plant-derived cellulose. But plant-derived cellulose consists of hemicellulose, lignin, and pectin, BC is free of other polymers. Each BC nanofiber or nano-bacterial cellulose (NBC) is a bundle of cellulose nanofibrils which are aggregates of extended cellulose chains, resulting in formation of hydrogel sheet with high surface area and porosity [6, 7, 9-13].

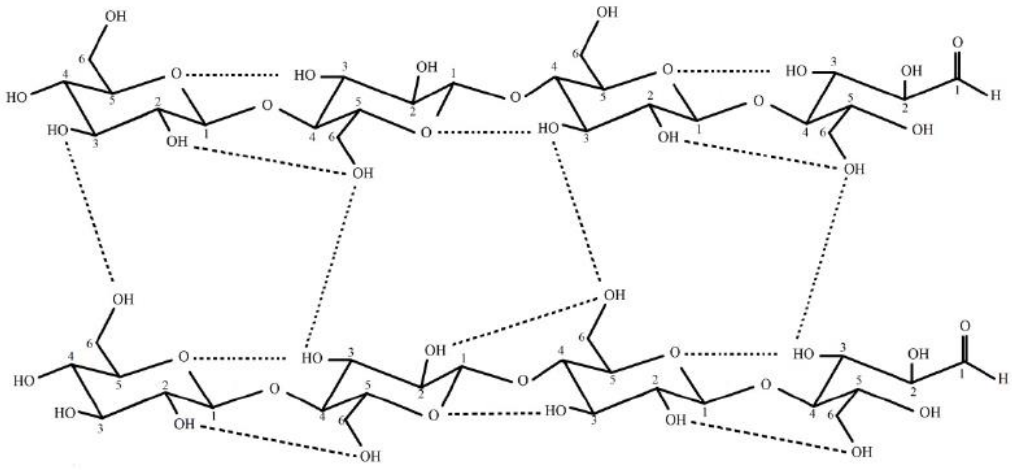

Figure 1: Inter- and intra-hydrogen bonding of bacterial cellulose [6].

This structural singularity of the BC fibrillated network results in unique mechanical characteristics, such as a high degree of polymerization, high crystallinity, high mechanical strength, high surface area and high water holding capacity. NBC fibers in the axial direction is similar to that of glass, the mechanical properties (Young's modulus and tensile strength) of NBC are almost equal to those of aramid

fibers (e.g., Kevlar). NBC has been applied in multiple field such as foods, cosmetics, nutraceuticals, cosmeceuticals and drug delivery. Although NBC has unique properties, there is limitation such as lack of antibacterial properties, optical transparency, and stress bearing capability. To overcome these limitations, NBC modifications has been introduced to adjustment of BC structural characteristics during biosynthesis process or post-synthetic material modification through chemical derivatization or preparation of composites.

2.2 Papermaking process

The papermaking process has several stages [2, 3]:

1. Stock preparation
2. Paper forming
3. Converting

Stock preparation

In the preparation of pulp for papermaking process, three major types of pulp fibers are wood fibers, recycled fibers, and non-wood fibers (i.e. rice grasses, sugar cane bagasse). A mixture of pulp fibers and water is called “Stock”. In this step, raw stock is converted into the finished stock for the paper machine. Stock preparation consists of several process steps as following:

1. Defibering or fiber disintegration; dry pulp is dispersed into water to form stock by Hydra-pulper.
2. Beating or refining is stock treatment step. It aims to develop the bonding ability of the fibers.
3. Blending; the addition of chemical additives such as fillers (GCC, talc, clay), sizing agents, dyes and pigments to improve paper properties.
4. Screening and Cleaning; the pulp fibers are cleaned to remove unwanted particles form pulp stock.
5. Consistency control; dilution of pulp stock. The stock consists of approximately 99.5% water and 0.5% pulp fibers. It is called “Thin stock”.

Paper forming

The next step after stock preparation is to form the stock into the paper at the wet-end of paper machine.

1. Head box; the thin stock is pumped into the head box of the paper machine. It is squirted through a thin horizontal slit across the machine's width onto a forming wire.
2. Wire part; Water is removed and fibers start to spread and consolidate into a thin mat.
3. Press section; the paper web is squeezed by two rotating rolls for water removal before drying. After leaving the press section, the sheet mostly has about 65% of moisture content.
4. Drying; the paper web passes through dryer. Dryer is a series of steam-heated cast-iron cylinders. The process evaporates many tons of water.

Converting

The process is now finish for papermaking process, but some grades of paper are required to treating by a surface sizing or coating process for improve the paper properties.

1. Surface sizing is the operation to strengthen the paper surface by applying surface strengthening agents onto the surface of the paper. Which the surface strengthening agent commonly used is starch.
2. Coating is the treatment of the paper surface with pigments (i.e. calcium carbonate, clay, titanium dioxide) to improve printing quality, optical properties.
3. Calendaring; the paper passes through a series of heated steel rolls to press and polish the paper. Calendaring can reduce variations of thickness and increase density and smoothness of the paper, but for papers that need more glossy or other surface characteristics will using super calendaring.

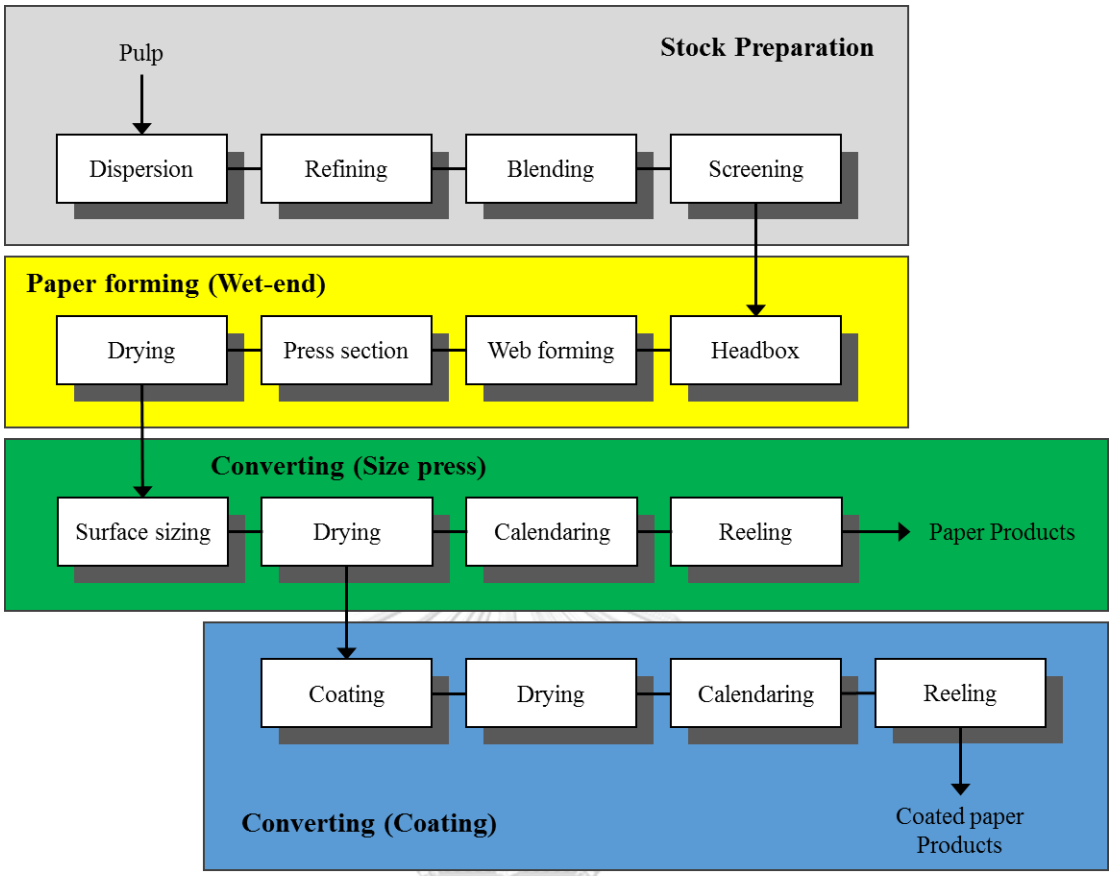

Figure 2: Papermaking process; block diagram.

2.3 Surface sizing process

Surface sizing is accomplished in a device called a “size press”. The most important type of surface treatment for paper strength improvement. Especially, packaging paper which made from 100% recycled fiber because starch applied to the surface is generally 100% retained, and surface sizing can improve paper strength up to 30-60%. Nevertheless, there are many factors influencing surface sizing. The paper characteristics (i.e. paper structure, porosity, level of internal sizing, and moisture content of paper, sizing solution properties (i.e. type of starch, solid content, viscosity, temperature, and pH), machine design and operational (i.e. nip pressure and roll hardness) can all affect the amount of surface sizing agent applied and how it performs [2, 3].

As mentioned above, machine design is one of the factors. There are several types of machine for applying starch solution onto the surface of paper.

1. Pond size press or conventional size press is the most common surface application method. It consists of two rolls pressed together to form a nip, where a pond of the sizing solution between the two rolls. The paper passes through this pond, the sizing solution is applied to the paper surface. Additionally, there are three types of the size press machine design: horizontal type, vertical type, and inclined type.

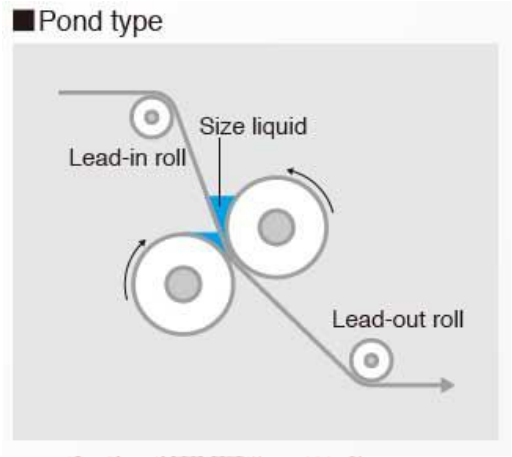

Figure 3: Pond size press [14].

2. Gate roll size press is aimed to reduce the turbulence in the size press pond. By install pre-metering rolls to store sizing solution and transfer to applicator rolls. The size press rolls are used as application rolls. However, the equipment is technically complex owing to the large number of rolls.

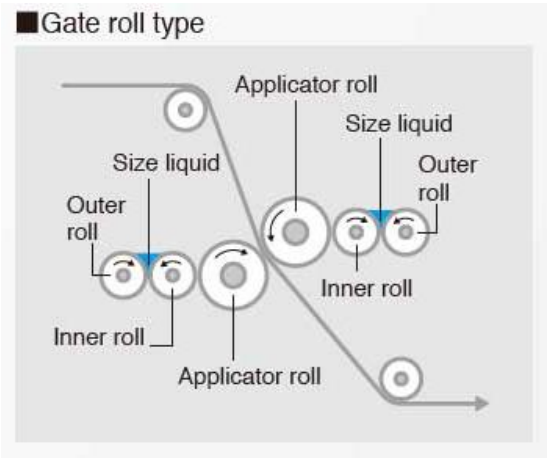

Figure 4: Gate roll size press [14].

3. Metered size press (also called SpeedSizer, SymSizer or Film press) is developed to overcome the pond size press problems. The size press rolls are used as applicator rolls. A film of sizing solution which metered by rod or blade metering, is applied to the applicator rolls. The film is transferred to the paper in the nip without pond formation and pressed into the paper. The advantage of metered size press is uniform coating and the quantity of water which has to be evaporated is reduced. This lead to reduce energy costs and to improve paper-machine speed.

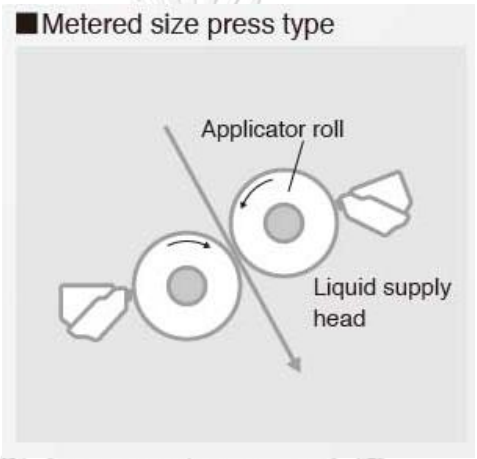

Figure 5: Metered size press [14].

2.4 Starch chemistry

Starch is high molecular weight polymer of anhydroglucose units ($C_6H_{10}O_5$) linked by α-D-glycosidic bonds. This polysaccharide is produced by most green plants as energy storage. It is the most common carbohydrate in human diets and is contained in large amounts in staple foods like potatoes, wheat, corn, rice, and cassava. Pure starch is a white, tasteless and odorless powder that is insoluble in cold-water or alcohol. It consists of two types of molecules: a linear fraction, amylose, and a branched fraction, amylopectin. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin by weight [15].

Amylose consists of α-1,4 linked anhydroglucose units (**Figure 6**). This linkage results in a flexible molecule with a natural extended helical twist that can reorganize into a collapsed helix (retrogradation). Amylopectin consists of a backbone structure of

α-1,4 linkage between anhydroglucose units but with branching at α-1,6 positions (**Figure 7**). This bonding results in a multi-branched or ramified structure. Knowledge of the chemical and physical structure of starch is helpful in understanding its role in the papermaking process.

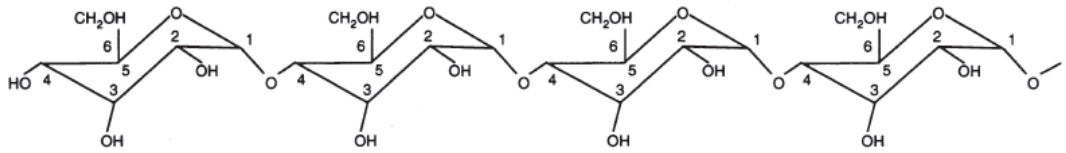

Figure 6: The chemical structure of amylose [3].

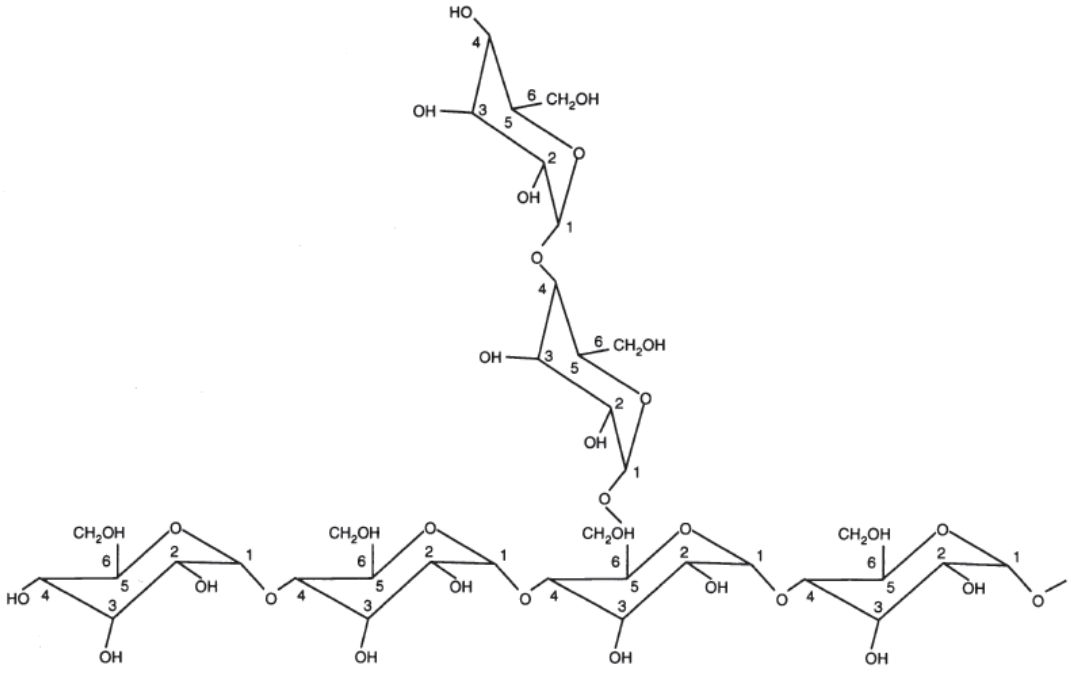

Figure 7: The chemical structure of amylopectin [3].

2.5 Starch cooking

For starch to function as an additive in various applications, its bonding capability must be fully developed. The starch has been converted into its hydrated form by “cooking”. Mixture of granular starch in water is prepared by starch slurry make-down system, as illustrated in **Figure 8**.

When starch is added to cold water, heat is applied to a starch suspension and the temperature rises. The water is absorbed into the starch granules and bonds between the starch molecules in the granule are broken, causing the granules to swell. The critical temperature at which swelling occurs is called the gelatinization or pasting temperature (about 55–80°C, depending on the type of starch). As heating continues, amylose leaches out and the starch becomes sticky. Thereafter, the swollen starch granules progressively disintegrate into swollen starch aggregates, eventually achieving a complete molecular dispersion. Complete solubilization of all starch present does not normally occur unless the starch paste is prepared at temperatures of 100-160°C (depending upon the type of starch) (**Figure 9**). After cooking, the starch paste may be diluted to the desired storage concentration. A biocide should be used to minimize risk for microbiological breakdown of starch. Storage at 60-70°C temperature is recommended [15, 16].

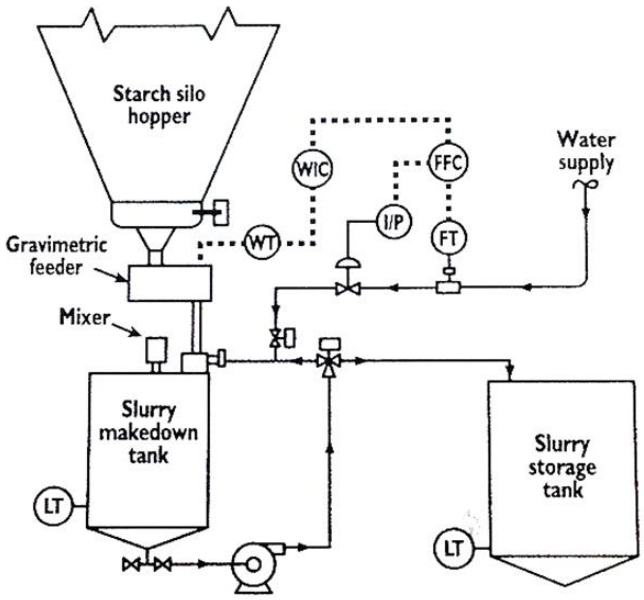

Figure 8: Starch slurry make-down system [15].

In paper industry, the starch cooking can be either by a batch or a continuous system:

Batch cooking

A basic batch cooker is a tank equipped with an agitator and a steam distribution pipe to heat the slurry to the required temperature. Throughout starch cooking, the starch slurry is heated by feeds steam directly into the cooker and agitation is needed to ensure adequate heat transfer and system homogeneity. Batch cooking is normally used when a papermill's starch consumption is small.

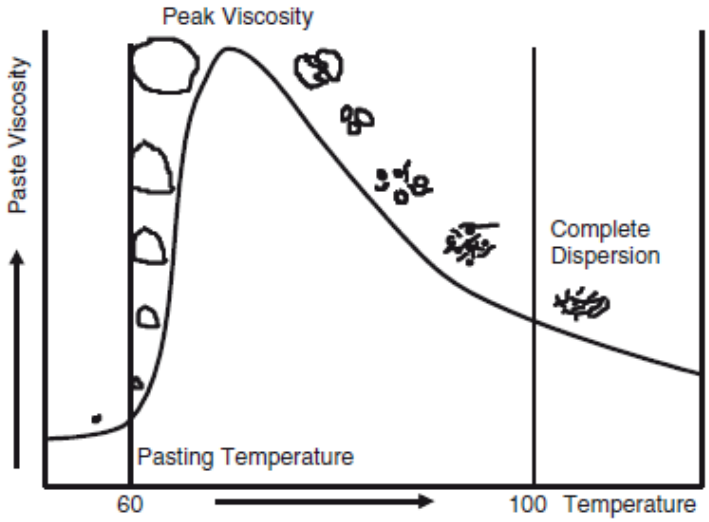

Figure 9: Starch gelatinization [16].

Continuous cooking

Jet-cooking is a continuous method of pasting starch in which steam under pressure mixes completely with starch slurry and rapidly heats it and cooks it within a few seconds. Jet cookers utilize direct steam injection. The jet cooker may be automatically controlled by the level in the cooked starch storage tank.

Jet cookers give a more uniform product as starch granules are completely fragmented and dispersed when cooked at high temperatures (>100°C) and at high pressure. Jet cookers are also more easily automated, and a more economical use of raw material is possible.

2.6 Starch in papermaking process

Starch is consumed in large volumes by the paper industry for various applications. The starch use is apportioned as follows: About 16% for wet-end process, 5% for spraying process, 68% for surface sizing process, and 11% as a coating binder in coating process [2, 3, 16].

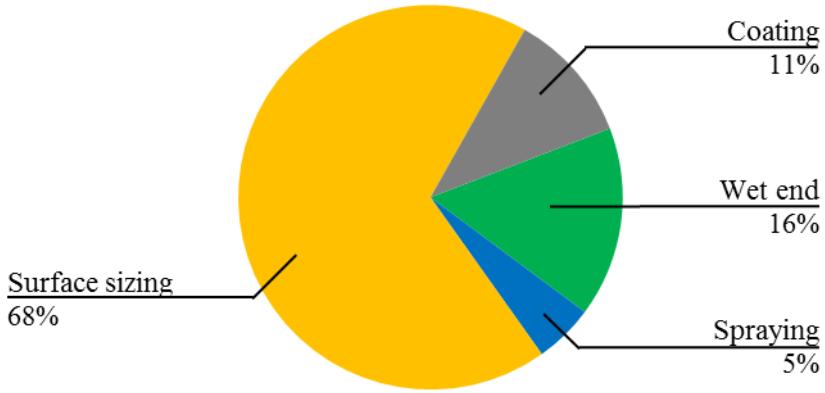

Figure 10: Starch consumption for various applications in the paper industry.

Starch is chemically similar to cellulose. It is the most used as a dry-strength additive for paper. However, there are several paper grades which the different requirements. Thus, the starches have been modified by several methods depend on applications or needs.

1. Wet-end starch; the major wet-end starch is cationic starch. Because the surface charge on the fibers and mineral fillers are oppositely charged to the cationic starch, so the cationic starch is adsorbed by fibers and fillers. It is added to the pulp stock to enhance dry-strength of the paper (inter-ply bond and stiffness), to improve the retention of fines, fibers, fillers and chemical additives, drainage, formation of paper, and to lower energy consumption and overall paper manufacturing costs.

2. Spray starch is uncooked starch that sprayed between the piles on multi-ply paper to improve inter-ply bonding. For sprayed starch is retained on paper by mechanical filtration, so a large particle size of starch is favored. The uncooked starch is cooked in the dryer section; thus, the gelatinization temperature of the starch is very significant in determining the onset of starch cooking in the dryer.

3. Surface sizing starch is a large portion of the total starch consumption in the paper industry. For improvement of paper strength, the starch solution is applied onto the paper to bind fibers more strongly to the surface. Moreover, the starch is penetrated paper sheet to improve internal strength. Thus, native starch is not suitable for surface sizing because there are large molecules. Before it can be use at the surface sizing the native starch must be modified the viscosity of the starch solution to decrease in the molecular weight of the starch by thermochemical conversion or enzyme conversion.

4. Coating starch is another starch for surface treatment application which is used as a coating binder. It is a very efficient chemical in coating colors both for binding pigment particles to the paper, and for controlling rheology and water retention. The modified types of the coating starch are similar to the surface sizing starch.

2.7 Properties of paper

There are many of the properties and characteristics that are important to paper depend on paper grades or end-use requirements. The most important property that are necessary for a paper to perform well as packaging paper is the strength of paper. The strength of paper prevents the packaging box from bulging the weight of boxes and pallets above it in a stack. Furthermore, some packaging box is required resistance and barrier properties. The most commonly test methods used to measure the properties of paper in the paper industry as following [17, 18]:

1. Bursting strength is used as a measure of resistance to rupture by pressure. The bursting test value is the maximum pressure, required to produce rupture of the paper. The most common instrument for measuring bursting strength is the Mullen tester, dating to the 1890s. The Mullen burst tester has also been modernized in recent years. Because of the common use of the Mullen testers, bursting strength has become known as “burst”.

2. Internal bond strength is used for measuring the force required to delaminate a sheet of paper in the z-direction. Gummed tapes that commonly experience z-direction stresses in use rely upon strong bonding within the sheet. A different test for measuring tensile strength in the z-direction is described in TAPPI Useful Method 403 under the title “Test for Interfiber Bond Using the Internal Bond Tester”. This test is commonly called the “Scott Bond Test”.

3. Tensile strength or tensile breaking strength is a direct indication of the durability and potential end-use performance of papers that receive direct tensile stresses in use, such as wrapping paper, bag, gummed tape, twisting paper, and printing paper. Tensile strength is reported as the force per unit width required to rupture the paper. This property is important in printing and other converting operations where the sheet is subjected to stresses that could lead to delamination.

4. Folding endurance tests have been used to estimate the ability of paper to withstand repeated bending, folding, and creasing. There are 2 types for the determination of the folding endurance i.e. MIT-type apparatus and Schopper-type apparatus. Folding endurance is the logarithm of the number of double folds required to break the paper when a strip of paper is tested under a standard tension. Which double fold is one complete oscillation of the test sample, during which it is folded first backwards then forwards about the same line.

5. Wax pick test is designed to measure the surface strength of paper or its resistance to picking, which uses calibrated sealing waxes of various adhesive power. The waxes are in the form of sticks which are numbered from 2A to 26A in the order of increasing tackiness. Report as the critical wax strength number (CWSN), the highest numerical designation of the wax that does not disturb the surface of the paper.

6. IGT pick test is used to determine the damage of the paper surface during the printing operation. At the time the printing form is lifted off the paper the ink is exerting a certain force on the paper. This force is increasing with an increase in the viscosity and tack of the ink and the printing speed. When this force exceeds a certain value, the surface of the paper will be damaged.

7. Cobb size test, describes a procedure for determining the quantity of water absorbed by sized paper. The results (Cobb value) are reported as the weight of water absorbed per area of paper surface, usually grams per 100 cm^2.

8. Air permeability measurements (Gurley method) or air resistance, is used to measure the volume of air that passes through the paper, along with any possible leakage of air across the surface. The results of the test are usually reported as the number of seconds it takes for 100 cm^3 of air to pass through the sheet of paper. Since a high-test value implies a low air permeability.

CHAPTER III
LITERATURE REVIEWS

3.1 Nanocellulose in paper applications

Cellulose nanocrystals are produces by breaking down the cellulose fibers and isolating the crystalline regions. Strong acid hydrolysis, a process described nearly 60 years ago by Randy has been used to isolate the cellulose nanocrystals. The cellulosic nanofibrillar structures have recently come into focus to be used as reinforcement material in nanocomposites because of their wide abundance, renewable and environmentally benign nature, and outstanding mechanical properties [19].

Yang et al. (2014) [1] had prepared and characterized starch-based composite suspensions/films reinforced with 0.1-0.5 wt% of nanocrystalline cellulose (NCC). Surface sizing application of the reinforced composite suspensions on cellulosic paper was subsequently studied for improving the mechanical properties and the resistance to air permeability of the paper. The result show that NCC can be effective in improving the mechanical properties and the resistance to air permeability of surface sized paper. When 0.3 wt% NCC was added to the starch-based composite suspensions, the surface sized paper exhibited increases of 6, 9, 23, and 4% in the tensile index, tear index, folding endurance, and burst index, respectively, as compared to the paper sized by NCC-free starch-based composite suspensions.

Table 1: Effect of NCC Dosage on Mechanical Properties of Surface-Sized Paper [1].

	tensile index (N·m/g)		tear index (mN·m²/g)		folding endurance (times)		
sample ID	MD[a]	CD[a]	MD	CD	MD	CD	burst index (kPa·m²/g)
base paper	58.90 ± 1.41	32.98 ± 1.04	6.02 ± 0.01	6.86 ± 0.05	39 ± 4	43 ± 9	2.82 ± 0.03
NCC-0%	61.09 ± 1.27	34.64 ± 0.16	6.24 ± 0.04	7.45 ± 0.07	43 ± 7	48 ± 9	2.83 ± 0.05
NCC-0.1%	63.09 ± 0.55	35.35 ± 0.23	6.67 ± 0.05	7.47 ± 0.02	44 ± 5	50 ± 11	2.86 ± 0.10
NCC-0.2%	63.47 ± 0.24	35.75 ± 0.34	6.68 ± 0.09	7.48 ± 0.06	46 ± 8	53 ± 4	2.88 ± 0.04
NCC-0.3%	64.74 ± 1.40	36.96 ± 0.84	6.77 ± 0.05	7.69 ± 0.08	53 ± 9	58 ± 7	2.95 ± 0.06
NCC-0.4%	63.86 ± 0.36	36.09 ± 0.46	6.71 ± 0.05	7.59 ± 0.08	46 ± 1	56 ± 8	2.92 ± 0.10
NCC-0.5%	63.59 ± 0.92	36.07 ± 0.14	6.69 ± 0.07	7.54 ± 0.08	50 ± 10	56 ± 3	2.91 ± 0.07

[a]MD means the direction of paper grain corresponding with the track of paper machine; CD means the direction of paper at right angles to the grain of the paper.

Luu et al. (2011) [8] had studied a new method to improve the print quality of ink-jet printing. The method involved applying a layer of nano-fibrillated cellulose (NFC) to the woodfree base sheet treated with AKD. Ink-jet pigments and dyes were able to penetrate through these NFC layers. The AKD treatment limits liquid penetration and reduces print-through. The combination of NFC and AKD gave a higher print density and at the same time reduced print-through compared to samples treated with AKD only.

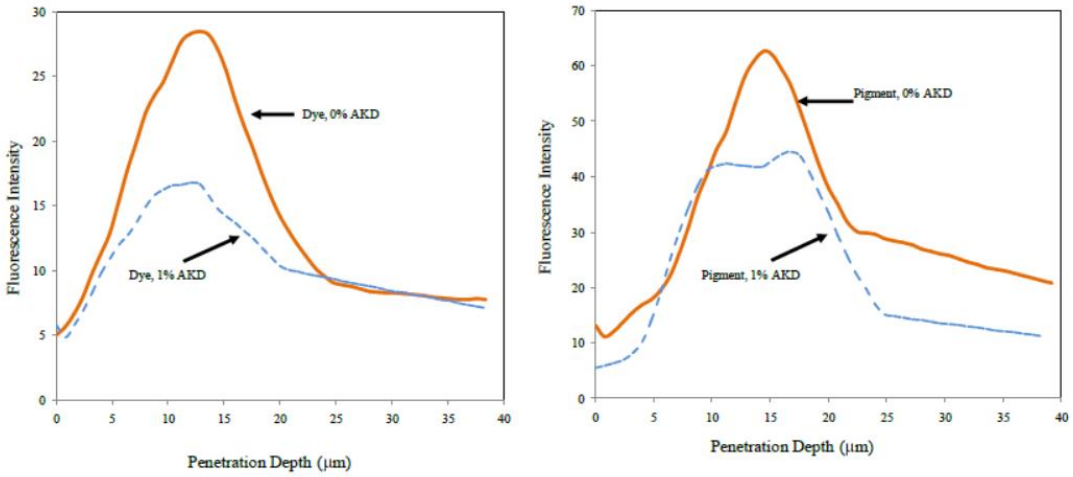

Figure 11: Penetration profiles of dye-based ink-jet ink (left) and pigment-based ink (right) in the untreated and AKD woodfree papers [8].

Richmond (2014) [20] coated cellulose nanofibers (CNF) on the paper to improve the properties of the paper. Papers were coated with CNF suspensions, CNF tends to decrease gloss and brightness. The stiffness of paper shows little increase even though films of CNF are quite stiff, the modest decrease in permeability, and the decrease in porosity all indicate that CNF penetrates into paper and does not stay at the surface as a coating.

Yang et al. (2016) [21] employed nanocrystalline cellulose (NCC) as an efficient dispersant to prepare alkyl ketene dimer (AKD) emulsion. AKD/NCC emulsion was used as the sizing agent for surface-sized cellulosic paper. It acted as a good reinforcing agent for improving the mechanical properties of the surface-sized paper, and reduced the air permeability by 96.83%.

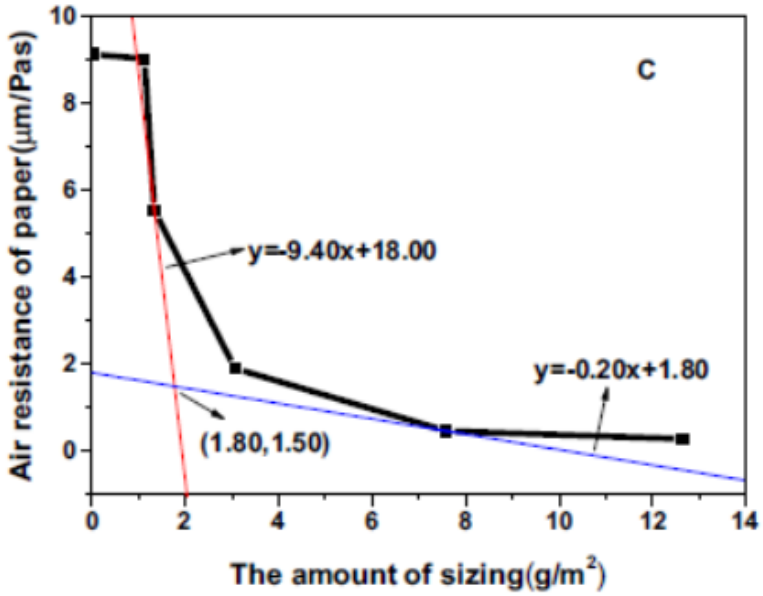

Figure 12: The air permeability of surface sized cellulosic paper [21].

Tabarsa et al. (2017) [22] used bacterial cellulose (BC) to reinforce softwood pulp (SP) to generate a sustainable biocomposite. The physical and mechanical properties showed that as the dosage of BC increased, the properties of tensile index, tear index, and burst index greatly improved, while the porosity and the elongation decreased. In particular, 15% of the BC with SP during sheet formation was found to significantly improve properties as compared to paper sheets produced from 100% SP (**Figure 13**).

Camaros et al. (2017) [23] used cellulose nanocrystals (CNC) based composite as an alternative material in the filling lacunae of documents and artworks on paper. Aqueous dispersion of CNC with propylene glycol, methylcellulose and $CaCO_3$ are the components of the developed paper pulp. The CNC-based paper showed a higher crystallinity index. The increase in the crystallinity of a material generally enhances its strength, along with the suitable visual aspects as well as the verified chemical compatibility with paper.

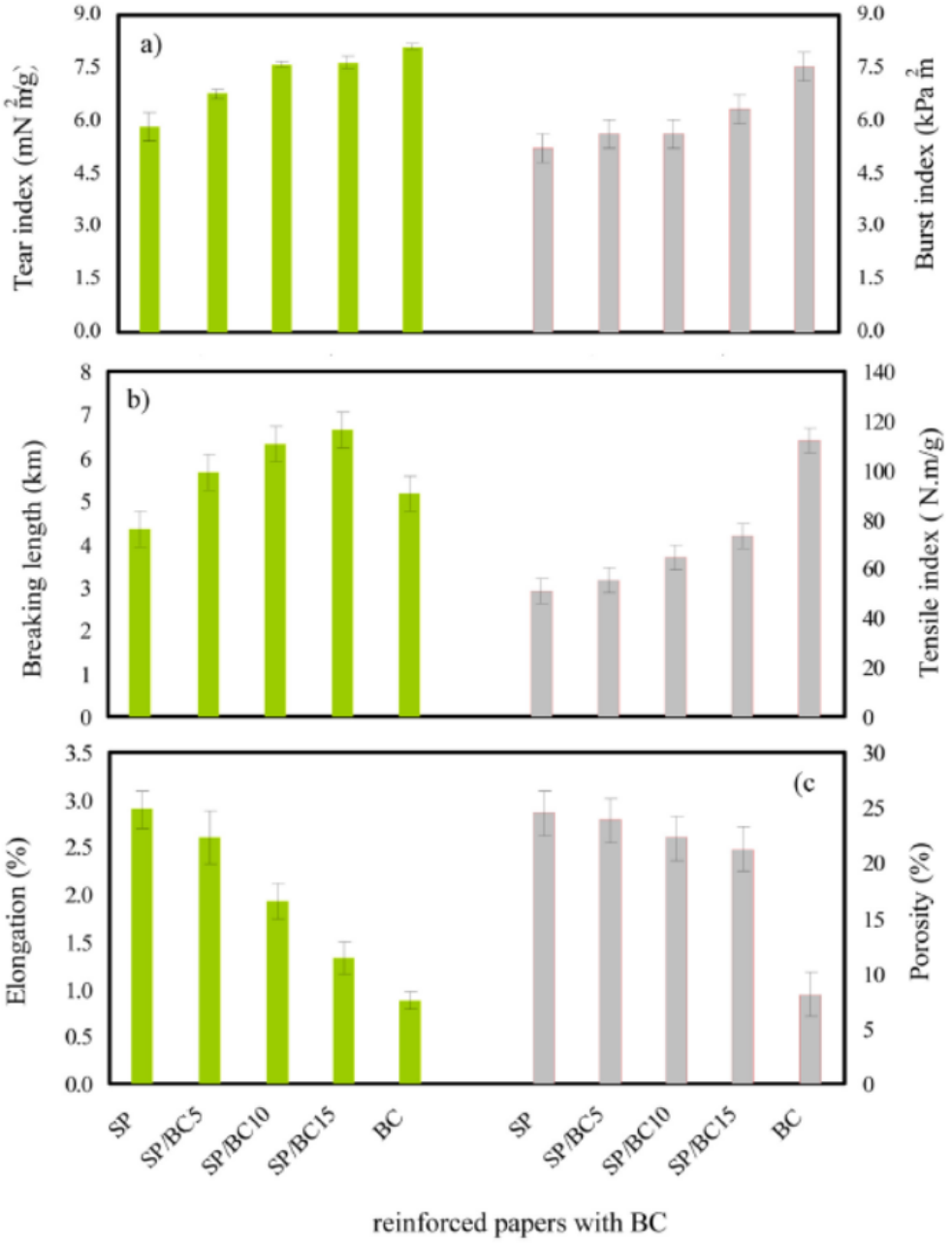

Figure 13: Physical and mechanical properties of pure SP, BC, and reinforced papers with BC [22].

3.2 Surface treatment of paper

Lee et al. (2002) [24] had prepared cationic starch as size press starch to solve the problems associated with conventional size press starches. Oxidized starches commonly used for surface sizing, but they act as anionic trash in the broke recycling process. When cationic starch was used as size press starch, the starch contents in headbox and white-water silo were decreased by 59-62% and 29%, respectively. This decreased COD load in white water by more than 50 ppm and increased fines retention and strengths of paper. Base papers surface sized with cationic starch also gave better stiffness, opacity, brightness, printing quality, and picking resistance than oxidized starch.

Lipponen et al. (2004) [25] had studied effect of concentration of starch solution on surface sizing. When the solids content of the starch solution was increased from 8 to 18%, less starch penetrates into the sheet and more starch remains on the paper surface. A decreased penetration of starch improves such paper properties as surface strength and bending stiffness. The porosity of paper decreases by almost 50%. Surface sizing at high solids can decreasing the wetting of the sheet will also increase the productivity of paper machines.

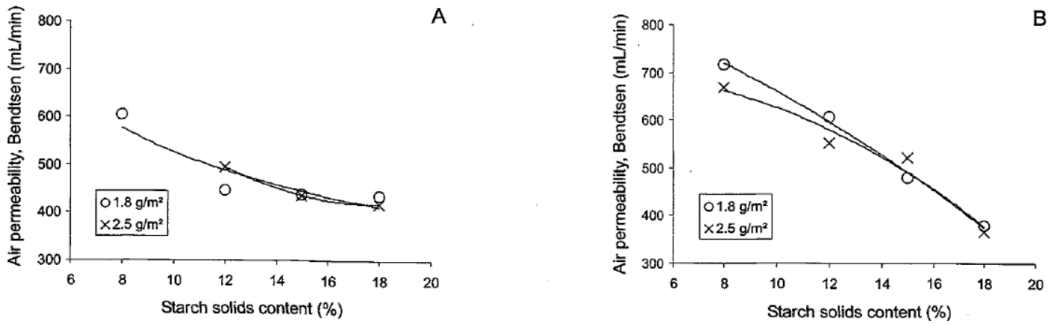

Figure 14: Effect of solids content on air permeability (Bendtsen) as a function of the total amount of starch applied with (A) a low-viscosity starch A and (B) a high-viscosity starch B [25].

Brenner et al. (2016) [26] used the ultrasonic treatment of a jet cooked starch solution to prepare degraded starch for surface sizing. Compared to commercial degradation processes (by enzymes or by thermos-oxidation). Starch solutions prepared by ultrasonic treatment show enhanced penetration into the paper with a higher starch quantity compared to paper that is sized with starches from common digestion processes. Paper sized with an ultrasonically treated starch solution shows the same strength properties compared to commonly sized paper. However, these benefits justify an economic evaluation of the new process.

Chen et al. (2017) [27] had prepared superhydrophobic paper with remarkable durability by a universal surface sizing technique. Starch-based composite was first coated onto the paper surface by surface sizing, immediately followed by spray coating of hexamethyl disilazane treated silica nanoparticles (HMDS-SiNPs) dispersed in ethanol on the surface of the wet starch-coated sheet. After drying, the obtained paper possesses excellent self-cleaning properties and exhibits an enhanced durability against multiple scratching, bending, and moisture.

CHAPTER IV
EXPERIMENTAL

4.1 Materials

1. Nano-bacterial cellulose (NBC) (The Institute of Food Research and Product Development, Kasetsart University, Thailand)
2. Sodium hydroxide (NaOH) (Merck Co., Ltd., Thailand)
3. Commercial tapioca based oxidized starch (EXCELSIZE 8, EXCELSIZE 15, and EXCELSIZE 22, SMS Corporation Co., Ltd., Thailand)
4. Cellulosic paper (CM180, Basis weight 180 gsm) (Panjapol Paper Industry Co., Ltd., Thailand)

4.2 Instruments

1. Laboratory blender (Model 8010S, Waring, USA)
2. K Control coater (Model K202, RK Print Coat Instrument Ltd., UK)
3. Oven (Model NDO-600ND, EYELA, Japan)
4. Water bath
5. Brookfield viscometer (Model DV2TLVTJ0, Brookfield, USA)
6. Digital refractometer (Model 3810 PAL-1, Atago, Japan)
7. Laboratory thermometer
8. Burst strength tester (Model PN-BSM160, Hangzhou Pnshar Technology Co., Ltd., China)
9. Universal tester vertical (Frank-PTI, Germany)
10. Internal bond tester (Model 1027A, Universal Engg. Corporation, India)
11. Folding endurance MIT tester (MIT#1, Tinius Olsen, USA)
12. Cobb tester (Water absorption tester)
13. Air permeability (Gurley type Densometer, H.E. Messmer Ltd., England)
14. Fourier-transform infrared spectrometer (FTIR) (Spectrum GX, Perkin Elmer, USA)
15. X-Ray diffractometer (XRD) (Model D8 Discover, Bruker AXS, Germany)
16. Scanning electron microscope (SEM) (Model JSM-7610F, JEOL, Japan)

4.3 Methodology

4.3.1 Preparation of starch solutions

The several oxidized starches with slurry concentration of 25 %w/w were cooked by direct steam batch cooker at temperature of 95°C for 20 min. The starch solutions obtained were diluted to concentrations of 10 %w/w and measured viscosity of the starch solutions by using the Brookfield viscometer. The starch solutions were stored in water bath at temperature of 60°C.

4.3.2 Preparation of NBC starch-based composite suspensions

The nano-bacterial cellulose hydrogel was first purified by washing with DI water for 1 hour and then treated with 1% w/w NaOH for 24 hours to remove remaining bacterial cells followed by rinsing with DI water until pH came to 7.

The purified wet NBC hydrogel was blended in water. The NBC suspension was mixed into the starch solution with various dosage levels (0.10, 0.25, 0.50, 0.75, 1.00, 2.50, 5.00, 7.50 and 10.00 %w/w based on dry weight of starch) and continuously stirred at temperature of 60°C, 500 rpm for 10 min.

4.3.3 Paper surface sizing

The NBC starch-based composites were sized on the surface of base paper using the K Control coater at a constant sizing speed of 13 m/min. The surface sized paper was dried at 105°C for 3 min. The surface sizing weight of the paper samples was about 4-6 g/m^2.

4.3.4 Characterization of films and papers

The starch solution, the NBC suspension, and the NBC starch-based composite suspension were prepared following by previous, then poured into plate and dried at room temperature for 1 day. The films were obtained and characterized by FTIR, XRD, and SEM.

4.3.4.1 Scanning electron microscopy (SEM)

Scanning electron microscopy will be employed to observe the morphology of the surface and cross-section of the starch, NBC, and NBC starch-based composite film. The JEOL JSM-7610F model at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University is used for this purpose.

4.3.4.2 Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was used primarily to identify the chemical structure of starch, NBC, and starch-based composite film. The FTIR spectra of the films were measured at wavenumbers ranging from 4000 to 400 cm^{-1} with a Perkin Elmer (United States) Spectrum GX FTIR spectrometer.

4.3.4.3 X-Ray diffraction spectroscopy (XRD)

X-ray diffraction of starch, NBC, and NBC starch-based composite film was measured with an X-ray diffractometer (model D8 Discover, Bruker AXS, Karlsruhe, Germany). X-ray diffraction patterns were recorded with Cu radiation (λ = 1.54 A°). The operating voltage and current were 40 kV and 40 mA, respectively. Samples were scanned from 10-40° 2θ at a scan speed of 7.5° min^{-1}.

4.3.5 Determination of properties of surface sized paper

The surface sized paper samples were treated for 24 hours at 27±1 °C and 65±2 %RH prior to mechanical measurement. The mechanical measurements including burst index (TAPPI T403), internal bonding (TAPPI T569), tensile index (TAPPI T494), and folding endurance (TAPPI T511) of paper samples. The resistance to water and air were determined by Cobb's test (TAPPI T441) and air permeability (TAPPI T460), respectively. All of measurements were followed TAPPI standard test methods.

4.3.6 Surface morphology of surface sized paper

The examination of the surface sized paper was performed by SEM. The samples were dried before experiment by oven at 60 °C for 2 hours then kept in desiccator for 1 hour. After that, cut test specimen in 1 cm^2 and sputtered with gold particle. The surface morphology of the paper was observed.

CHAPTER V
RESULTS AND DISCUSSION

5.1 Characterization of films

5.1.1 Scanning electron microscopy (SEM)

The surface structure of NBC, oxidized starch, and NBC starch-based composite films was then analyzed by scanning electron microscopy (SEM). The SEM investigation on the dried films represented the structure of surface morphology and cross-sectional of these films (**Figure 15-18**). In definition, starch film refers to oxidized starch (EXCELSIZE 15) film without NBC adding, NBC film refers to nano-bacterial cellulose film with no starch, whereas the E15-NBC refers to the NBC starch-based composite film with the dosage of NBC was varied at 0.50% and 1.00% on dry starch.

The SEM of the NBC film (**Figure 15**) shown the well-organized fibril networks. The similar result was reported by Phisalaphong, M. et al. (2008) [28]. The starch film presented surface and cross-section with greater homogeneity and continuity (**Figure 16**). The homogeneity of the oxidized starch film was attributed to the effect of depolymerization of the starch molecules [29]. The morphology of E15-NBC films with the addition of NBC suspension at various concentration of 0.50% and 1.00% w/w as shown in **Figure 17 and 18**, displays homogeneous film as same as starch film which indicated a good dispersion of the NBC in the starch matrix, without the agglomeration of NBC.

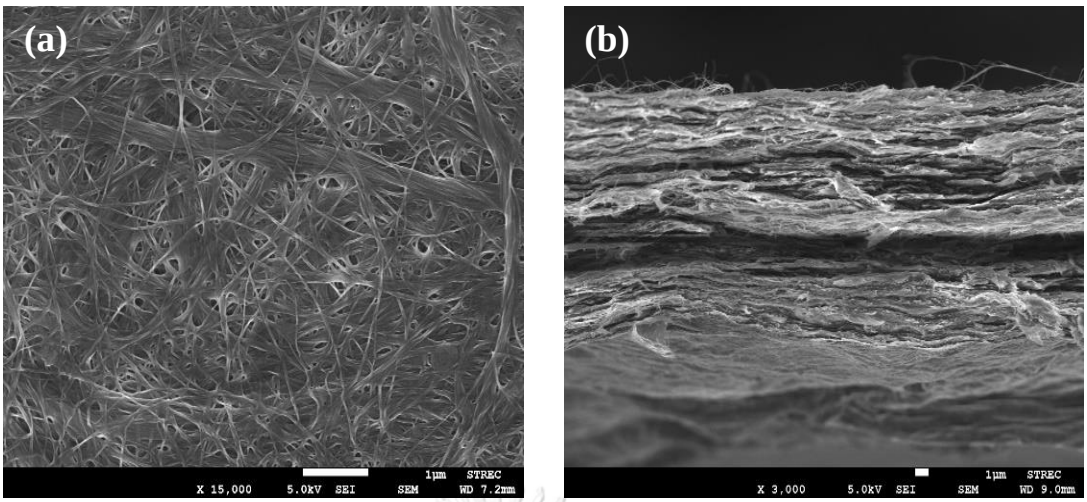

Figure 15: SEM images of (a) surface morphology at 15000X magnification and (b) cross-sectional morphology at 3000X magnification of NBC film.

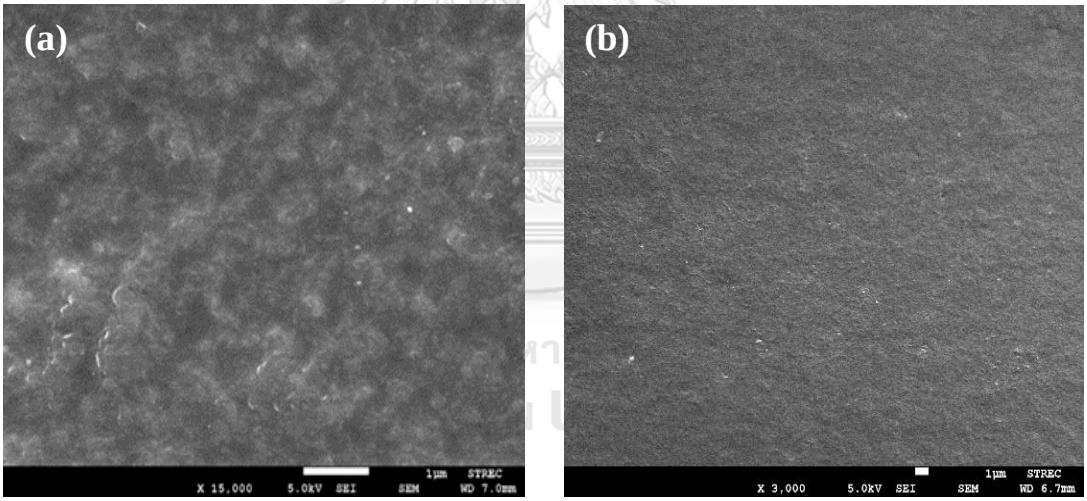

Figure 16: SEM images of (a) surface morphology at 15000X magnification and (b) cross-sectional morphology at 3000X magnification of starch film.

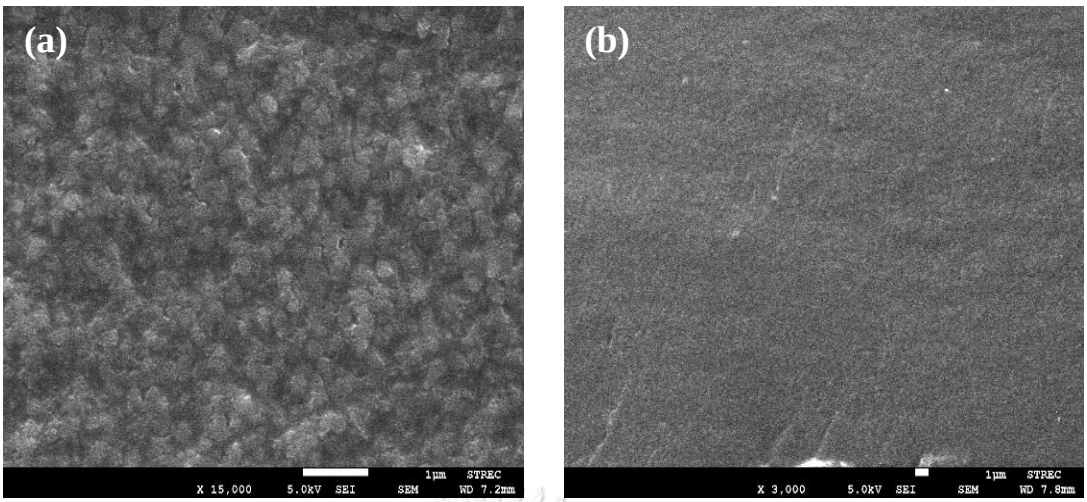

Figure 17: SEM images of (a) surface morphology at 15000X magnification and (b) cross-sectional morphology at 3000X magnification of E15-NBC 0.50% film.

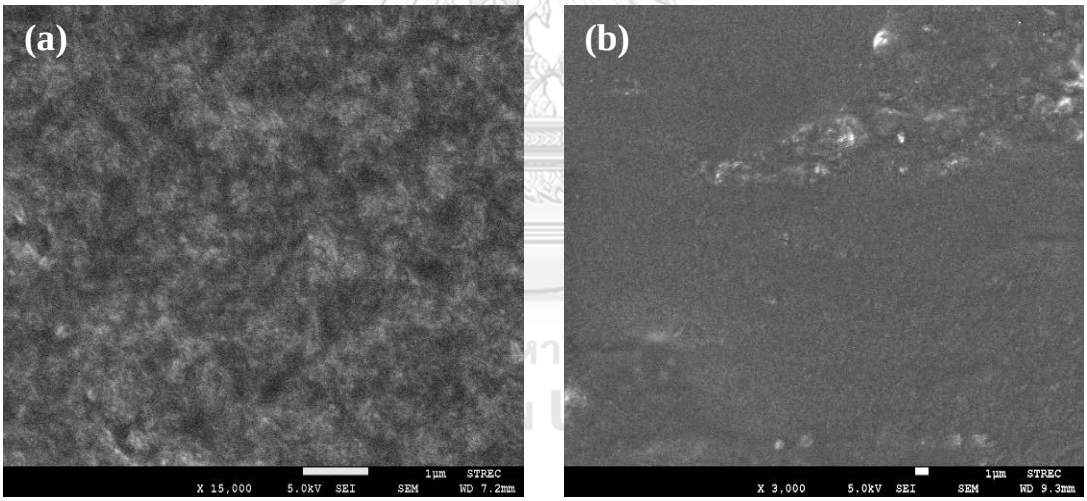

Figure 18: SEM images of (a) surface morphology at 15000X magnification and (b) cross-sectional morphology at 3000X magnification of E15-NBC 1.00% film.

5.1.2 Fourier transform infrared spectroscopy (FTIR)

In this research, the chemical functions of oxidized starch, NBC, and NBC starch-based composite films were analyzed by FTIR spectroscopy. The results of FTIR (**Figure 19**) demonstrated the specific functional group or chemical bonds of films. FTIR spectra of the oxidized starch (EXCELSIZE 15) film, NBC starch-based composite film with the addition of 0.50% NBC, and NBC film are shown as spectra (a), (b), and (c), respectively. The FTIR of oxidized starch film (**Figure 19a**) exhibited a high intensity of absorption peak, which was assigned to depolymerization of the starch molecules by oxidation of hydroxyl group to aldehyde and carboxyl group [30, 31]. The characteristic of NBC as shown in **Figure 19c** was the bands at 3200-3400 cm^{-1} and 1642 cm^{-1}, which were assigned to the intramolecular O–H stretching and glucose carbonyl of cellulose, respectively [28, 32].

The FTIR spectra of NBC starch-based composite films (**Figure 19b**) were quite similar to the FTIR spectra of the oxidized starch film, because starch was the main component of the film. Since NBC starch-based composite film were prepared with a combination of NBC and starch, the FTIR spectra of NBC starch-based composite films were combined with characteristic absorption bands on **Figure 19a** and **Figure 19c**. There was a new band at 1634 cm^{-1} which indicated the glucose carbonyl of cellulose as same as shown in NBC film, but it has shifted from 1642 cm^{-1} to 1634 cm^{-1} and broad peak. The shift of broad absorption band of the film could be attributed to the intermolecular hydrogen bonding might take place between starch and NBC [33, 34], leading to a good miscibility film. The FTIR result was in good agreement with the conclusion from the previous analysis of surface morphology (SEM).

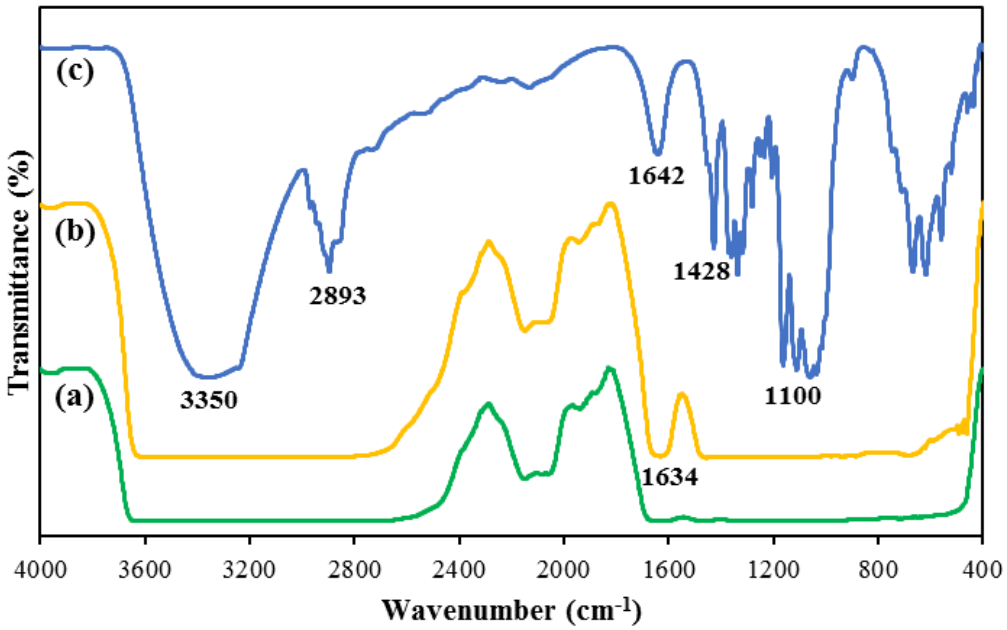

Figure 19: The FTIR spectra of the films: (a) Starch (EXCELSIZE 15), (b) E15-NBC 0.50%, and (c) NBC.

5.1.3 X-Ray diffraction spectroscopy (XRD)

The XRD patterns of starch, NBC starch-based composite, and NBC films are shown in **Figure 20**. The oxidized starch film in **Figure 20a** shows the intense peaks appeared at 2θ values of 17.4°, meaning that the crystalline structure of the native starch is destroyed during the oxidation, exhibiting an amorphous phase [35]. For the XRD pattern of NBC film in **Figure 20d**, the peaks observed at 14.5° and 22.8° were attributed to the NBC cultured in static circumstance. The board diffraction peaks observed for NBC were because NBC is not a completely crystalline material [28]. The diffractograms of the starch-based composite film with the additions of 0.50% and 1.00% of NBC showed nearly no difference from that of oxidized starch film.

The degree of crystallinity (**Table 2**) of the oxidized starch film was slightly higher than that of NBC starch-based composite films. The degree of crystallinity of the oxidized starch, NBC starch-based composite with 0.50% and 1.00% NBC, and NBC was 28.94%, 21.24%, 28.54%, and 81.28%, respectively. The NBC starch-based composite film showed the decreased in degree of crystallinity to 21.24% cause by the distribution of 0.50% NBC in the oxidized starch matrix. However, higher degree of

crystallinity at 28.54% was observed with the increase of NBC supplement to 1.00% (E15-NBC 1.00%). Crystallinity could indicate to the degree of structural order in a solid film. The compositions of crystalline/amorphous components in the film can also affect its crystallinity.

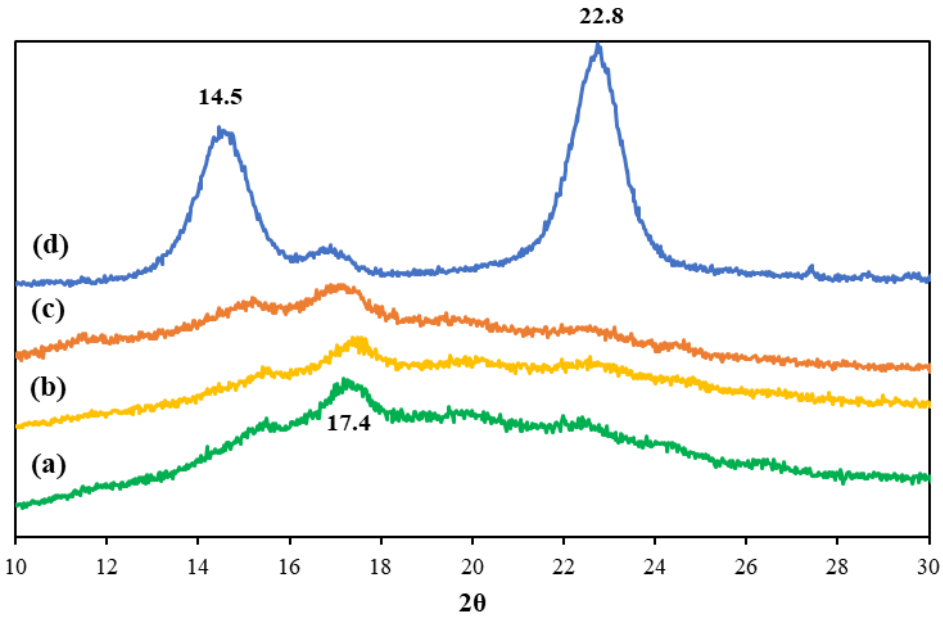

Figure 20: The X-ray pattern of the films: (a) Oxidized starch (EXCELSIZE 15), (b) E15-NBC 0.50%, (c) E15-NBC 1.00%, and (d) NBC.

Table 2: Degree of crystallinity of films.

Film sample	Crystalline area	Amorphous area	Degree of crystallinity (%)
Oxidized starch (E15)	3462.8	8504.5	28.94
E15-0.50% NBC	1916.0	7103.0	21.24
E15-1.00% NBC	3003.0	7517.8	28.54
NBC	9237.9	2127.4	81.28

5.2 Effect of oxidized level of starch on properties of paper

Oxidized level affects the molecular weight of starch which exhibits to viscosity of starch solution. The different viscosity of starch that used as surface sizing agents could have effect on the physical properties of the surface sized papers. In this study, the various viscosities of oxidized starches, which are high, middle, and low viscosity, respectively (**Table 3**), were used to prepare the NBC starch-based composite suspensions with the addition of 0.00%, 0.50% and 1.00% w/w NBC. The mechanical properties in terms of burst index, internal bonding, tensile index, and folding endurance, and the barrier properties in terms of water absorption (Cobb value) and air permeability of the surface sized paper were determined in order to investigate the effect of viscosity of starch on encouragement to performance of NBC as a reinforcing material.

Table 3: The viscosity of starch solution.

Starch	Brookfield viscosity 60 rpm at 50°C (cP)	Solids content (%)
EXCELSIZE 8	36	10
EXCELSIZE 15	14	10
EXCELSIZE 22	9	10

The mechanical properties of the surface sized paper are shown in **Figure 21-26**. As compared to base paper (Blank), by surface sizing with the high-viscosity of starch (EXCELSIZE 8, E8) without NBC, the mechanical properties of surface sized paper in terms of burst index, internal bonding, tensile index in machine direction (MD) and cross-machine direction (CD), and folding endurance in machine direction (MD) and cross-machine direction (CD) were increased by 29%, 26%, 1%, 5%, 27% and 21%, respectively. For the middle-viscosity of starch (EXCELSIZE 15, E15), the mechanical properties were increased by 21%, 25%, 2%, 4%, 30%and 16% in terms of burst index, internal bonding, tensile index in MD and CD, and folding endurance in

MD and CD. And by using the low-viscosity of starch (EXCELSIZE 22, E22), the mechanical properties were increased by 19%, 22%, 8%, 2%, 30% and 18%, respectively.

From the previous results, the viscosity of starch is effect to improve each mechanical properties of paper. For example, the burst index of paper by using the high-viscosity starch was higher than the lower one. On the other hand, the folding endurance of paper by using the low-viscosity was higher than that by using the high-viscosity starch.

In addition, the incorporation of NBC into starch-based composite suspension considerably increased the overall mechanical properties of surface sized paper. There was no significant difference in effects of NBC supplement under the variation of viscosity of starch, i.e. EXCELSIZE 15 with 1.00% NBC and EXCELSIZE 22 with 1.00% NBC are increased the burst index in same ratio of 10%.

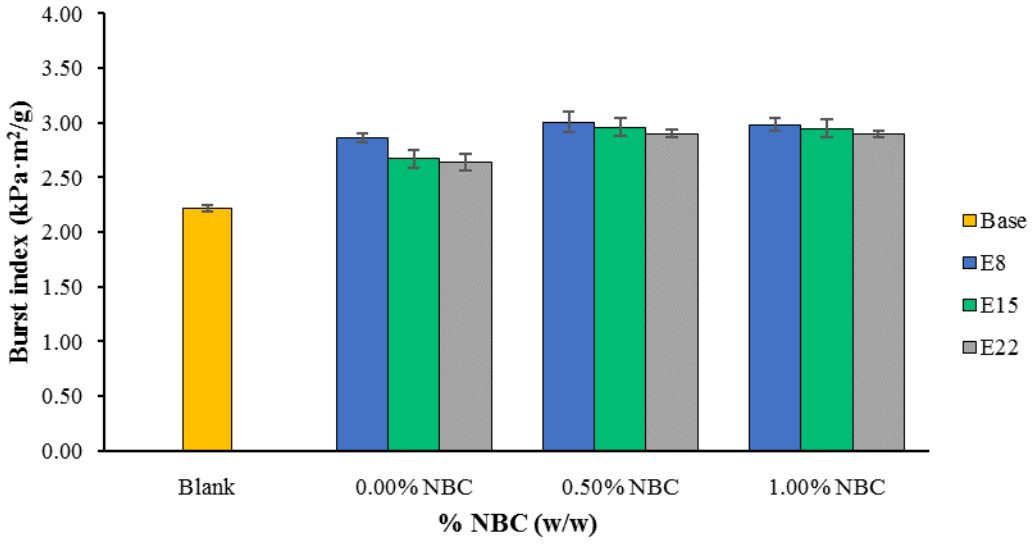

Figure 21: Burst index of surface sized paper with various starches as a function of NBC content in starch-based composites.

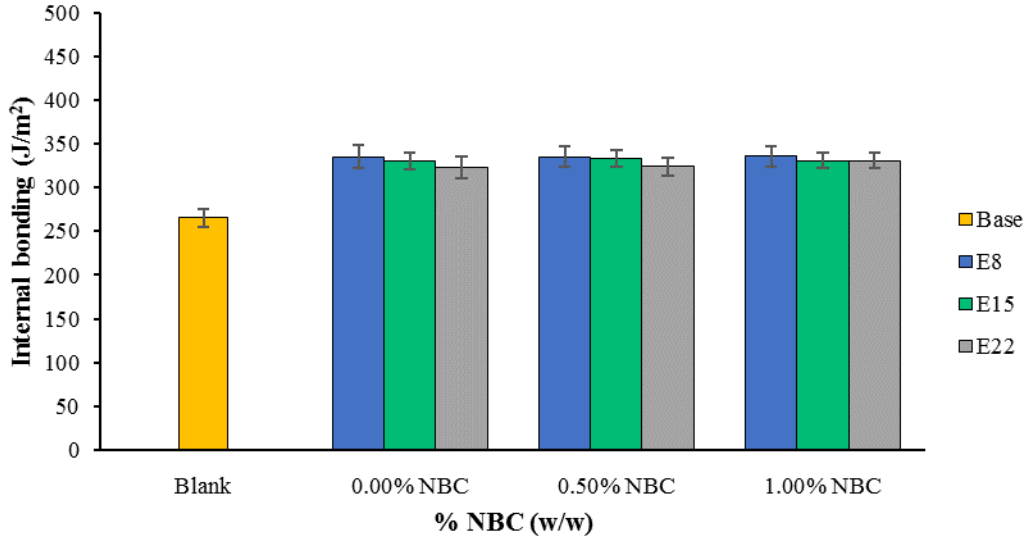

Figure 22: Internal bonding of surface sized paper with various starches as a function of NBC content in starch-based composites.

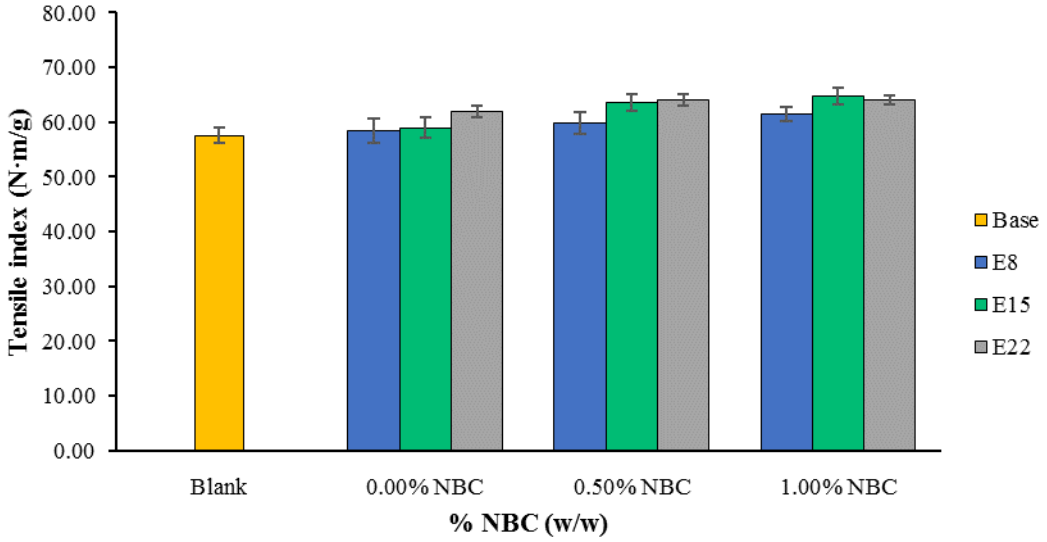

Figure 23: Tensile index (MD) of surface sized paper with various starches as a function of NBC content in starch-based composites.

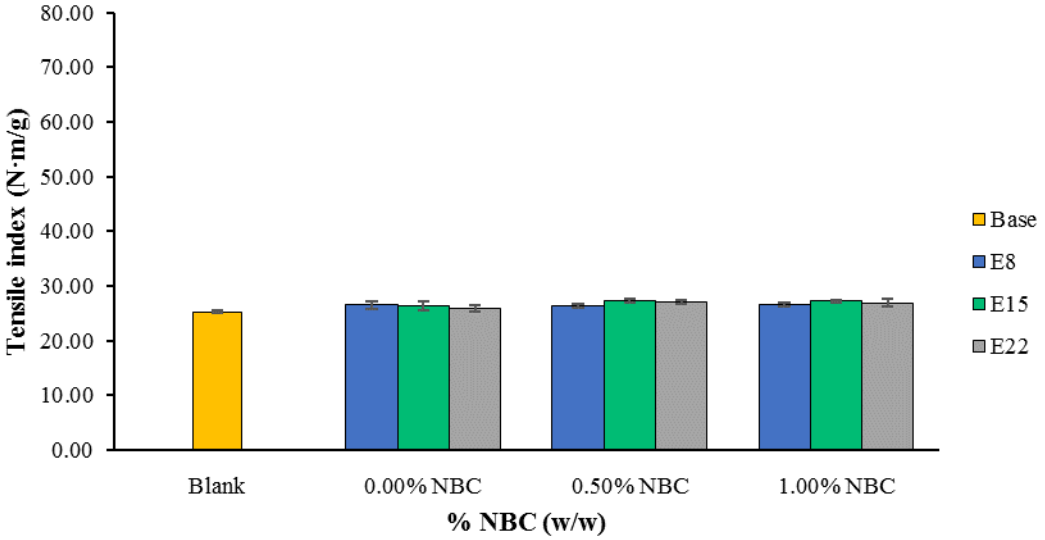

Figure 24: Tensile index (CD) of surface sized paper with various starches as a function of NBC content in starch-based composites.

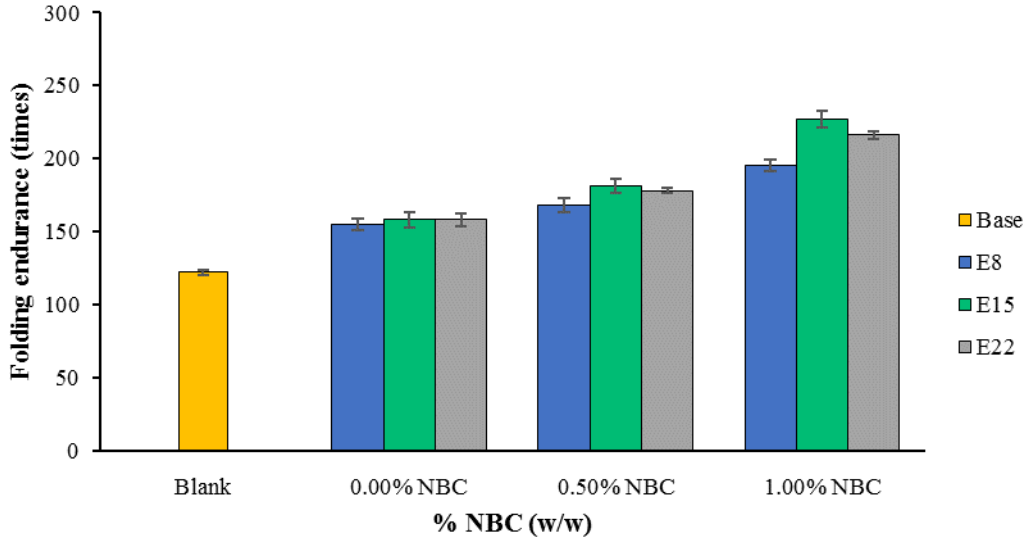

Figure 25: Folding endurance (MD) of surface sized paper with various starches as a function of NBC content in starch-based composites.

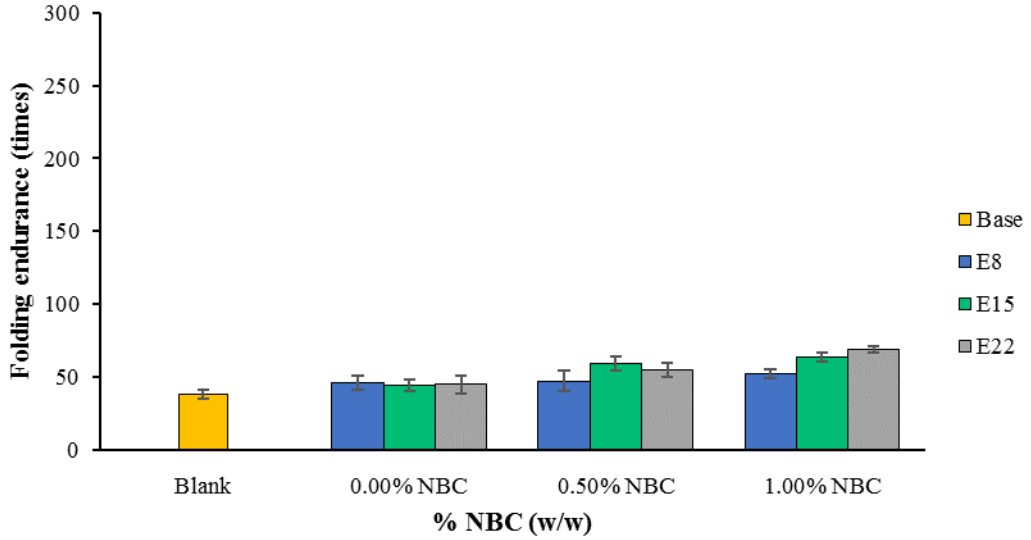

Figure 26: Folding endurance (CD) of surface sized paper with various starches as a function of NBC content in starch-based composites.

The barrier properties of surface sized paper in term of the water absorption of surface sized paper which was evaluated by Cobb value (**Figure 27**) was slightly decreased as compared to base paper. Nevertheless, all of samples still shown high Cobb value because starch and NBC have hydrophilic character, especially NBC has high water holding capacity. The air resistance of the papers was significantly enhanced by surface sizing. As shown in **Figure 28**, the air resistance was increased by 188%, 101%, and 86% as compared to based paper, when surface sizing with the high, middle, and low-viscosity starch, respectively. Furthermore, the air resistance tends to increase when the dose of NBC is higher. Due to viscosity of the applied starch, the air resistance of surface sized paper with the high-viscosity starch (EXCELSIZE 8) was higher than the lower one, by more effect on pore size reducing of the paper.

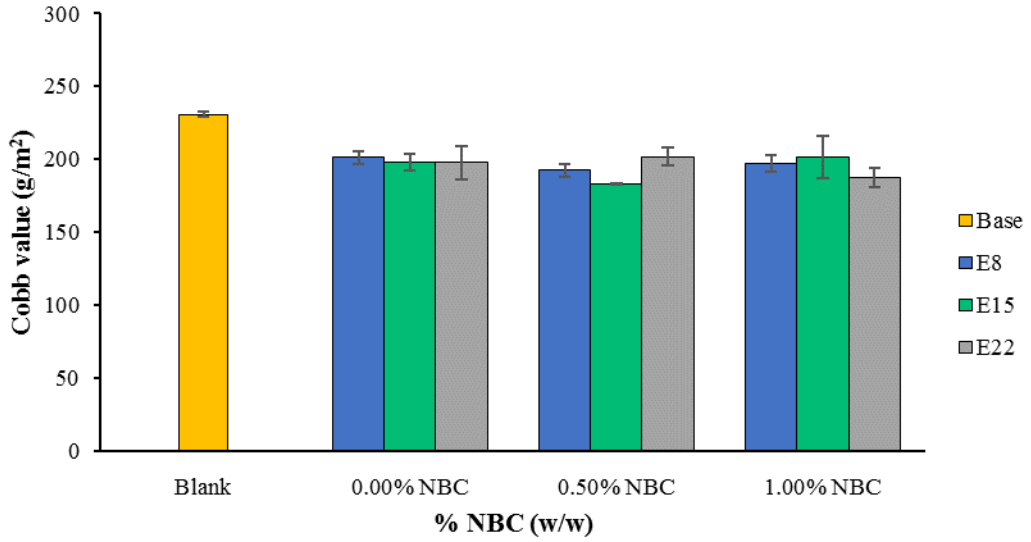

Figure 27: The water absorption of surface sized paper with various starches as a function of NBC content in starch-based composites.

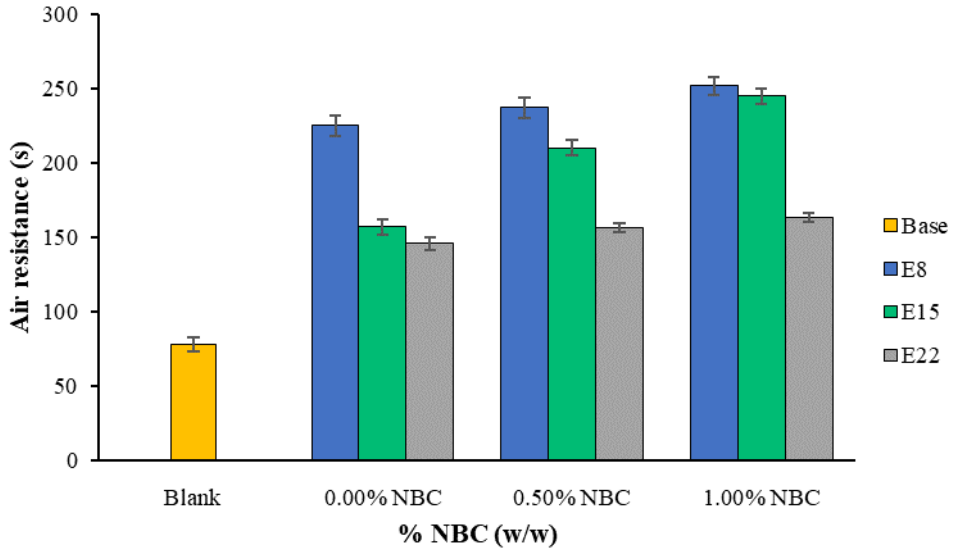

Figure 28: Air resistance of surface sized paper with various starches as a function of NBC content in starch-based composites.

According to results, the high-viscosity of starch can enhance the burst index and the air resistance which related to the effects of surface coating. On the other hand, the low-viscosity of starch can enhance the tensile index and the folding endurance which related to the inter-fiber bonding of paper. Because low-viscosity of starch can penetrate into the paper. However, the starch viscosity did not show any significant effect on the performance of NBC as reinforcement material in starch-based composite.

5.3 Effects of NBC dosage in starch composite on properties of paper

This section demonstrates the effects of varying dosage of NBC from 0.10-10.00%, mixed into EXCELSIZE 15, which is the middle-viscosity starch. The effect of NBC dosage on the mechanical properties (**Figure 29-34**) and the barrier properties (**Figure 35-36**) of surface sized paper were investigated.

Figure 29 presents the burst index of paper after surface sizing with NBC starch-based composite, tends to increase up to 10% with the addition of 0.50% NBC. The burst index was not increased even though the NBC dosage was increased more than 0.50%. Subsequently, there was no significantly improvement in the internal bonding (**Figure 30**) when NBC was added. The tensile index in machine direction (MD) (**Figure 31**) was slightly increased approximately 10% with the addition of NBC was 1.00% and gradually increasing with the increase of NBC from 1.00 to 10.00%. But the tensile index in cross-machine direction (CD) was not found improvement (**Figure 32**). In case of the folding endurance, the increased NBC content in starch-based composite could be increase the folding endurance in both directions (MD and CD) (**Figure 33 and 34**). With the addition of 10.00% NBC, the surface sized paper exhibited the increases in the folding endurance in MD and CD by 60% and 48%, respectively as compared to the surface sized paper without NBC.

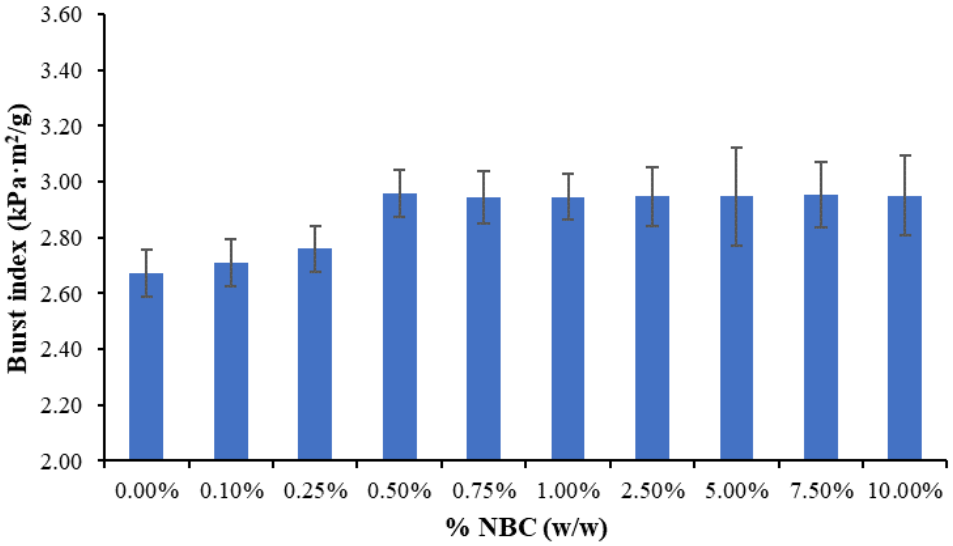

Figure 29: Burst index of surface sized paper as a function of NBC content in starch-based composite.

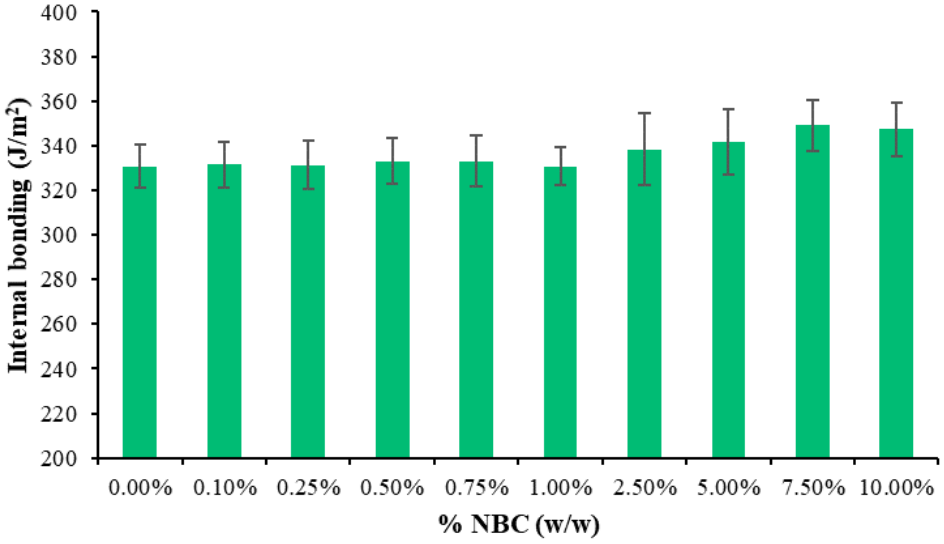

Figure 30: Internal bonding of surface sized paper as a function of NBC content in starch-based composite.

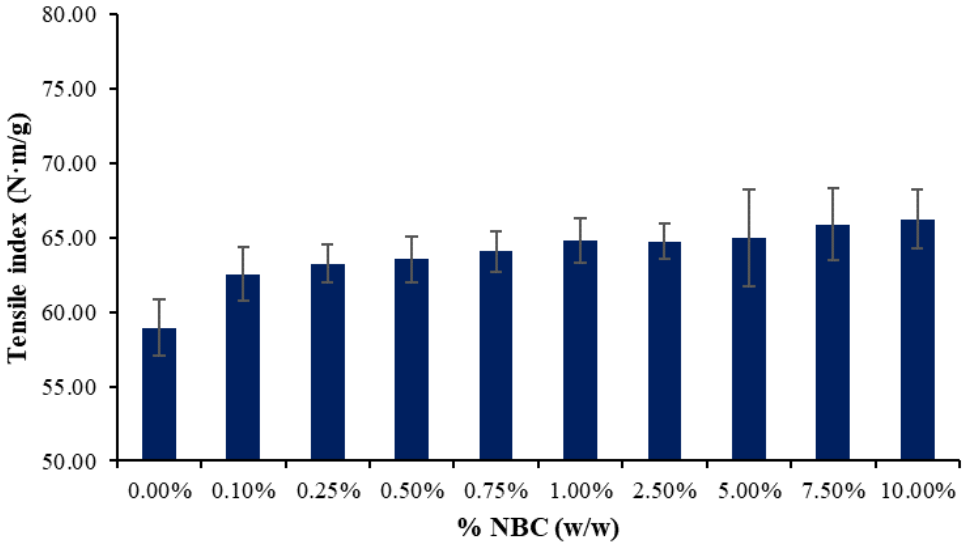

Figure 31: Tensile index of surface sized paper (MD) as a function of NBC content in starch-based composite.

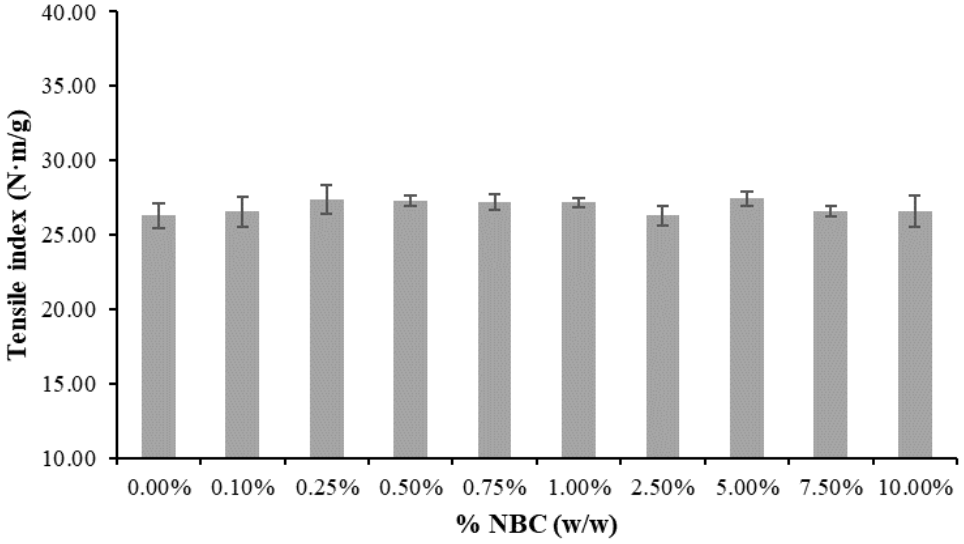

Figure 32: Tensile index of surface sized paper (CD) as a function of NBC content in starch-based composite.

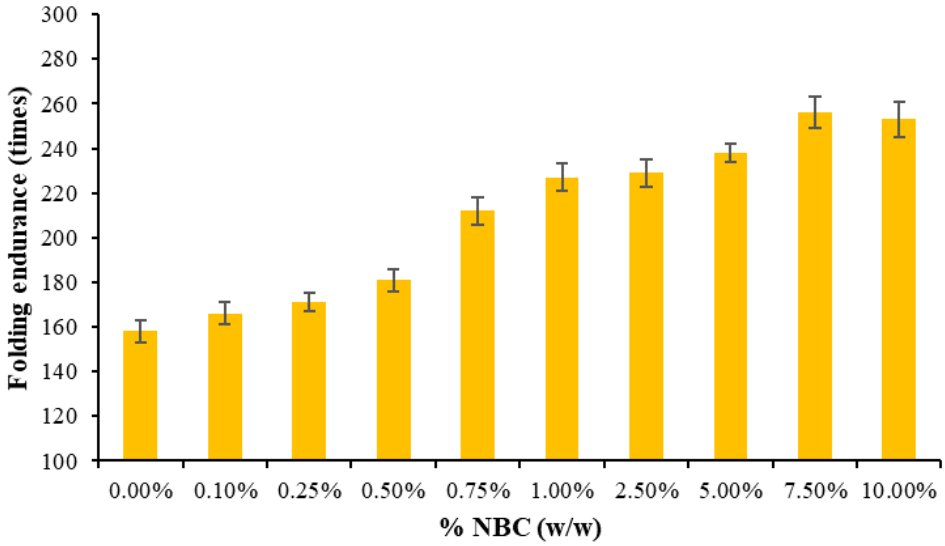

Figure 33: Folding endurance of surface sized paper (MD) as a function of NBC content in starch-based composite.

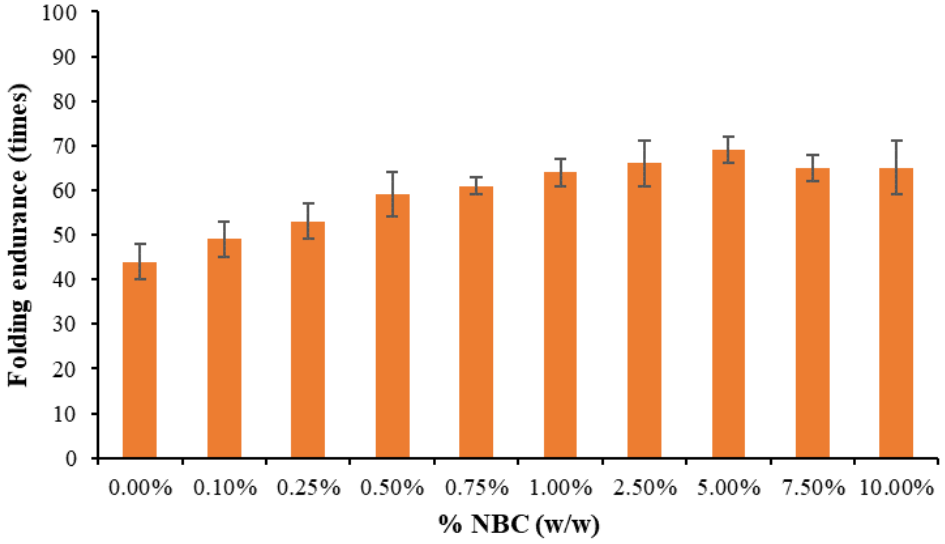

Figure 34: Folding endurance of surface sized paper (CD) as a function of NBC content in starch-based composite.

The effect of the NBC supplement in starch-based composite on the barrier properties of surface sized paper is shown in **Figure 35**. There was no significant difference in the water resistance even though NBC was added. Alternatively, it can be observed that the incorporation of NBC into starch-based composite had obvious effect on the air resistance of the surface sized paper as shown in **Figure 36**. With the additions of 1.00% and 10.00% NBC, the air resistance was particularly improved by 56% and 61%, respectively as compared to surface sizing without NBC. Therefore, NBC could be able to seal the pores that might exist within the papers, which served as the major path for permeating air molecules [36]. This result is supported by the report of Yang, S. et al (2014) [1], that the paper sized by starch-based composite suspensions with 0.3 wt. % nanocrystalline cellulose showed a 33% decrease in air permeability.

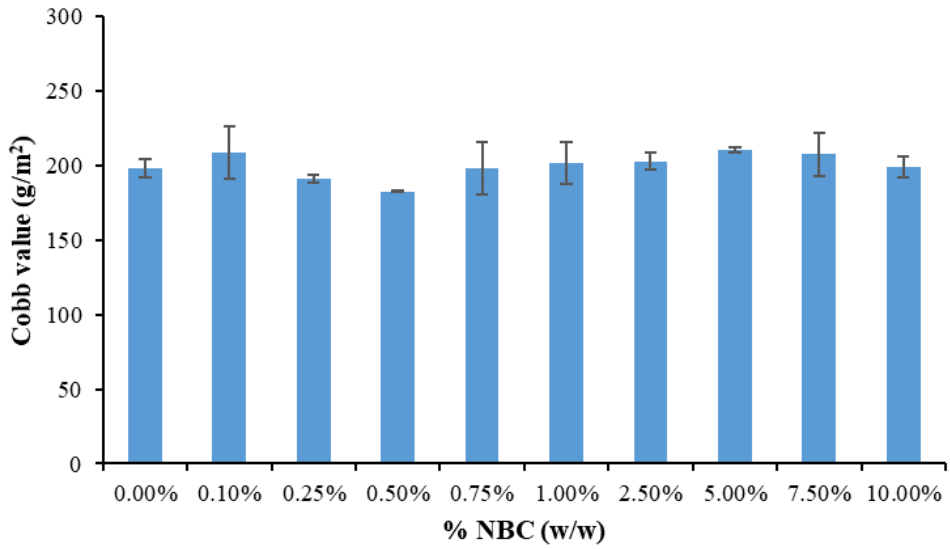

Figure 35: The water absorption of surface sized paper (Cobb value) as a function of NBC content in starch-based composite.

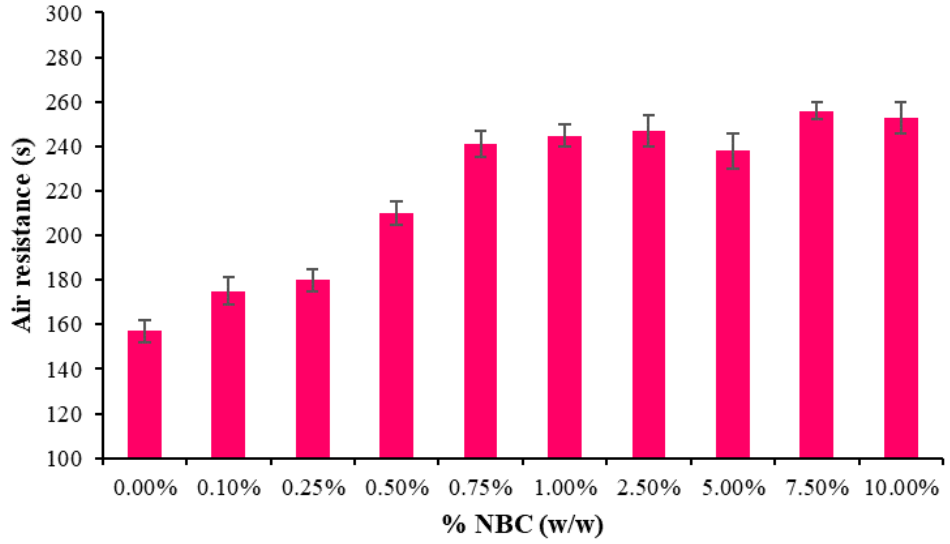

Figure 36: Air resistance of surface sized paper as a function of NBC content in starch-based composite.

5.4 Surface morphology of paper

The surface morphology of based paper, surface sized paper without and with addition of NBC at 0.50% and 1.00% was observed by SEM at 500X magnification. SEM images of based paper (**Figure 37**) demonstrate that cellulose fiber is formed the fiber network structure and there are gaps between the fiber. **Figure 38** presented the SEM image of surface sized paper without the addition NBC. The cellulose fiber was coated with starch resulting in bridging to connected between each fiber. In addition, by adding NBC 0.50% and 1.00% (**Figure 39 and 40**), the gap between fiber were filled with NBC and bridged by starch, leading to pore size reducing.

The SEM results supported the results from the previous analysis of mechanical properties and barrier properties of surface sized paper. In general, paper is essentially a hydrogen bonded fibrous composite. The strength mechanism is primarily through reinforcement of the inter-fiber joints via hydrogen bonds. The starch penetrates into paper according to the void space between fibers. Then attaches to fibers and reinforces the paper sheet. The NBC provide more inter-connection between fibers and more reactive group for interaction with starch. Moreover, the incorporation of NBC in paper structure sealed the paper pores, leading to the air resistance were enhanced.

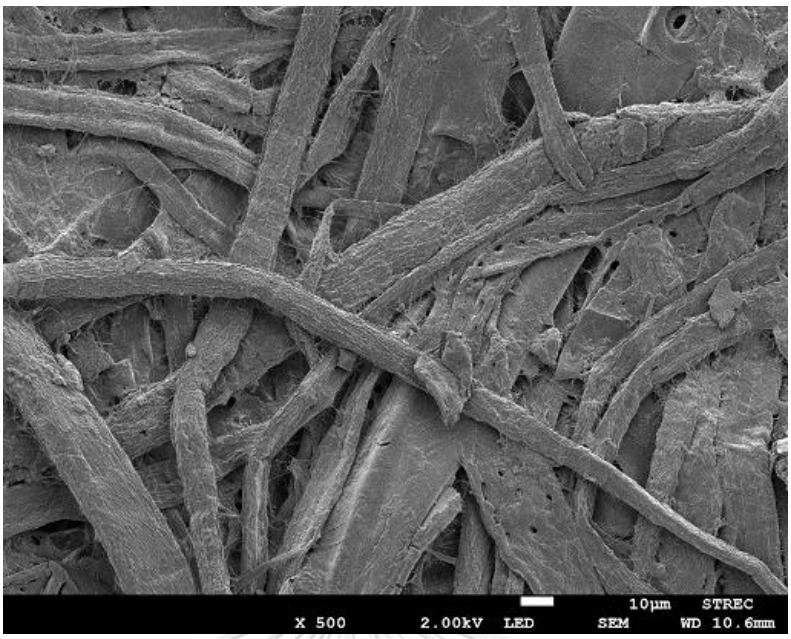

Figure 37: SEM image of surface morphology of based paper at 500X magnification.

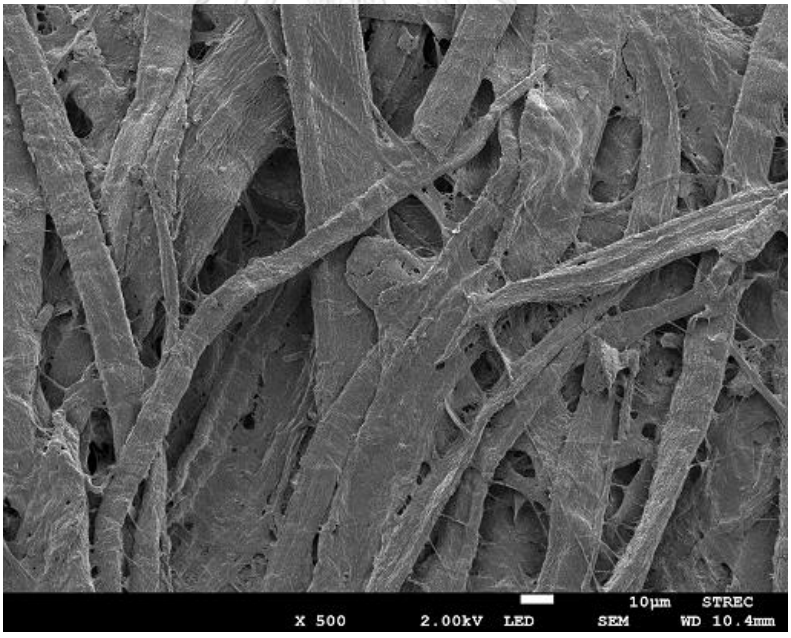

Figure 38: SEM image of surface morphology of surface sized paper without NBC at 500X magnification.

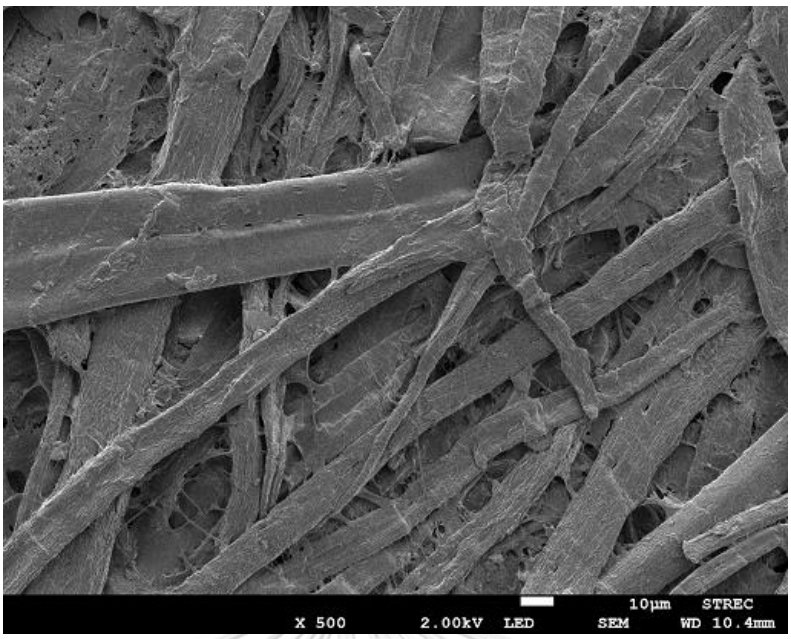

Figure 39: SEM image of surface morphology of surface sized paper with addition of 0.50% NBC at 500X magnification.

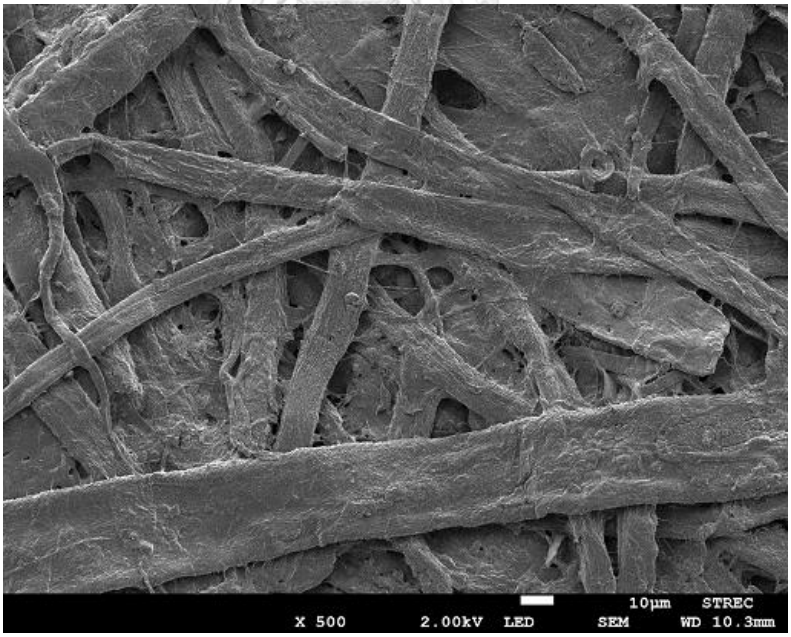

Figure 40: SEM image of surface morphology of surface sized paper with addition of 1.00% NBC at 500X magnification.

CHAPTER VI
CONCLUSION

In case of the limitations of starch in surface treatment process, to reduce these disadvantages. The starch-based composite reinforced with nano-bacterial cellulose (NBC) which was isolated from nata de coco, been developed. With addition of NBC 0.10-10.00% w/w, the composites were prepared and used as surface sizing agents for cellulosic paper. The FTIR spectra indicated the intermolecular interactions between NBC and oxidized starch. The NBC starch-based composite films were homogeneous that indicated NBC should be well-dispersed in the starch. NBC starch-based composite which used in surface treatment of paper can improve properties of paper. When 1.00% NBC was added, the mechanical properties increase up to 10% in terms of burst index, tensile index and 45% in term of folding endurance. The barrier property was particularly improved resulting in the enhanced air resistance up to 56%, as compared to surface sized paper without NBC. However, when the NBC dosage was further increased up to 10.00%, the mechanical and barrier properties of paper did not show considerably more improvement. Thus, the optimal dosage of NBC in starch-based composite for obtain good paper strength and air resistant property of paper was 1.00%.

Results revealed that the resistance to air was significantly enhanced by the addition of NBC in starch-based composite for surface treatment. Therefore, NBC has good potential uses as the additive to replace paraffin wax or synthetic polymer coating for food packaging products in order to protect oxidation for foods or fruits. However, more improvement for water and oil resistance is suggested for next development.

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APPENDICES

APPENDIX A
THE OXIDIZED STARCH SPECIFICATION

Oxidized starch specification

Starch	Brookfield viscosity* (cP)	Solid contents (%)	Temperature (°C)
EXCELSIZE 8	30-50	10	50
EXCELSIZE 15	30-50	15	50
EXCELSIZE 22	80-130	25	50

Remark: *Brookfield viscosity was measured LV-type at 60 rpm, spindle S61.

APPENDIX B
SURFACE TREATMENT METHOD

The surface treatment of cellulosic paper with NBC starch-based composite suspensions by K Control Coater as following:

1. Turn on the K Control Coater.
2. Set the coating parameters:
    a. Select coating speed (1-10).
    b. Select K meter bar (Bar No. 0-9).

    Note: In this study, coating speed No. 10 (13 m/min) and K meter bar No. 0 were selected in order to control coated weight of 4-6 g/m^2.
3. Place the based paper on glass bed and clipped.
4. Insert the selected K meter bar to bar holder on base paper.
5. Pour the coating substrate onto base paper, close to K meter bar and along the paper width. In this case, the coating substrate was NBC starch-based composite suspensions.
6. Turn the switch from STOP to FWD. for start coating process. The K meter bar was moved straightforward, then the base paper was coated. After that, turn the switch back to STOP.
7. Coated paper was dried by oven at 105°C for 3 min.
8. Remove K meter bar and clean with sponge by using tap water, then make it dried.
9. Clean glass bed. Make sure it was dried before the next coating.
10. Turn the switch to REV. for set bar holder in initial position, then turn switch back to STOP.
11. Next coating, repeat process from 3 to 10.

APPENDIX C
PAPER PROPERTIES TEST METHOD

C1. Preparation for testing

The most important prerequisite for paper testing is conditioning of the paper sample for its moisture content. Because wood fibers are naturally hygroscopic, paper easily absorbs moisture from the ambient atmosphere or releases moisture if the atmosphere in drier than that corresponding to equilibrium moisture content of the paper. Moisture content of paper influences almost all its physical properties. Paper samples therefore require careful conditioning before testing.

According to TAPPI T 400 “Standard conditioning and testing atmosphere for paper, board, pulp handsheets, and related products”, the preferred conditioning climate is 50 ± 2% RH and 23 ± 1°C. Another alternative allowed in tropical countries is 65% RH and 27°C. The normal conditioning time for paper is usually four hours minimum.

C2. Bursting strength

Bursting strength is the maximum pressure that the paper can resist without breaking with pressure applied perpendicular to the plane of the test piece. The unit for bursting strength is kilopascal, kPa. Calculation of the material related burst index uses the following formula:

Burst index = bursting strength / basis weight [$kPa \cdot m^2/g$]

The bursting test for paper is described in TAPPI T 403. The most common tester used for bursting strength measurements is the Mullen tester. A test specimen placed over a circular elastic diaphragm. Avoid areas including watermarks, creases, or visible damage. Clamp a specimen securely in position, overlapping the specimen at all points. Apply the hydrostatic pressure as specified until the specimen ruptures, and record the maximum pressure registered. Watch carefully for any movement of the unclamped margin of the specimen. If slippage is indicated, discard the test and increase

the clamping pressure. If it appears that excessive clamping pressure damaged the specimen, discard the test and reduce the clamping pressure.

C3. Internal bond strength

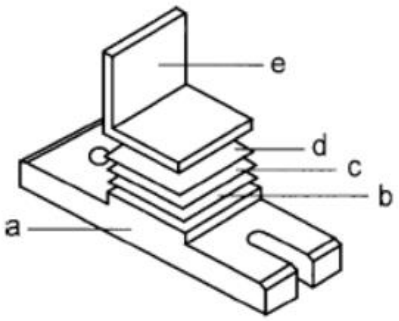
Internal bond strength or Z-directional strength refers to the ability of a paper to resist tensile loading in a direction perpendicular to the plane of the paper (Z-direction). After exceeding the Z-directional strength of the paper, a break in the paper structure occurs in the sheet but not at its surface.

The most common apparatus for measuring internal bond strength is the Scott bond tester, TAPPI T 569. The test specimens were accurately cut to 1.00 inches wide and 5.5 inches long. For accurate alignment in some specimen preparation stations, the specimens should be 7.0 inches long. Handle specimens by the extreme ends of the strip only. Ensure that strips are free from abnormalities, creases, or wrinkles.

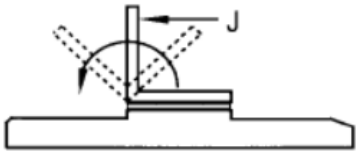
The specimen is mounted between the steel anvil and the aluminum platen. A double-sided tape mounts the specimen on the metal pieces. Cut the tape-paper-tape sandwich with knife to five pieces of sample. A pendulum then hits the aluminum platen and loads the paper sample until it breaks.

The loss of kinetic energy of the pendulum after it hits the aluminum platen indicates the strength of the paper. However, in the Scott bond tester, the loading case is not as well defined as in the real Z-directional tensile testing.

The unit for internal bond strength is Joule per square meter, J/m^2.



a steel anvil
b double coated tape
c specimen
d double coated tape
e aluminum platen



J = Pendulum Impact

C4. Tensile strength

Tensile strength is a very useful property to describe the general strength of any material. For paper, it is the maximum force per unit width that a paper strip can resist before breaking when applying the load in a direction parallel to the length of the strip. Measurement uses testers applying either a constant rate of loading, or a constant rate of elongation for loading the strip. Tensile strength expression uses kN/m. From the tensile strength measured, calculation of the tensile index uses the following formula:

Tensile index = tensile strength / basis weight [N·m/g]

The tensile strength test for paper is described in TAPPI T 494. This method describes the procedure, using constant-rate-of-elongation equipment, for determining four tensile breaking properties of paper and paperboard: tensile strength, stretch, tensile energy absorption, and tensile stiffness. In the tensile strength teste, the test specimen is cut in each principal direction of the paper 25 ± 1 mm wide and long enough to be clamped in the jaws when the test span is 180 ± 5 mm, leaving enough length so that any slack can be removed from the strip before clamping. Set the clamps to an initial test span (distance between line contacts) of 180 ± 5 mm. Set the controls for rate of separation of the jaws to 25 ± 5 mm/min. The test specimen is stretched to the point where rupture occurs. The maximum tensile force the test specimen can withstand before it breaks and corresponding elongation of the strip are measured and recorded.

C5. Folding endurance

Folding endurance or folding strength is the ability of a strip of paper to resist breaking when folded under a certain load. This load is constant but is generally only a small fraction of the tensile strength of the paper. The folding strength is expressed directly as the number of double folds that the paper can stand. Folding endurance is the ten-based logarithm of the number of double folds.

Physically, folding strength does not have a clear definition. It relates to the tensile strength, elasticity, and elongation of the paper. Higher tensile strength and elongation of a paper equate to higher folding strength. The most common folding testers are following:

- Schopper
- MIT
- Köhler-Molin
- Lhomargy

Although the testers all use the same principle, the numerical results obtained with different testers are different.

The folding endurance of paper (MIT tester) is described in TAPPI T 511. A specimen was cut accurately to a width of 15 ± 0.02 mm and a length of not less than 130 mm. A 150-mm or longer strip is preferable to provide easier insertion in the clamps. Select specimens that are free from wrinkles or blemishes not inherent in the paper and make sure that the area where the folding is to take place does not contain any portion of a watermark and appears to be of average opacity. The long edges shall be clean cut and parallel.

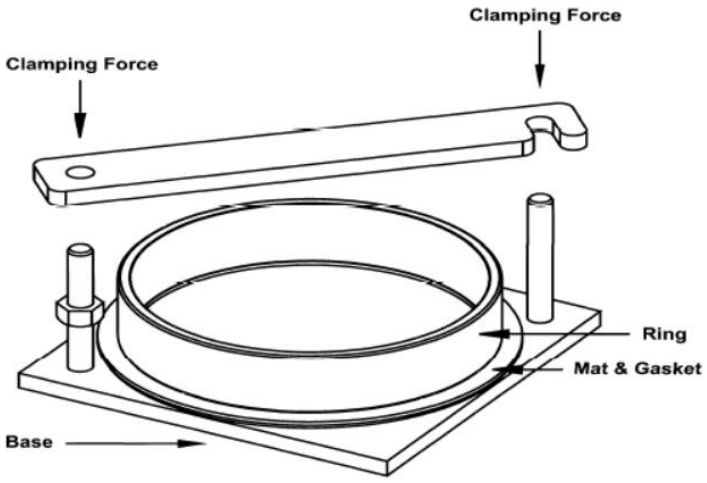
Turn the oscillating folding head so that the opening is vertical. Turn motor control switch to the off position. Place a 1-kg weight on the top of the plunger (equivalent to the tension desired on the specimen); tap the plunger sideways to minimize friction effects and lock it in position. Without touching the part of the strip to be folded, clamp the specimen lying wholly within one plane, i.e., flat, and with the sides, parallel to, and not touching the oscillating jaw-mounting-plate. Remove the weight and unscrew the plunger lock to apply the specified tension to the test strip. If the reading of the load indicator changes, re-clamp the specimen to give it its proper tension. Zero counter, then start motor.

Set the counter to zero and place the centrifugal fan so that its inlet is almost touching and is across the specimen and oscillating head. Start the fan and the instrument motor. Fold the strip at a uniform rate of 175 ± 25 double folds per minute until it breaks. Record the number of double folds made before fracture. If there is any appreciable delay between tests on successive specimens, keep the fan running to prevent the head warming by conduction from its shaft.

C6. Water absorptiveness

Water absorptiveness is used for determining the quantity of water absorbed by non-bibulous paper, paperboard, and corrugated fiberboard in a specified time under standardized conditions. It is based on studies by Cobb. It is a function of various characteristics of paper such as sizing, porosity, etc. This method is generally applicable to sized paper, paperboard and corrugated fiberboard, but it is not recommended as a sizing test for writing paper.

Water absorptiveness (Cobb value), the mass of water absorbed in a specific time by 1 m^2 of paper under 1 cm of water. The specimens are cut to a size slightly greater than the outside dimensions of the ring of the apparatus, the standard test area is 100 cm^2. Then weigh each specimen. Place a dry rubber mat on the metal plate and lay a weighed specimen on it. After wiping the metal ring, dry (do not use heat), place it upon the specimen, and fasten it firmly enough in place with the crossbar to prevent any leakage between the ring and the specimen.



Pour 100 mL of water into the ring as rapidly as possible thus giving a head of 1.0 cm. Start the stopwatch immediately. The standard test time is a period of 120 s for a paper. At 10 ± 2 s before the expiration of the predetermined test period, pour the water quickly from the ring, Carefully, but quickly, remove the ring and place the specimen with its wetted side up on a sheet of blotting paper resting on a flat rigid surface. Place a second sheet of blotting paper on top of the specimen and remove the surplus water by moving the hand roller once back and once forward over the pad. Fold the specimen with the wetted area inside. Immediately reweigh it. Calculation and report the water absorptiveness (Cobb value) uses the following formula:

$$\text{Cobb value} = (\text{Final weight [g]} - \text{Conditioned weight [g]}) \times 100 \qquad [g/m^2]$$

C7. Air resistance

The air resistance of paper may be used as an indirect indicator of Z-directional fluid permeance, as well as other variables such as: degree of refining, absorbency (penetration of oil, water, etc.), apparent specific gravity, and filtering efficiency for liquids or gases. Air resistance is the resistance to the passage of air, offered by the paper structure, when a pressure difference exists across the boundaries of the specimen. It is quantified by obtaining the time for a given volume of air to flow through a specimen of given dimensions under a specified pressure, pressure difference, temperature, and relative humidity.

The Gurley method is described in TAPPI T 460. This method is used to measure the air resistance of approximately 6.45 cm^2 circular area of paper using a pressure differential of 1.22 kPa. The recommended range of the liquid column instrument is from 5 to 1800 seconds per 100 mL cylinder displacement. For more impermeable papers the time requirements become so excessive that other techniques are preferable.

APPENDIX D

Table D1 Data of Figure 21

Sample	Burst index (kPa·m^2/g)					Average	SD
Base paper	2.18	2.24	2.20	2.23	2.23	2.21	0.03
	2.16	2.24	2.20	2.24	2.23		
E8-NBC 0.00%	2.85	2.79	2.86	2.90	2.76	2.87	0.07
	2.99	2.89	2.91	2.84	2.88		
E8-NBC 0.50%	2.92	3.00	3.12	3.01	2.91	3.01	0.11
	3.02	3.21	3.07	2.93	2.86		
E8-NBC 1.00%	3.08	2.87	2.93	2.98	3.09	2.98	0.08
	3.03	2.93	3.07	2.93	2.95		
E15-NBC 0.00%	2.68	2.74	2.62	2.69	2.62	2.67	0.08
	2.63	2.70	2.51	2.72	2.82		
E15-NBC 0.50%	2.91	3.04	2.89	2.83	2.85	2.96	0.08
	2.96	2.99	3.02	3.05	3.04		
E15-NBC 1.00%	2.92	2.88	2.91	2.83	2.88	2.95	0.08
	3.03	3.08	3.04	2.97	2.92		
E22-NBC 0.00%	2.63	2.46	2.58	2.34	2.64	2.64	0.07
	2.76	2.75	2.76	2.72	2.76		
E22-NBC 0.50%	2.90	2.87	2.92	2.95	2.90	2.90	0.03
	2.89	2.85	2.90	2.96	2.87		
E22-NBC 1.00%	2.96	2.90	2.93	2.91	2.81	2.90	0.03
	2.90	2.89	2.89	2.87	2.90		

Table D2 Data of Figure 22

Sample	Internal bonding (J/m^2)					Average	SD
Base paper	271	257	271	263	265	265	10
E8-NBC 0.00%	322	330	337	341	347	335	13
E8-NBC 0.50%	332	343	332	340	328	335	12
E8-NBC 1.00%	345	330	338	330	336	336	12
E15-NBC 0.00%	332	326	326	345	329	331	10
E15-NBC 0.50%	341	332	333	328	332	333	10
E15-NBC 1.00%	328	325	330	336	334	331	9
E22-NBC 0.00%	326	322	326	328	315	323	12
E22-NBC 0.50%	324	326	326	319	326	324	10
E22-NBC 1.00%	337	324	334	330	330	331	8

Table D3 Data of Figure 23

Sample	Tensile index (MD) (N·m/g)					Average	SD
Base paper	58.64	55.51	58.59	56.84	58.35	57.59	1.38
E8-NBC 0.00%	61.30	55.84	59.10	59.01	56.87	58.43	2.13
E8-NBC 0.50%	61.29	60.59	61.69	58.48	57.10	59.83	1.96
E8-NBC 1.00%	59.57	63.04	60.59	61.73	62.21	61.43	1.37
E15-NBC 0.00%	56.58	60.29	61.36	58.38	58.14	58.95	1.88
E15-NBC 0.50%	63.47	61.08	64.50	64.98	63.64	63.53	1.51
E15-NBC 1.00%	63.37	67.13	63.50	65.17	64.86	64.81	1.52
E22-NBC 0.00%	61.55	60.70	63.14	61.53	63.06	62.00	1.06
E22-NBC 0.50%	63.42	64.36	64.78	64.87	62.55	64.00	0.99
E22-NBC 1.00%	62.98	64.29	64.15	63.44	65.35	64.04	0.91

Table D4 Data of Figure 24

Sample	Tensile index (CD) (N·m/g)					Average	SD
Base paper	25.45	24.96	25.33	25.09	25.65	25.29	0.28
E8-NBC 0.00%	25.46	26.24	26.57	27.31	26.84	26.49	0.70
E8-NBC 0.50%	26.49	26.99	26.41	25.91	26.09	26.38	0.41
E8-NBC 1.00%	26.16	26.57	26.56	27.07	26.53	26.58	0.32
E15-NBC 0.00%	25.09	25.92	26.57	26.64	27.34	26.31	0.85
E15-NBC 0.50%	27.72	27.26	27.37	26.72	27.24	27.26	0.36
E15-NBC 1.00%	27.01	26.95	26.97	27.65	27.32	27.18	0.30
E22-NBC 0.00%	26.70	25.24	25.63	25.53	26.42	25.91	0.62
E22-NBC 0.50%	26.60	26.85	26.99	27.81	27.01	27.05	0.46
E22-NBC 1.00%	26.58	26.87	26.78	26.11	28.00	26.87	0.70

Table D5 Data of Figure 27

Sample	Cobb value (g/m^2)		Average	SD
Base paper	232	230	231	2
E8-NBC 0.00%	198	204	201	4
E8-NBC 0.50%	189	195	192	4
E8-NBC 1.00%	193	201	197	6
E15-NBC 0.00%	194	202	198	6
E15-NBC 0.50%	182	183	183	0
E15-NBC 1.00%	191	212	202	14
E22-NBC 0.00%	206	190	198	11
E22-NBC 0.50%	206	197	202	6
E22-NBC 1.00%	192	183	188	7

Table D6 Data of Figure 29

% NBC	Burst index (kPa·m^2/g)					Average	SD
0.00%	2.68	2.74	2.62	2.69	2.62	2.67	0.08
	2.63	2.70	2.51	2.72	2.82		
0.10%	2.67	2.74	2.61	2.81	2.72	2.71	0.09
	2.58	2.62	2.78	2.78	2.80		
0.25%	2.71	2.75	2.71	2.76	2.68	2.76	0.08
	2.84	2.95	2.73	2.79	2.68		
0.50%	2.91	3.04	2.89	2.83	2.85	2.96	0.08
	2.96	2.99	3.02	3.05	3.04		
0.75%	2.90	3.09	2.86	2.87	3.03	2.95	0.09
	2.93	2.95	3.10	2.87	2.86		
1.00%	2.92	2.88	2.91	2.83	2.88	2.95	0.08
	3.03	3.08	3.04	2.97	2.92		
2.50%	3.02	3.02	2.96	3.02	3.15	2.95	0.11
	2.86	2.88	2.82	2.90	2.84		
5.00%	3.15	3.03	2.77	3.00	3.18	2.95	0.18
	2.75	2.90	2.78	3.15	2.77		
7.50%	2.96	2.86	3.19	3.03	2.96	2.95	0.12
	2.82	2.90	2.86	3.08	2.87		
10.00%	2.94	2.77	3.03	3.08	2.74	2.95	0.14
	3.08	2.75	2.99	3.02	3.09		

Table D7 Data of Figure 30

% NBC	Internal bonding (J/m^2)					Average	SD
0.00%	332	326	326	345	329	331	10
0.10%	331	325	325	348	328	332	10
0.25%	338	324	347	322	326	331	11
0.50%	341	332	333	328	332	333	10
0.75%	324	339	320	335	348	333	11
1.00%	328	325	330	336	334	331	9
2.50%	329	358	323	330	352	338	16
5.00%	331	355	328	335	360	342	15
7.50%	342	346	362	336	360	349	11
10.00%	330	357	340	353	357	347	12

Table D8 Data of Figure 31

% NBC	Tensile index (MD) (N·m/g)					Average	SD
0.00%	56.58	60.29	61.36	58.38	58.14	58.95	1.88
0.10%	64.97	60.08	63.32	62.08	62.27	62.54	1.80
0.25%	63.11	61.09	64.25	64.15	63.73	63.26	1.30
0.50%	63.47	61.08	64.50	64.98	63.64	63.53	1.51
0.75%	63.32	65.43	65.06	62.08	64.43	64.06	1.37
1.00%	63.37	67.13	63.50	65.17	64.86	64.81	1.52
2.50%	63.68	63.99	65.80	66.20	64.04	64.74	1.17
5.00%	60.18	63.21	67.78	67.05	66.72	64.99	3.21
7.50%	68.72	62.93	64.97	64.74	68.00	65.87	2.42
10.00%	65.21	67.74	63.58	66.27	68.44	66.25	1.95

Table D9 Data of Figure 32

% NBC	Tensile index (CD) (N·m/g)					Average	SD
0.00%	25.09	25.92	26.57	26.64	27.34	26.31	0.85
0.10%	25.21	26.50	26.21	26.94	27.86	26.54	0.97
0.25%	26.83	26.45	26.76	28.34	28.51	27.38	0.97
0.50%	27.72	27.26	27.37	26.72	27.24	27.26	0.36
0.75%	27.04	27.78	27.27	27.49	26.47	27.21	0.50
1.00%	27.01	26.95	26.97	27.65	27.32	27.18	0.30
2.50%	25.50	27.21	26.50	25.75	26.46	26.28	0.68
5.00%	27.82	27.84	26.60	27.26	27.59	27.42	0.51
7.50%	26.84	26.74	26.56	26.02	26.84	26.60	0.34
10.00%	27.56	27.79	25.93	25.49	26.09	26.57	1.03

Table D10 Data of Figure 35

% NBC	Cobb value (g/m^2)		Average	SD
0.00%	194	202	198	6
0.10%	196	221	209	18
0.25%	193	189	191	3
0.50%	182	183	183	0
0.75%	211	186	199	18
1.00%	191	212	202	14
2.50%	207	199	203	6
5.00%	209	212	210	2
7.50%	197	218	208	15
10.00%	204	194	199	7

VITA

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His academic publication is as follow:

DEVELOPMENT OF STARCH-NANOCELLULOSE COMPOSITE OF USING IN SURFACE TREATMENT OF PAPER in the Proceedings of the 2017 Technology Innovation Management and Engineering Science International Conference (TIMES-iCON2017) on November 20-21, 2017 at Bangkok, Thailand.