Potential Application of Alkyd Resin for Production of Liner Board Coating: Some Parameters on the Properties of Coating and Coated Liner Board

Widchuda Chantaramee

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Packaging Technology
Prince of Songkla University
2010

Thesis Tiltle Potential Application of Alkyd Resin for Production of Liner Board Coating: Some Parameters on the Properties of Coating and Coated Liner Board

Author Miss Widchuda Chantaramee

Major Program Packaging Technology

Major Advisor

………………………………………..
(Dr. Thawien Wittaya)

Co-advisor

……………………………………......
(Dr. Waranyou Sridach)

Examining Committee

....Chairperson
(Dr. Supachai Pisuchpen)

………………………………………..
(Asst. Prof. Dr. Tanyarut Jinkarn)

………………………………………..
(Dr. Waranyou Sridach)

………………………………………..
(Dr. Thawien Wittaya)

The Graduate School, Prince of Songkla University, has approved this thesis as partial fulfillment of the requirements for the Master of Science Degree in Packaging Technology.

..…………………………………..……
(Assoc. Prof. Dr. Krerkchai Thongnoo)
Dean of Graduate School

ชื่อวิทยานิพนธ์ การศึกษาความเป็นไปได้ในการประยุกต์ใช้อัลคิดเรซินเพื่อผลิตเป็นสารเคลือบสำหรับกระดาษปะผิว : ปัจจัยบางประการที่ส่งผลต่อสมบัติของสารเคลือบและกระดาษปะผิวที่ผ่านการเคลือบ
ผู้เขียน นางสาววิชชุดา จันทรมี
สาขาวิชา เทคโนโลยีบรรจุภัณฑ์
ปีการศึกษา 2552

บทคัดย่อ

จากการศึกษาผลของ coating mediums (oxidized starch, octanyl succinate starch, hydroxypropyl starch, starch acetate and polyvinyl alcohol; PVOH) ที่ระดับความเข้มข้นต่างๆ (1-6 % w/v) ต่อความคงตัวของสารเคลือบจากอัลคิดเรซินและสมบัติของกระดาษปะผิวที่ผ่านการเคลือบ พบว่าสารเคลือบจากอัลคิดเรซินมีความคงตัวเพิ่มขึ้นเมื่อความเข้มข้นของ coating mediums เพิ่มขึ้น ขณะที่ค่าการต้านทานการดูดซับน้ำของกระดาษปะผิวที่ผ่านการเคลือบลดลงสาเหตุจากสมบัติการชอบน้ำของแป้งดัดแปร เมื่อเปรียบเทียบความเข้มข้นที่ระดับเดียวกันของ coating mediums ชนิดต่างๆต่อความหนืดและความคงตัวของสารเคลือบจากอัลคิดเรซิน พบว่าสารเคลือบที่ใช้ oxidized starch ร้อยละ 1%, octanyl succinate starch ร้อยละ 1-2% และ polyvinyl alcohol ร้อยละ 1-3% มีความเหมาะสมต่อการใช้งานมากที่สุด และพบว่าค่าการดูดซับน้ำของกระดาษปะผิวที่ผ่านการเคลือบด้วยสารเคลือบจากอัลคิดเรซินที่ใช้ oxidized starch ร้อยละ 1% มีค่าต่ำที่สุดและเมื่อพิจารณาผลของความเข้มข้นของอัลคิดเรซิน (2-5% w/v) ต่อสมบัติของสารเคลือบพบว่า เมื่อความเข้มข้นของอัลคิดเรซินเพิ่มขึ้นส่งผลให้ความคงตัวของสารเคลือบจากอัลคิดเรซินและค่าการดูดซับน้ำของกระดาษที่ผ่านการเคลือบลดลง และเมื่อพิจารณาความเร็วในการผสมโดยการโฮโมจิไนซ์ที่ระดับ 5,000, 10,000 และ 15,000 rpm เป็นเวลา 1, 2 และ 3 นาที พบว่าเมื่อความเร็วในการผสมเพิ่มขึ้นส่งผลให้ความคงตัวของสารเคลือบผิวจากอัลคิดเรซินและการต้านทานการดูดซับน้ำของกระดาษสูงขึ้น โดยพบว่าการผสมที่ระดับ 15,000 rpm เป็นเวลา 3 นาทีทำให้สารเคลือบจากอัลคิดเรซินมีความคงตัวดีที่สุด เมื่อศึกษาการเปลี่ยนแปลงสารเคลือบผิวจากอัลคิดเรซินระหว่างการเก็บรักษา พบว่า เมื่อระยะเวลาการเก็บรักษาสารเคลือบจากอัลคิดเรซินเพิ่มขึ้นส่งผลให้เกิดการแยกชั้นของสารเคลือบเพิ่มขึ้น เมื่อพิจารณาผลของปัจจัยที่ศึกษาการเตรียมสารเคลือบผิวจากอัลคิดเรซินต่อสมบัติเชิงกลซึ่งประกอบด้วยค่าการต้านทานแรงดึงและค่าแรงดันทะลุของกระดาษปะผิวที่ผ่านการเคลือบ พบว่า ชนิดและความเข้มข้นของ coating mediums, ความเข้มข้นของอัลคิดเรซินและระดับการผสมไม่มีผลต่อค่าการต้านทานแรงดึงและค่าแรงดันทะลุของกระดาษปะผิวอย่างมีนัยสำคัญ

$(p>0.05)$ แต่อย่างไรก็ตามพบว่ากระดาษปะผิวที่ผ่านการเคลือบด้วยสารเคลือบจากอัลคิดเรซินมีค่าการต้านทานแรงดึงสูงกว่ากระดาษปะผิวที่ไม่ผ่านการเคลือบอย่างมีนัยสำคัญ $(p<0.05)$ เมื่อเปรียบเทียบประสิทธิภาพค่าการดูดซับน้ำของกระดาษปะผิวระหว่างสารเคลือบจากอัลคิดเรซินกับสารเคลือบผิวทางการค้าพบว่ากระดาษปะผิวที่เคลือบด้วยสารเคลือบจากอัลคิดเรซินมีค่าการดูดซับน้ำสูงกว่าสารเคลือบผิวทางการค้าอย่างมีนัยสำคัญ (20.09 and 16.60 g/m^2) อย่างไรก็ตามเมื่อทำการเปรียบเทียบประสิทธิภาพการพิมพ์ของกระดาษปะผิวพบว่ากระดาษที่ผ่านเคลือบด้วยแว็กซ์ทางการค้าจะให้สีที่ซีดจางกว่า นอกจากนี้ยังทำให้ค่าการต้านทานแรงดึงต่ำกว่ากระดาษปะผิวที่ผ่านการเคลือบด้วยสารเคลือบจากอัลคิดเรซินอีกด้วย

Thesis Title Potential Application of Alkyd Resin for Production of Liner Board Coating: Some Parameters on the Properties of Coating and Coated Liner Board
Author Miss Widchuda Chantaramee
Major Program Packaging Technology
Academic Year 2009

ABSTRACT

Effect of coating mediums (oxidized starch, octanyl succinate starch, hydroxypropyl starch, starch acetate and polyvinyl alcohol) and concentrations (1-6 % w/v) on coating stability and coated liner board properties were studied. The results demonstrated that increasing of coating mediums concentrations, overall resulted in a high stability, but increased in water absorptiveness of coated liner board. This profile is primarily due to the hydrophilicity of modified starches. Comparing effect of the same amount of coating mediums on viscosity and stability which suitable for coating process, the results exhibited that coating formulated of 1% of oxidized starch, 1-2% of octanyl succinate starch and/or 1-3% of polyvinyl alcohol was suitable for application. The lowest water absorptiveness of coated liner board was obtained when 1% w/v of oxidized starch was applied. Regarding the effect of alkyd resin content (2-5% w/v) on the coatings properties, increasing of alkyd resin content resulted in lowers both stability and water absorptiveness. Different mixing conditions were also determined (5,000, 10,000 and 15,000 rpm for 1 and 3 min) on coating properties. The results showed that increasing of mixing speed yielded increasing of coating stability and water resistance of coated liner boards, besides mixing speed at 15,000 rpm for 3 min showed the best stability of coatings. Moreover, investigated alkyd resin coatings during storage period founded that separation of alkyd resin coating increased when storage period increased. The mechanical properties were characterized by tensile index and bursting test. The results demonstrated that types and concentrations of coating mediums, concentration of alkyd resin and mixing conditions were not significantly ($p>0.05$) effect tensile index and bursting strength of coated liner board. However, tensile strength of uncoated liner board presented lower than liner board coated with alkyd resin coating ($p<0.05$). Comparing the efficiency of the alkyd resin coating with commercial coating exhibited that alkyd resin coating and commercial wax showed significantly different ($p<0.05$) are 20.09 and 16.60 g/m^2, respectively on the water absorptiveness of coated liner board However, comparing the printing quality and mechanical properties of coated liner board demonstrated that coated linerboard by commercial wax provided the fader color and lower tensile index than alkyd resin coating.

CONTENT

Page

Contents…………………………………………………………………... viii

List of Tables…………………………………………………………... ix

List of Figures………………………………………………………… x

Chapter

1. Introduction……………………………………………………... 1

   Review of Literature

   1. Paper and paperboard ……………………………………… 2
   2. Surface coating ……………………………….……... 11
   3. Starch ………………………..……………………….. 18
   4. Alkyd resin ……………………………...…………. 28
   5. Poly (Vinyl Alcohol) ……………………………………… 35

   Objectives……………………………………………………… 39

2. Materials and Methods……………………………………...... 40
3. Results and Discussion
   1. Effect of type and concentration of coating mediums on the properties of alkyd resin coating and coated liner boards …. 49
   2. Effect of alkyd resin content on the properties of alkyd resin coating and coated liner boards ……………………………. 59
   3. Mixing speed on compatibility between alkyd resin and coating mediums and properties of coating and liner board coated ………………………………………………………. 63
   4. Comparison of the efficiency of the alkyd resin coating and commercial wax …………………………………………… 68
   5. The microbiological changed of alkyd resin coating during storage ……………………………………………………… 76
4. Conclusions……………………………………………………... 78

References…………………………………………………………... 80

Vitae………………………………………………………………….... 89

LIST OF TABLES

Table **Page**

1 The chemical structures, molecular weights and acid values of anhydrides used ……………………………………………………. 32

2 Physico-chemical properties of short oil alkyd resin ……................ 41

3 Effect of types and concentration of coating medium formulated in alkyd resin coating on the water absorptiveness of coated liner board ……………………………………………………………... 50

4 Effect of types and concentration of coating medium formulated in alkyd resin coating on the viscosity (cP) of alkyd resin coating …… 53

5 Effect of alkyd resin content on the viscosity of coating ………….. 61

6 Effect of mixing condition on the viscosity and particle size of alkyd resin coating ………………………………………………… 66

7 Effect of coating on the color value of liner boards: (a) Uncoated, (b) Commercial wax and (c) Alkyd resin coating formula ………… 75

LIST OF FIGURES

Figure **Page**

1 Contact angle between a sessile drop and a flat surface …………….. 9

2 Schematic of apparatus for the Cobb test ……………………………. 10

3 Arrangement of the starch chains in the starch granule……………… 19

4 The revised cluster model of the amylopectin organization; (φ) denotes the single reducing end of the molecule…………………….. 20

5 Chemical and biochemical modifications of starch ……..………….. 22

6 Schematic representation of starch oxidation ………………….…….. 23

7 Chemical reactions during starch acetylation ……………………..…. 25

8 Starch which has been hydrophobically modified with octenyl succinicanhydride (OSA). The figure shows the hydrophobic/anionic substituent esterified to the starch polymer backbone ……………….. 26

9 Structure of starch octenyl succinate ………………………………… 27

10 Structure of a typical alkyd resin …………………………………….. 30

11 Preparation of alkyd resins …………………………………………... 34

12 Properties of poly (vinyl alcohol) ……………………………………. 36

13 Double roll coating machine………………………………………….. 43

14 The preparation of alkyd resin coating solution ……………………... 44

15 Effect of types and concentration of coating medium formulated in alkyd resin coating on the mechanical properties of coated liner board: (a) Tensile index in machine direction, (b) Tensile index in cross direction and (c) Bursting strength ……………….…………. 52

16 Effect of types and concentration of coating medium formulated in alkyd resin coating on the stability of alkyd resin coating: (a) octanyl succinate starch, (b) oxidize starch, (c) polyvinyl alcohol starch, (d) hydroxy propyl starch, (e) starch acetate …………………………….. 55

LIST OF FIGURES (CONTINUED)

Figure **Page**

17 SEM of coated liner board surface as a function of types and concentrations of coating medium: (a) uncoated liner board, (b) commercial wax, (c) 1%Oxi, (d) 2%Oxi, (e) 3%Oxi, (f) 4%Oxi, (g) 5%Oxi and (h) 6%Oxi ……………………………………………….. 57

18 Printing quality of coated liner board as a function of oxidized starch concentrations of coating medium: (a) 1%Oxi, (b) 2%Oxi, (c) 3%Oxi, (d) 4%Oxi, (e) 5%Oxi and (f) 6%Oxi ………………………. 58

19 Effect of alkyd resin content on the water absorptiveness of coated liner boards ……………………………………………………... 59

20 Effect of alkyd resin content on the mechanical properties of coated liner boards: (a) Tensile index in machine direction, (b) Tensile index in cross direction and (c) Bursting strength ….…………..………….. 60

21 Effect of alkyd resin content on the stability of alkyd coating ……… 62

22 Effect of mixing condition on the water absorptiveness of coated liner boards ……………………………….............................. 64

23 Effect of mixing condition on the mechanical properties of coated liner boards: (a) Tensile index in machine direction, (b) Tensile index in cross direction and (c) Bursting strength ……………………….……. 65

24 Effect of mixing condition on the stability of alkyd coating: (a) 5,000 rpm for 1 min, (b) 5,000 rpm for 2 min, (c) 5,000 rpm for 3 min, (d) 10,000 rpm for 1 min, (e) 10,000 rpm for 2 min, (f) 10,000 rpm for 3 min, (g) 15,000 rpm for 1 min, (h) 15,000 rpm for 2 min and (i) 15,000 rpm for 3 min ………………………………………………… 67

25 Effect of coating type on the water absorptiveness of coated liner boards……………………………………………………………. 68

26 Effect of types of coating liner board on the mechanical properties of coated liner boards: (a) Tensile index in machine direction, (b) Tensile index in cross direction and (c) Bursting strength ………..… 69

LIST OF FIGURES (CONTINUED)

Figure **Page**

27 TGA thermograms of alkyd resin coating and commercial wax ....…. 70

28 FT-IR spectrum of the alkyd resin (A), oxidized starch solution (B), and alkyd resin coating using oxidized starch as a medium (C) …….. 72

29 SEM of liner boards surface: (a) uncoated liner board, (b) commercial wax, (c) alkyd resin coating …………………………….. 73

30 Effect of coating on the printing quality of liner boards: (a) Uncoated, (b) Commercial wax and (c) Alkyd resin coating formula... 74

31 Effect of storage period on microbiological quality of alkyd resin coating ……………………………………………………………….. 76

32 Effect of storage time on alkyd resin coating stability: (a) 2 day, (b) 4 days, (c) 6 days and (d) 8 days ………………………………………. 77

CHAPTER 1

INTRODUCTION

Packaging is the enclosing that requires protection from tampering, whether by physical, chemicals, or biological needs. It also shows the product that is labeled to show any nutrition information on the food being consumed. Because of environmental concerns from consumers and the limitation of future fossil fuels impel efforts to search for alternative polymers to replace synthetic polymers for packaging. The desire to prolong shelf-life and boost food quality whilst reducing packaging waste creates an interest in using edible and biodegradable polymers from renewable resources (Tharanathan, 2003). Abundant renewable cellulose fiber based packaging materials are corrugated board, paperboard and paper (Sothornvit, 2009). Liner paper is the most widely used corrugated material (Robertson, 1993; Han and Krochta, 2001). Besides their undeniable practical qualities, paperboard is manufactured from natural and renewable raw materials and offers the advantage of being both recyclable and biodegradable. However, because of their poor functional barrier properties and, particularly, high moisture sensitivity, (Gastaldi *et al*., 2007) barrier coating is one of the most important properties for paper packaging containers (Sun *et al*., 2007).

Generally, paper is coated with non-degradable polymer coating materials such as polyethylene (PE), wax (Wenzel *et al*., 1997), polyethylene terephthalate (PET) (Sun *et al*., 2007) and polybutylene terephthalate (PBT) (Overcash and Elsebaumer, 2001) to provide barrier properties. These materials are difficult to dispose and cause environmental problems. Moreover, paperboard is coated with waxes to meet these requirements. Unfortunately, most of commercial waxes are synthesis from synthetic polymer that will cause environmentally undesirable and a contributing factor to the growing solid waste disposal problem (Zou *et al*., 2007), moreover the wax cost is very expensive. Materials based on agro-polymers can be considered as an alternative source of raw materials for packaging. Several natural coatings have been used with the aim of to reduce the hygroscopicity and improving the water vapor barrier of papers, with a focus on the impregnation of papers with non-hygroscopic and biodegradable materials, like alkyd resin from soy bean oil. For coating medium preparation, the compatibility and distributed between alkyd resin and starch as coating paper is importance. Previous study, paper coating was successful formulated by dispersing 3% of alkyd resin from soy bean in octanyl succinate starch involved with addition of gelatin and xanthan gum as emulsifier and stabilizer, respectively. However, the efficiency of coating is still not acceptable regarding to the water absorptiveness of coated liner board and stability of coating. Then, the main objective of this study was to improve and develop the coating formulation by evaluated the effect of types and concentrations of coating medium (modified starch and polyvinyl alcohol) on coating properties and physical strength and water resistance properties of coated liner paper used in corrugated boxes. In addition, the amounts of alkyd resin and mixing speed on the properties of coating and coated paper were also examined. Moreover, the efficiency of the commercial wax was compared with the alkyd resin coating.

Review of Literature

1. Paper and paperboard

Paper and paperboard is widely used in food packaging applications and is generally more appreciated by consumers than plastic films because of its characteristics of recyclability and biodegradation related to environmental respect (Dury-Brun *et al.*, 2006). Paper is made from wood chips broken into tiny fibers, which make paper pulp when mixed with water. There are two main methods of breaking wood into fibers. Dissolving wood chips by a chemical process produces chemical pulp. Mechanical pulp is produced by the mechanical breakage (refining) of wood into fibers. Mechanical pulp has suitable strength and produces paper of suitable brightness at low energy cost (El-Sadi *et al.*, 2004). A network of natural cellulosic fibers of paper made up of microfibrils which are composed of long chain cellulose molecules in a crystalline state, with amorphous regions regularly disrupting the crystalline structure (Dury-Brun *et al.*, 2006).

1.1 Structure of paper

Paper and paperboard are considered to include all fibrous structures felted from a fluid suspension onto a grid, without limitation as to raw material, suspending fluid, or the nature of the grid. Although this definition specifies any type of suspending fluid, including air and any type of fibrous material, organic or inorganic, most paper is manufactured from cellulose fiber suspended in water. However, it must be formed by the felting process. Paper is a three-dimensional structure and when manufactured in a continuous process, its properties will differ markedly in the three dimensions.

In the process of felting the fibers into a sheet of paper, the extent of the entanglement of the fibers into a matrix depends on the dimensions of the fibers, the shape of the fibers, and their flexibility. To obtain strength in paper, the operation must go beyond felting and must include bonding of the fibers in the matrix. This bonding is obtained by mechanical treatment of the cellulose fibers in the presence of water, which increases fiber flexibility and provides bonding when the sheet is dried.

1.1.1 Functional properties

Many of the properties of paper are dependent on the fact that the basic constituent is cellulose fiber; these are called functional properties. Cellulose readily absorbs water; therefore, paper will absorb water unless it is given some special treatment to minimize the absorptive power of the cellulose. Cellulose is white; therefore, paper is white unless it contains lignin as an impurity or unless some dye or other material has been added to give it color. Cellulose is hygroscopic; therefore, paper is hygroscopic and will pick up and give off moisture with changes in relative humidity. A cellulose fiber expands and contracts with changes in moisture content; therefore, paper expands and contracts with changes in relative humidity. A cellulose fiber has the ability to form hydrogen bonds; therefore, fibers can be bonded together in paper without the addition of adhesives. A cellulose fiber has high strength; therefore, paper with high strength can be made from it. A cellulose fiber is flexible; therefore, paper is flexible. Cellulose burns; therefore, paper burns. This is a property of paper that is very valuable under certain circumstances.

The pulping and papermaking processes are designed to treat the cellulose fibers in such a way that the desirable properties of the cellulose are enhanced and the undesirable properties minimized. Rosin size is added to minimize the absorption of water; fillers are added to increase opacity, printing-ink absorption, and smoothness; dyes are added to give desirable colors; wet-strength resins are added to overcome the loss of bonding when wet; and coatings are added to give better printing qualities. The type of fiber used; the extent of cooking and bleaching, and the degree of bonding between fibers determine, to a large degree, the physical and optical properties of the paper. The amount of fiber treatment, formation on the wire, amount of wet pressing, method of drying, and amount of calendaring are the principal factors that affect the degree of bonding. These variables must be controlled to obtain a finished paper of the desired properties, which often means sacrificing one property to obtain another.

1.1.2 Machine and cross direction in paper

Paper has a definite grain caused by

- The greater orientation of fibers in the direction of travel of the paper machine.
- The greater strength orientation that results partly from the greater fiber alignment and partly from the greater tension exerted in the paper in this direction during drying.

This grain detection is known as the machine direction. The cross direction is the direction of the paper at right angles to the machine direction. The grain of paper must be taken into account in measuring all physical properties. In measuring tensile strength, folding endurance, and tearing resistance, strips of paper are cut in both directions to measure the strength in both the machine and cross directions. Confusion sometimes exists in reporting machine and cross-direction strength values. The general rule is that the direction of the test refers to the direction in which the test force is applied, and not to line of rupture. In the tearing resistance test, the force applied and the rupture are in the same direction, but in the fold and tensile tests the force is applied at right angles to the final rupture. The grain of the paper must be taken into account in measuring optical properties of the paper, such as brightness and gloss, as well as in measuring physical properties.

Most papers are made with machine-direction and cross-direction strength as nearly equal as possible. There are exceptions, however, where it is desirable to have maximum tensile strength in the machine direction. All papers should be used to take the greatest advantage of the grain of the paper. It is desirable to cut printing papers with the machine direction in the longer direction and to feed the sheet to the press with the machine direction parallel to the axis of the press roll.

1.2 Physical properties of paper

Most of the important properties of paper are physical rather than chemical. Structure properties discussed in the last section and strength properties discussed in the next section are physical properties but are important enough to be considered separately. This section will be limited to such physical properties as weight, thickness, density, porosity, smoothness, softness, hardness, dimensional stability and curl.

1.2.1 Grammage (Basis weight)

Weight is the most common specification made on paper. Because paper is used in sheet form and area is more important than volume, weight of paper is expressed per unit of area rather than unit of volume, as is the case with most other materials. Weight of paper is expressed as grams per square meter in the metric system and is termed grammage. In the English system it is termed basis weight and is expressed as pounds per ream, pounds per thousand sheets, or pounds per thousand square feet. A ream can be 480 or 500 sheets and can have many different sizes for the sheet.

The moisture content of the paper is dependent on the relative humidity of the air in contact with it. Because grammage or basis weight is always expressed as the total weight of the paper including the moisture, the weight must be determined at standard conditions if it is to be reproducible. Weight affects all physical properties and many of the optical and electrical properties of paper. In evaluating these properties it is important to distinguish between variations caused by variations in weight and variations caused by other differences in the papers. For this reason the grammage or basis weight should always be determined if weight-sensitive properties are being measured.

1.2.2 Density

The density of paper is probably the most important fundamental paper property. Density is related to porosity, rigidity, hardness and strength of the paper; in fact, density influences every optical and physical property except sheet weight. Because of its fundamental nature, sheet density has been suggested as the most satisfactory basis for comparing the strength and other properties of different papers.

1.2.3 Porosity

Paper is a highly porous material, as indicated by its low specific gravity compared with that of cellulose. Commercial papers contain as much as 70 percent air, which is due to true pores, those openings that extend entirely through the sheet, recesses, those openings connected to one surface only, and voids, those air spaces connected to neither surface. Porosity is a property of direct importance in writing and printing papers since it is a factor in the absorption of inks. It is an important property of coating raw stock for pigment-coated papers where it affects the absorption of adhesive. It is definitely related to the oil resistance and hence is an important property of greaseproof and oil-resistant papers.

1.2.4 Smoothness

Smoothness is concerned with the surface contour of the paper. It is related to gloss because both gloss and smoothness are affected by calendaring, but the two properties are not the same. A pigment-coated sheet that has not been calendered will be relatively smooth but will have a low gloss, whereas an uncoated sheet with poor formation that has been calendered will have a gloss higher than that of the coated sheet but will be rougher. Gloss is discussed under optical properties.

1.3 Strength properties of paper

Strength is a very important property because paper is often used under conditions where it must withstand considerable stress, but paper strength is a vague term that means nothing unless the use to which the paper is to be put and particular property desired are carefully specified. There are many strength tests made on paper; the most common are bursting strength, tearing resistance, tensile strength, folding endurance and stiffness. None of these is a fundamental measurement but rather a combination of such factors as flexibility, bonding strength and fiber strength. These factors are, in turn, dependent on the type of fibers, the length and thickness of the fibers, the imperfections in the fibers, the flexibility of the individual fibers, the pattern of the fiber network, the number of bonds, the strength of the individual bonds, the weight of the paper, the apparent density, the moisture content, and many other factors.

1.3.1 Tensile strength

Tensile strength more nearly approaches a fundamental measurement than other conventional strength measurements made on paper. Tensile strength is a component of the more complex bursting, folding, and tearing strength, which are discussed in the following sections. Tensile strength of paper is always greater in the machine direction than in the cross direction because of the greater alignment of fibers in the machine direction. The amount and quality of fiber bonding is the most important factor affecting tensile strength. Increased bonding caused by either increased beating or increased wet pressing will increase the tensile strength, but the tensile strength will always be much less than the tensile strength of a fiber when both are expresses in terms of cross-sectional area. Moreover, fiber length is believed to play a role in tensile strength of paper. The peak tensile strength was reached at shorter fiber lengths when the fiber diameter was decreased.

1.3.2 Bursting strength

Bursting strength is a highly empirical test that is defined in the TAPPI standard as the hydrostatic pressure required rupturing paper when deformed in an approximate sphere 30.5 mm in diameter at a controlled rate of loading. Bursting strength is complex function of tensile strength and stretch. The stress exerted in the test is largely one of tension resulting from a pressure differential across the sheet at the time of rupture. The strain is approximately equal in all directions, thus building up unequal stresses in the paper. The fact that paper ordinary ruptures in a line that is at right angles to the machine direction is primarily due to the fact that the paper has a lower stretch in the machine direction which directs the stress caused by the bulging rubber diaphragm into a machine direction tension. Two factors are responsible for bursting strength: fiber length and interfiber bonging. Increased fiber length makes for a higher bursting strength, but bursting strength is even more affected by fiber bonding. Beating increases the bursting strength over most of the range. However, a decrease in bursting strength occurs with excessive beating; past of this loss on excessive beating can be attributed to disintegration of the fiber, but since bursting strength is also lowered when a very high density is obtained by wet pressing, at least part of this loss must be attributed to a loss in stretch. Bursting strength is predominantly an internal sheet property, although it is influenced to some extent by surface sizing. Surface sizing with starch will give some increase, but surface sizing with glue will produce a very significant increase in bursting strength.

1.4 Optical properties of paper

The optical properties of paper are sometimes more important than the physical properties. The appearance of the paper depends on the optical properties, and much paper is sold on the basis of its appearance. In addition, the optical properties determine the ability of some papers to function in the intended manner. The most important optical properties are color, brightness, opacity and gloss.

1.5 Barrier properties of paper

There are many properties of paper that are classified as resistance properties. Many of these are related to the properties of the cellulose fibers used to manufacture the paper.

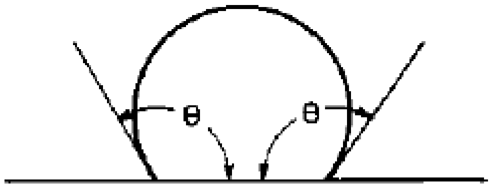
1.5.1 Oil and grease resistance

Oil resistance is important in many type of paper. Most printing inks are oil bases; therefore, the oil resistance is a measure of the degree to which the printing ink will penetrate into the paper. Common tests for oil resistance are castor oil test, which measures the time required for a drop of castor oil to penetrate through the sheet, and the surface oil test, in which a drop of linseed oil is placed on the paper and spread into an oblong shape by passing a roller across it. The time required for the sheen to disappear is taken as an indication of the rate of penetration into the surface.

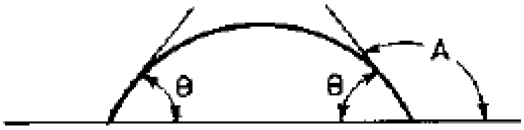
1.5.2 Water and writing-ink resistance

The resistance to the penetration of water and water-based inks is quite different from the resistance to oil and oil-based inks. Oil resistance is controlled primarily by the formation of the sheet and is related to the air resistance. Water resistance is obtained by adding sizing materials that reduce the ability of the water to wet the sheet. These sizing agents have little effect on the rate of oil penetration.

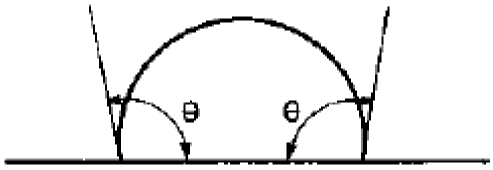
Contact angle measurements between sessile drops and the surface of paper have long been used as an indication of wettability (Figure 1), the contact angle θ for a drop of aqueous liquid increases as the paper surface becomes more hydrophobic and conversely, decreases as the surface becomes more wettable.



HARD-SIZED PAPER



SOFT-SIZED PAPERBOARD



WRITING PAPER

Figure1. Contact angle between a sessile drop and a flat surface.
Source: Lyne (2001)

The Cobb size test is widely used and has been adopted as an international standard The Cobb test amounts to sealing on side of the paper sample to a rubber mat by means of a cylindrical ring clamped over the upper surface of the sample. The cylindrical ring has an inside area of 100 cm^2 (11.28 cm inside diameter) and a height of 2.5 cm (Figure 2). The aqueous liquid is poured into the right to a depth of 1 cm (100 cm^3), and 10 s before the end of a specified time interval the liquid is poured off. The sample is removed and blotted with a standardized blotting paper. Exactly at the end of the present time interval, a second blotter is put on top of the first and a 10 kg roller is passed over the three sheets to extract the free water. The weight increase in the paper sample is taken to be the amount of liquid absorbed in the present time interval.

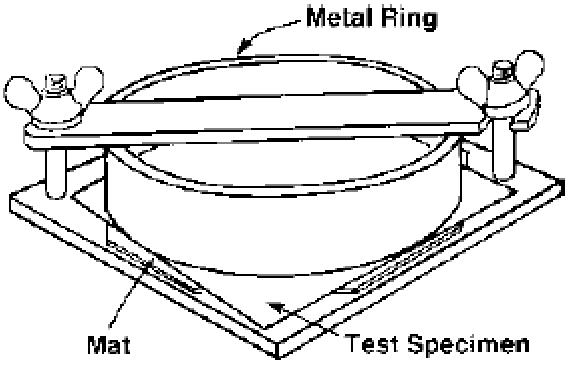


Figure 2. Schematic of apparatus for the Cobb test.

Source: Lyne (2001)

1.5.3 Water-vapor permeability

Water-vapor permeability is a very important property of packaging papers. Packages for dry hygroscopic materials such as crackers and breakfast cereals must resist the penetration of water vapor or the food will become soggy and unappetizing. Water-vapor resistance and water resistance are two different properties. Water resistance is developed by adding sizing material, but sizing has little affected on water-vapor transmission. Water vapor is a gas and a good water-vapor resistance is obtained by adding a material such as wax that fills all the pores of the paper, thus leaving no passageway for the gaseous water vapor. Some water vapor will still be transmitted by being absorbed in the fiber exposed on one surface, migrating through the fiber as water and then being released on the other side of the paper or board (Brandon, 1979). Due to its composition of cellulose, the hydrophilic nature of cellulose causes it to be less water resistant. Paper and paperboard are prone to absorb water vapor from the environment, especially when stored under high humidity conditions or when coming into contact with high-moisture food materials such as fresh agricultural produce. Absorption of moisture reduces physical and mechanical strength of the paperboards, causing corruption of boxes during storage and distribution. Surface treatments such as sizing and coating are usually used to improve physical strength as well as water barrier properties (Rhim *et al.*, 2006).

2. Surface coating

Surface treatments such as sizing and coating are extensively applied to improve the appearance of paper. Paper may be coated either on equipment that is an integral part of the paper machine (i.e., on-machine coating), or on separate converting equipment. The most common method for the application of chemicals to the surface of a paper web is with a size press, where dry paper is passed through a flooded nip and a solution or dispersion of the functional chemical contacts both sides of the paper. Excess liquid is then squeezed out on the press and the paper is re-dried.

The sizing agent penetrates far enough into the paper to increase the fiber bonding and the dependent properties (Robertson, 1946). Surface-sizing agents prevent excess water penetration and improve the strength of the paper such as tensile strength, surface strength, surface evenness, printability, reduced dusting, etc. This makes the use of cheaper pulps and increase filler addition in paper manufacture possible (Gigac *et al.*, 2008). An additional effect is an improvement in the scuffing resistance of the paper surface (Robertson, 1946). The most commonly used materials for surface sizing are starches, usually chemically modified (e.g., oxidized starches, cationic starches and hydroxyl-ethylated derivatives). Other film-forming materials that can be used for surface sizing include animal glue, methyl cellulose (MC), carboxymethyl cellulose (CMC), polyvinyl chloride (PVC) and wax emulsions, and certain resin polymers that are sometimes used to obtain special effects (Cushing, 1979), which provide oil and grease repellent coating and improve paper strength. Other polymeric sizing agents such as polyurethanes are used as surface-sizing and strength-enhancing agents, but their cost is relatively high compared with other sizing agents. Surface-sizing agents can be applied in assize press, in a size tub, by spraying, as foam, or (in the case of heavy papers) at the calenders (Cushing, 1979).

2.1 Factors affecting surface sizing

To ensure picking up a uniform amount of size, the sheet going to the size press or size tub should be uniform in regard to moisture content, internal sizing, and density. Furthermore, the size solution itself should be uniform as to concentration of sizing agent, viscosity, and temperature. Some of the important factors are discussed in the following paragraphs. Sizing tests made in samples of paper taken just ahead of the size press and immediately after the size press are of value in indicating the percentage of the total sizing value that is the result of the internal and surface-sizing operations.

2.1.1 Effect of sheet moisture content

Some machines are running as low as 3 to 3.5percent moisture before the size press because of problems of wrinkles during drying if the sheet enters the press wetter. A sheet that is wetter or dryer than the optimum will not pick up the maximum amount of size. If the sheet is relatively dry before entering the size, it will come out wider as the fibers readjust themselves in dimensions.

The moisture in the sheet leaving the size press is generally about 30 to 35 percent in lightweight papers. This means that about 25 percent moisture must be dried out of the sheet a second time, which makes surface sizing a rather expensive operation.

2.1.2 Effect of basis weight

The basis weight of the sheet being surface sized is an important factor since the amount of size picked up and the penetration into the sheet are practically independent of the sheet weight. This means that the surface-size: fiber ratio varies as the weight of the sheet is changed, assuming that the size solution is not changed. Thus a lower size: fiber ratio will be obtained on heavier sheets, and there will be less improvement in the strength properties of the paper, such as bursting and tensile strength.

2.1.3 Effect of sheet density and smoothness

The density has an important effect on the penetration of surface size since high-density papers pick up less size than do porous papers. The density of the paper is also a factor in the overall sizing value, as previously explained. In highly porous papers the size replaces air in the sheet and this air is absorbed by the size, thus contributing to foaming troubles. It is important that the surface of the paper before sizing be as smooth and as free from fuzz as possible. If the sheet is fuzzy, the final paper will contain bare fibers protruding above the surface, regardless of how much size is applied. These fibers will serve as wicks for the conduction of water or other liquids through the surface film into the body of the paper, thereby defeating the purpose of sizing. Under adverse conditions the paper may show feathering beneath the surface of the size when written in with ink. Steaming of the surface-sized sheet with wet steam just before the calenders will sometimes reduce fuzz by cementing protruding fibers back onto the sheet. This can be done conveniently on the underside only.

The sizing value is related to the finish of the paper surface. As a general rule, surfaces with a positive wetting tendency will wet mote readily with rougher surfaces, and, conversely, surfaces with a negative wetting tendency become more water-repellent with rougher surfaces. This explains why machine-finished papers with a relatively grainy surface usually show a higher contact angle with water than do highly calendered papers. For the same reason, sizing agents that are ineffective on smooth surfaces may show excellent water repellent properties when applied to fibrous surfaces.

2.1.4 Effect of viscosity, solids content and temperature of the size

The properties of the size itself are of the utmost importance in determining the amount of penetration of size into the paper. Cobb's equation shows that the important properties of the size solution are surface tension, wetting properties and viscosity. The times of exposure of the paper to the size solution and the concentration or solids content of the solution are the remaining important variables. The particular importance in determining the amount of size penetration is the viscosity since the penetration varies inversely as the square root of the viscosity of the solution. For this reason, the viscosity of the sizing solution should be regulated with considerable care to obtain the proper penetration for the grade of paper being made. The important practical considerations are the concentration and the temperature of the size, since these variables are not only important by themselves but also determine the viscosity of the solution. Instruments for the automatic control of temperatures and Baume of the size at the size tub have been developed and are in successful operation. Instrumentation of this operation is extremely helpful in attaining uniform, satisfactory results. Starch size changes viscosity on aging and this may produce curl if there is a difference in pickup on the different sides of the sheet. Automatic viscosity control is helpful in controlling this curl. If the surface sizing is not adequate, the first thing the paper maker will do is increase the concentration of the size. A very low concentration (0 to 1.25 percent) produces a light finish, medium concentration (1.25 to 5.0 percent) produces good surface sizing and high concentration (5.0 to 12.0 percent) produces an increase in internal strength and wax pick resistance. Drying of the paper becomes more difficult at the higher concentrations. If drying becomes too difficult, it may be made easier by adding some water to the size.

The temperature of the size used in a size press has a practical upper limit imposed by what the rubber-covered press rolls can stand without checking. Also, incases when the paper dips into the size and no automatic feeding devices are in use, it is very difficult to feed the paper manually at temperatures above 52 to 54° and this imposes a limit on operating temperature. If the size-tub temperature is not controlled automatically nor adjusted manually, an equilibrium temperature is attained after a period of continuous operation since the hot paper entering the size continually adds heat. The equilibrium established depends in the temperature of the paper and the machine speed. Too low an operating temperature resulted in excessive pick up of size in the surface of the sheet, thus resulting in sticking to the rolls. Starting up with cold rolls can produce the same result; therefore, when starting up, the size should be run on the press long enough to warm the rolls. In calendering sizing the size is generally applied at the first, or “wet,” stack at a point as close to the top as is convenient. Since the paper is at a very high temperature at that point, the sizing solution generally picks up heat and consequently has a high equilibrium temperature of about 82 to 88°C. It has been suggested that this high temperature causes air to be squeezed out of the sheet under the pressure of the nip at the critical instant that the size is being applied, thus interfering with film formation and producing foam

2.1.5 Effect of drying and calendering

Careful drying is important in surface sizing. Most surface-sized paper is dried on the paper machine under rather adverse conditions. Some glue-sized papers are packed in a wet condition and then are dried slowly in an air drier at relatively low temperature. This produces much contraction and cockling of the paper but result in the fullest benefits in the way of strength and sizing. Two rapid drying resulted in cracking and checking of the surfaces film. Another potential difficulty that may result from inadequate drying conditions is a picking or a flaking off of the surface film of size on the driers. Poor results due to improper drying may be corrected by remoistening the sheet and drying again under more favorable conditions, but this is an expensive procedure. Flaking of the sized paper during drying may be prevented by operating the first driers at low temperature (Cushing, 1979).

2.2 Surface sized with starch

Starch is the most used additive derived from renewable raw material in the paper industry. Of the 2.8 million tones of starch used in industry within the European Union in 1995, more than 46% - 1.3 million - tones was consumed by the biggest customer group of the starch industry: the paper industry. The consumption of starch has almost double in the past of 10 years. This increase is not just the result of the growth of the paper industry, but also the increased use of starch in the different paper grades. Some 1.8 kg of starch was used on average per ton of paper in 1995. This statistical average value, specific starch demand, also covers paper grades where no starch is used. Thus, some paper some consumed as much as 50-70 kg starch per ton. After fibers and pigments, starch is the third most important material for the paper industry as regards quantity. The use of starch distributed as follows:

- Surface application, 68%
- Wet-end addition, 16%
- Coating, 11%
- Spray, 5% (Bergh, 1997).

Considerable starch is used for surface sizing. Starch is much cheaper than animal glue and has replaced it as a surface size on all but the highest grades of papers (Cushing, 1979). The starch used in the paper industry is derived from different plants. Potato, maize and wheat are the most frequently used starch sources in Europe, though small quantities come from tapioca, barley and waxy maize (Bergh, 1997). The application of surface sizing may also be made at the calendar starch. In surface sizing, a continuous film is deposited on the sheet. All material added on the size press stays in the sheet. Surface sizing improves the finish, produces a better printing surface, minimizes scuffing and listing (Mentzer, 1984)

2.2.1 General properties of starch for surface sizing

Starch is a white – to buff – colored material that is sold in powdered, pearl or crystal form. Starch exists in the physical form of small grains or granules whose size, shape and physical marking are sufficient to indentify the variety of starch. Chemically speaking, starch contains two major chemical entities, amylose (a strength-chain polymer of glucose) and amylopectin (a branched-chain polymer of glucose), although certain starches (waxy varieties) contain only amylopectin. All starches contain minor amounts of fatty acids, other lipids, proteins and inorganic salts.

Before starch can be used for surface sizing, it must gelatinize on heating of its granules in the presence of water about 88 to 98°C and held there for approximately 10 to 20 min (Cushing, 1979). The granules take on water and start to swell, absorbing water and eventually their crystallinity is irreversibly lost. At the same time, due to part of the granule dissolves and the granule starts to disintegrate, amylose leaches out of the granules and forms a continuous matrix in which the gelatinized granules, mainly consisting of amylopectin, are embedded. One of the properties which are of paramount importance for the starch based food and chemical industry is the considerable increase in viscosity of gelatinized starch dispersions (Raphaelides, 2006). The degree of granule disintegration and the viscosity of the starch solution depend on the type of starch, degree of modification, time and temperature of heating, and amount of agitation. Starch solutions are reasonably stable, but there is some retrogradation on aging, thus causing the solution to cloud up, increase in viscosity, and even set back or gel if the concentration is high enough. Retrogradation is increased by low pH, low temperature, presence of certain cations (e.g., calcium or aluminum) and slow cooling. The leaching of alum from the paper as it passes through the size is a factor in this connection. Solutions of native or unmodified starch have too high a viscosity for ordinary surface sizing and hence modified starches of reduced viscosity are generally used.

2.2.2 Chemically modified starches

The types of chemically modified starch most generally used are the oxidized starches, cationic starches and hydroxyethyl ether derivatives (HE). Chemically modified starches are generally superior to other types. A choice might be made on the basis that chemically modified starches work best on rag papers, whereas enzyme-converted starches produce acceptable results on chemical wood pulp and rag-contented papers. The enzyme-converted starches are considerably cheaper to use and naturally are preferred when there is no significant difference in results. Ordinarily, if there is any difference in results between these types of starch, the difference shows up in the degree of sizing of, rather than in the strength of the paper.

Oxidized starch is made by the starch manufacturer in a wide range of viscosities by treating slurry of native starch with alkaline sodium hypochlorite at a temperature no higher than 54°C. During conversion, soluble products are formed, and these are later removed by filtering and washing, after which the starch is dried and packed for shipment. Hydroxyethyl ether starches are made by reacting starch with ethylene oxide in alkaline medium. Both of these starches must be cooked in water at the paper mill by heating to a temperature of 88 to 98°C for about 15 to 20 min. they form solutions of improved colloidal properties compared to most other forms of modified starch. No great difference in results is obtained from the use of oxidized versus hydroxyethyl starches, except that oxidized starches tend to penetrate the sheet more whereas hydroxyethyl starches tend to form a better surface film, particularly when low solids solutions are used. Methods of acetylation have made available low-cost acetylated starches in a range of viscosity for surface sizing.

Oxidized starch, which at one time was the major type of modified starch used for surface sizing is now used to a lesser extent. Two factors have been responsible for this move away from oxidized starches. The first factor is that the anionic nature of oxidized starched results in a decrease in the retention of filler and fines when the dry or wet machine broke containing oxidized starch is returned to the stock system. Second, since these starches are not well retained on paper fibers during repulping they cause a rise in the BOD content of the mill effluent waters. Hydroxyethyl ether starches are better retained by paper fibers and do not seriously reduces filler retention in comparison to oxidized starches (Cushing, 1979).

3. Starch

Starch is the lowest priced and most abundant worldwide commodity. It is produced in most countries and is available at low cost in all countries. Its level price over many years is impressive and makes it especially attractive as an industrial raw material (Whistler, 1984). Starch has been a subject of academic as well as of industrial interest for the past few decades because of its renewability and biodegradability (Chen and Wang, 2006).

3.1 Structure of starch

Starches are polymers of anhydroglucose units with the general formula of $(C_6H_{10}O_5)_n$ in which these units are joined by α-glucosidic linkages (Zobel, 1992). Starch granules are composed primarily of amylose and amylopectin. Amylose is essentially a linear polymer consisting of (1→4)-linked α-D-glucopyranosyl units (Shannon and Garwood, 1984), thus making the molecule linear or slightly branched. Though amylose is the minor component in most granules, it has a large influence on the properties of starch. Amylopectin, the major component of most starches, consists of a large number of shorter chains that are bound together at their reducing end side by a (1→6)-linkage, which makes this very large polysaccharide extensively branched (Bertoft, 2004). Figure 3 shows linear and branched of the starch chains in the starch granule.

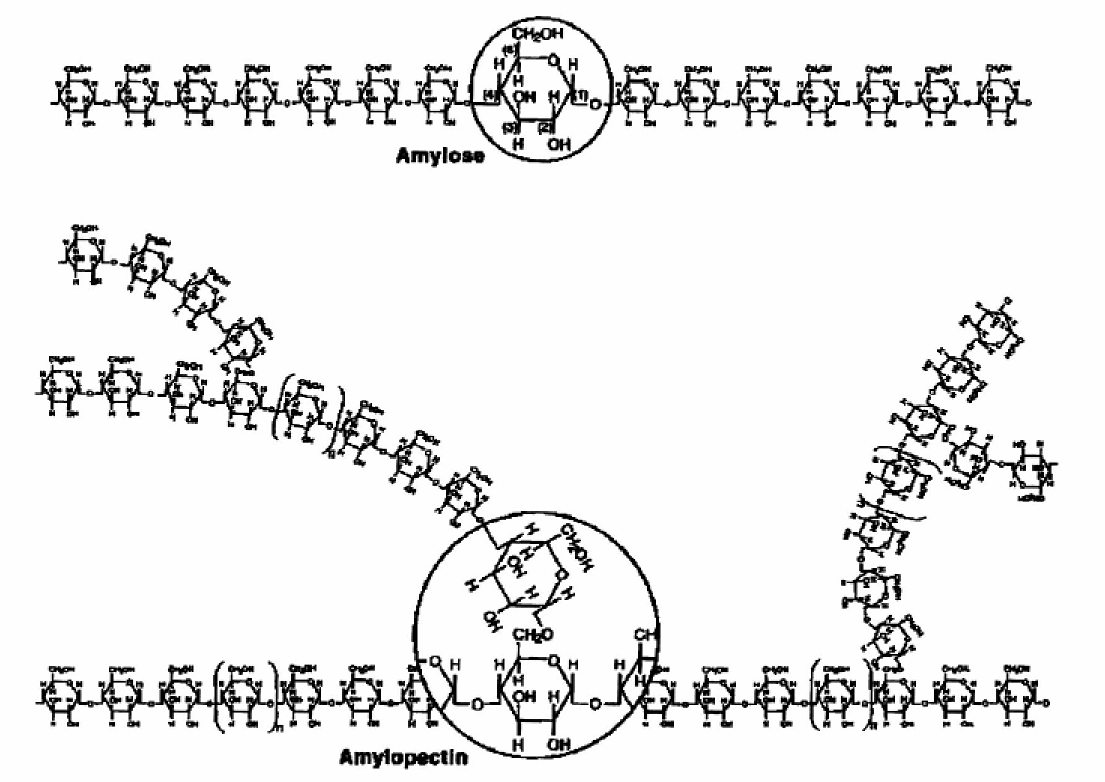


Figure 3. Arrangement of the starch chains in the starch granule.
Source: Viswanathan (1999)

In fact, the linear amylose has a small degree of branching but it is predominantly regarded as a single chain. The chain length can vary with the botanical origin of the starch but will be of the order of 500 to 6,000 glucose units. Because of its more simple polymeric structure, amylose has a greater propensity to deposit in a regular manner forming crystals. In nature, three crystalline forms of amylose, A, B and C exist, depending upon the source: cereals (A), tuber (B) and certain pea and bean varieties (C). Precipitated starch complexes (with iodine, long-chain alcohols and fatty acids) are found in the V form. The so-called linearity of the amylose is further complicated by a twisting of the polymer into a helix. It is different degrees of hydration of the helix that gives rise to the A, B and C forms.

In contrast to amylose, each branched chain of amylopectin contains only up to 30 glucose units. However, the multitude of branching in amylopectin gives it a molecular weight that is 1,000 times that of amylose. Indeed, amylopectin is a titan of a molecule from nature: one of the largest with a molecular weight of 400 million. The ratio of amylose and amylopectin in any native starch is dependent not only on its source (Murphy, 2000). The branching structure of amylopectin has been studied extensively and a variety of models of the molecular architecture have been proposed. Cluster model was presented based on the suggestion that the branching points occur in groups (clusters) (Figure 4). The cluster model of the amylopectin structure describes the branched structure as three different chains: A, B and C, which are grouped according to their location in the amylopectin molecule (Figure 2). A chains are linked to B chains only through the reducing end and do not carry any other chains. The B chains carry A chains and/or other B chains through one or more (1 → 6)-α-d-glucosidic linkages. They are linked via their reducing ends to other B chains or the sole C chain, which carries the only reducing end of the whole molecule. The A chains and short B chains form left-handed, parallel double helices that constitute the clusters, whereas the longer B chains interconnect the clusters into larger structures (Richardson and Gorton, 2003).

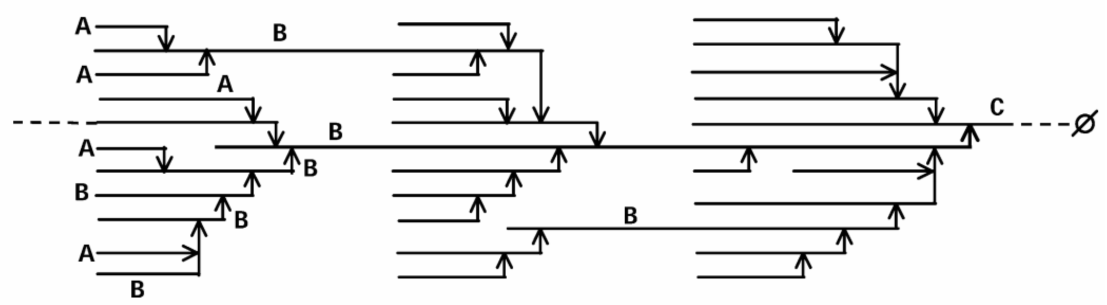


Figure 4. The revised cluster model of the amylopectin organization; (φ) denotes the single reducing end of the molecule.

Source: Richardson and Gorton (2003)

3.2 Starch characteristics

Native starch granules are insoluble in cold water, due to their semi-crystalline structure. Heating of a dilute aqueous suspension of starch resulted in a swelling of the granules, disruption of the crystalline parts and loss of birefringence. As the temperature increases, irreversible swelling occurs, and the granular order is destroyed. In addition, the viscosity increases with increasing swelling of the granules. This process is known as gelatinization and is an important property of starch, resulting in the use of starch as thickeners in foods (Richardson and Gorton, 2003). The gelatinization is a two-stage process. At the first stage, granules absorb water mostly in their amorphous regions, which swell dramatically and at the same time part of amylose, if it is present, diffuse out of the granule. The second stage is reached when this swelling causes, with the help of hydration, the disruption of crystallinity within the crystalline regions. The degree of granule swelling and the amount of amylose or even amylopectin leached out is governed by a number of factors such as the amount of available water, the temperature and the time of heating, the presence of other substances which may or may not interact with either the starch components or the water, such as lipids, surfactants, sugars, salts and so on (Raphaelides and Georgiadis, 2007). Another important physical property of starch is retrogradation, which occurs when the polymer chains, after gelatinization, re-associate and return to a more ordered state. Retrogradation results in gels or precipitates and is related to storage stability properties. For example, the aggregated structures that are formed when amylose self-associates in an aqueous dispersion are utilized in the formation of films. Another example is the retrogradation of amylopectin, which is partially responsible for staling of bread (Richardson and Gorton, 2003).

3.3 Starch modification

Native starch is a good texture stabilizer and regulator in food systems but constraints, such as low shear resistance, thermal resistance, thermal decomposition and high tendency towards retrogradation, limit its use in some industrial food applications (Hui *et al.*, 2009). Native starches contain free hydroxyl groups in the 2, 3 and 6 carbons of the glucose molecule, making them highly reactive. This allows them to be modified by different chemical treatments and thus regulate their properties (Bao *et al.*, 2003). Starch modification, which involves the alteration of the physical and chemical characteristics of the native starch to improve its functional characteristics, can be used to tailor starch to specific food applications (Hermansson and Svegmark, 1996). Each chemical and biochemical modification described below is represented schematically in Figure 5. Modified starches have been investigated and developed for more than a century and have various applications in food, paper and textile industries (Miyazaki *et al.*, 2006).

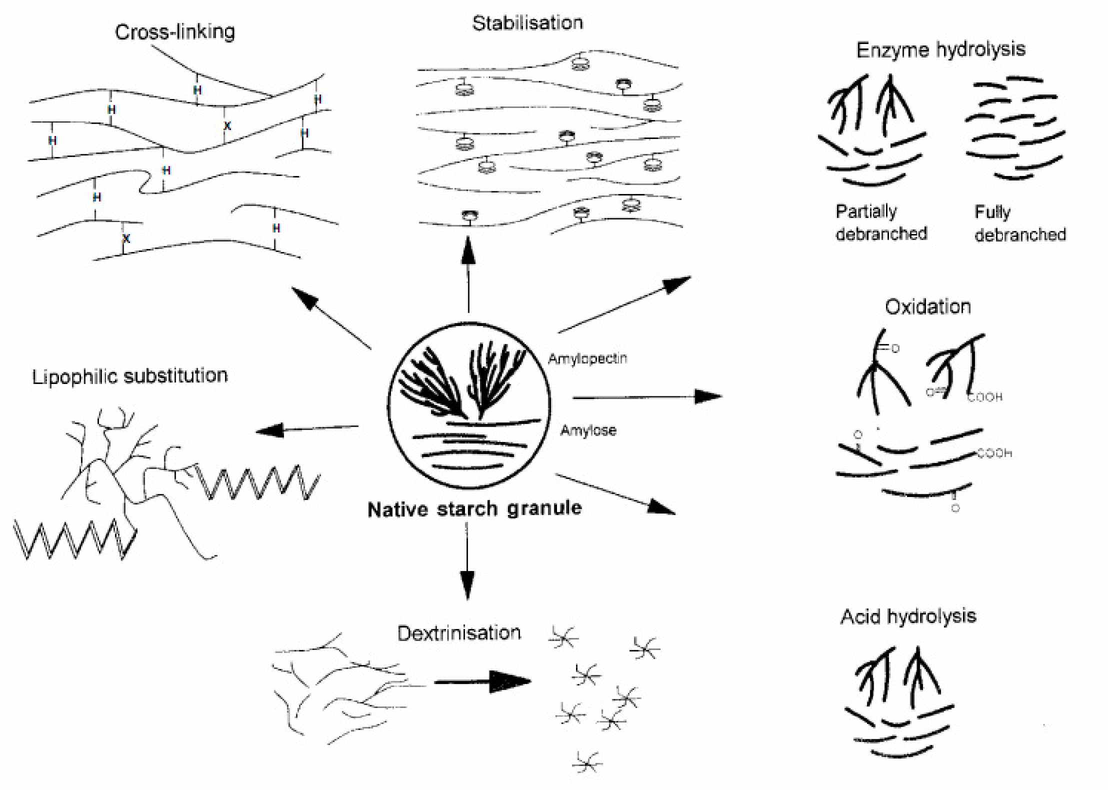


Figure 5. Chemical and biochemical modifications of starch.
Source : Murphy (2000)

3.3.1 Oxidized starch

Oxidized starch is widely used in paper industries (Sorokin *et al.*, 2004) where its specific properties are used to close the pores of paper to lay fuzz on the surface, to increase the tensile fold and bursting strength of the paper (Kweon *et al.*, 2001). The production of oxidized starches employs alkaline hypochlorite is the most common commercial reagent (Rutenberg and Solarek, 1984). Two important modifications occur: the relatively bulky carboxyl (COOH) and carbonyl (C=O) groups are introduced together with partial depolymerisation of the starch chains. (Murphy, 2000). The oxidation occurs at the C_6 primary hydroxyl group or at the vicinal diols on C_2 and C_3 involving a cleavage of the C_2–C_3 bond to give carbonyl and carboxyl functions (Figure 6).

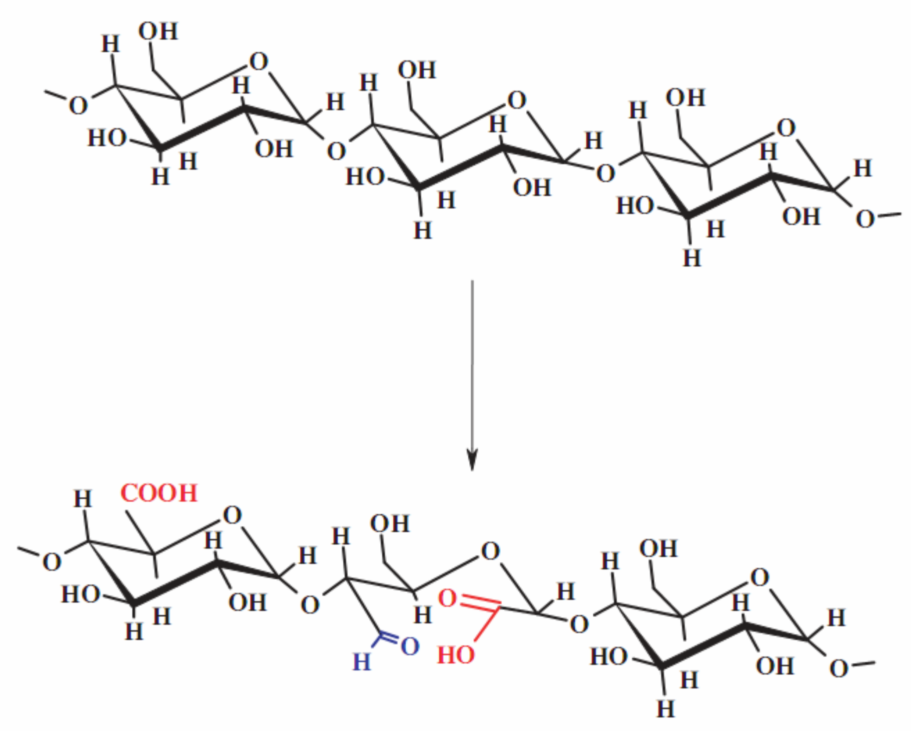


Figure 6. Schematic representation of starch oxidation.

Source: Sorokin *et al*. (2004)

Starch is oxidized to obtain low-viscosity, high-solids dispersions and resistance to viscosity dispersion, and introduces carbonyl and carboxyl groups, which minimize retrogradation of amylose, thus giving viscosity stability (Rutenberg and Solarek, 1984). About 80-85% of the hypochlorite-oxidized starch produced is used in the paper industry. It is primarily a paper coating binder where it is high fluidity and good binding and adhesive properties make it effective in high solids pigmented coating colors. Compatibility with the pigment, usually clay, is important and it should not adversely affect water-holding capacity and rheology of the coating color.

Until recently, large quantities of oxidized starches were used for paper and paperboard surface sizing to seal pores, tie down loose surface fibers, improve surface strength, and provide holdout of printing inks. Viscosity stability of oxidized starch dispersion as well as the range of viscosities available made them particularly suitable. However, the on-site conversion of native pearl starch by continuous enzyme conversion or thermal-chemical conversion has led to a decrease in the use of oxidized starch in surface sizing and has had some effect on coating use.

Thermochemical-converted starch does not have the viscosity stability of the oxidized starch and tends to retrograde on storage making it difficult to use in coating. Methods developed to overcome this retrogradation tendency may lead to a decrease in the use of hypochlorite-oxidized starch in paper coating. Oxidized starch in the wet end of the paper machine, mainly introduced in repulped coated paper (broke), has a detrimental effect on pigment retention by acting as a dispersant (Rutenberg and Solarek, 1984).

2.3.2 Starch ester

Starch esters of commercial value are those which provide sol stability and functional properties such as hydrophobic, cationic or anionic character at relatively low cost. Currently, these esters are the starch acetates and the half-ester of some dibasic carboxylic acids, particularly the alkenylsuccinic acids. As mentioned in the preceding section, the diesters of the dibasic carboxylic acids are valuable because of the cross-linking introduced. Because the tendency of a starch dispersion to increase in viscosity on cooling and aging and finally to gel is related to the association of the amylose molecules, any treatment which retards or eliminates this crystallization or retrogradation phenomenon will affect stabilization of the starch sol.

3.3.2.1 Starch Acetate

Acetylated starch has also been known for more than a century (Miyazaki *et al.* 2006). Acetylation prevents or minimizes association of outer branches of amylopectin molecules. This is of practical value in food applications where it prevents cloudiness and syneresis in aqueous dispersions of waxy starches stored at low temperature. Although there has been considerable interest in the higher DS acetate, particularly amylose acetate, because of their organic solvent solubility, thermoplasticity and film properties they have not developed commercially. The major use of starch acetate in the paper industry is in surface sizing for improved printability and functional properties by imparting low and uniform porosity, surface strength, abrasion resistance, oil holdout and solvent resistance, as well as by adhering stray fibers to the substrate. Matsui *et al.* (2004) reported that impregnation of hygroscopic materials with starch acetate of cassava bagasse with 10% Kraft paper added had a great influence on the reduction of water absorption. Similarly, Larotonda *et al.* (2005) demonstrates that cassava starch acetate impregnation of Kraft paper is an interesting alternative for the improvement of the hygroscopic properties and water vapor permeability of the Kraft paper. Starch acetates compete with oxidized starches, hydroxyethyl starches and low-viscosity starches prepared via enzymes or thermochemical processes. Other competitive products are other film-formers such as carboxymethyl cellulose, poly (vinyl alcohol) and alginates. When paper containing starch acetates is reintroduced into the paper-making system, there is no adverse dispersant effect on the retention of fillers and pigments, as noted with oxidized starches (Rutenberg and Solarek, 1984).

During acetylation, three free hydroxyl groups at C_2, C_3 and C_6 of the starch molecule can be substituted with acetyl groups. Therefore, the theoretical maximum DS is 3. The expected chemical reactions are illustrated in Figure 7 (Miyazaki *et al.* 2006). Depending on the degree of substitution (DS), properties of starch esters e.g. solubility varies significantly. The degree of substitution is defined as the number of moles of substituents per d-glucopyranosyl structural unit of starch. (Rudnika *et al.*, 2005). Therefore, acetylated starch has typically physicochemical characteristics such as low gelatinization temperature, high solubility, good cooking and storage stabilities (Miyazaki *et al.* 2006).

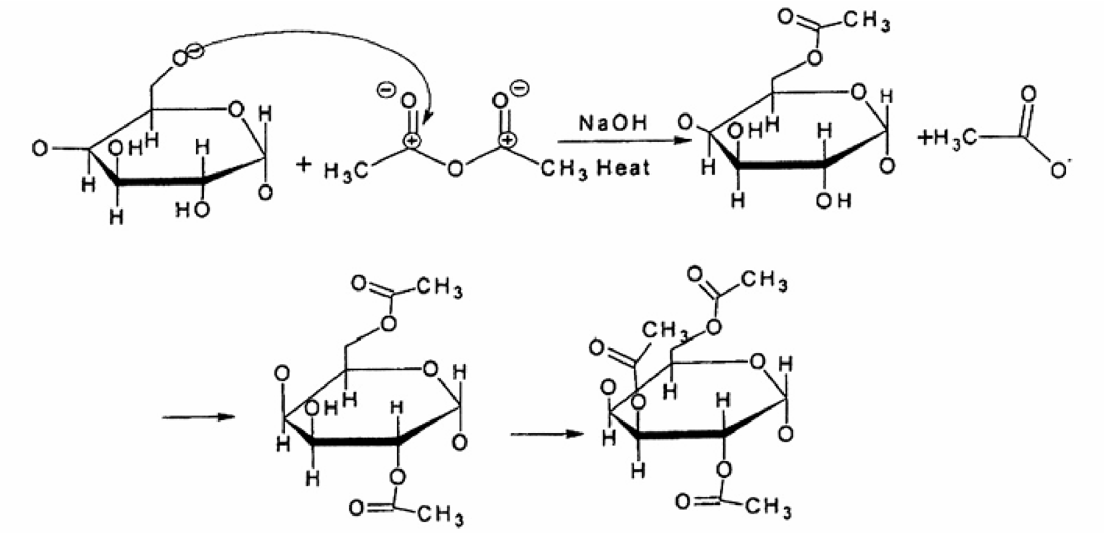


Figure 7. Chemical reactions during starch acetylation.
Source: Miyazaki *et al.* (2006)

3.3.2.2 Octanyl succinate starch

The hydrophilicity of starch, its propensity to interact with water, can be transformed into a schizophrenic hydrophilic-hydrophobic duality. This is particularly useful for stabilizing interactions between materials such as oil and water. To achieve this already hydrophilic starch must be given a characteristic that mirrors that of oil, namely, a long hydrophobic, i.e. lipophilic, hydrocarbon chain. Octanylsuccinate groups containing an eight-carbon chain provide the lipid-mimicking characteristic (Murphy, 2000). Starch octanylsuccinates can be prepared by treating starches with octanyl succinic anhydride (Bhosale and Singhal, 2006), are produced oil-in-water emulsions as the sole emulsifier that are resistant to re-agglomeration. (Tesch *et al.*, 2005; Bhosale and Singhal, 2006; Nilsson and Bergenståhl, 2006; Thirathumthavorn and Charoenrein, 2006; Nilsson and Bergenståhl, 2007). The glucose part of starch binds the water while the lipophilic, octenyl part binds the oil. In this way complete separation of the oil and water phases is prevented (Murphy, 2000). However, the hydrophobic substituent (Figure 8) also contains a carboxylic acid which can be negatively charged. (Nilsson and Bergenståhl, 2007).

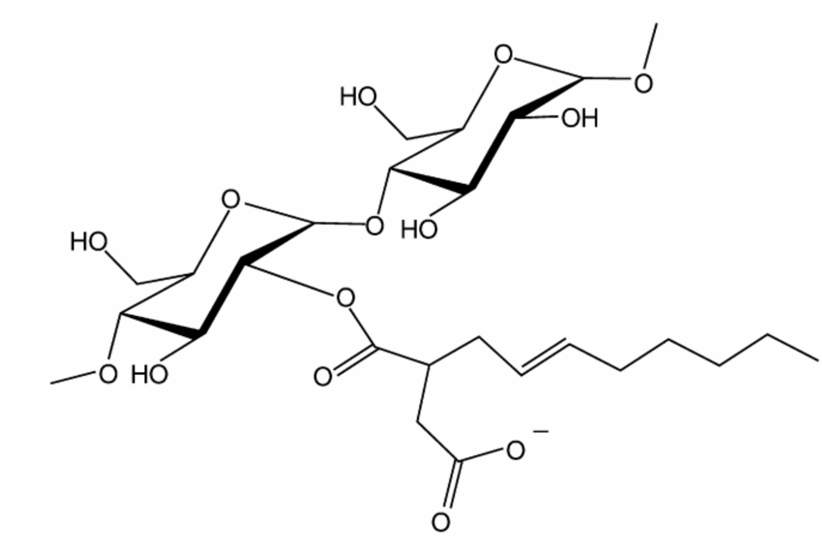


Figure 8. Starch which has been hydrophobically modified with octanyl succinicanhydride (OSA). The figure shows the hydrophobic/anionic substituent esterified to the starch polymer backbone.

Source: Nilsson and Bergenståhl (2007)

The chemical structure of starch octanyl succinate is shown in Figure 9. The incorporation of bulky OSA grouping to hydrophilic starch molecules confers surface active properties to the modified starch so obtained. Unlike typical surfactants, OSA starch forms strong films at the oil–water interface giving emulsions that are resistant to reagglomeration. As a result, aqueous solutions of OSA starches have been used to stabilize flavour emulsion in beverages, oil in salad dressings and to encapsulate flavour and fragrances (Bhosale and Singhal, 2006).

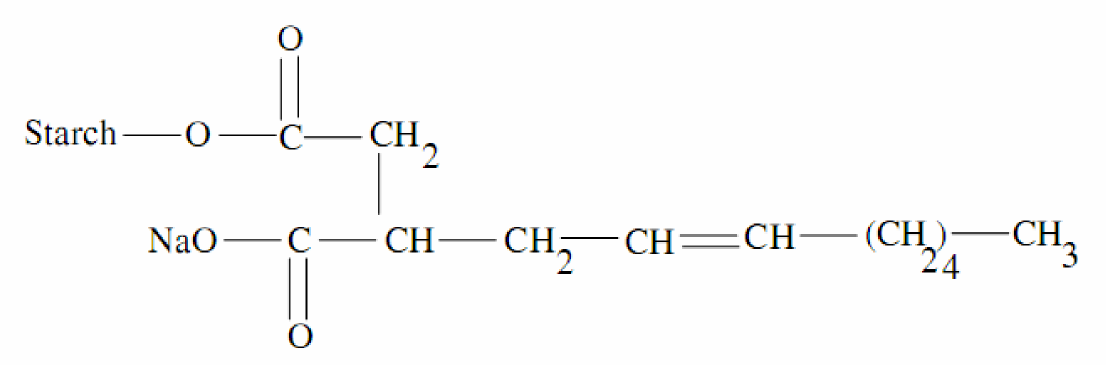


Figure 9. Structure of starch octanyl succinate.
Source: Bhosale and Singhal (2006)

According to, Cadwell and Wurzburg (1953) patented modification of starches with OSA. This groundbreaking work was based on the esterification of starch with OSA under mild alkaline conditions. (OSA) is permitted for food applications. (Bhosale and Singhal, 2006) In the United States, FDA approved OSA starch for food use in 1972. The maximum level of OSA treatment allowed is 3% or degree of substitution (DS) ≈ 0.02 (Song *et al.,* 2006; Bhosale and Singhal, 2007).

In addition, starch octanylsuccinates are starch derivatives used as binders and thickening agents in foods, tablet disintegrants in pharmaceuticals, surface sizing agents and coating binders in paper (Wang *et al.*, 1997; Bhandari and Singhal, 2002; Shogren, 2003).

3.3.3 Starch ether

The reaction of starch with etherifying reagent, propylene oxide, results in the introduction of hydroxypropyl group onto the polymeric chain of starch. The alignment of polymers that causes a change in the structure, leading to an opaque, gelled, and/or chunky texture with “weeping” of liquid from the gel. The reactive nature of propylene oxide is due to its highly strained three-membered epoxide ring. Bond angles in the ring average 60° resulting in a very unstable (reactive) molecule.

In substitution reactions by etherification, the starch molecule should first be activated to make the O–H bond nucleophilic and to facilitate the formation of starch–O^-. Alkaline reagents in this regard are excellent as catalysts. This is followed by reaction of starch–O^- and propylene oxide which results in bimolecular substitution producing hydroxypropyl starch (Pal *et al.* 2000).

Hydroxypropyl starches are widely used in the food industry. They are prepared by reacted a starch with propylene oxide to low levels of etherification, a molar substitution (MS) of 0.1 being common. (Kavitha and BeMiller, 1998). When starch is hydroxypropylated, internal hydrogen bonding is weakened. Hydroxypropylated starch gives improved shelf life, freeze/thaw stability, cold storage stability, cold water swelling, and a reduced gelatinization temperature, as well as retarded retrogradation. Therefore, hydroxypropylated starch has a wide spectrum of applications in the food industry (Tuschhoff, 1987; Kim, 2003). Hydroxypropylated starches are generally prepared by etherification of native starch with propylene oxide in the presence of an alkaline catalyst. The hydroxypropyl groups introduced into the starch chains are capable of disrupting the inter- and intra-molecular hydrogen bonds, thereby weakening the granular structure of starch, leading to an increase in motional freedom of starch chains in amorphous regions (Wootton and Manatsathit, 1983; Seow and Thevamalar, 1993; Choi and Kerr, 2003). Hydroxypropyl groups are known to be hydrophilic in nature. Therefore, the hydroxypropylated starch absorbed more water and increased water absorption of starch (Pal *et al*., 2002; Miyazaki *et al*., 2006). Choi and Kerr (2003) studied the effects of hydroxypropylation on water sorption isotherms and molecular mobility of both starch and water molecules using pulsed ^{1}H-MMR techniques and reported that the water absorption capacity of hydroxypropylated wheat starch increases with increasing degree of molar substitution of hydroxypropylated group in a specific water activity range.

4. Alkyd resin

Producing of low solvent amount, high-quality organic coatings for industrial applications are important target in coating industry. Formulation of a low solvent amount coating requires the use of a low molecular weight polymer that has low viscosity. One of the most widely used types of organic coatings is alkyd resin. Alkyd resins are widely used as binders in surface coating due to their unique properties such as colour and gloss retention, film flexibility and durability, and good adhesion. The resins offer high gloss and are easily applied under variable environmental conditions (Aigbodion *et al.*, 2003). Even though they have been used in protective coating resins for over 50 years, they still belong among the most important synthetic coating resin (Vareckova *et al.*, 2006). Additionally, they are to a greater extent biologically degradable polymers because of the oil and glycerol parts (Aydin *et al.*, 2004).

Alkyd resins belong to a class of polymers that are used in surface coating formulations because of their low cost and versatility and provide a major source of protective and decorative coating materials (Hackmann, 2001). Alkyd resins in a broad sense refer to polymers. By convention, however, polyesters with unsaturation in the backbone are not referred to as alkyds but are termed “unsaturated polyesters.” The specific definition of alkyds that has gained wide acceptance is that alkyds are polyesters modified with fatty acids (Holmberg, 2006).

4.1 Classification

The name ‘alkyd’ is derived from the alcohol and acid monomers used to make the polyester polymer, and an alkyd resin is oil modified alkyd polyester. Alkyd resins are made by condensation polymerization of polyols (at least three hydroxyl groups), polybasic acids and a source of fatty acids (either siccative oils or free fatty acids) (Figure 10). The final resin is composed of a polyester backbone, on its own a highly branched polymer, and dangling fatty acids, which serve to reduce the amount of cross-linking creating a more flexible polymer (Ploeger *et al.*, 2008).

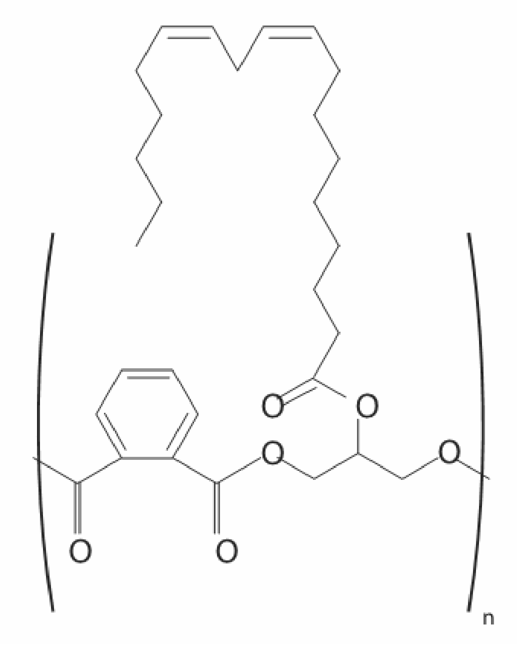


Figure 10.Structure of a typical alkyd resin.
Source: Haveren *et al.* (2007)

The nature and proportions of these components control the properties of the resin. The amount of combinations is enormous and specification of an alkyd resin must involve several parameters. The most important ways of classifying are given below (Holmberg, 2006).

4.1.1 Oil length and type of oil

Depending on the weight percentage of fatty acid in the resin, alkyds are referred to as short oil (<45%), medium oil (45 to 55%) or long oil (>55%). However, some confusion exists regarding the terminology. The type of fatty acid used also governs the properties of the alkyds. The resins are classified as drying, semidrying and nondrying, depending on the degree of unsaturation in the fatty acid residues (iodine number of >140, 125 to 140, and < 125, respectively) (Holmberg, 2006). The fatty acid portion gives many important properties to the resin, including, cross-linking potential, flexibility, compatibility with solvents and control of solubility (Ploeger *et al.*, 2008). Oxidative drying of alkyds, which involves air oxidation of polyene structures in fatty acid residues, is at maximum around 50% oil length. After drying, film hardness is inversely proportional to the degree of fatty acid modification. Short oil alkyds generally give films of high quality with regard to color and gloss retention but with low flexibility and with poor adhesion. Long oil alkyds are usually superior in terms of pigment dispersion, rheological properties, and storage stability.

4.1.2 Percentage of phthalic anhydride

Phthalic anhydride is the most commonly used raw material in alkyd compositions, and the weight percentages are usually stated. There is an inverse relationship between percentages of phthalic anhydride and degree of fatty acid modification, short oil alkyds having above 35%, medium oil alkyds between 20 and 35% and long oil alkyds below 20% phthalic anhydride.

4.1.3 Acid value and hydroxyl number

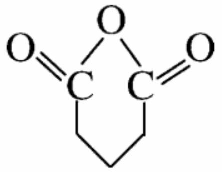
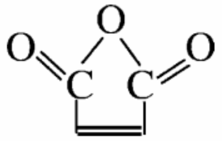
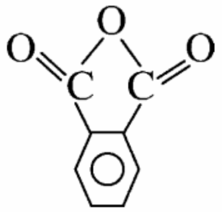
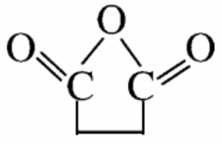
The acid value is defined as milligrams of potassium hydroxide required to neutralize 1 g of resin. For alkyds resin, 0.1 M KOH in ethanol is normally employed. The hydroxyl number (sometimes called hydroxyl value) is the milligram of potassium hydroxide equivalent to the amount of acyl groups reacted in the acylation of 1 g of resin. A known amount of acylating reagent (often acetic anhydride or phthalic anhydride in pyridine) is added to the resin sample, and the hydroxyl number is obtained by backtitration with alkali. Usually, the hydroxyl number is considerably higher than the acid values. Baking alkyds require a certain concentration of hydroxyl groups to react with the amino acids, and for air drying alkyds, the concentration of hydroxyl groups determines pigment wetting properties. The concentration of carboxyl groups is of particular interest in alkyds for water-borne coatings. To achieve water solubility without excessive use of cosolvents, these resins are processed to a high acid value, and the carboxyl groups are subsequently neutralized with ammonia or an amine.

4.2 Raw materials

4.2.1 Polybasic acids

Due to ease of handling, good balance of properties and economy, orthophthalic acid is the most important polybasic acid for alkyds. It is almost exclusively used in its anhydride form. Isophthalic acid is used as a replacement for phthalic anhydride when a tougher, faster drying and more chemical and heat resistant coating are required. The meta position of its carboxyl groups makes the formation of intramolecular cyclic esters more unlikely with isophthalic acid, leading to higher molecular weights and high viscosities of the alkyds. The chemical structures of the anhydride with molecular weight and acid value are shown in Table 1.

Table 1 The chemical structures, molecular weights and acid values of anhydrides used.

Component	Formula	Molecular weight	Acid value (mg KOH/g)
Glutaric anhydride		114.1	983.4
Maleic anhydride		98.06	1144.2
Phthalic anhydride		148.12	757.5
Succinic anhydride		100.8	1121.1

Source: Aydin *et al.* (2004)

4.2.2 Polyols

Usually, a mixture of polyols having a functionality of 2 to 4 is used in an alkyd formulation. Ethylene glycol, propylene glycol and neopentyl glycol are the most important duols; glycerol and trimethylol propane are commonly used triols; and pentaerythrital is the tetraol of choice. The choice of polyol components is mainly responsible for the degree of branching of the alkyd. The flexibility of the resin is also influenced by the distance between the hydroxyl groups-diethylene glycol, for instance, gives a more flexible product than ethylene glycol. Neopentyl glycol, because of its branched structure, gives heat-and hydrolysis-resistant films (Holmberg, 2006).

4.2.3 Fatty acids and oils

Alkyds are classified by ‘oil length’, i.e. the weight percent of oil or triglyceride equivalent or fatty acids in the finished resin, and oil type (Ploeger *et al.*, 2008). The vast majority of the nonbasic acids used in alkyd compositions are derived from vegetable oils. Fish oil also is used to a small degree. Rosin, which is a mixture of resinous monobasic acids having a molecular weight of about 330, is sometimes incorporated to improve hardness, initial drying and water resistance. Synthetic aromatic acids, such as benzoic acid, can provide greater hardness and improve gloss retention.

The degree of unsaturation in the fatty acid governs the drying properties of alkyds. In general, the higher the iodine numbers of the oil or the fatty acid, the faster the drying. The position of the double bonds is also of importance, with conjugated bonds being much more reaction in auto-oxidation than non-conjugated. Soybean oil is the workhorse among the vegetable oils. Linseed oil is used for fast drying alkyds. Tall oil, sunflower oil and safflower oil are also common as raw materials for drying alkyds. Coconut oil and castor oil are extensively used in nondrying alkyds.

4.3 Manufacturing process

Alkyds are prepared by polycondensation of the acid and alcohol components until a predetermined acid value-viscosity relationship has been achieved. The reaction is normally performed under inert gas or solvent vapor to minimize oxidation of unsaturated components. In the initial phases of the reaction, the drop in acid value is rapid, and the increase in viscosity is slow. Alkyd coatings are produced in two processes; fatty acid process and the alcoholysis or glyceride process (monoglyceride process).

4.3.1 Monoglyceride process

When triglyceride oil is heated together with polyols and polybasic acids, the polyols react preferentially with the acids, and a heterogeneous mixture of triglyceride and unmodified polyester is obtained. The way to overcome this problem is to perform a controlled tranesterification of the fatty acids prior to the condensation step. This is usually done by reacting 1 mole of triglyceride with 2 moles of glycerol (or another polyol) at a temperature of 220 to 250°C until the monoglyceride stage is obtained. The preferred catalysts are PbO, $Ca(OH)_2$, and Ca-soaps.

After formation of monoglycerides, the polybasic acids and the polyols are added, and the condensation is carried out until the desired viscosity-acid value relationship is reached.

In the two-stage process shown in Figure 11, oil is initially subjected to a reaction with glycerol to obtain a monoglyceride precursor, which in the second step, is reacted with phthalic anhydride to obtain the alkyd resin (Ogunniyi and Odetoye, 2007).

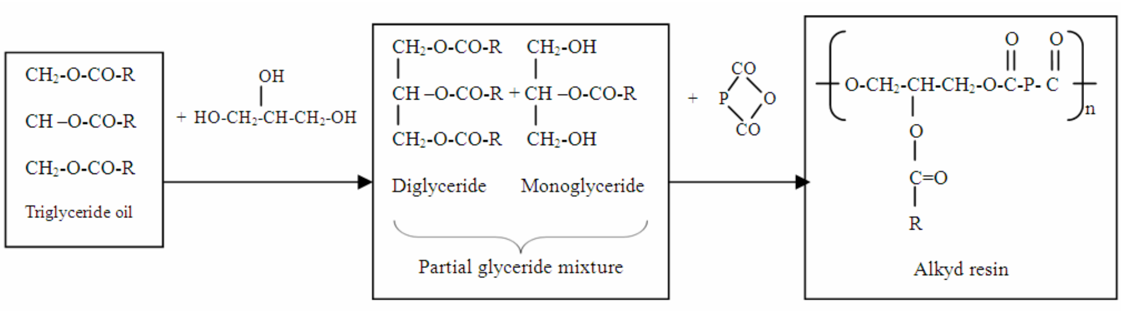


Figure 11.Preparation of alkyd resins.
Source: Aydin *et al.* (2004)

4.3.2 The fatty acid process

The fatty acid process uses not the triglyceride but the fatty acid itself. Apart from giving a greater freedom in the choice of polyol components, this process is more reproducible and gives better control over molecular weight and molecular weight distribution of the resin. In addition, this process enables the condensation to be carried on to lower acid value, which is advantageous for the drying properties.

The choice of manufacturing process is not only a matter of finding the most suitable synthesis procedure. There exist distinct differences in film properties between alkyds of the same composition but prepared by different processes (Holmberg, 2006).

5. **Poly (Vinyl Alcohol)**

Poly (vinyl alcohol) (PVOH) is a water-soluble synthesis resin. It is produced by the hydrolysis of poly (vinyl acetate); the theoretical monomer, CH_2=CHOH, does not exist. PVOH, also known as polyvinyl alcohol, is a dry solid and is available in granular or powdered form. Grades include both the fully hydrolyzed form on poly (vinyl acetate) and products containing residual, i.e. unhydrolyzed, acetate groups. Resin properties vary according to the molecular weight of the parent poly (vinyl acetate) and the degree of hydrolysis. A wide range of grades is offered by PVOH manufacturers.

The wide range of chemical and physical properties of PVOH resins has led to their broad industrial use. They are excellent adhesives and highly resistant to solvents, oil and grease. Poly (vinyl alcohol) forms tough, clear films that have high tensile strength and abrasion resistance. Its oxygen-barrier qualities are superior to those of any known polymer; However, PVOH must be protected from moisture, which greatly increased its gas permeability. Poly (vinyl alcohol) also contributed to emulsification and stabilization of aqueous dispersions. The main uses of PVOH in the United States are in textile and paper sizing, adhesives and emulsion polymerization. Significant volumes are also used in such diverse application as joint cements for hospital laundry bags, emulsifiers in cosmetics, temporary protective film to prevent scratching of highly polished surfaces and soil binding to control erosion. Poly (vinyl alcohol) is an intermediate in the interlayer in laminated safety glass. Outside the United States, PVOH is also used for textile fiber, although it must be chemically treated to become water-insoluble.

5.1 Physical properties

The physical properties of PVOH are controlled by molecular weight and the degree of hydrolysis. The upper portion of Figure 12 shows the variation in properties with molecular weight at a constant degree of hydrolysis. Since hydrolysis and molecular weight can be independently controlled in the manufacturing process, a product matrix has evolved that provided the property balance needed for different applications.

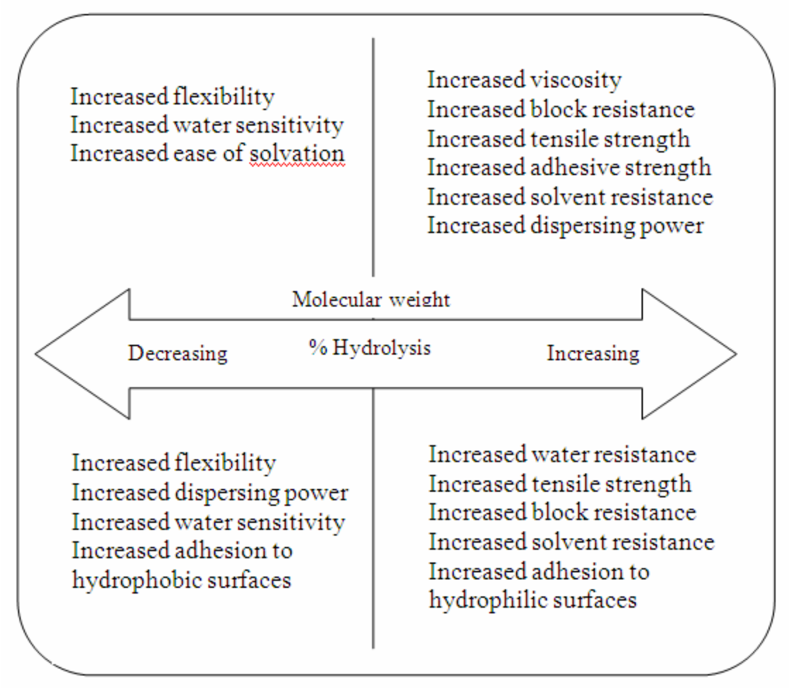


Figure 12. Properties of poly (vinyl alcohol).

Source: Jaffe and Rosenblum (1990)

5.2 Solubility

All commercial PVOH grades are soluble in water, the only practical solvent. The ease with which PVOH can be dissolved is controlled primarily by the degree of hydrolysis. Fully hydrolyzed products must be heated close to the atmospheric boiling point of water to dissolve completely. Lower temperatures are required as the degree of hydrolysis is decreased until 75-80% hydrolysis is reached, at which point the product is fully cold-water soluble but precipitated upon heating. The hydrolysis range of 87-89% is considered optimum for both cold and hot water solubility. Products with this optimum degree of hydrolysis are commonly referred to as partially hydrolyzed poly (vinyl alcohol). Regardless of the degree of hydrolysis, all commercial PVOH grades remain dissolved upon cooling. Solubility is also influenced by particle size, i.e. surface area, molecular weight and crystallinity. Decreasing particle size and molecular weight improves the solubility weight. Crystallinity is induced by heat treatment and retards the solubility rate. Because the presence of residual acetate groups reduces the extent of crystallinity, low hydrolysis grades are much less sensitive to heat treatment.

Poly (vinyl alcohol) cannot be dissolved by most common organic solvents, e.g. gasoline, kerosene, benzene, xylene, trichloroethylene, carbon tetrachloride, methanol, ethylene glycol, acetone and methyl acetate. It has limited solubility in dimethyl sulfoxide; the solubility is in proportion to the residual acetate content. Although there are no good solvents for PVOH other than water, up to 50% of lower alcohols can be added to PVOH solutions without causing precipitation.

5.3 Solution viscosity

The viscosity of a PVOH solution is controlled by molecular weight, concentration and to lesser degree, temperature. Degree of hydrolysis does not strongly affect viscosity, although the viscosity is proportional to degree of hydrolysis at constant molecular weight. Viscosity relationships for low, medium and high molecular weight grades are shown in Fig 3. Viscosity, rather than solubility, limits the concentration of PVOH solutions. With conventional batch-mixing equipment, the practical concentration limits for low, medium and high molecular weight resins are 30 wt %, 20 wt % and 15 wt %, respectively. The viscosities of partially hydrolyzed PVOH solutions remain stable if the solutions are stored at high temperature over a wide range of concentrations. However, viscosities of concentrated solutions of fully hydrolyzed PVA gradually increase over a period of days when stored at room temperature and gelation occurs in products that contains < 1 mol % acetate groups. This viscosity increase or gelation can be reversed by reheating. Lower solution concentrations and lower degrees of hydrolysis eliminate viscosity instability associated with long-term solution storage.

5.4 Manufacture

All PVOH manufacture involves poly (vinyl acetate) as the starting material. The theoretical monomers, vinyl alcohol (CH_2=CHOH), does not exist. Conversion of poly (vinyl acetate) to PVOH is generally accomplished by base-catalyzed methanolysis; sodium hydroxide is the usual base. Poly (vinyl acetate) polymerization is accomplished by conventional processes, e.g., solution, bulk or emulsion polymerization. Solution polymerization is favored because the subsequent alcoholysis reaction requires solvent addition. The polymerization step determines the ultimate molecular weight of the PVOH. Catalyst concentration, temperature and solvent control the degree of polymerization; acetaldehyde is an effective chain-transfer agent. It is the agent commonly used.

The degree of hydrolysis of PVOH is controlled during the alcoholysis and is independent of molecular weight control. Fully hydrolyzed PVOH is obtained if methanolysis is allowed to go to completion. The reaction can be terminated by neutralizing or removing the sodium hydroxide catalyst. The addition of small amounts of water to the reactants promotes saponification of poly (vinyl acetate), which consumes sodium hydroxide. The extent of hydrolysis is inversely proportional to the amount of water added. A disadvantage of water addition is an increase in byproduct sodium acetate, which is present as ash in all commercially available grades of PVOH. The alcoholysis reaction can be carried out in a highly agitated slurry process; a fine precipitate forms as the poly (vinyl acetate) converts into PVOH. The product is then washed with methanol and is filtered and dried. A moving belt process allows the PVOH to form a gel and subsequently to be cut into granular form.

The alcoholysis process yields methyl acetate as a byproduct. The methyl acetate can be used as a solvent or it can be processed to recover methanol and acetic acid. One such process involves mixing the methyl acetate with water and passing them through a cation-exchange resin to catalyze the hydrolysis reaction. Methanol recovered from this process can be totally recycled to the methanolysis step and the acetic acid is sold as a byproduct (Jaffe and Rosenblum, 1990).

Objectives

1. To evaluate the effect of type and concentration of mediums on the properties of alkyd resin coating and coated liner board.
2. To evaluate the alkyd resin concentration on the properties of alkyd resin coatings and coated linerboard.
3. To determine the effect of mixing speed on the properties of alkyd resin coating and coated linerboard.
4. To compare the efficiency of the alkyd resin coating with commercial wax.
5. To investigate the microbiological changed of alkyd resin coating during storage.

CHAPTER 2

MATERIALS AND METHODS

1. Materials

1.1 Liner board

Liner board (KS170) used was obtained from Thai Containers Songkhla (1994) Co., Ltd. (Songkhla, Thailand) with an average thickness of 0.252 mm and basis weight of 170 g/m^2.

1.2 Chemicals

The following chemical materials were used to prepare the alkyd resin coating liner boards: coating medium oxidized starch (ExcelSize 5), hydroxyl propyl starch (HT8), starch acetate (SMS FT) were obtained from Siam Modified Starch Co., Ltd., (Pathumthani, Thailand) octanyl succinate starch was obtained from Thai Containers Songkhla (1994) Co., Ltd. (Songkhla, Thailand) and polyvinyl alcohol (BF-05) with average molecular weight of 22,000 – 27,000 g mol^{-1} and degree of hydrolysis of 98.5 – 99.2%, gelatin, locust bean gum as emulsifier and stabilizer, respectively. Short oil alkyd resin (SA 7713-70) was purchased from Diforce Cheme Co., Ltd (Bangkok, Thailand) and physico-chemical properties are presented in Table 1. The alkyd resin was a chain stopped short oil alkyd resin based on soybean fatty acids. Commercial wax (WR390) was obtained from Thai Containers Songkhla (1994) Co., Ltd. (Songkhla, Thailand)

Table 1 Physico-chemical properties of short oil alkyd resin.

Properties	**Value**	**Unit**
Viscosity	6,300 – 9,800	cP
Color	Y = 74	
	x = 0.3558	CIE
	y = 0.3480	
Solid content	70.8	%
Acid value	9.36	mg KOH / g

Source : Diforce Cheme Co., Ltd

2. Instruments

Instruments	Model	Company/Country
Magnetic stirrer model	RO 10 power	IKA LABORTECHNIK, Germany
Stirrer	RW 20n	IKA LABORTECHNIK, Germany
Homogenizer	T 25	Ultra Turrax, Malaysia
Hot air oven	Memmert UM-500	Memmert, Germany
Dry cabinet	AD-050C	Wonderful, Philippine
Double roll coating machine	-	-
Brookfield viscometer	DV-II	Brookfield Engineering Laboratory, U.S.A.
Water absorption tester	GT-6015	GOTECH TESTING MACHINE, Taiwan
Universal testing machine	LR 30K	Lloyd Instruments Ltd, UK
Scanning electron microscope	JSM-5800 LV	JEOL, Japan
Flexography Printer	3FM115	Yueli, Taiwan
Laser particle size analyzer	LS-230	Coulter, U.S.A.
Thermogravimetric analyzer	TGA-7	Perkin-Elmer, U.S.A.
FTIR spectrometer	Equinox 55	Bruker, Japan
Hunter associates laboratory	ColorFlex	Hunter Associates Laboratory, U.S.A.

3. Effect of type and concentration of coating mediums on the properties of alkyd resin coating and coated liner boards

3.1 Preparation of alkyd resin coating solution and liner board coating

Coating medium (oxidized starch, octanyl succinate starch, hydroxypropyl starch, starch acetate and polyvinyl alcohol) were prepared at various concentrations (1, 2, 3, 4, 5 and 6 w/w) in filtered water, heated until starches were gelatinized or PVOH was dissolved completely. In order to gelatinize the starches, the slurry must be heated to a temperature of at least 80°C for a sufficient amount of time. In the part of the PVOH dissolution, the slurry was stirred about 30 minutes at room temperature. After that the slurry was heated until PVOH dissolved in filtered water completely. Gelatin and locust been gum (10% and 3% w/w of alkyd resin, respectively) were dissolved in coating medium. After cooling, 3% of alkyd resin was added. The suspensions were homogenized at 10,000 rpm for 3 minutes. Then the coating was applied on the white side of liner board (0.3–0.8 g/m^2) by double roll coating machine (Figure 13) and drying at 160–170°C. All coated liner boards were conditioned at 65% RH ambient room temperature in a constant humidity chamber before testing. The summary of the preparation of alkyd resin coating solution and liner board coating was presented in Figure 14.

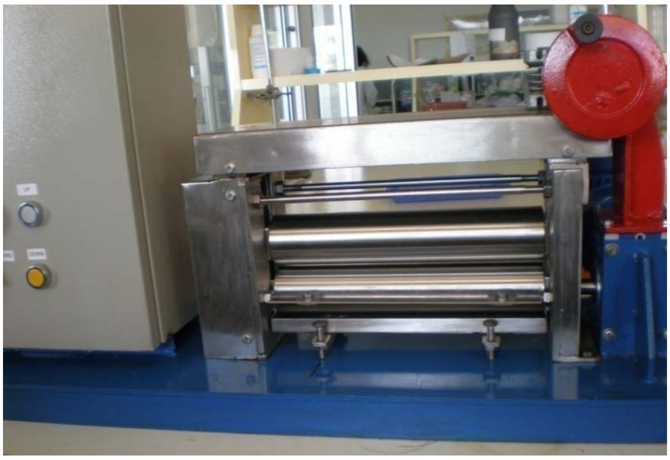


Figure 13. Double roll coating machine

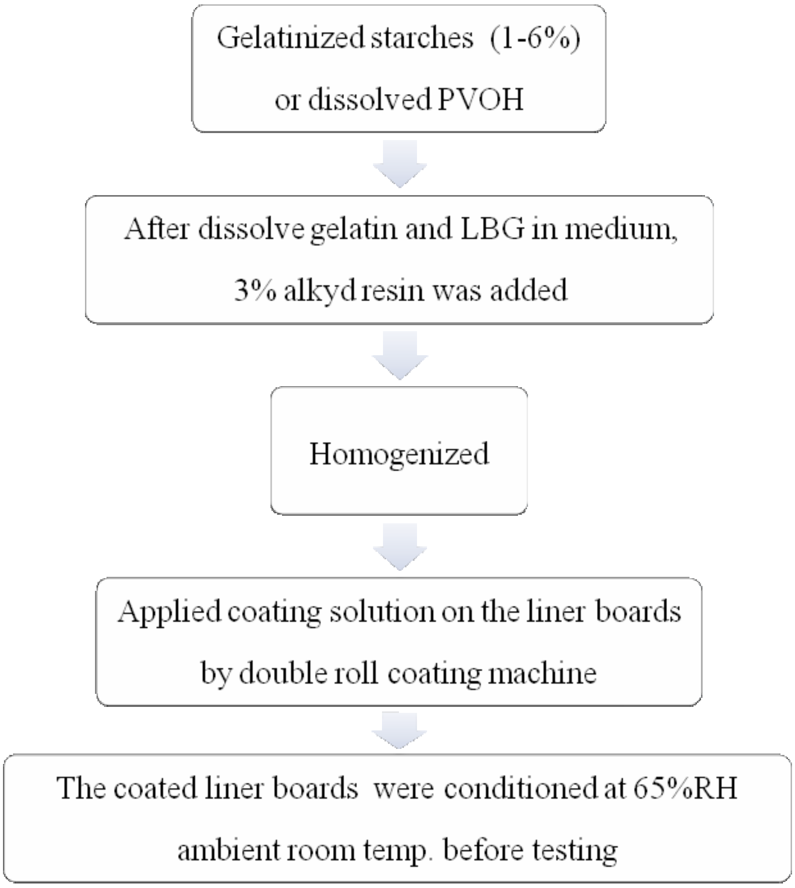


Figure 14. The preparation of alkyd resin coating solution.

3.2 Coated liner board testing

3.2.1 Water absorptiveness

The apparatus used in water absorptiveness tests was a Cobb Tester. The Cobb_{60} value was performed according to TAPPI Standard T441/ ISO 535. It consists of a gravimetrical analysis in which a sample is weighed before and after poured distilled water in for 1 min (Matsui *et al*., 2004). The procedure, including the duration of certain stages, is specified in each standard. A dry test piece of suitable size is weighed and placed under the cylinder. Then 100 ml of water is poured over the test piece. After a specified time the water is poured off and the test piece is placed on a standardized blotting paper. Another blotting liner board is placed on top of the test piece and the excess water is removed by means of the couch roller. The test piece is weighed again and the results are calculated and reported as absorptiveness in grams, per m^2 according to the standard method.

3.2.2 Mechanical properties

Tensile index was measured with a Universal testing machine (LLOYD Instrument Ltd, Model LR30K, Hampshire, England) in accordance with the TAPPI T 494 (ASTM D 882 method A). The clamp separation was 100 mm and the strain rate was set at 15 mm/min. This test method describes the procedure, using constant rate of elongation equipment, for determining tensile breaking properties of paper and paperboard. Tensile index was calculated by dividing the tensile strength which maximum force at break by basis weight. The reported results are the average of ten measurements. Bursting strength was a measure of resistance against rupture of paper. It was defined as the hydrostatic pressure to rupture the paper as the pressure was increased at a constant rate. Bursting strength is expressed in kilopascal (kPa) or psi (pounds per square inch) by Mullen tester.

3.2.3 Scanning electron microscopy

The selected coated liner boards were observed surface morphology by scanning electron microscopy (SEM). To visualize the surface of the materials, small pieces of sample (10mm×10mm) were cut and directly mounted on stub with double-sided carbon tape. After degassing and gold coating (5 nm thick), samples were examined with JEOL JSM-5800 LV scanning electron microscope (Gastaldi *et al.*, 2007).

3.2.4 Printing quality

Coated liner boards were printed with red color by flexography printing machine (Yueli, Model 3FM115, Taiwan) that supported from Thai Containers Songkhla (1994) Co., Ltd. (Songkhla, Thailand). After printed, coated liner boards were measured the rectangular coordinates (L*, a* and b*) and the total color difference (ΔE*) was calculated by equation (1):

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

3.3 Coating characteristics

3.3.1 Viscosity

The viscosity of alkyd resin coatings were determined by Brook Field Viscometer. All the measurements were conducted at 25 °C for 30 min after the sample was loaded. Mean viscosity values were calculated as the average of three measurements made on the three separately prepared samples.

3.3.2 Coating stability

Coating stability value was determined by Drakos and Kiosseoglou's method (2008). A quantity (250 mL) of coating was poured into a cylindrical glass container that covered with aluminum foil, and stored at room temperature for 24 hours. The stability of the coating was measured by measuring the height of the visible serum separation layer, with storage time.

4. Effect of alkyd resin content on the properties of alkyd resin coating and coated liner board

The selected type and concentration of coating medium from section 3 was prepared in filtered water, heated until starches were gelatinized completely. Then 1-5% of alkyd resin was added after gelatin and locust been gum (10% and 3% of alkyd resin, respectively) were completely dissolved in the medium. The suspensions were homogenized at 10,000 rpm for 3 minutes. Later, the coating was applied on the white side of liner board (0.3–0.8 g/m^2) by double roll coating machine and drying at 160–170°C. All coated liner boards were conditioned at 65% RH ambient room temperature in a constant humidity chamber before testing. The properties of coating and coated liner boards were tested similar to section 3.

5. Effect of mixing speed on the properties of alkyd resin coating and coated liner board

The selected type and concentration of coating medium from section 3 was prepared in filtered water, heated until starches were gelatinized completely. Then the optimum concentration of alkyd resin (selected from section 4) was added after gelatin and locust been gum (10% and 3% of alkyd resin, respectively) were completely dissolved in the medium. The suspensions were homogenized at 5,000, 10,000 and 15,000 rpm for 1, 2 and 3 min. Then, the coating was applied on the white side of liner board (0.3–0.8 g/m^2) by double roll coating machine and drying at 160–170°C. All coated liner boards were conditioned at 65% RH ambient room temperature in a constant humidity chamber before testing. The properties of coating and coated liner boards were tested similar to section 2

6. Comparison of the efficiency of alkyd resin coating with commercial wax

The selected type and concentration of coating medium from section 3 was prepared in filtered water, heated until starches were gelatinized completely. Then the optimum concentration of alkyd resin (selected from section 4) was added after gelatin and locust been gum (10% and 3% of alkyd resin, respectively) were completely dissolved in the medium. The suspensions were homogenized at the optimum mixing speed (selected from section 5). Then, the coating was applied on the white side of liner board (0.3–0.8 g/m^2) by double roll coating machine and drying at 160–170°C. All coated liner boards were conditioned at 50% RH and 27$\pm$2^{o}C in a constant humidity chamber before testing. The commercial wax was prepared by adding filtered water in ratio of 1:12 (commercial wax: water). Then the coating was applied on the liner boards by double roller coater and drying at 160–170°C. All coated liner boards were conditioned at 65% RH ambient room temperature in a constant humidity chamber before testing. Then the coated liner boards from alkyd resin and commercial wax were compared.

7. Effect of storage period on the stability of alkyd resin coatings

The selected type and concentration of coating medium from section 2 was prepared in filtered water, heated until starches were gelatinized completely. Then the optimum concentration of alkyd resin (selected from section 3) was added concomitant with gelatin and locust been gum (10% and 3% of alkyd resin, respectively). The suspensions were homogenized at the optimum mixing speed (selected from section 4). Coating stability value was measured by Drakos and Kiosseoglou’s method (2008). A quantity (250 ml) of coating was filled into a cylindrical glass container that covered with aluminum foil, and stored at room temperature for 1, 3, 5 and 7 days. The TVC (Total Variable Count) of coating and stability of the coating were determined.

8. Statistical Analysis

Completely randomized experimental design (CRD) was used in section 2 – 6. Analysis of Variance (ANOVA) was used to compare mean difference of the sample. If the difference in mean is existed, multiple comparisons will be performed using Duncan' New Multiple Rang (DMRT)

CHAPTER 3

RESULTS AND DISCUSSION

1. Effect of type and concentration of coating mediums on the properties of alkyd resin coating and coated liner boards

1.1 Water absorptiveness

Water absorption is important properties of paper, not only for writing and printing results, but also for the appearance of the material after handling and practical use in real life. It is particular important when the material being packaged is subject to a wet environment. This method for measuring water absorption of sized papers is used all over the world. Sizing can also affect other aspects of the box making process. Table 3 shows effect of coating mediums formulated in alkyd resin coating on the water absorptiveness of coated liner boards. At 1% of medium concentration of all treatments provided the lowest water absorptiveness of coated liner board. It was observed that, increasing of coating medium concentration yielded a thicker of coating layer, revealed increasing the water absorptiveness of coated liner board. Han and Krochta (1999) reported that the water absorptiveness of paper increased by coating with WPI and they also reported that the thicker the coating, the higher water absorptiveness was obtained. Comparing the effect of type of medium on the water absorptiveness of coated liner boards, founded that using oxidized starch as a medium provided the lower water absorptiveness of coated liner board than other mediums. The water absorptiveness of coated liner board using 1% of oxidized starch, starch acetate, octanyl succinate starch, polyvinyl alcohol and hydroxypropyl starch as a medium were 19.56 g/m^2, 21.91 g/m^2, 22.27 g/m^2, 24.69 g/m^2 and 24.97 g/m^2, respectively. Besides, the water absorptiveness of liner board coated with alkyd resin containing oxidized starch, starch acetate and octanyl succinate starch as a medium showed significantly ($p \leq 0.05$) lower than control or uncoated liner board (25.54 g/m^2). According to these results, the lowest water absorptiveness of coated liner board was obtained at 19.56 g/m^2 when 1% w/v of oxidized starch was applied as coating medium. The different mediums formulated from alkyd resin coating provided a different in water absorptiveness of coated liner board can be described. Oxidation of starch allows carboxyl and carbonyl groups to be substituted on the polymer backbone, replacing the hydroxyl groups (Tolvanen *et al.*, 2009). The presence of carboxyl and carbonyl groups in the oxidized-starch might produce hydrogen bridges with the OH groups of the amylose and amylopectin molecules, and these linkages gave more structural integrity in the polymeric matrix (Hu *et al.*, 2009). As a result, spacing between the macromolecules may be decreased, leading to a reduction in water absorptiveness of coated liner board. Moreover, specific properties of oxidized starch are used to fill up the pores of paper (Kweon *et al.*, 2001). Although, starch acetate and hydroxylpropyl starch were hydrophobic starch which expected to give low water absorptiveness of coated liner boards, but the degree of substitution of these starches was not appropriated for this study.

Table 3. Effect of types and concentration of coating medium formulated in alkyd resin coating on the water absorptiveness of coated liner board.

Conc. w/v	**Oxidized starch**	**Octanyl succinate starch**	**Polyvinyl alcohol**	**Hydroxy propyl starch**	**Starch acetate**
1%	50.69^{k}±2.48	49.16^{ij}±2.15	50.35^{fghi}±1.75	49.78^{fgh}±3.01	52.49^{j}±3.62
2%	50.29^{j}±2.35	49.66^{fghij}±2.40	49.95^{efgh}±2.10	51.66^{efgh}±4.38	52.31^{hij}±3.63
3%	50.32^{hij}±2.80	49.77^{ghij}±1.91	49.72^{bcd}±1.78	49.54^{cde}±3.86	51.42^{fghi}±3.74
4%	50.25^{fghi}±2.53	49.49^{fghij}±2.03	49.47^{bcde} ±1.87	49.98^{bcd}±3.38	52.00^{cdef}±3.82
5%	50.19^{ef}±2.36	49.63^{fgh}±2.01	49.64^{fghi}±2.01	51.61^{a}±4.48	51.40^{defg}±3.40
6%	50.06^{b}±2.74	50.38^{defg}±2.15	51.87^{fghi}±1.77	52.18^{a}±3.45	52.07^{cde}±3.26

*Control = 43.22^{efgh}±2.87

1.2 Mechanical properties of coated liner boards

Tensile index is one of the most basic strength properties of packaging materials. Tensile index is a measure of the ability of paper to resist breaking under tension (Rhim *et al.*, 2006). When measuring strength properties MD refers to the test force applied in the machine direction and CD is force applied in the cross machine direction. Many paper properties depend on the orientation of the paper since the MD and CD properties are not identical (Biermann, 1996). Bursting strength tells how much pressure paper can tolerate before rupture under specific conditions on a piece of testing equipment called a Mullen tester (Brittain *et al.*, 2000). Figure 15 shows the mechanical properties testing of coated liner board comprise of tensile index in machine direction, tensile index in cross direction and bursting strength. The mechanical properties of liner board coated with alkyd resin coating were significantly different to control sample ($p \leq 0.05$). However, the result showed that types and concentrations of coating mediums were not significantly affect ($p>0.05$) the tensile index and bursting strength of coated liner board. From these results can be described to bursting strength of liner board depends on basis weight and TS is dependent on the strength of fibers, their surface area and length, and the bonding strength between them. (Rhim *et al.*, 2006). Therefore, coating did not affect mechanical properties of coated liner board.

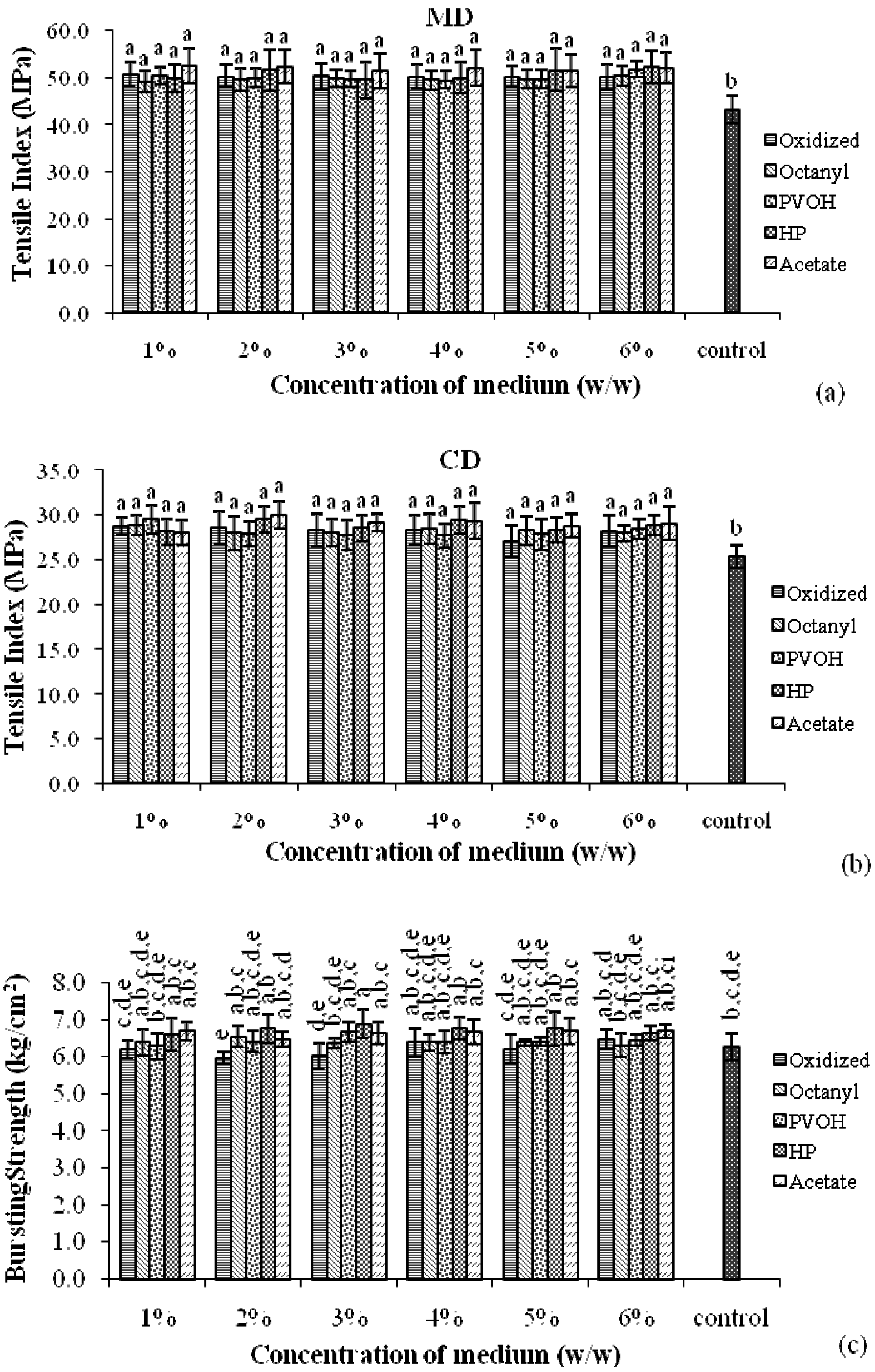


Figure 15. Effect of types and concentration of coating medium formulated in alkyd resin coating on the mechanical properties of coated liner board: (a) Tensile index in machine direction, (b) Tensile index in cross direction and (c) Bursting strength.

1.3 Coating characteristics

Viscosity is the important factor and affects the coating weight (Sothornvit, 2009) which effected to the properties of coated liner board. Table 4 shows the viscosity of coating formulated which various types and concentrations of coating medium, it was found that the viscosity of the coating was increased with increasing the medium concentration. Comparing with the same concentration, shows that alkyd resin coating formulated with PVOH provided the lowest viscosity, while using hydroxylpropyl starch and starch acetate showed higher viscosity than oxidized starch, octanyl succinate starch and polyvinyl alcohol, respectively. According to the viscosity is the important factor and affects the coating weight and also influence the coating process. Regarding to this study revealed that coating formulated with 1% of oxidized starch, 1-2% of octanyl succinate starch and/or 1-3% of polyvinyl alcohol was suitable for application.

Table 4. Effect of types and concentration of coating medium formulated in alkyd resin coating on the viscosity (cP) of alkyd resin coating.

	Concentration (w/v)					
Polymer based	1%	2%	3%	4%	5%	6%
Octanylsuccinate	8-11	9-13	10-16	11-17	12-18	13-19
Oxidized	9-10.5	12-13	18-19	26-28	35-37	60-61
PVOH	6-9	7-10	8-12	10-14	11-16	13-18
Hydroxypropyl	18-23	25-29	52-56	171-174	328-331	957-960
Acetate	16-21	29-35	66-68	231-232	405-406	1564-1568

**Japan Wax = 5.5 cP

The coating stability was influenced by the type and concentration of coating medium. The result demonstrated that increasing concentration of coating medium provided a good stability of coating which was observed by decreasing of serum phase layer of coating. Comparing with the same content of coating mediums, the results exhibited that starch acetate and hydroxylpropyl starch provided higher stability than oxidized starch, octanyl succinate starch, polyvinyl alcohol, respectively (Figure 16). Using starch acetate and hydroxylpropyl starch as a coating medium presented the best stability. This seems to indicate that, acetyl and hydroxypropyl groups prevents or minimizes association of outer branches of amylopectin molecules. This is of practical value in food applications where it prevents cloudiness and syneresis in aqueous dispersions of waxy starches stored at low temperature (Rutenberg and Solarek, 1984). Although the best stability of coating derived from using starch acetate and hydroxypropyl starch, too high coatings viscosity were occurred cause surface roughness of coated liner board. The results showed that 1% of oxidized starch formulated in coating medium shows fairly stability than octanyl succinate starch and polyvinyl alcohol in the same concentration, respectively (Figure 14) and had been selected for using as a medium of coating for next study. Figure 14a and 14c shows effect of octanyl succinate starch and polyvinyl alcohol as coating medium on coating characteristics. The results showed that the alkyd resin in the mixture was separated and float to the surface of alkyd resin coating. This is attributable to the oil and water phases normally have different densities, and so it is necessary to include a free energy term that accounts for gravitational effects, that is, the tendency for the liquid with the lowest density to move to the top of the emulsion. This term contributes to the thermodynamic instability of emulsions and accounts for the observed creaming or sedimentation of droplets (McClements, 2004). However, creaming or sedimentation will occur slowly when the concentration of coatings increased. This can attribute that high viscosity of coating was retarded molecules movement.

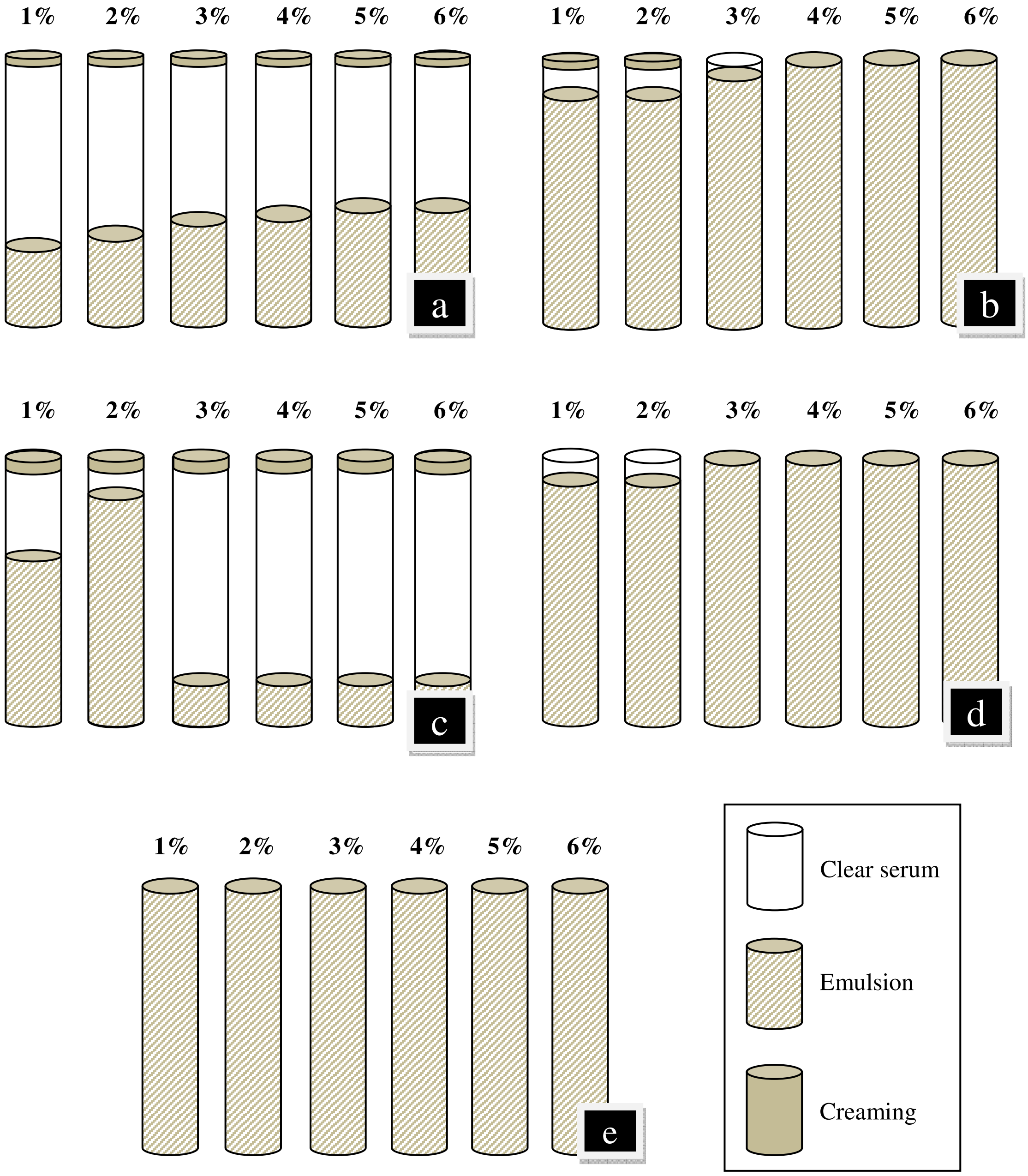


Figure 16. Effect of types and concentration of coating medium formulated in alkyd resin coating on the stability of alkyd resin coating: (a) octanyl succinate starch, (b) oxidize starch, (c) polyvinyl alcohol starch, (d) hydroxy propyl starch, (e) starch acetate.

1.4 Surface morphology of liner boards

According to the previous results, coated liner board using oxidized starch as medium was selected for this experiments. The morphology of the coated liner board was identified by Scanning electron microscopy (SEM). The results demonstrated that uncoated liner board had roughness and porosity higher than coated liner boards (Figure 17). The results showed that coating medium affected the morphology of liner board. The SEM images provided very smooth surfaces for coated liner board when concentration of coating medium increased. However, too high coating medium concentration seemed to be more irregular with a rougher surface of coated liner board, which had an effect on printing quality of coated liner board. Figure 18 showed the printing quality of coated liner board as a function of oxidized starch concentrations as coating medium. The results showed that low concentration of oxidized starch provided a better printing appearance of coated liner board than high oxidized starch concentration. Moreover, roughness surface of coated liner board initial appeared when increasing concentration of oxidized starch access than 2% caused further reduced the printing quality of coated liner board. It is speculated that the roughness surface of coated liner board might be due to a high thickness of coating layer on the liner board resulting from a high viscosity of coating. Thus the viscosity is the important factor and affects the coating surface. Generally, the concentration of most hydrocolloids coating solution applied on paper is not access than 10% (Han and Krochta, 2001; Trezza and Vergano, 1994; Lin and Krochta, 2003; Gallstedt *et al.*, 2005; Khwaldia *et al.*, 2005). Moreover, Sothornvit, (2009) offered using hydroxypropyl methylcellulose concentration only 2.5%, which was adequate to provide the appropriate viscosity for coating on paper in their study.

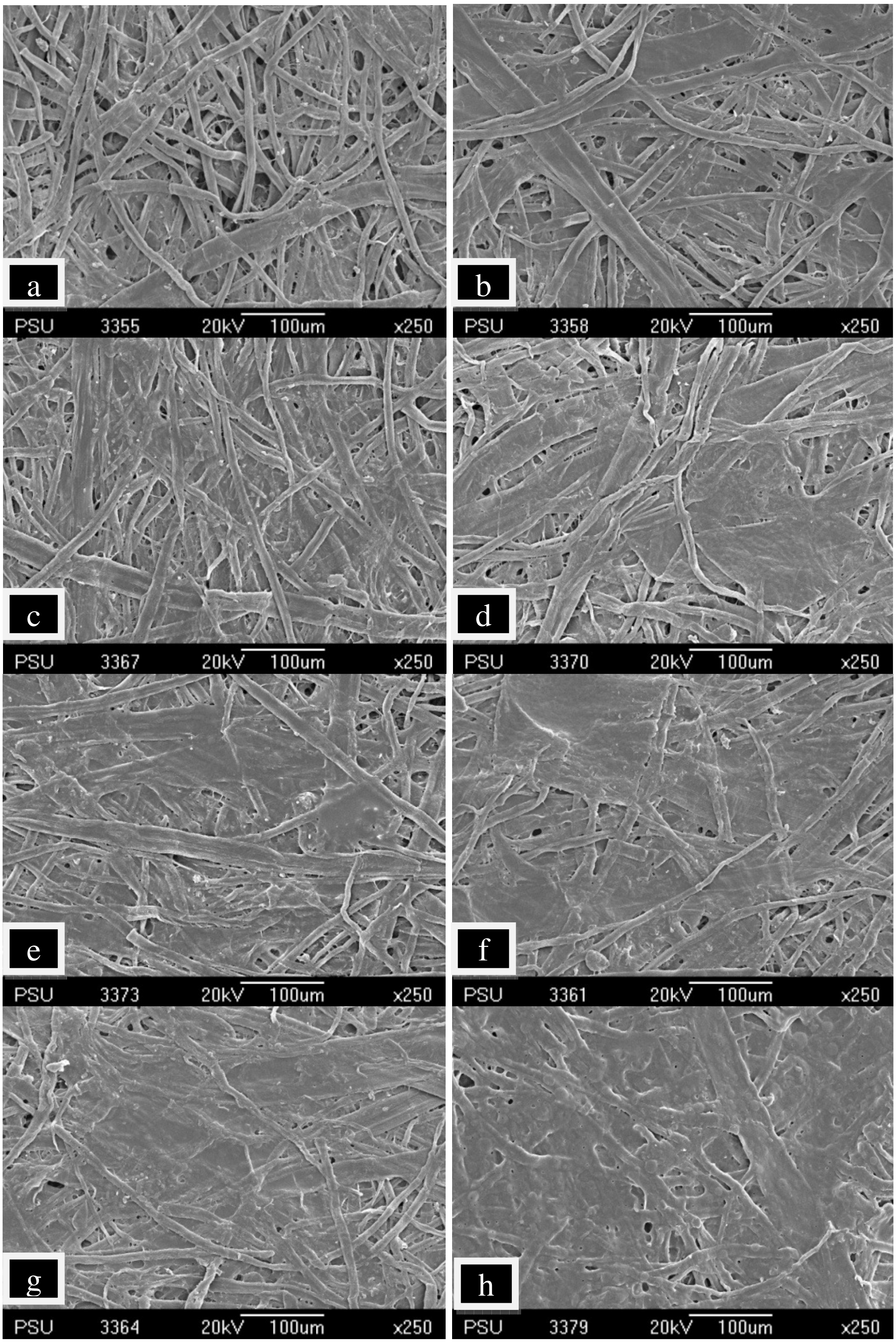


Figure 17. SEM of coated liner board surface as a function of types and concentrations of coating medium: (a) uncoated liner board, (b) commercial wax, (c) 1%Oxi, (d) 2%Oxi, (e) 3%Oxi, (f) 4%Oxi, (g) 5%Oxi and (h) 6%Oxi.

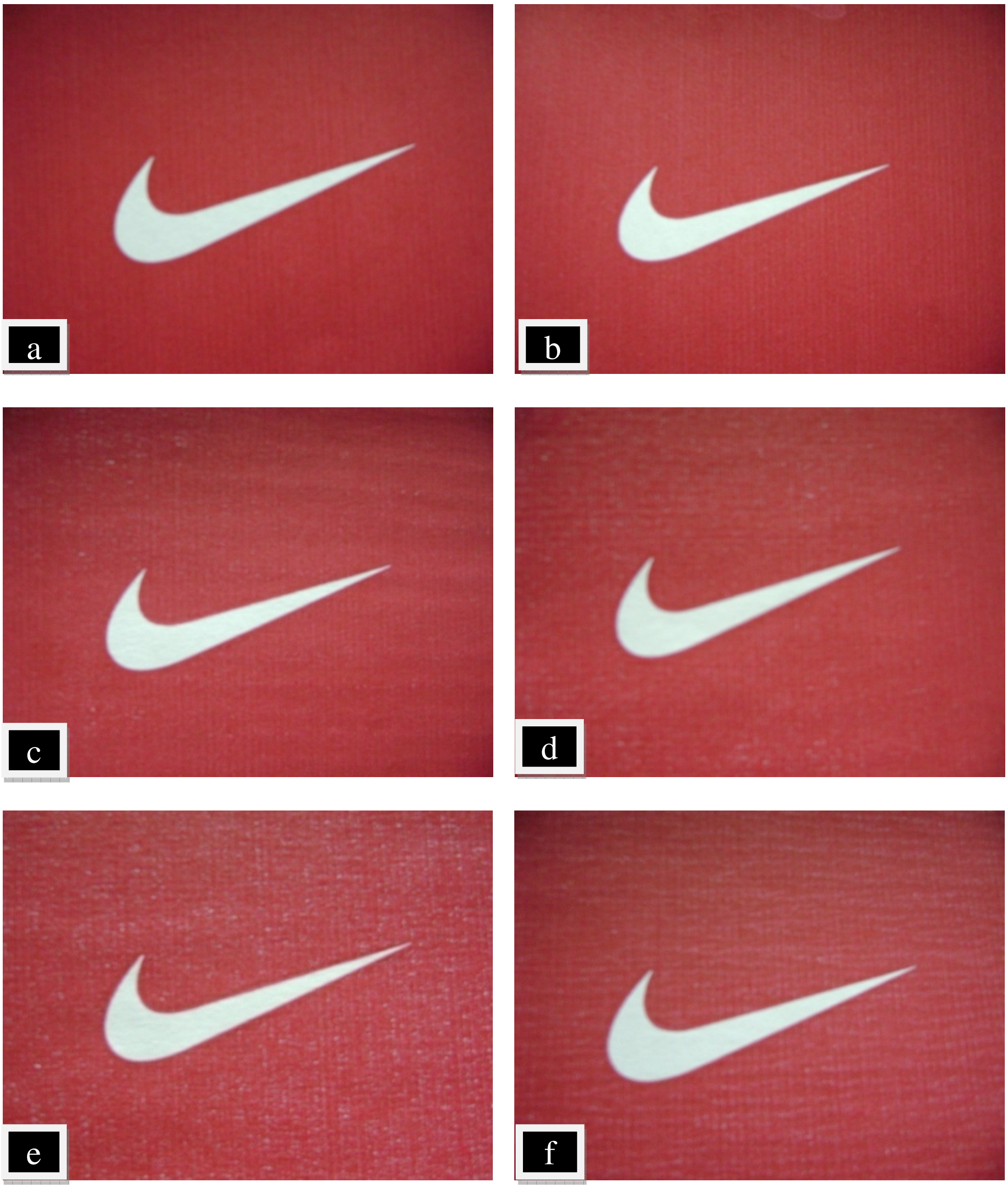


Figure 18. Printing quality of coated liner board as a function of oxidized starch concentrations of coating medium: (a) 1%Oxi, (b) 2%Oxi, (c) 3%Oxi, (d) 4%Oxi, (e) 5%Oxi and (f) 6%Oxi.

2. Effect of alkyd resin content on the properties of alkyd resin coating and coated liner boards

According to the result of the effect of type and concentration of coating mediums on the properties of alkyd resin coating and coated liner boards revealed that using 1% as a coating medium yielded the lowest water absorptiveness of coated liner boards then 1% of oxidized starch was selected for this study.

2.1 Water absorptiveness

The effect of alkyd resin content on the water absorptiveness of coated liner board was presented Figure 19. As expected, improving of water barrier properties of liner board coating can be achieved by addition hydrophobic substances to the coating formula. Addition of alkyd resin caused a decrease in water absorptiveness of coated liner board because its hydrophobicity. The results exhibited that increasing of alkyd resin content resulted in decreasing of water absorptiveness of coated liner boards. The lowest of water absorptiveness of coated liner board was obtained at 18.95 g/m^2 when 5% w/v of alkyd resin was applied. Moreover, in the study by Sztuka and Kołodziejska (2009) reported that the improving of water barrier properties can be achieved by an addition of hydrophobic substances to the film structure.

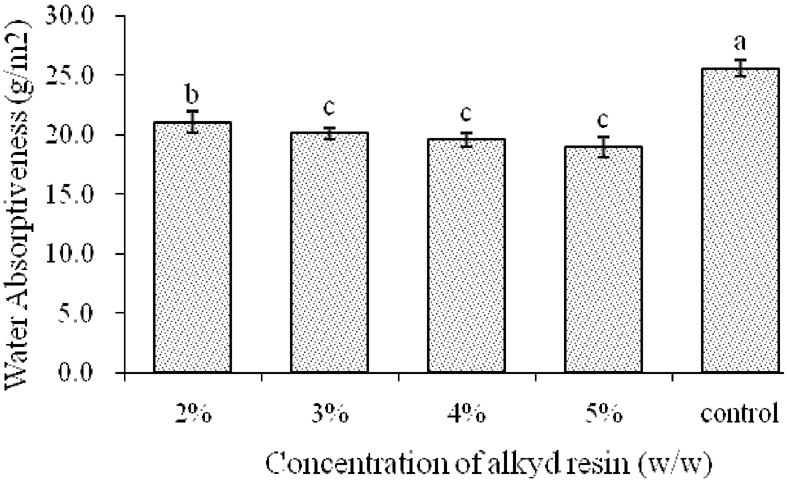
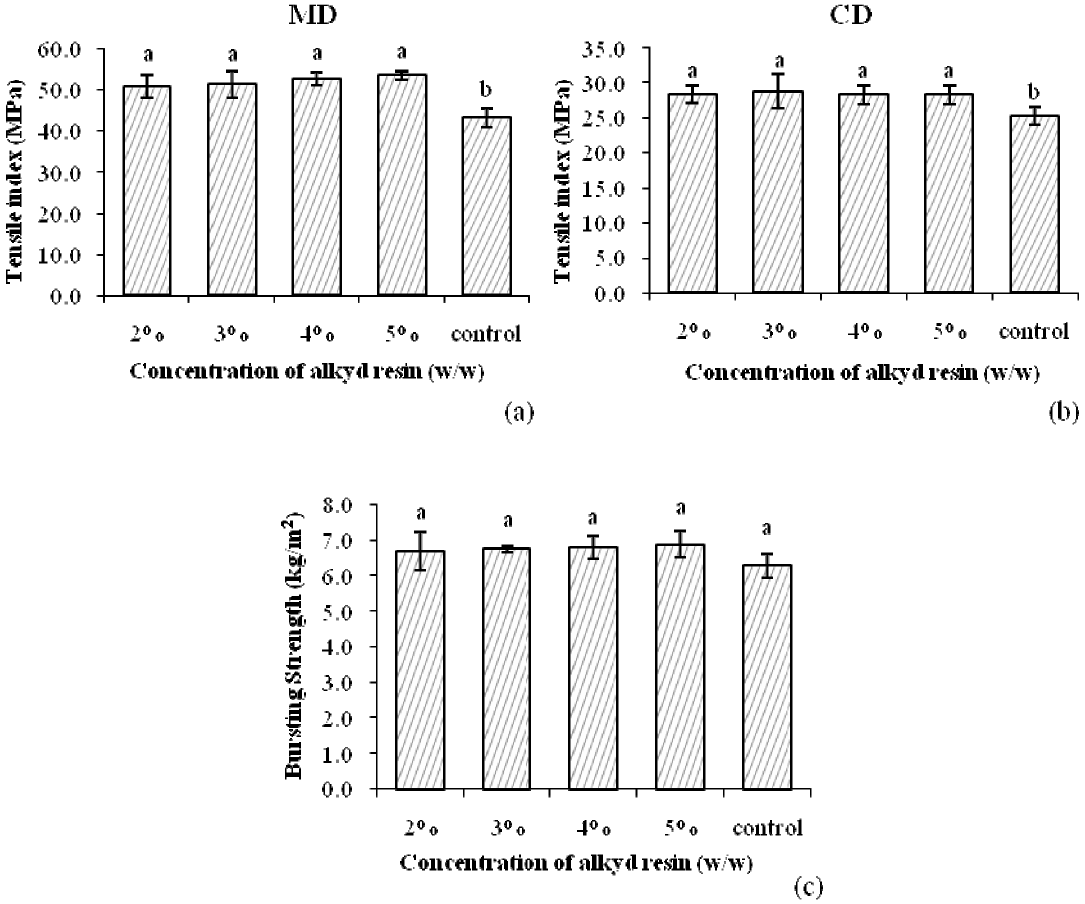


Figure 19. Effect of alkyd resin content on the water absorptiveness of coated liner boards.

2.2 Mechanical properties of coated liner board

The effect of alkyd resin content on mechanical properties of coated liner boards comprises of tensile index in machine direction, tensile index in cross direction and bursting strength were investigated. The mechanical properties of coated liner boards were significantly different to control ($p \leq 0.05$). However, the results showed that alkyd resin content were not significant effect ($p>0.05$) in tensile index and bursting strength of coated liner boards (Figure 20). From these results can be described to bursting strength of liner boards depends on basis weight and tensile index is dependent on the strength of fibers, their surface area and length, and the bonding strength between them. (Rhim *et al.*, 2006). Therefore, alkyd resin content did not affect mechanical properties of coated liner boards.



(a) (b) (c)

Figure 20. Effect of alkyd resin content on the mechanical properties of coated liner boards: (a) Tensile index in machine direction, (b) Tensile index in cross direction and (c) Bursting strength.

2.3 Coating characteristics

The viscosity of alkyd resin coating prepared from various concentrations was showed in Table 5. From the result, showed increasing amounts of alkyd resin were not significant affect the viscosity of alkyd resin coating. Similarly, Yilmaz *et al.* (1999) measured the viscosity of the aqueous starch solutions with different glycerol concentrations under several shear rates. The results found the changing glycerol concentration did not have any significant effect on the viscosities under the conditions as applied during study. This was attributed the alkyd resin content is only a small percentage in the coating system when compared with the water content. In such a system it is understandable that changes in alkyd resin concentration do not have significant effects on viscosity of the coating system.

Table 5. Effect of alkyd resin content on the viscosity of coating.

Alkyd resin conc.	Viscosity
2%	8.10
3%	10.50
4%	10.70
5%	12.70

In Figure 21 revealed the alkyd resin coating stability with various content of alkyd resin. The result demonstrated that increasing of alkyd resin content resulted in lowers stability of alkyd resin coating. Addition of 5% of alkyd resin provided the lowest coating stability of alkyd resin coating. This was attributed to amount of alkyd resin which comprised of hydrophobicity was not compatible to coating medium.

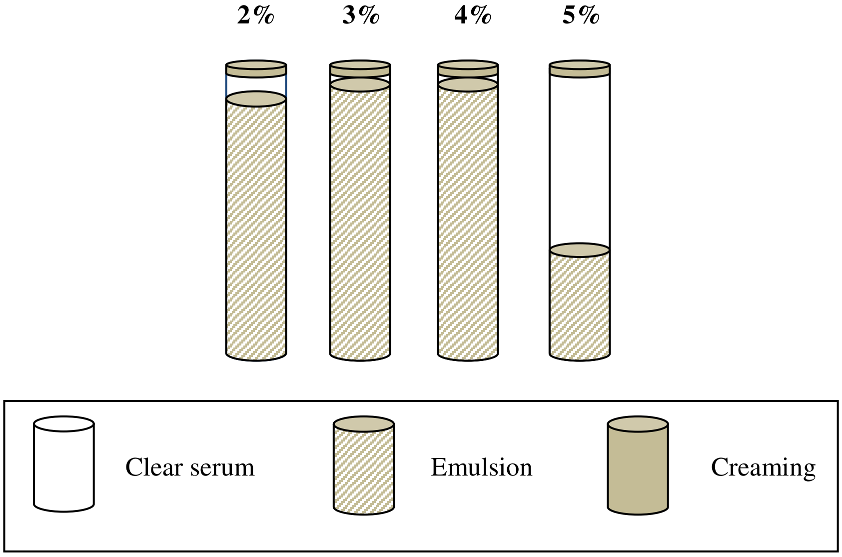


Figure 21. Effect of alkyd resin content on the stability of alkyd resin coating.

According to the results, using 3, 4 and 5% of alkyd resin showed not significant different in water absorptiveness of coated liner boards. However, the alkyd resin coating formulated with using 3% and 4% of alkyd resin provided the best coating stability. Hence, coating formulated with 3% of alkyd resin was selected for next study.

3. Mixing speed on compatibility between alkyd resin and coating mediums and properties of coating and liner board coated

Regarding to the result of the effect of alkyd resin content on the properties of alkyd resin coating and coated liner boards showed that using 3% provided the lower water absorptiveness of coated liner boards and best stability of alkyd resin coating then 3% of alkyd resin was selected for this study.

3.1 Water absorptiveness

Generally starches are incompatible with alkyd resin in solution, phase separation usually occurs resulting in a change of functional behavior of the alkyd resin and starches, a visual separation of a clear serum and a loss of desired quality. The stability of the alkyd resin coating and distribution of alkyd resin plays an important role in the properties of water absorptiveness of coated liner boards. The hydrophobicity of alkyd resin particle which thoroughly distributed into coating emulsion caused reduction water absorptiveness of coated liner board. Water absorptiveness of coated liner boards was decreased when increasing of mixing speed (Figure 22). At 10,000 and 15,000 rpm of mixing speed provided lower water absorptiveness than mixing speed at 5,000 rpm at the same mixing time. Comparison effect of mixing time on water absorptiveness of coated liner boards founded that increasing of mixing time showed decreasing of water absorptiveness of coated liner boards. These results can be attributed to the increasing compatibility of alkyd resin coating by increasing mixing speed and mixing time provided the good distribution of alkyd resin which affected to the water absorptiveness of coated liner boards. Furthermore, the results founded that mixing condition at 10,000 rpm for 2 and 3 minutes and 15,000 rpm for 1, 2 and 3 minutes were not significant different ($p>0.05$) on water absorptiveness of coated liner boards.

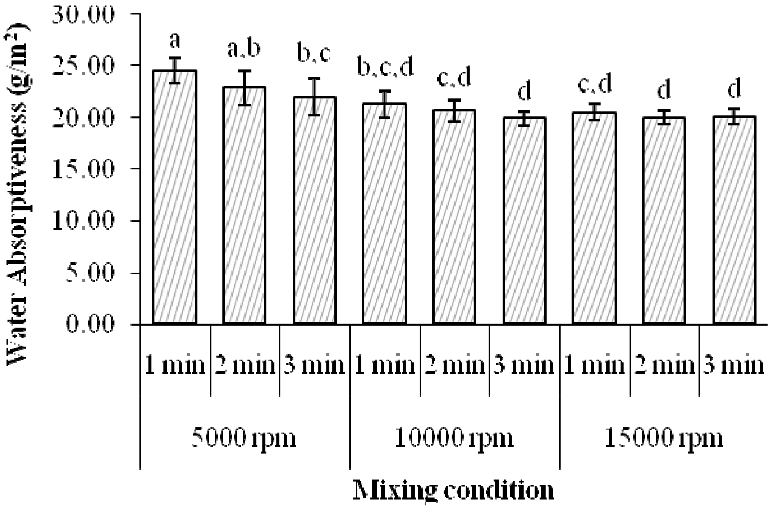


Figure 22. Effect of mixing condition on the water absorptiveness of coated liner boards.

3.2 Mechanical properties of liner board

Figure 23 exhibited the effect of mixing condition of alkyd resin coating on mechanical properties testing of coated liner boards comprise of tensile index in machine direction, tensile index in cross direction and bursting strength. The mechanical properties of liner board coated with alkyd resin coating were significantly different to control ($p \leq 0.05$). However, the result showed that mixing speed and mixing time of in this study were not significant effect ($p>0.05$) in tensile index and bursting strength of coated liner boards (Figure 23). From the results indicated that bursting strength of liner board was depended on basis weight and tensile index is dependent on the strength of fibers, their surface area and length, and the bonding strength between them. (Rhim *et al.*, 2006).

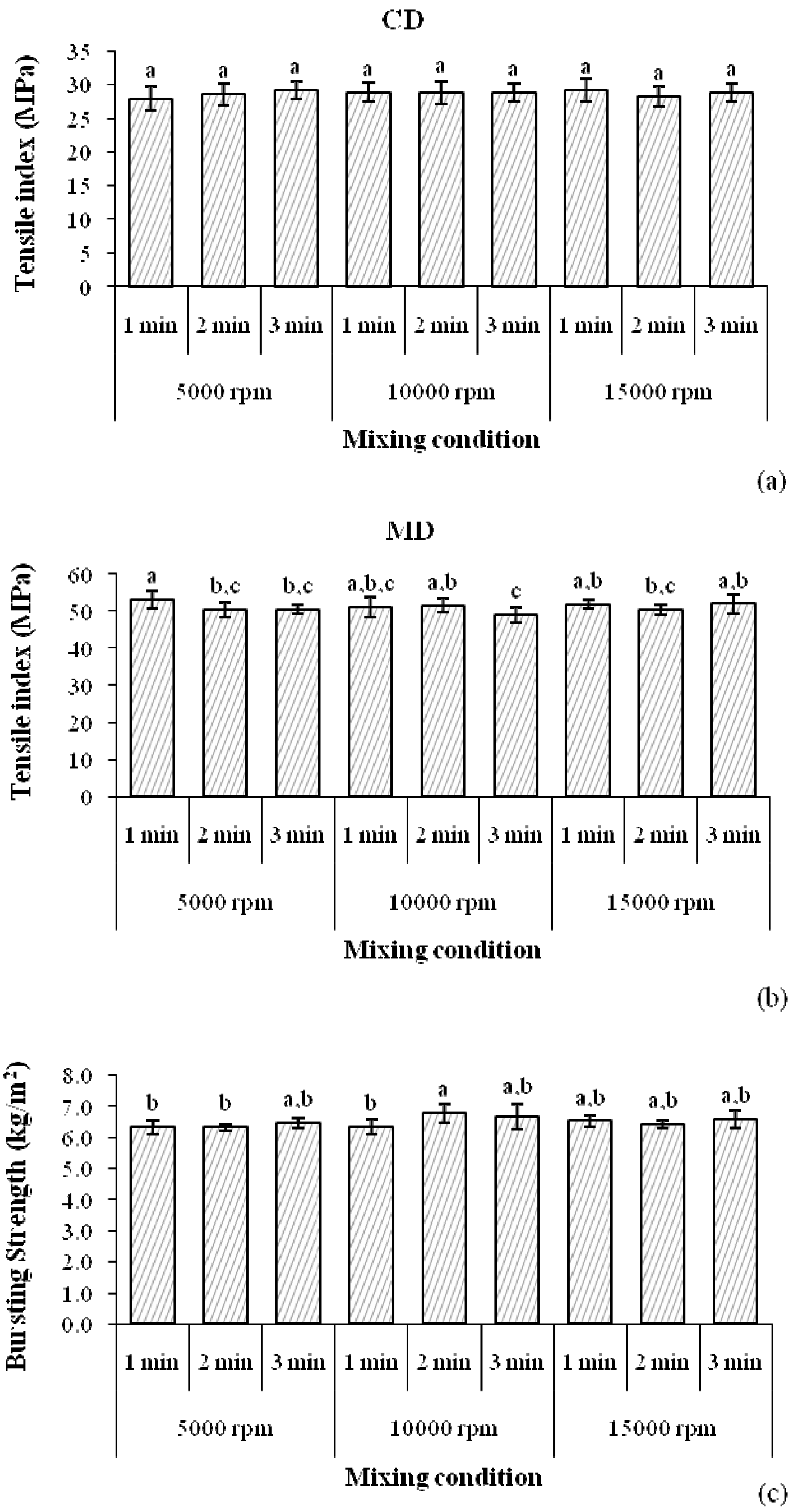


Figure 23. Effect of mixing condition on the mechanical properties of coated liner boards: (a) Tensile index in machine direction, (b) Tensile index in cross direction and (c) Bursting strength.

3.3 Coating characteristic

According to the suitable properties of alkyd resin coatings depend on the coatings compatibility. Therefore mixing speed on compatibility between alkyd resin and coating mediums was evaluated. Table 6 exhibits viscosity and particle size of alkyd resin coating, showed that increasing of mixing speed and mixing time caused smaller size of particle had an effect on the stability of alkyd resin coating (Figure 24). Beside the results founded that increasing of mixing speed and mixing time resulted in increasing of coating stability. The highest stability of alkyd resin coatings was obtained when mixing speed and mixing time was 15,000 rpm for 3 min. This seems to indicate that, as high level of mixing condition produced smaller particle size of alkyd resin coating and then provided the stability of alkyd resin coating. However, mixing speed and mixing time were not had an effect on the viscosity of alkyd resin coating. Due to mixing time at 15,000 rpm for 3 min provided the smallest size of particle, hence these mixing condition were selected for further study.

Table 6. Effect of mixing condition on the viscosity and particle size of alkyd resin coating.

Mixing speed (rpm)	Mixing time (min)	Viscosity (cP)	particle size (µm)
5,000	1	10.8	21.340
	2	9.80	19.345
	3	9.80	17.350
10,000	1	9.52	11.910
	2	9.80	10.527
	3	9.82	9.143
15,000	1	11.50	8.710
	2	10.50	6.504
	3	10.10	4.298

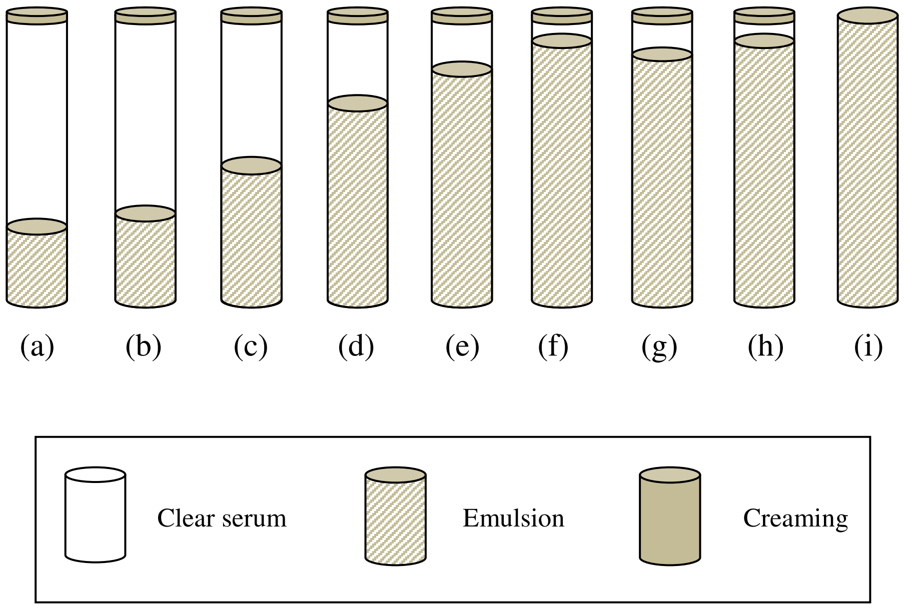


Figure 24. Effect of mixing condition on the stability of alkyd resin coating: (a) 5,000 rpm for 1 min, (b) 5,000 rpm for 2 min, (c) 5,000 rpm for 3 min, (d) 10,000 rpm for 1 min, (e) 10,000 rpm for 2 min, (f) 10,000 rpm for 3 min, (g) 15,000 rpm for 1 min, (h) 15,000 rpm for 2 min and (i) 15,000 rpm for 3 min.

4. Comparison of the efficiency of the alkyd resin coating and commercial wax

4.1 Water absorptiveness

Figure 25 exhibited the comparison of the efficiency of the alkyd resin coating (prepared by using 1% of oxidized starch as a coating medium and using 3% of alkyd resin then homogenized at 15,000 rpm for 3 min) and commercial wax on water absorptiveness of coated liner boards. The result showed that the water absorptiveness of alkyd resin coated liner board had significantly ($p \leq 0.05$) higher water absorptiveness than commercial wax coated liner board (20.09 and 16.60 g/m^2, respectively). This was attributed to the difference in hydrophobicity between alkyd resin coating and commercial wax.

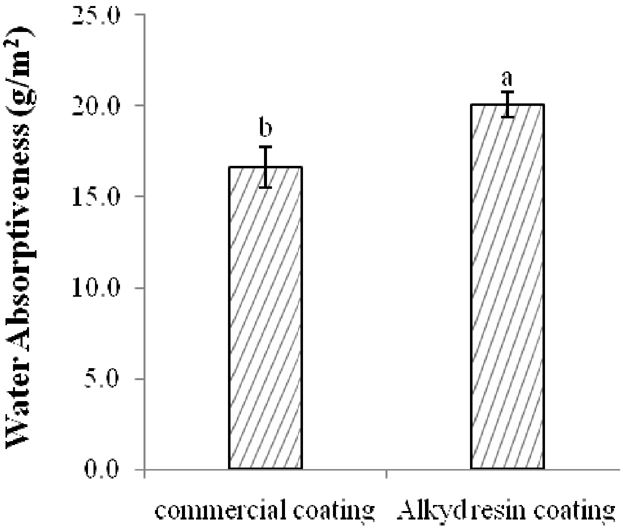


Figure 25. Effect of coating type on the water absorptiveness of coated liner boards.

4.2 Mechanical properties of liner board

Figure 26 exhibited the comparison of alkyd resin coating and commercial wax on mechanical properties testing of coated liner boards comprise of tensile index in machine direction, tensile index in cross direction and bursting strength. The tensile strength in MD and CD of alkyd resin coated liner board were significantly different to commercial wax coated liner board ($p \leq 0.05$). However, the result showed that were not significantly affect ($p>0.05$) the bursting strength of coated liner board (Figure 26).

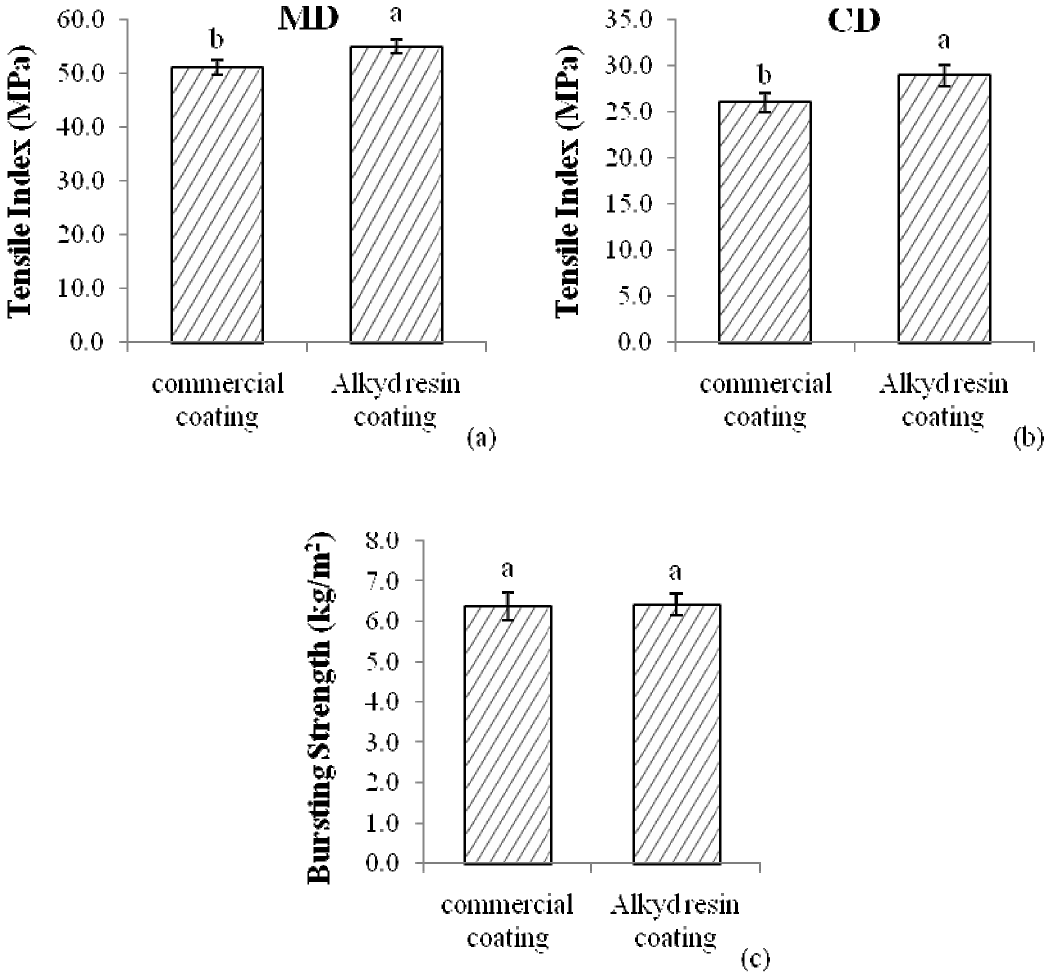


Figure 26. Effect of types of coating liner board on the mechanical properties of coated liner boards: (a) Tensile index in machine direction, (b) Tensile index in cross direction and (c) Bursting strength.

4.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is usually employed to determine the temperature of initial weight loss, which can be viewed as the onset of degradation (Xie *et al.*, 2002). TG is also used to identify components in a sample (Caoa *et al.*, 2004). TGA thermograms and the char yields (600 ℃) of alkyd resin coating and commercial wax under nitrogen were showed in Figure 27. The alkyd resin coating showed a two-stage weight loss below 600 ℃, with the first major one underwent 96.53% weight loss represents the evaporation/dehydration that begins immediately after the temperature is increased and finishes at around 100 ◦C, and the second one range (280–350°C) corresponds to the degradation of starch and alkyd resin with a weight loss of 3.11%. Further heating up to 600 ℃ resulted in carbonization and ash formation. Commercial wax exhibited three different degradation processes. Due to water-based formula, the initial stage peak of commercial wax showed the major peak began at 58 °C with a weight loss of 96.24% which similar to the initial peak of alkyd resin coating. The second stage, slightly decompose range (170-250°C) revealed 1.48% of the weight loss. Furthermore, the next decomposition began at 338°C showed 1.74% of weight loss.

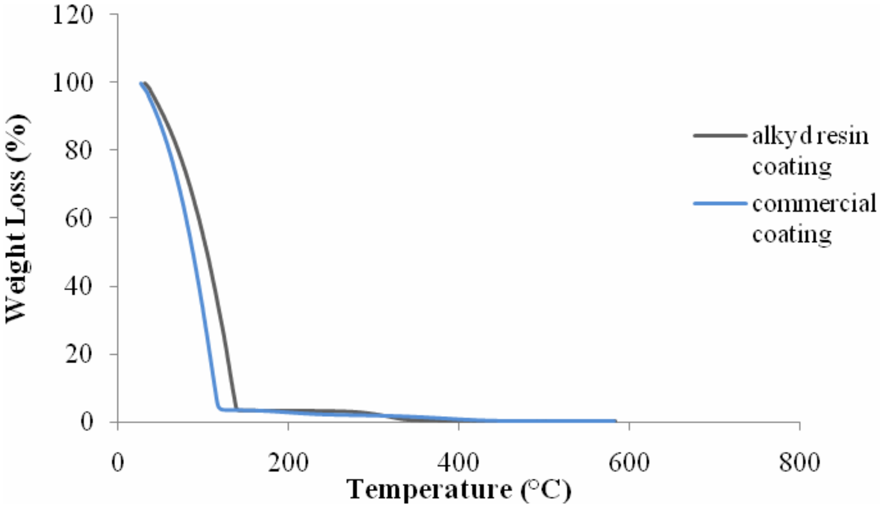


Figure 27. TGA thermograms of alkyd resin coating and commercial wax.

4.4 Fourier Transform Infrared Spectroscopy (FT-IR)

Infrared spectroscopy is one of the most often used spectroscopic tools for the study of polymers. The method is rapid and sensitive, with a great variety of sampling techniques, and yet the instrumentation can still be considered inexpensive. The infrared absorption spectrum of a compound is probably its most unique physical property and the spectrum is often called the fingerprint of a molecule (Kacurakova and Wilson, 2001). Fourier Transform Infrared Spectroscopy (FT-IR) is an analytical technique extensively applied to various substances including liquid, gas and solid matter to identify the unknown materials. This technique measures the absorption of various infrared light wavelengths by the material of interest. These infrared absorption bands identify specific molecular components and structures. FTIR technique not only can be used to make qualitative analyses for the substance identification, but also can be used to obtain the content of composition in the sample (Song *et al.*, 2007). The spectrum of the alkyd resin, starch solution and alkyd resin coating samples was investigated. Figure 28A exhibited the alkyd resin characteristic absorption peaks of C=O stretching groups at 1729 cm^{-1} and 1682 cm^{-1} appeared in alkyd resin (Figure 28C). A strong and broad absorption of starch solution and alkyd resin coating samples was found at 3300 cm^{-1}. This implies the presence of –OH groups in the starch and hydrogen bonding between those –OH groups. Moreover, characteristic absorption peaks at 1022 cm^{-1} were found for starch solution and alkyd resin coating samples. Similarly to the characteristic FT-IR bands for starch gels have been found at 1046 and 1019 cm^{-1} (Kacurakova and Wilson, 2001).

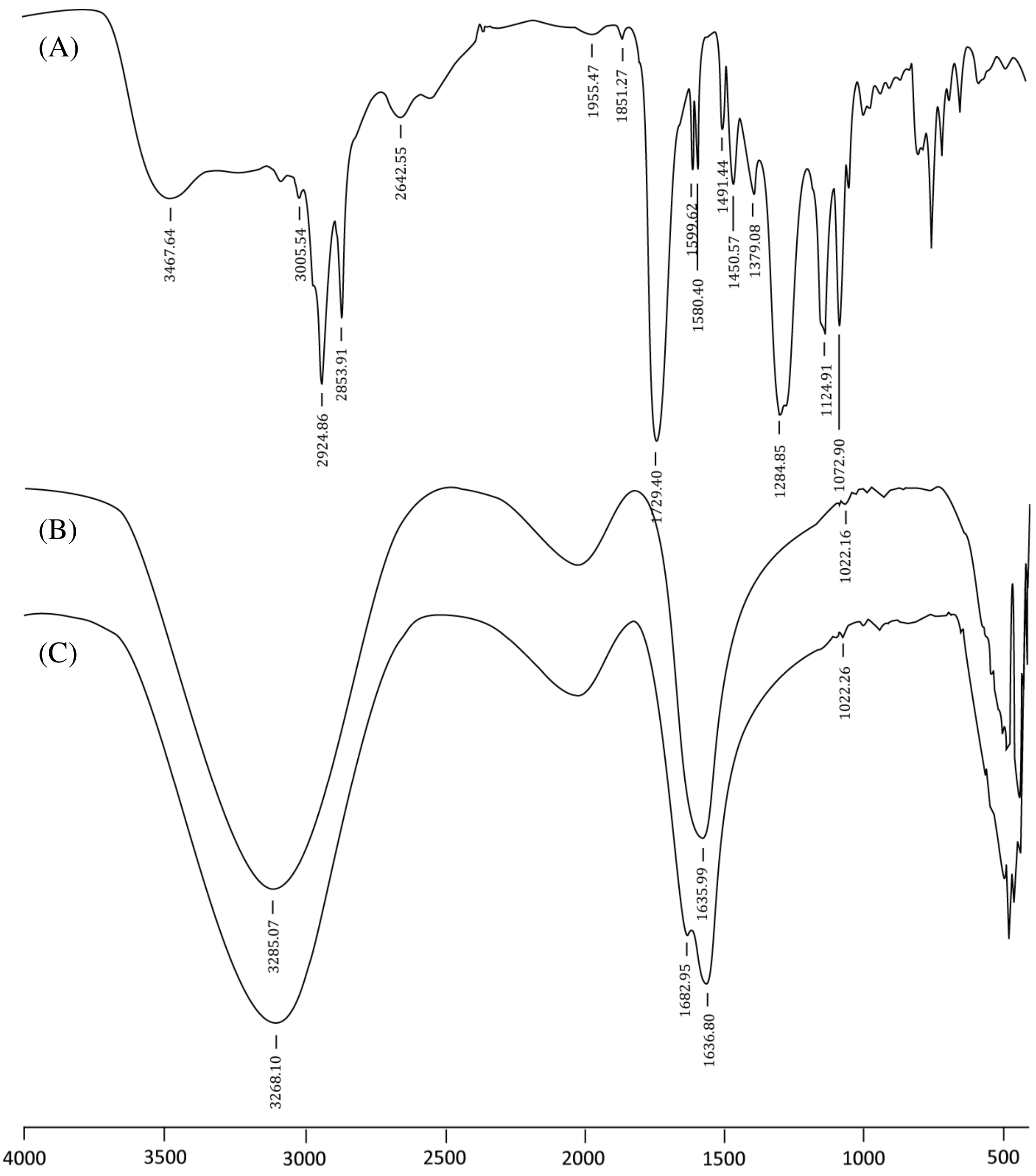


Figure 28. FT-IR spectrum of the alkyd resin (A), oxidized starch solution (B), and alkyd resin coating using oxidized starch as a medium (C).

4.5 Surface morphology of liner boards

SEM observation of coated liner boards in cross-section displayed differences from uncoated liner board, commercial wax coated liner board and alkyd resin coated liner board. The results founded that liner board coated with commercial wax was homogeneous and smoother surface than alkyd resin coated liner board and uncoated liner board, respectively (Figure 29). This suggested that commercial wax was able to form a continuous film on the surface which covered and filled the porous structure of liner board while alkyd resin coating was penetrated into the liner board appeared rather dense structure of liner board and showed irregular of porous fiber on the surface.

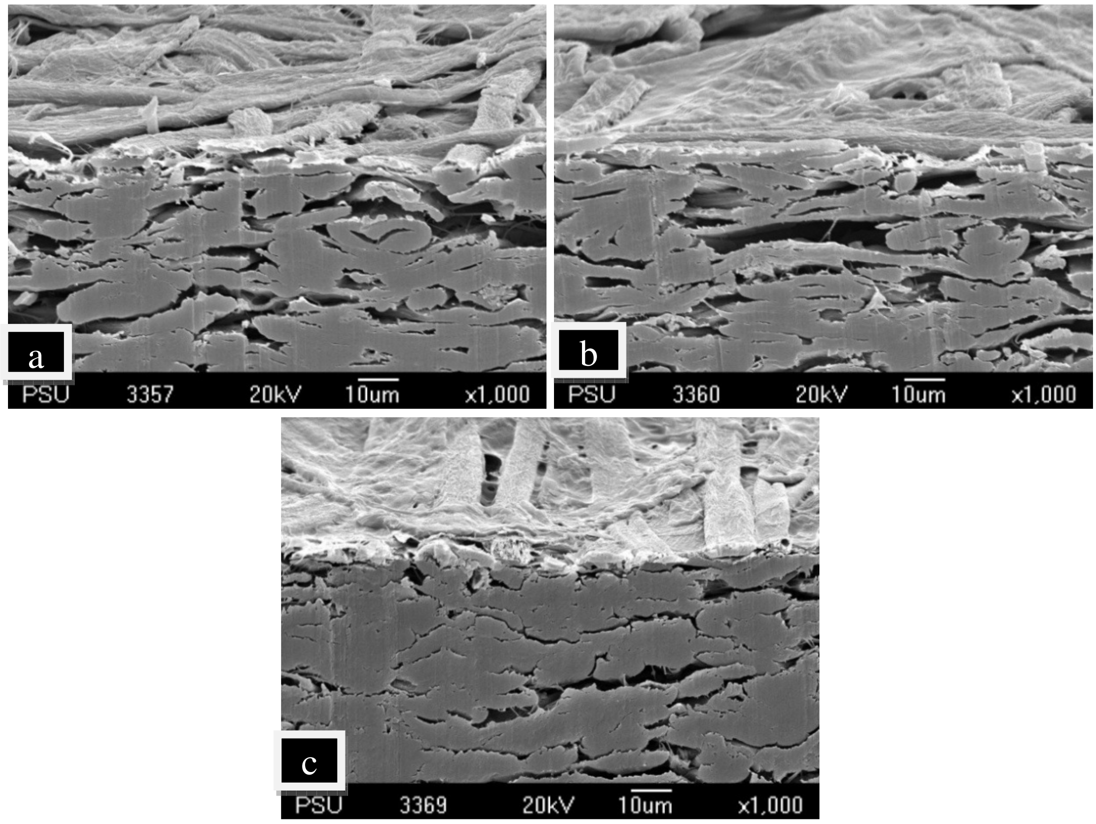


Figure 29. SEM of liner boards surface: (a) uncoated liner board, (b) commercial wax, (c) alkyd resin coating.

4.6 Printing quality of coated liner board

Figure 30 showed the printing quality of coated liner board comparison between uncoated liner board, commercial wax and coated liner board with alkyd resin coating. It founded that commercial wax coated liner board provided fader color than uncoated liner board and alkyd resin coated liner board. The result was possibly due to high hydrophobicity of commercial wax showed incompatibility with water-based dye which comprised of hydrophilic groups. Due to starch containing of alkyd resin showed well compatibility with water-based dye provided better printing quality of coated liner board than those treatments.

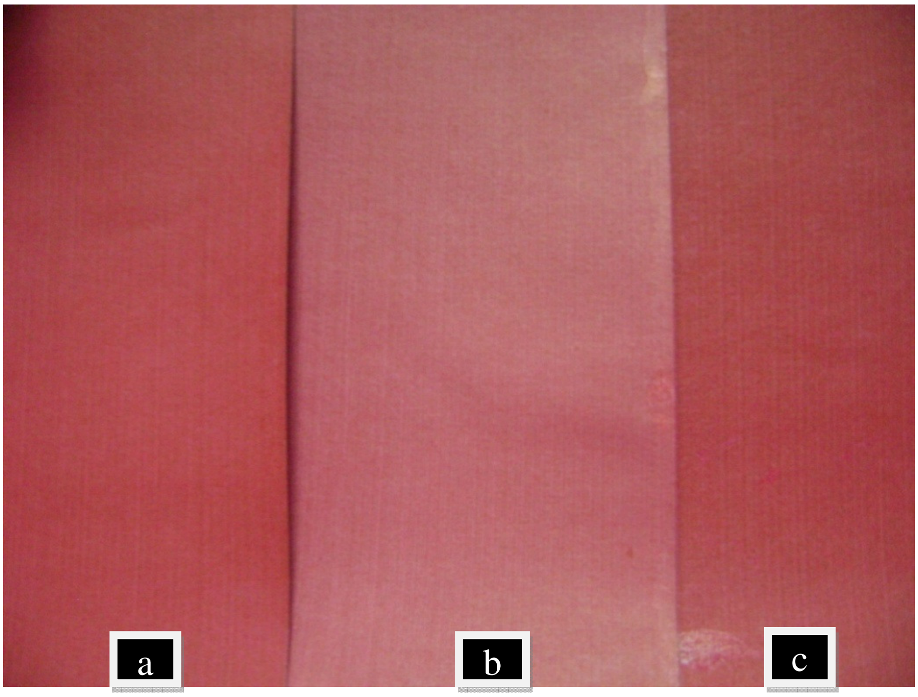


Figure 30. Effect of coating on the printing quality of liner boards: (a) Uncoated, (b) Commercial wax and (c) Alkyd resin coating formula.

The measured color value of uncoated liner board, coated liner board with commercial wax and alkyd resin coating by CIELAB system was showed in Table 6, the color of uncoated liner board was 42.88, 45.17 and 13.49 of L*, a* and b* value, for the color of coated liner board with commercial wax were 44.40, 42.89, 10.32 and 4.19 of L*, a*, b* and ΔE* value, for the color of coated liner board with alkyd resin coating were 42.51, 45.58, 14.28 and 0.96 of L*, a*, b* and ΔE* value, respectively. The difference colors between standard (uncoated liner board) and samples (commercial wax and alkyd resin coating) were presented to the ΔE* value. The result demonstrated that color value of uncoated liner board was similar to coated liner board with alkyd resin coating which considered from less than 1.0 of ΔE* value. This coincided with uncoated liner board and coated liner board with alkyd resin coating was indistinguishable in color (Figure 30).

Table 6 Effect of coating on the color value of liner boards: (a) Uncoated, (b) Commercial wax and (c) Alkyd resin coating formula.

Liner boards	color value			
	L*	a*	b*	ΔE*
Uncoated (Std.)	42.88±0.14	45.17±0.13	13.49±0.10	-
Commercial wax	44.40±0.08	42.89±0.12	10.32±0.13	4.19
Alkyd resin coating	42.51±0.18	45.58±0.10	14.28±0.16	0.96

5. The microbiological changes of alkyd resin coating during storage

The microbial quality of alkyd resin coating during storage at ambient temperature was investigated by using total viable count (TVC) (BAM 2001) and Drakos and Kiosseoglou's method (2008). Figure 31 shows the curves referred to the growth of TVC in the alkyd resin coating stored for 2, 4, 6 and 8 days. The TVC counts were founded slowly increasing from approximately 15 cfu/ml initial 3 days but sharply rising from then on, reaching values of 25 cfu/ml at approximately 8 days. Due to starch is the main component of alkyd resin coating, indicating that these microorganisms may have utilized this carbohydrate as a source of energy (Durango *et al.*, 2006).

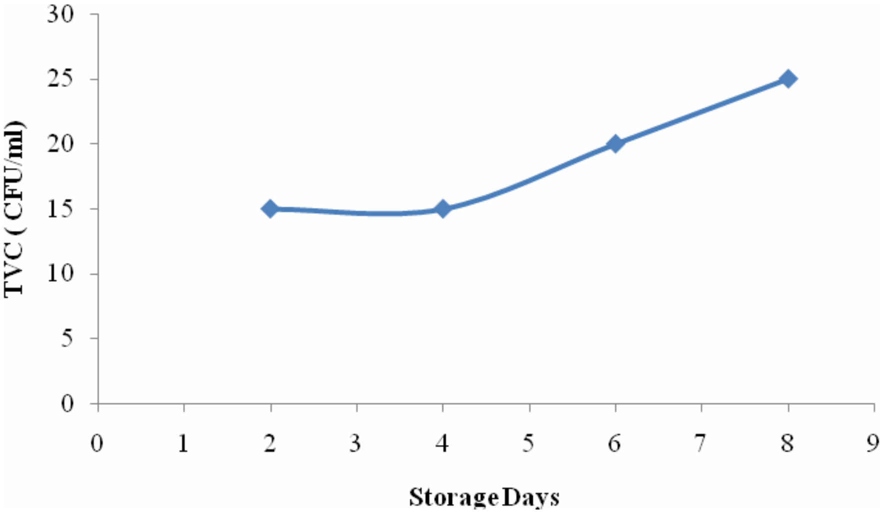


Figure 31. Effect of storage period on microbiological quality of alkyd resin coating.

The alkyd resin coating stability was influenced by the storage time (Figure 32). The result demonstrated that the alkyd resin coating was separated and floated on the surface of coating. However, when storage time increased yielded an increasing of clear serum phase of alkyd resin coating. This is attributed to the oil and water phases normally have different densities, and so it is necessary to include a free energy term that accounts for gravitational effects, that is, the tendency for the liquid with the lowest density to move to the top of the emulsion. This term contributes to the thermodynamic instability of emulsions and accounts for the observed creaming or sedimentation of droplets (McClements, 2004). Moreover, the alkyd resin coating began to spoilage when stored up to 3 days observed from the smell and agglomeration.

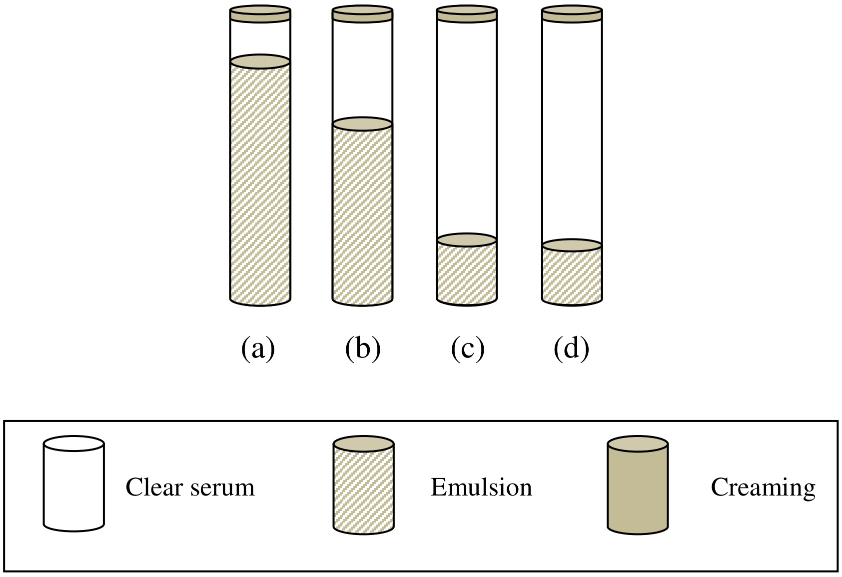


Figure 32. Effect of storage time on alkyd resin coating stability: (a) 2 day, (b) 4 days, (c) 6 days and (d) 8 days.

CHAPTER 4

CONCLUSIONS

1. Increasing of coating mediums concentrations, overall resulted in a high stability, but increased in water absorptiveness of coated paperboard.

2. Alkyd resin coating formulated with 1% oxidized starch was suitable for alkyd resin coating preparation, by the reason of providing applicable viscosity and the lowest water absorptiveness of coated paperboard.

3. Increasing of alkyd resin content in the alkyd resin coating showed lower both alkyd resin coatings stability and water absorptiveness of coated paperboard.

4. Mixing speed at 15,000 rpm for 3 min showed the best stability of alkyd resin coatings and lowest water absorptiveness of coated paperboard.

5. Total viable count (TVC) and phase separation of alkyd resin coating increased when the storage period increased.

6. Types and concentrations of coating mediums, concentration of alkyd resin and mixing conditions were not significantly ($p>0.05$) affected tensile strength and bursting strength of coated paperboard.

7. Tensile strength of uncoated paper presented lower than alkyd resin coated paperboard.

8. Alkyd resin coating (1% of oxidized starch as a medium, 3% of alkyd resin which mixing conditions at 15,000 rpm for 3 min) showed higher water absorptiveness (20.09 g/m^2) of coated paperboard than commercial coating (16.60 g/m^2). However, the printing quality and mechanical properties of alkyd resin coated paperboard demonstrated superior than coated paperboard with commercial coating. Besides, the cost of alkyd resin coating is cheaper than commercial wax (50 and 120 baht, respectively)

Suggestions

1. The another coating medium such as cationic starch, and emulsifying agent and stabilizer are needed to be studied in the future.

2. The wet strength and ring crush test of liner board should be determined to represent the mechanical properties of corrugated box.

REFERENCE

Aigbodion, A.I., Okieimen, F.E., Obazee, E.O. and Bakare I.O. 2003. Utilisation of maleinized rubber seed oil and its alkyd resin as binders in water-borne coatings. Prog. Org. Coat. 46: 28–31.

Aydin, S., Akçay, H., Özkan, E., Güner, F.S. and Erciyes, A.T. 2004. The effects of anhydride type and amount on viscosity and film properties of alkyd resin. Prog. Org. Coat. 51: 273–279.

BAM, 1998 BAM, Bacteriological analytical manual (8th ed.), US Food and Drug Administration, Gaithersburgh, MD (1998).

Bao, J., Xing, J., Phillips, D. and Corke, H. 2003. Physical properties of octenyl succinic anhydride modified, rice, wheat and potato starches. J. Agric. Food Chem. 51: 2283–2287.

Bergh, 1997. Starch. *In* Surface Application of Papers Chemicals. (Brander, J. and Thorn, I., ed.). p. 69-108. Blackie Academic & Professional. London.

Bertoft, E. 2004. Analysing Starch Structure. *In* Starch in Food. (Eliasson, A.C., ed.). p. 57-96. CRC Press. Baca Raton.

Bhandari, P.N. and Singhal, R.S. 2002. Studies on the optimization of preparation of succunate derivatives from corn and amaranth starches. 2002. Carbohydr. Polym. 47: 277 – 283.

Bhosale, R. and Singhal, R. 2006. Process optimization for the synthesis of octenyl succinyl derivative of waxy corn and amaranth starches. Carbohydr. Polym. 66: 521–527.

Bhosale, R. and Singhal, R. 2007. Effect of octenylsuccinylation on physicochemical and functional properties of waxy maize and amaranth starches. Carbohydr. Polym. 68: 447–456.

Biermann, J. C. 1996. Handbook of Pulping and Papermaking. 2nd ed. Academic Press. San Diego.

Brandon, C. E. 1979. Properties of Paper. *In* Pulp and Paper Chemical Technology. Vol. III. 3rd ed. (James, P. C., ed.). p. 1715-1955. Jonh Wiley & Sons. New York.

Brittain, J.A., Perkins, S.R., Schnell, P.G. 2000. The Corrugated Containers Manufacturing Process. TAPPI Press. Atlanta.

Caldwell, C.G. and Wurzburg, O.B. 1953. Polysaccharides Derivative of Substituted Dicarboxylic Acids. U.S. Pat. 2,661,349.

Caoa, R., Nayaa, S., Artiagab, R. Garcia, A. and Varela, A. 2004. Logistic approach to polymer degradation in dynamic TGA. Polym. Degrad. Stabil. 85: 667 – 674.

Chen, Y. X. and Wang, G. Y. 2006. Adsorption properties of oxidized carboxymethyl starch and cross-linked carboxymethyl starch for calcium ion. Colloids Surf., A. 289: 75–83.

Choi, S. G., and Kerr, W. L. 2003. Effects of chemical modification of wheat starch on molecular mobility as studied by pulsed ^{1}H-NMR. Lebensmittel-Wissenchaft Und-Technologie. 51: 1–8.

Cushing, M. L. 1979. Surface Sizing. *In* Pulp and Paper Chemical Technology. Vol. III. 3rd ed. (James, P. C., ed.). p. 1667-1714. Jonh Wiley & Sons. New York.

Debeaufort, F. and Voilley, A. 1995. Effects of surfactants and drying rate on barrier properties of emulsified edible films. Int. J. Food Sci. Tech. 30: 183–190.

Drakos, A. and Kiosseoglou, V. 2008. Depletion flocculation effects in egg-based model salad dressing emulsions. Food Hydrocolloid. 22: 218–224.

Durango, A.M., F Soares, N.F. and Andrade, N.J. 2006. Microbiological evaluation of an edible antimicrobial coating on minimally processed carrots. Food Control 17: 336–341.

Dury-Brun , C., Jury , V., Guillard, V., Desobry , S., Voilley , A. and Chalier, P. 2006. Water barrier properties of treated-papers and application to sponge cake storage. Food Res. Int. 39: 1002–1011.

El-Sadi, H., Carreau, P. and Esmail, N. 2004. Changes in the rheological and colloidal properties of paper coating liquids with paper-yellowing inhibition additives. J. Colloid Interface Sci. 271: 496–503.

Gastaldi, E., Chalier, P.,Guillemin, A. and Gontard, N. 2007. Microstructure of protein-coated paper as affected by physico-chemical properties of coating solutions. Colloids Surf. A. 301: 301–310.

Gigac, J., Fiserova, M. and Rosenberg, M. 2008. Improvement of paper strength via surface application of sugar beet pectin. Chem. Pap. 62: 509-512.

Hackmann, C. 2001. Expanding the coatings industry with soy. Paint Coat. Ind. 17: 74-75.

Han, J. H., and Krochta, J. M. 1999. Wetting properties and water vapor permeability of whey-protein-coated paper. Trans. ASAE. 42: 1375–1382.

Han, J.H., and Krochta, J.M. 2001. Physical properties and oil absorption of whey-protein-coated paper. J. Food Sci 66:1-6.

Haveren, J. van, Oostveen, E. A., Miccichè, F.B., Noordover, A. J., Koning, C. E., Benthem, R. A. T. M. van, Frissen, A. E. and Weijnen, J. G. J. 2007. Resins and additives for powder coatings and alkyd paints, based on renewable resources. J. Coat. Technol. Res. 4: 177–186.

Hermansson, A. M. and Svegmark, K. 1996. Developments in the understanding of starch functionality. Trends Food Sci. Tech. 7: 345–353.

Holmberg, K. 2006. Alkyd Resins. *In* Coatings Technology Handbook. 3rd ed. (Tracton, A. A., ed.). p. 51. CRC Press. Boca Raton.

Hu, G., Chen, J. and Gao, J. 2009. Preparation and characteristics of oxidized potato starch films. Carbohydr. Polym. 76: 291–298.

Hui, R. Qi-he, C., Ming-liang, F., Qiong, X. and Guo-qing, H. 2009. Preparation and properties of octenyl succinic anhydride modified potato starch. Food Chem. 114: 81–86.

Kavitha, R. and BeMiller, J.N. 1998. Characterization of hydroxypropylated potato starch. Carbohydr. Polym. 37: 115–121.

Kim, M. 2003. Evaluation of degradability of hydroxypropylated potato starch/polyethylene blend films. Carbohydr. Polym. 54: 173–181.

Kweon, D. K., Choi, J. K., Kim, E. K. and Lim, S. T. 2001. Adsorbtion of divalent metal ions by succinylated and oxidized corn starches. Carbohydr. Polym. 46: 171-177.

Jaffe, H. L. and Rosenblum. F. M. 1990. Poly (Vinyl Alcohol) for Adhesives. *In* Handbook of Adhesives. (Skeist, I., ed.,). 401-407.

Kacurakova, M. and Wilson, R.H. 2001. Developments in mid-infrared FT-IR spectroscopy of selected carbohydrates. Carbohydr. Polym. 44: 291–303.

Larotonda, F.D.S., Matsui, K.N.. Sobral, P.J.A. and Laurindo, J.B. 2005. Hygroscopicity and water vapor permeability of Kraft paper impregnated with starch acetate. J. Food Eng. 71: 394–402.

Lyne, M. B. 2001. Wetting and the penetration of liquids into paper *In* Handbook of Physical Testing for Paper. 2nd ed. (Borch, J., Lyne, M. B., Mark, R. E. and Habeger, Jr., C., C., ed.) p. 298–328. Marcel Dekker Inc. New York.

Matsui, K.N., Larotondaa, F.D.S., Paes, S.S. Luiza, D.B. Pires, A.T.N. and Laurindoa, J.B. 2004. Cassava bagasse-Kraft paper composites: analysis of influence of impregnation with starch acetate on tensile strength and water absorption properties. Carbohydr. Polym. 55: 237–243.

McClements, D. J. 2004. Food emulsions: principles, practice, and techniques. 2nd Ed. CRC Press. USA.

Mentzer, M. J. 1984. Starch in the Paper Industry. *In* Starch Chemistry and Technology. 2nd ed. (Whistler, R. L., Bemiller, J. N. and Paschall, E. F., ed.). p. 543–574. Academic Press. San Diego.

Miyazaki, M., Hunga, P. V., Maedad T. and Morita N. 2006. Recent advances in application of modified starches for breadmaking. Trends Food Sci. Tech. 17: 591-599.

Morillon, V., Debeaufort, F., Blond, G., Capelle, M. and Voilley, A. 2002. Factors Affecting the Moisture Permeability of Lipid-Based Edible Films: A Review. Crit. Rev. Food Sci. Nutr. 42: 67–89.

Murphy, P. 2000. Starch. *In* Handbook of Hydrocolloids. (Phillips, G. O. and Williams, P. A., ed.). p. 41–65. CRC Press. Boca Raton.

Nilsson, L. and Bergenståhl, B. 2006. Adsorption of hydrophobically modified starch at oil/water interfaces during emulsification. Langmuir. 22: 8770–8776.

Nilsson, L. and Bergenståhl, B. 2007a. Emulsification and adsorption properties of hydrophobically modified potato and barley starch. J. Agric. Food Chem. 55: 1469-1474.

Nilsson, L. and Bergenståhl, B. 2007b. Adsorption of hydrophobically modified anionic starch at oppositely charged oil/water interfaces. J. Colloid Interface Sci. 308: 508–513.

Ogunniyi, D.S. and Odetoye, T.E. 2007. Preparation and evaluation of tobacco seed oil-modified alkyd resins. Bioresour. Technol. 99: 1300–1304.

Overcash, D. T., and Elsebaumer, R. L. (2001). Coated sheet method. U.S. Pat. 6,193,831.

Pal, J., Singhal, R. S. and Kulkarni P. R. 2000. A comparative account of conditions of synthesis of hydroxypropyl derivative from corn and amaranth starch. Carbohydr. Polym. 43: 155-162.

Ploeger, R., Scalarone, D. and Chiantore O. 2008. The characterization of commercial artists' alkyd paints. J. Cultural Heritage 9: 412-419.

Raphaelides, S. N. and Georgiadis, N. 2006. Effect of fatty acids on the rheological behavior of maize starch dispersions during heating. Carbohydr. Polym. 65: 81–92.

Raphaelides, S.N. and Georgiadis, N. 2007. Effect of fatty acids on the rheological behaviour of pea starch dispersions during heating. Food Hydrocolloids 21: 1188–1200.

Rhim, J.W., Lee, J.H. and Hong, S.I. 2006. Water resistance and mechanical properties of biopolymer (alginate and soy protein) coated paperboards. LWT. 39: 806–813.

Richardson, S. and Gorton, L. 2003. Characterisation of the substituent distribution in starch and cellulose derivatives: Review. Anal. Chim. Acta. 497: 27–65.

Robertson, G.L. 1993. Paper and Paper-Based Packaging Materials. *In* Food Packaging, Principles and Practice. p 103-120. Marcel Dekker. Inc. New York.

Rudnika, E., Matuschekb, G., Milanovb, N. and Kettrup, A. 2005. Thermal properties of starch succinates. Thermochim. Acta. 427: 163–166.

Rutenberg, M. W. and Solarek, D. 1984. Starch Derivatives: Production and Uses. *In* Starch Chemistry and Technology. 2nd ed. (Whistler, R.L., Bemiller, J.N. and Paschall, E. F., ed.), p. 312–388. Academic Press. San Diego.

Seow, C. C. and Thevamalar, K. 1993. Internal plasticization of granular rice starch by hydroxypropylation: Effects on phase transitions associated with gelatinization. Starch. 45: 85–88.

Shannon, J.C. and Garwood, D. L.1984. Genetics and Physiology of Starch Development. *In* Starch Chemistry and Technology. 2nd ed. (Whistler, R.L., Bemiller, J.N. and Paschall, E. F., ed.), p. 26–86. Academic Press. San Diego.

Shogren, R. L. 2003. Rapid preparation of starch esters by high temperature/pressure reaction. Carbohydr. Polym. 52: 319 – 326.

Slager, T.L. and Prozonic, F.M. 2004. Simple methods for calibrating IR in TGA/IR analyses. Thermochim. Acta. 426: 93–99.

Simkovic, I., Laszlo, J. A. and Thompson, A. R. 1996. Preparation of a weakly basic ion exchanger by crosslinking starch with epichlorohydrin in the presence of NH4OH. Carbohydr. Polym. 30: 25–30.

Song, X. Y., Chen, Q. H., Ruan, H., He, G. Q. and Xu, Q. 2006. Synthesis and paste properties of octenyl succinic anhydride modified early Indica rice starch. J. Zhejiang Univ. Sci. B. 7: 800–805.

Song, Z., Zhang, M. and Ma, C. 2007. Study on the oxidation of calcium sulfide using TGA and FTIR. Fuel Process Technol. 88: 569–575.

Sorokin, A. B., Kachkarova-Sorokina, S. L., Donze, C., Pinel, C. and Gallezot, P. 2004. From native starch to hydrophilic and hydrophobic products: a catalytic approach. Top. Catal. 27: 67–76.

Sothornvit, R. 2009. Effect of hydroxypropyl methylcellulose and lipid on mechanical properties and water vapor permeability of coated paper. Food Res. Intern. 42: 307–311.

Sun, Q., Schork, F. J. and Deng, Y. 2007. Water-based polymer/clay nanocomposite suspension for improving water and moisture barrier in coating. Compos. Sci. Technol. 67: 1823–1829.

Sztuka, K. and Kolodziejska, I. 2009. The influence of hydrophobic substances on water vapor permeability of fish gelatin films modified with transglutaminase or 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC). Food Hydrocolloid. 23: 1062–1064.

Tesch, S., Gerhards, C. and Schubert, H., 2002. Stabilization of emulsions by OSA starches. J. Food Eng. 54: 167 – 174.

Tharanathan, R. N. 2003. Biodegradable films and composite coatings: Past, present and future. Trends Food Sci. Tech. 14: 71–78.

The ,D. P., Debeaufort, F., Voilley, A. and Luu, D. 2009. Influence of hydrocolloid nature on the structure and functional properties of emulsified edible films. Food Hydrocolloid. 23: 691–699.

Thirathumthavorn, D. and Charoenrein, S. 2006. Thermal and pasting properties of native and acid-treated starches derivatized by 1-octenyl succinic anhydride. Carbohydr. Polym. 66: 258–265.

Tolvanena, P., Maki-Arvela, P., Sorokin, A.B., Salmi, T. and Murzin, D.Yu. 2009. Kinetics of starch oxidation using hydrogen peroxide as an environmentally friendly oxidant and an iron complex as a catalyst. Chem. Eng. J. 154: 52-59.

Tuschhoff, J. V. 1987. Hydroxypropylated starches. *In* Modified starches: Properties and uses. (Wurzburg, O. B., ed.). p. 90–95. CRS Press. Florida.

Vareckova, D., Podzimek, S. and Lebduska, J. 2006. Characterization of alkyd resins by size exclusion chromatography coupled with a multi-angle light scattering photometer. Anal. Chim. Acta 557: 31–36.

Vargas, M., Albors, A., Chiralt, A. and Martınez, C. G. 2009. Characterization of chitosan–oleic acid composite films. Food Hydrocolloid. 23: 536–547.

Viswanathan, A. 1999. Effect of Degree of Substitution of Octenyl Succinate Starch on Enzymatic Degradation. J. Environ. Polym. Degrad.. 7: 185 – 190.

Wang, L., Shogren R.L. and Willett, J.L. 1997. Preparation of Starch Succinates by Reactive Extrusion. Starch . 49: 116 – 120.

Wenzel, D. J., Bartholomew, W., Quick, R., Delozier, M. S., and Klass-Hoffman, M. 1997. Recyclable and compostable coated paper stocks and related methods of manufacture. U.S. Pat. 5,654,039.

Whistler, R.L.1984. History and Fututure Expectation of Starch Use. *In* Starch Chemistry and Technology. 2nd ed. (Whistler, R.L., Bemiller, J.N. and Paschall, E. F., ed.), p. 2–12. Academic Press. San Diego.

Wootton, M. and Manatsathit, A. 1983. The influence of molar substitution on the water binding capacity of hydroxypropyl maize starches. Starch. 35: 92–94.

Yılmaz, G., Jongboom, R.O.J., Soest, J.J.G. and Feil, H. 1999. Effect of glycerol on the morphology of starch–sunflower oil composites. Carbohydr. Polym. 38: 33–39.

Xie, W., Heltsley, R., Cai, X., Deng, F., Liu, J. Lee, C. and Pan W. P. 2002. Study of stability of high-temperature polyimides using TG/MS technique. J. Appl. Polym. Sci. 83: 1219–1227.

Zobel, H. F. 1992. Starch: Source, Production and Properties. *In* Starch Hydrolysis Products: Worldwide Technology, Production and Application. (Schenck, F.W. and Ronald, E., ed.). p. 23-44. VCH. New York.

Zou, Y., Hsieh, J. S., Mehnert, E. and Kokoszka, J. 2007. The effect of pigments and lattices on the properties of coated paper. Colloids and Surfaces A: Physicochem. Eng. Aspects. 294: 40–45.

VITAE

Name Miss Widchuda Chantaramee

Student ID 5011020033

Educational Attainment

Degree	Name of Institution	Year of Graduation
Bachelor of Science (Material Product Technology)	Prince of Songkla University	2006

List of Publication and Proceedings

Chantaramee, W. and Bourtoom. T. 2009. Effect of coating mediums on alkyd resin coating stability and coated paperboard properties. In Proceedings of The 10th Annual Conference of Thai Society of Agricultural Engineering. Suranaree University of Technology Thailand. 1-3 April 2009. P. 251-254.