

**A DISSERTATION FOR THE DEGREE OF DOCTOR OF PHILOSOPHY**

**Application of Suspension-polymerized Latexes in  
Surface Sizing and Pigment Coating of Paper**

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## **ABSTRACT**

### **Application of Suspension-polymerized Latexes in Surface Sizing and Pigment Coating of Paper**

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Fold cracking of coated paper is one of the most frequent and troublesome problems affecting the use of coated paper and boards. Paper industry is facing more fold cracking problem because substantial amount of filler is being used in papermaking and heavier coatings are applied to substitute the use of expensive fibers with pigment coating.

Fold cracking of coated paper is highly dependent on the properties of coating layer. The coating composition including pigments and binders affects the properties of coating layer. A latex with a good extensional property could improve the flexibility of coating layer and result in a less crack area after folding of coated paper. To minimize fold cracking of coated paper and board, a method to improve the extensional property and tensile strength of the base sheet and coating layer is necessary. Improving the fold crack resistance by optimization of surface sizing or paper coating by use of additives seems a practical method. Hence application of additives which provide both strain and strength might be a useful method to minimize the fold crack.

The physical and chemical properties of latexes depend upon various factors

including polymerization methods, and monomers and stabilizer used in the polymerization. In this research, sterically stabilized suspension-polymerized acrylate (SP) latexes were used as additives for surface sizing and pigment coating of paper. A protective shell containing oxidized starch and polyvinyl alcohol (PVA) provided the steric hindrance to the SP latexes.

The property of the suspension-polymerized latex was examined and compared with that of conventional emulsion-polymerized ones. As an approach to decrease the fold cracking of coated paper, SP latexes were tested as a surface sizing additive. By preparation of starch films, it was possible to compare the film properties without variability caused by the base sheet. The strength and stretch properties of starch films without and with SP latex were measured. The effect of using SP latexes as a surface sizing additive on the mechanical properties of the paper was examined.

SP latexes with different acrylic acid content were used as cobinders for paper coating. The physical properties of these latexes including viscosity, particles size and zeta potential as a function of pH were compared. The viscoelastic properties of the coating color containing SP latex as a cobinder were evaluated. Moreover effect of partial substitution of the styrene butadiene (S/B) latex with SP latex on porosity, surface and optical properties of dried coating composite was investigated.

The coating layers containing SP latex as a cobinder were prepared and the tensile strength and strain property of the coating layers were evaluated. Finally the effect of SP latex on fold cracking of low- and high- basis weight coated paper in machine direction (MD) and cross machine direction (CD) was investigated.

The SP latex showed less tendency to generate foam than conventional styrene-butadiene and styrene-acrylate latexes, and they were highly compatible with the conventional surface sizing solution as the strength and

stretch of the starch films increased. The SP latex resulted in a greater tensile strength and extensional properties of sized paper than the emulsion-polymerized latexes, which suggested their potential applicability for reducing the fold cracking of coated paper.

Acrylic acid monomer was found to be an important factor affecting viscosity, particle size and zeta potential of SP latexes. As a result of partial substitution of S/B latex with SP latexes in coating color, the viscoelastic properties of coating color was influenced by interaction between coating components. Because of this interaction, a weakly flocculated structure was built up in coating color which affected the formation of coating layer and thereby a more porous coating layer with higher opacity and brightness was formed.

Use of SP latex in coating layer, improved the strength and strain of the coating layer which was attributed to the protective shell and monomer composition of the SP latex. The extensional properties of the coated papers were improved when SP latex was used in coating formulation. Higher tensile strength and extensional properties of coating layer and coated paper, resulted in less crack area after folding. A base paper with higher basis weight gave a larger crack area as did the CD fold. Presence of SP latex in pre- and top-coating reduced the fold crack area, however it was found more effective in top-coating layer. Starch amount and total binder content of pre-coating layer contributed to appearance of larger fold crack area.

**Keywords:** Suspension-polymerized (SP) latex, surface sizing, paper coating, coating layer, extensional properties, fold cracking, folding direction

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## **Chapter 1**

### Introduction

## **1. Introduction**

Different paper products are pigment coated to improve optical and printing properties. In this competitive market, the quality of the paper is a critical issue, and it should meet the consumer demand. During converting operations, coated paper and board undergo folding processes which results in the appearance of cracks along the folded area that is called fold cracking. The issue of fold cracking most often arises when the tensional or compressional stress or strain exceeds the level that the coated product can withstand.

Fold cracking of coated paper has been recognized as one of the most frequent and troublesome problems affecting the use of coated paper and boards these days. Fold cracking is becoming more common in the paper industry because more filler is being used in papermaking and heavier coatings are applied to substitute the use of expensive fibers with pigment coating (Im et al., 2013; Seo et al., 2016; 2012). As the paper with high ash content are being used as a base stock for pigment coating, fold cracking problem on the coated surface is frequently observed (Seo et al., 2015). Fold cracking occurs when coated paper and paperboard are folded or creased during the converting operation.

Many studies have investigated the factors that affect the fold cracking of coated papers, such as the fiber composition, coating pigments and binders, coating layer structure, folding direction. Sim et al. (2012) evaluated the influence of the fiber composition and showed that fold cracking of coated paper was minimized when the base paper consisted of 90% hardwood fiber and 10% softwood fiber was used. They also showed that beating exacerbated fold cracking, even though it increased tensile strength. Clay has been found to give greater fold cracking than ground calcium carbonate (GCC) (Rättö and

Hornatowska, 2010a).

An increase of the starch binder in the coating increases the modulus of elasticity (MOE) and decreases the strain of the coating (Oh et al., 2015; Okomori et al., 2001; Rioux et al., 2011). This change in mechanical properties of the coating layer accompanies with starch binder influences the fold cracking of the coating layer. The use of starch as a coating binder has been found to increase the fold crack area while decreasing the total number of fold cracks (Oh et al. 2015), and this was attributed to the greater occurrence of strain-based failure of coatings with higher starch binder contents.

Many studies have been done to improve the coating layer property and make coatings more resistive to fold cracking. The importance of the extensional strain property of the coating layer in decreasing the fold cracking has been shown by Okomori et al. (2001) and Oh et al. (2015). The use of latex with a low glass transition temperature or reducing the starch binder in the coating color reduced the MOE while increasing the strain of the coating layer, which eventually led to a smaller length, width, and area of the cracks in the coating after folding. Oh and co-workers (2016) studied the effect of latex monomer on the extensional properties of coating layer and fold cracking of coated papers. They showed that S/A latex was more favorable to improve the strain of coating layer and consequently increased the fold cracking resistance because of the less crosslinked gel structure of this latex.

Although numerous studies have been conducted on fold cracking, and many researchers investigated the effect of base paper and coating color composition on fold crack resistance, few approaches have been made to improve the fold crack resistance of the base paper by surface treatment. Surface sizing of paper

is usually carried out to adjust adsorption properties of base paper and control coating color penetration during coating process. Starch is widely used for surface sizing of coating base stocks because it has many advantages of improving the tensile strength, burst strength, and stiffness of the coating base stock. However, starch has a high glass transition temperature ( $T_g$ ) and is a brittle polymer by itself, which gives a rigid and brittle film after drying (Orford et al., 1989). Hence, surface sizing with starch often increase the fold cracking of coated paper. This indicates that there is a clear need to find a way to reduce the brittleness of the starch film to obtain positive effect in reducing the fold cracking of coated paper by surface sizing of coating base stock.

To minimize fold cracking, methods to improve the extensional property and tensile strength of the base paper and coating layer is necessary. Many strategies like increasing the porosity of the paper, reducing the thickness, and increasing the coating color penetration might be useful to reduce the fold cracking. These strategies, however, requires a number of manipulation in the papermaking process and often changes other properties of the products. Therefore, it might be useful to find a simple and reliable way to improve the fold crack resistance. A new surface sizing additive or paper coating cobinder may provide a simple and practical approach in reducing the fold cracking. Because base paper or coating layer with better extensional and strength properties would be more favorable to reduce fold cracking, it is necessary to find an additive to make these property changes possible.

Several types of emulsion-polymerized latexes, including styrene/butadiene (S/B) latex, and styrene/acrylate (S/A) latex, have been used not only as binders for pigment coating but also as additives for surface sizing of paper to improve printability and to reduce linting and dusting. Surface treatment of paper with

latexes can enhance the internal bonding strength and flexibility (Blackley, 1997; Gray and Rende, 2005; Sajbel, 2005). Use of latex materials as surface sizing additives does not increase the solution viscosity, thus it is possible to increase the solids level of sizing solution. S/B latexes with lower  $T_g$  or S/A latexes were found very effective to reduce the fold cracking problem (Kim et al., 2010; Oh et al., 2016), mainly because of their high extensional property.

The colloidal stability of emulsion-polymerized latexes is usually obtained via electrostatic protection provided by the surfactant and functional monomers (Arshady, 1992; Bacquet and Isorad, 1997). These surfactants, however, reduce the surface tension of the latex dispersions and coating formulation, and thereby cause foaming in the size pressing or coating operations. When using synthetic latexes as surface sizing additives or coating binders, they should be compatible with the starch solution or other coating components.

Sterically stabilized suspension-polymerized latex is another type of latex. This latex is stabilized by a protective shell that surrounds the core polymer particle and provides steric hindrance to the particle. The protective shell of the suspension-polymerized latex is obtained by the hydrophilic polymers like starch, PVA, carboxymethyl cellulose, etc. (Arshady, 1992; Blackley, 1997; Horák, Pelzbauer, Švec, & Kálal, 1981). Because these hydrophilic polymers have similar hydrophilic properties as starch molecules used in surface sizing, they provide a high compatibility of the latexes with surface sizing starch solution or coating color components. It is also possible to impart a good extensional property to the brittle surface sizing starch film if the latex is designed to be highly flexible and stretchable.

## 2. Objectives

This study was aimed to reduce the fold cracking problem by the optimization of the surface sizing and pigment coating components. To minimize fold cracking, a method to improve the extensional property and tensile strength of the base sheet and coating layer is necessary. For this purpose, sterically stabilized latexes with better extensional properties were designed and prepared based on the suspension polymerization. In the polymerization of these latexes, a protective shell containing starch and PVA was employed to obtain strength, compatability, and runnability in size sizing and coating operation.

In the first part of this study, application of sterically stabilized latexes as a surface sizing additive was examined. The effect of sterically stabilized suspension-polymerized latex on the extensional properties of starch film was studied, and its potential on stiffness and MOE reduction of sized papers was evaluated. Moreover, the change in surface tension and foam generation with the use of the suspension-polymerized latex was examined.

The second part of this research was aimed to study the effect of sterically stabilized latexes as a cobinder in coating formulation. The effect of the suspension-polymerized latex on the rheological and foaming properties of coating color was investigated. The interaction between coating color components that influences the structure formation of coating layer, hence surface properties, porosity and optical properties of the coating layer were also examined.

Fold crack resistance is affected by the extensional properties of coating layer. Hence the influence of sterically stabilized suspension-polymerized latex

cobinder on the tensile properties of the coating layer and coated paper was studied. The coated papers were folded with a constant pressure and the fold crack areas were determined to examine the potential of using sterically stabilized latexes as a cobinder to decrease the fold cracking of coated paper.

Surface characteristics of coated paper are of importance for printability. Hence the last part of this research was carried out to understand the effect of sterically stabilized latexes on the surface properties of coated paper. Optical properties of the coated paper including opacity and brightness were evaluated. Finally, the ink absorbency and ink distribution of the coated papers were measured.



### **3. Literature reviews**

#### **3.1 Suspension-polymerized latexes**

Synthetic polymer latexes have been developed and used to bind the mineral particles to each other and to the base paper and provide the strength of the coating layer after drying. Emulsion polymerization is widely used to prepare the latex binders for coating. The colloidal stability of emulsion-polymerized latexes is usually provided by electrostatic protection by the surfactants and functional monomers (Arshady, 1992; Bacquet and Isoard 1997). It has been shown that the conventional latex binders are very effective as a coating binder because it provides good binding strength, surface smoothness, optical and rheological properties and allows high solids coating. A number of products have been developed to maximize certain properties or optimize the overall properties of the latex. Even though the conventional latex has been a predominant binder for paper coating, it is true that there is a need of further improvement. For instance, conventional emulsion-polymerized latex often generates a huge amount of foam if it is not handled carefully because it contains surfactants as stabilizer. These surfactants reduce the surface tension of the surface sizing solution or coating color and thereby cause foaming in the size pressing or coating operations.

Emulsion polymerization method is being used to produce the many latex products used for coating because it allows the rapid polymerization of high molecular weight polymers without the loss of temperature control, and gives a product low in viscosity irrespective to the molecular weight. Another polymerization method, which is called suspension polymerization, involves

polymerizing the monomers and sterically stabilizing the polymer particles using hydrophilic stabilizers, e.g. starch, PVA, carboxymethyl cellulose, etc. (Blackley, 1997; Horák et al., 1981; Vivaldo-Lima et al., 1997). This is schematically illustrated in Figure 1-1.

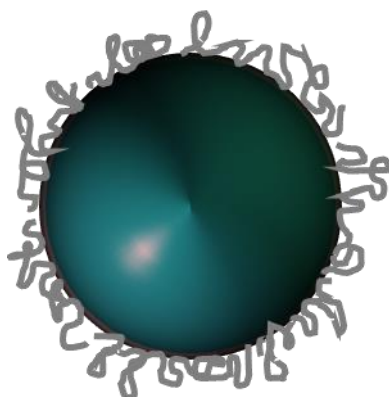


Fig.1-1. Schematic representation of a suspension-polymerized latex particle.

In suspension polymerization, drops of a monomer containing phase are dispersed in a continuous water phase and polymer is produced inside of the drops. The polymerization usually proceeds by a free-radical mechanism that produces polymer beads, whose size distribution is often similar to that of the polymerizing drops in the reactor (Brooks, 2010). The suspension-polymerized latexes are stabilized with the use of hydrophilic polymers as stabilizers. Water-miscible polymers, both naturally occurring and synthetic, are often used as stabilizers (Borwanker et al., 1986). This is the main and unique characteristics of the suspension-polymerized latexes. This suggests that the use of sterically stabilized suspension-polymerized latex (SP latex) as an additive for surface sizing provides several advantages. For instance, foaming may be reduced

because no surfactants are used in polymerization. The compatibility of SP latex with surface sizing solution can be improved because hydrophilic polymers, being similar to starch molecules in structure, can be used as stabilizers in the polymerization.

Block type polymers with a linear arrangement of different monomers or graft copolymers consisting of a backbone and several grafted chains are most common polymeric stabilizers. The block type polymeric stabilizers consisted of hydrophobic and hydrophilic blocks and the graft copolymer types have a hydrophobic backbone and hydrophilic chains. To provide stability for the latexes, the hydrophobic parts of the polymers which are very insoluble in the medium, dissolve or absorb on the core polymer of latex and the hydrophilic segment remains in the medium (Tadros, 2015; 2014). Besides of providing steric repulsion, the hydrophilic segment of the polymeric stabilizers determines the volume fraction of the disperse phase which affects the viscoelastic properties of the latex (Tadros, 2012).

### **3.2 Surface sizing**

Surface sizing refers to the application of a film forming material onto the surface of paper to improve surface properties and enhance certain physical properties of the paper sheet (Bajpai, 2015; Lee et al., 2002). The base paper is usually surface sized prior to pigment coating to improve the coating holdout on the paper product. Starch solutions are the most commonly used material for this purpose because of their favorable cost and performance. Surface sizing with starch improves the strength of paper as a result of the abundant hydroxyl groups in starch, which are capable of forming hydrogen bonds with papermaking fibers. Starch also provides rigidity and stiffness to paper products,

thereby improving their runnability in printing and converting operations.

To improve the rheology of surface sizing solution and interaction with papermaking fibers, various additives have been used. For instance, polyvinyl alcohol (PVA), sodium alginate, polyacrylamide, carboxymethyl cellulose, etc. have been used along with starch to improve the film-forming properties and control the penetration of starch solution into base paper. Seo et al. (2013) investigated the effect of PVA or polyDADMAC (polydiallyldimethylammonium chloride) addition on surface sizing with oxidized starch, and showed that electrostatic interactions between the high molecular weight polyDADMAC and oxidized starch increased the viscosity of the surface sizing solution and gave gelatinous blobs, while low molecular weight PVA was most effective in improving folding endurance and internal bond strength without the problems associated with high molecular weight polyDADMAC. Cationic polyacrylamide (cPAM) (Jeon and Lee 2003) or cationic starch (Lee et al., 2002) have been used to increase the interaction of surface sizing solution with papermaking fiber thereby to limit the penetration of the surface sizing solutions into the paper. Dextrin-poly(acrylic acid) copolymer has been examined as a surface sizing additive to improve paper properties (Kim et al., 2017; Rajabi Abhari et al., 2017).

Use of water soluble polymers, however, often gives a problem of increasing the starch solution viscosity, which limits the solids level of surface sizing solution (Jeong et al., 2013). Because the solids level of sizing solution is closely associated with the drying energy after surface sizing, it is preferred to have a sizing additive that does not increase the solution viscosity. Several types of latexes have been used as surface sizing additive to improve printability and reduce linting and dusting problem. Surface treatment of paper with latexes can

improve the internal bonding strength and flexibility (Blackley, 1997; Gray and Rende, 2005; Sajbel, 2005).

### **3.3 Rheological properties of coating color and its effect on structure formation of coating layer**

Coating colors containing pigments and binders usually show a complicated viscoelastic behavior that affects the runnability of the coating process and property of the coated paper (Ascanio et al., 2006; Carreau, 1993; Grön and Dahlvik, 1997; Page et al., 2002). Solids content, pigment shape, pigment size distribution, latex level, and latex size could affect the rheology of the coating color (Bousfield, 2008; Bruun, 2009). For instance, viscosity of a coating color containing kaolin clay is higher than that of calcium carbonate based coating color (Conceição et al., 2005). The plate shape particles need more volume than round shape particle to rotate in the dispersion that results in a higher viscosity of coating color. Narrow particle size distribution also increased the viscosity (Roper, 2000).

The interaction between components of the coating color affects the viscoelastic properties by formation of a network in coating color (Husband, 2000; Yziquel et al., 1999). Coating colors usually contain water soluble cobinders and thickeners like starch, polyvinyl alcohol (PVA) and carboxymethyl cellulose (CMC) that affect rheology and water retention properties of disperse systems ( Bruun, 2009; Choi et al., 2015; Fadat et al., 1988; Gron and Dahilvik, 1997). These highly water soluble polymers interact with other components and affect the runnability of the coating process and viscoelastic properties of the coating color by flocculation of the components

and formation of a network that is shear-dependent (Husband, 1998; McGenity et al., 1992; Oh et al., 2017; Wallström & Järnström, 2004; Whalen-Shaw and Gautam, 1995).

Water retention property of a coating color is also an important property which affects drying process and property of the dried coating composite. The water retention property is highly dependent on the hydrophilicity and viscoelastic properties of the disperse system interaction between components of the coating color (Page et al., 2002). Thickeners with more hydroxyl or carboxyl groups tend to improve the water holdout of the coating color via hydrogen bond formation. Interaction of coating color components results in flocculation and formation of a network which entraps bulk water and influences the water retention of the disperse system (Li, et al., 2001; Gron and Dahlivik, 1997).

Previous studies showed that flocculation of coating color containing mineral pigments affects the structure of the coating layer after drying and would result in the formation of a porous coating layer after drying (Choi et al., 2015; Oh et al., 2017). Porosity of the coating layer is an important factor which is influenced by pigment type, size, size distribution, and interaction between components of coating color. Porosity and void structure of a coating layer affect the light scattering and improve the optical properties of the coating layer, like brightness and opacity (Alince and Lepoutre, 1980). When a coating color containing pigments and latexes is dried, the voids between pigments are filled with latex film and a less porous structure is formed which influences the light scattering and optical properties. Hence the formation of a more porous dried coating composite is favored for better optical properties of the coated surface. On the other hand, mechanical properties of a coating layer are affected by its porosity and void structure. A more porous coating layer deteriorates the

mechanical properties by reducing the strength and stiffness of the coating composite (Lepoutre and Rigdahl, 1989).

### **3.4 Fold cracking**

Fold cracking of coated papers is critical damage which causes a quality problem. Crack size and area and the number of cracks can affect the appearance of the coated paper. Besides of appearance of cracks, fold cracking could result in a strength reduction which leads to deterioration of the quality. During the folding process, the outer layer of paper subjected to tension and the inner layer undergoes a compressive stress and both of the base stock and coating layer might be ruptured and damaged (Alam et al., 2009; Guyot et al., 1992; Oh et al., 2016; Sim et al., 2012). Ratto and Hornatowska (2010a) suggested the beam theory for illustration of the folding crack. The strain,  $\varepsilon$ , at a distance,  $z$ , from the neutral axis and a radius of curvature,  $R$ , can be expressed by Equation 1-1.

$$\varepsilon = \frac{z}{R} \quad \text{Eq. (1-1)}$$

This equation reveals that the largest strain is obtained in the top layer of the coating. During the bending process, as the radius of curvature decreases the compressive stress increases in the bottom layer of paper and the strain increases in the upper coating layer. In the case of a single coated layer in which the mechanical properties don't vary through the thickness, the cracks start from the surface of the coating layer and propagate to the internal parts. Multiple coating layers, however, might have different behaviors. The tensile strain will also increase with the thickness of the paper. Paperboards, however,

show a different behavior when it is subjected to a creasing process. Paperboards internally delaminate and enable to relief some of the compressive forces and strain in the inside and outside of the coated board respectively (Barbier, 1999; Rättö & Hornatowska, 2010a; 2010b).

Deformation of coated paper or board during folding inhibits the complete bending but could exhibit shear strains and shear stresses which are negligible in most cases. However in some cases which the coated paper is weak or consists of pigment with weak structure, the shear stresses during bending or creasing might break and delaminate the coating layer (Rättö, 2006). In a sandwich beam, the maximum and zero shear stresses are obtained at the center and the surface of the beam respectively, so the shear stress in the coating layer is maximum near the coating layer and paper interface (Zenkert, 1992).

#### **3.4.1 Effect of base paper on fold cracking**

Base paper is an important factor which affects the fold cracking of coated paper. Similar coating color composition on the different base stocks might result in different cracking mechanisms and the cracks with different patterns would appear (Barbier et al., 2002; Guyot et al., 1992; Colley, 1982). Base stock composition and properties and its role in fold cracking of coated paper have been the subject of the previous studies. Effect of the composition and strength of base paper on fold cracking of coated paper was investigated by Sim et al. (2012). They mixed different ratios of hardwood bleached kraft pulp (Hw-BKP) and softwood bleached kraft pulp (Sw-BKP) and increased mechanical strengths of base paper by beating pulp fibers. The result showed that increase in the beating degree and content of Sw-BKP improved the mechanical



properties of the base paper. However, this increase in mechanical properties resulted in increased fold cracking. Colley (1982) reported the effect of the base paper on fold cracking and suggested that optimizing the beating process could reduce the risk of the fold crack appearance.

Barbier et al. (2002) and Oh and coworkers (2016) reported that the thickness of the base paper is an important factor in the appearance of the folding cracks. A decrease in base paper thickness results in fold crack reduction because the coating layer subjects to a small strain. Porosity of base paper also influences the fold cracking. A low-density and porous paper might facilitate the coating color penetration into the paper. According to Kamel et al. (2009) an increase of mechanical property of paper is obtained by the penetration of different polymers into the paper. Guyot et al. (1992) studied the effect of coating color penetration into the base paper and showed that the fold crack resistance improved as the coating color penetrated more and the base paper resisted more to the damage during the folding operation.

### **3.4.2 Effect of coating color components on fold cracking**

Coating color composition like pigment and binder has a significant influence on the fold cracking tendency of coated paper. Pigment shape, structure, orientation, and size affect the crack area. Pigment properties also influence the appearance of cracks and their sizes. Binders are mainly used in the coating color to bind the pigment particle to each other and to the base paper. Cohesion of the coating layer which is provided by binder also plays an important role in the appearance of fold cracking. Binder type and amount in the coating color, the presence of cobinder and its ratio could affect the fold crack resistance of the coated paper. A coated paper becomes stiffer when a rigid binder is used in

the coating color. Binders ranging from natural one like starch to synthetic one like latex might be used for coating color preparation which also affect fold cracking.

#### **3.4.2.1 Effect of coating pigments on fold cracking**

Pigment particles have different strengths and stiffness due to the variation in their shape and orientation. Compared to GCC, clay imparts higher in-plane stiffness and strength. On the other hand, GCC gives a higher out-of-plane strength due to the oriented shape (Husband et al., 2007; Lepoutre and Rigdahl, 1989; Prall et al., 2000; Toivakka and Bousfield, 2001). Guyot et al. (1992) investigated the effect of coating color composition on the fold cracking. They applied various ratio of clay and calcium carbonate and the result showed that by increasing the clay proportion in coating color, the fold crack decreased. Ratto and Hornatowska (2010) studied the relationship between the crack area with GCC and clay-based coating and the result showed that clay in coating color resulted in greater crack area. They also reported that in GCC-based coating, release of the tension resulted in fold cracking which initiates at the surface of the coating layer and then expands into the z-direction. In clay-based coating, however, cracks would be appeared parallel to the plane which is the weakest direction. Moreover, because of the layered structure of the clay, clay-based coating layer was subjected to shear stress and broken which indicated that delamination is might be happened due to shear failure rather than to energy release due to cracking.

### **3.4.2.2 Effect of coating binder on fold cracking**

Binder type and amount affect the fold cracking. A coated paper becomes more stiff by using a rigid binder with higher  $T_g$  in the coating color (Bacquet and Isoard, 1997). According to Ratto and Hornatowska (2010a), replacement of S/B latex with starch in clay and GCC based coating increased the crack area of coated paper after creasing. In another research Ratto and Hornatowska (2010b), investigated the crack area and initiation time and propagation speed of cracks in coating layers after creasing. The result showed that the replacing 50% of the S/B latex with starch, increased the crack are and shortened crack initiation time. Moreover, increasing binder content increased crack initiation time but due to the cohesion of the coating layer, crack area decreased. Oh et al. (2015) used starch in pre-coating color and studied its effect on fold cracking of the coated paper. The result showed that as the starch content increased, the number of cracks decreased but the total crack area increased. They also investigated the effect latex  $T_g$  on fold cracking and pointed out that increasing  $T_g$  of S/B latex increased fold cracking area as a result of strain reduction in the coating layer. Moreover, latexes with higher  $T_g$  resulted in the formation of very large cracks in the coating layer (Figure 1-2).

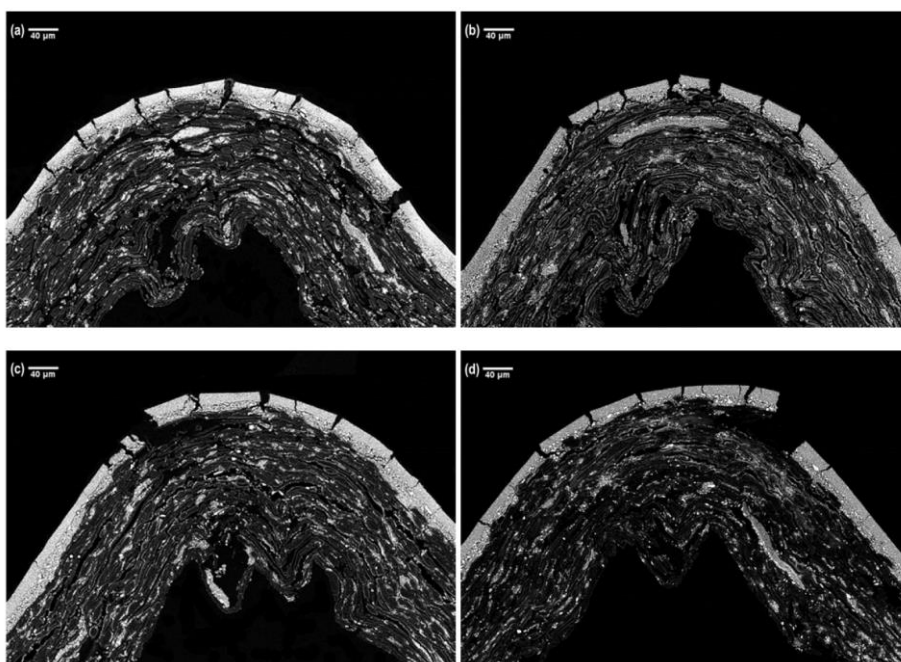


Fig. 1-2 Cross-sectional images of the cracked coated paper. Latex with  $T_g$  of  $-3\text{ }^{\circ}\text{C}$  was used as top coating binder in (a) and (b). Latex with  $T_g$  of  $24.3\text{ }^{\circ}\text{C}$  was used as top coating binder in (c) and (d) (Oh et al., 2015).

Using a binder with low  $T_g$  improves the flexibility of the coating layer. Oh et al. (2016) evaluated the tensile properties of the coated paper containing different latex binders and showed that S/A latexes gave high elongation. Presence of one double bond in acrylate monomer resulted in low cross-linking level in the latex structure. Presence of two double bonds in butadiene monomer makes S/B latexes have highly crosslinked gel structure, which resulted in a low strain characteristics in the coating layer.

### 3.4.3 Strengths and characteristics of the coating layer and its effect on fold cracking

Several studies have been reported on the effect of bending stiffness of paper on fold cracking. They showed that fold crack reduces when bending stiffness of coated paper decrease (Alam et al., 2009; Salminen et al., 2008a; 2008b). The coated paper is a heterogeneous material and its Young's modulus differs between the base paper and the coating. The stiffness of the coated paper is given by the equation 1-2:

$$R = \sum_i E_i I_i = \sum_i E_i \left( E_i x_i^2 + \frac{h_i^3}{12} \right) \quad \text{Eq. (1-2)}$$

Where

$E_i$  is Young's modulus of layer i (MPa);

$I_i$  is the moment inertia of layer i with respect to the bending plane ( $\text{Kg m}^2$ );

$X_i$  is the distance from the center of layer I to the bending plane (m);

$H_i$  is the thickness of layer i (m).

The thickness of the paper increase after coating, therefore, a coated paper's bending stiffness is greater than that of the base paper. Thus as the elastic modulus of the coated layer increase, the bending stiffness of coated paper increases as well. Coating color composition like binder and pigment has a significant effect on the bending stiffness of the coating and consequently on bending stiffness of coated paper and could influence the fold cracking. It should be noted that a coating color with similar component might result in

different fold cracking behaviors on different base papers (Bacquet and Isoard, 1997).

Structure and characteristics of the coated paper are determined by the structure of the base paper and strength and properties of the coating layer. Characteristics and strengths of the coating are affected by coating color composition like type and amount of pigments, binders, and other ingredients. The number of the coating layers, Strengths and thickness of each layer also plays an important role in fold crack resistance. Jopson and Towers (1995) evaluated a combined effect of the base stock and coating layer on fold cracking. They suggested a weak base paper and a stiff coating layer could increase the folding crack.

Application of high coat weight or multi-layer coating could increase the fold cracking (Sim et al., 2012). In order to optimize the bending stiffness and fold crack resistance, modeling and experimental studies were carried out by Salminen and coworkers (2008a, 2008b) and Alam et al. (2009). They optimized the crack resistance and raw material cost by applying triple coating layers consisted of a very stiff and thin pre-coating layer, a medium stiff and thick middle-coating layer. Since the outer layer of the coating undergoes the highest strains, a flexible and thin layer is suitable for the top-coating layer. Oh et al. (2015) evaluated the effect of latex content in the top coating layer. The result showed that increasing S/B latex content in the top coating layer would not reduce fold cracking due to the minimal changes in tensile properties of coating layers obtained with changing latex content. To make the outer layer more flexible with lower rigidity usage of a softer binder with lower  $T_g$  might be a practical strategy. Salminen et al. (2008a) suggested that a softer binder in the outer layer of a double-coated paper.

Tensile strengths of coating layers involving different types of clay were evaluated by Husband et al. (2009; 2006) and the result showed that a coating layer prepared with a high shape factor clay had high tensile stress and elastic modulus. Moreover, they compared coating layers of clay and GCC and reported that clay coating layers showed higher tensile stress and strain than GCC coating layers. Tensile properties of the coating layer are also affected by the type of coating binder. Application of starch as a coating binder increases the elastic modulus but decreases the strain of coating layer (Okomori et al. 2001, Rioux et al. 2011, Oh et al. 2015). In general, a high glass transition temperature of latex increases the elastic modulus of the coating layer while it decreases the strain of coating layer (Okomori et al. 2001, Oh et al. 2015). Alam and Toivakka (2012) studied the mechanical properties of the coating layer using a finite element method and reported that the type of pigment and spreading characteristic of latex affected the mechanical properties of the coating layer.

## **Chapter 2**

Suspension-polymerized latex as an additive for surface sizing  
of paper with oxidized starch



## 1. Introduction

Surface sizing refers to the application of a film forming material onto the surface of paper and paperboard to increase the wetting resistance against liquids and to improve surface and physical properties of paper (Bajpai, 2015; Lee et al., 2002). Although many studies have been done to improve the coating layer property and to make coatings more resistive to fold cracking, few approaches have tried to make the base stock more forgiving to the folding and converting operation. Starch is widely used for surface sizing of coating base stocks because it has many advantages for improving the tensile strength, burst strength, and stiffness of the coating base stock. However, the use of starch as a coating binder is one of the major causes of fold cracking for coated products because of its stiffness and low resilience properties. A question has been raised if the use of starch in surface sizing and not as a coating binder would have a detrimental effect during the folding operation of coated papers. If this is so, another question is raised whether or not it is possible to reduce the fold cracking problem by using an additive that provides a good extensional property to the surface sizing layer.

It was found that water-soluble polymers like PVA, CMC or emulsion-polymerized latexes can be used to improve film forming and extensional properties of starch. However, these additives often gives a problem of increasing the starch solution viscosity or foam generation.

In this study, sterically stabilized suspension-polymerized (SP) latexes were tested as surface sizing additives. The physical properties of these polymer suspensions including surface tension and foaming tendency were investigated and compared with conventional emulsion-polymerized latexes. Finally, the

effect of the SP latexes on the mechanical properties of the surface sized papers was examined and compared with the paper surface sized using conventional emulsion-polymerized latexes as additives.

## **2. Experimental**

### **2.1 Materials**

A commercial oxidized starch (C 3011) was provided by Samyang Genex (Seongnam, Korea). Sterically stabilized suspension-polymerized latex (SP latex) was kindly provided by SongKang Industrial Co. Two commercial emulsion-polymerized latexes, i.e. a styrene-butadiene latex (S/B latex; Lutex 760, LG Chemical, Korea) and a styrene acrylate latex (S/A latex; SAL 105, LG Chemical, Korea) were used for comparison. Fine papers with a basis weight of 85 g/m<sup>2</sup> from Moorim paper (Jinju, Korea) were used as base paper for surface sizing.

### **2.2 Viscosity measurement**

A Brookfield viscometer (DV-2, USA0) was used to determine the low-shear viscosity of the latexes and the sizing solutions at 100 rpm using a spindle No. 61 and 62. Viscosity of the latex was measured at 25 °C, and the viscosity of starch solution was measured at 50 °C before surface sizing.

### **2.3 Particle size measurement**

The particle size of the latex was measured using a Malvern Zetasizer (Nano-ZS, UK). Latex samples were diluted with deionized water to a concentration of 0.01 wt.% for particle size measurement.

## **2.4 Transmission electron microscopy (TEM)**

Images of the latexes were obtained using a LIBRA 120 (Carl Zeiss) transmission electron microscope with an operation voltage of 120 kV. Latex particles were deposited on Formvar film coated grids and then the grids were exposed to a drop of uranyl acetate solution (UA) for 10 s for staining and then washed for 1 s in two drops of DI water. The residual DI water was then removed using a filter paper and the sample was dried at room temperature.

## **2.5 Fourier transform infrared spectroscopy (FTIR)**

FT-IR spectra of the latexes were obtained using a Nicolet 6700 Spectrometer (Thermo Electron Corporation, USA) in attenuated total reflectance (ATR) mode in the range of 600-4000  $\text{cm}^{-1}$ . The latex films were prepared by drying the latex dispersion in aluminum dishes at 70 °C.

## **2.6 Surface tension of latexes**

The surface tension of the latex at several concentrations was measured using a KRÜSS tensiometer (K-12, Germany). The latex dispersions were diluted with deionized water to concentrations of 0.001, 0.01, 0.1, 1, and 10 wt.%.

## **2.7 Foaming tendency of latexes**

The foaming tendency of the latexes was evaluated by measuring the height

of the foam after free falling of 100 g of the latex dispersion at 1% into a 100 mL graduated cylinder from a reservoir, following the principle of the Ross-Miles method (Ross & Miles, 1941).

## **2.8 Zeta potential of the latexes as a function of pH**

The zeta potential of the latexes was measured using a Malvern Zetasizer (Nano-ZS, UK). A latex sample was diluted with deionised water to a concentration of 0.01 and 0.1 wt zeta potential measurement.

## **2.9 Effect of pH on the stability of latexes**

The effect of pH on the stability of the latex dispersions was studied by measuring the Brookfield viscosity. A stress-controlled rotational rheometer (CVO, Bohlin Instruments, USA) with cone-plate geometry (R: 40 mm, angle: 4°) was used to measure the viscoelastic property. For this experiment the latex dispersions were diluted with deionised water to 40% and 27% for the emulsion-polymerized and SP latexes, respectively. HCl and NaOH solutions were used to change the pH of the latex dispersions.

## **2.10 Effect of salt concentration on the stability of latexes**

The effect of the salt concentration on the stability of the latex dispersions was studied by measuring the zeta potential and particle size distribution at different NaCl concentrations. The zeta potential and particle size were measured using a Malvern Zetasizer (Nano-ZS, UK). For this experiment the latex dispersions were diluted with deionized water to 0.1% in the NaCl solutions, which had

concentrations that ranged from 0 M to 4 M.

### **2.11 Effect of polyelectrolytes on the stability of latexes**

To study the effect of polyelectrolytes on the stability of the latexes, a cationic PAM was used. A solution with 1% cationic PAM was prepared and added to the latex dispersion at dosages of 0.005%, 0.01%, 0.05%, and 0.1% based on the weight of the latex dispersion. The latex and cationic PAM were mixed at a stirring speed of 400 rpm for 5 min and the low-shear viscosity (Brookfield viscometer, DV-2, USA) and particle size were measured.

### **2.12 Preparation of sizing solution**

A surface sizing solution at a solids content of either 5% or 16% was prepared by cooking oxidized starch slurries at a temperature of 95 °C for 30 min. Then the oxidized starch paste was cooled down to 65 °C and 3 or 5 parts of latex per 100 parts of starch was added to the starch solution. The mixture was then cooled down to 50 °C.

### **2.13 Starch film preparation**

To investigate the effect of the latex addition on the tensile property of the starch film, the prepared starch solution or the starch solution mixed with SP or S/B latex was poured in a polystyrene dish and dried in an oven at 50 °C under vacuum at 0.009 MPa.

## 2.14 Tensile property of starch film

The dried starch film with a thickness of  $\sim 100\ \mu\text{m}$  was carefully separated and cut for the tensile measurement. The samples were conditioned at 50% RH and 23 °C for 24 hours prior to testing. Tensile strength was measured using a Universal Testing Machine, Instron 5943 (Instron Int. Ltd., USA). The width and length of the samples were 15 mm and greater than 40 mm, respectively. The span length for the tensile testing was 30 mm. The oxidized starch films or starch films containing S/B or SP latexes were tested at a cross head speed of 3 mm/min. Figure 2-1 shows the starch samples for tensile measurement.



Fig. 2-1. Starch samples for the tensile strength measurement.

### **2.15 Surface sizing**

Surface sizing was carried out using an automatic bar coater (GIST Co. Ltd., Korea) on the base paper. The prepared sizing solution at a temperature of 50 °C was coated on the paper and then the sized papers were dried in a hot-air drying oven at 120 °C for 2 min.

### **2.16 Mechanical properties of surface sized papers**

The sized papers were conditioned at constant temperature of 23 °C and relative humidity of 50% for at least 24h. The tensile strength, bending resistance, and internal bond strength were determined according to TAPPI standards (T 1009 om-92, T 556 pm-95, T 569 pm-00).

### **2.17 Mill trial**

A Mill trial studied the effect of using the SP-M latex as a surface sizing additive, which was made at Moorim Paper Co. (PM1, Jinju, Korea) on a Fourdrinier type paper machine with a conventional inclined size press. The fiber composition of the base paper was 84% bleached hardwood kraft pulp, 4% bleached softwood kraft pulp, and 12% bleached chemi-thermomechanical pulp. The oxidized starch solution was cooked in a jet cooker and 2.9 pph of SP-M latex was added to the cooked starch solution and applied to the base paper with a basis weight of 198 g/m<sup>2</sup>. A high-grammage grade was used for the trial run because this would show the fold cracking phenomena more clearly. The mechanical properties of the sized papers were measured according to TAPPI standards. To investigate the distribution of the surface sizing starch in



the Z-direction of the sized papers, cross-sectional samples of the sized papers were prepared using razor blades. Then, the samples were immersed in a 0.1-M iodine potassium iodine solution for staining according to the method described by Lipponen et al. (2004). The cross-sectional images of the samples were obtained using a video microscope (i Megascop 1080 P, Alphastec Co., Anyang, Korea). The pre-coating color was prepared using coarse-grade GCC as a pigment. Additionally, 6 pph of S/B latex and 5 pph of starch were used as binders. The top-coating color was prepared using 90 parts of fine-grade GCC (Setacarb HG, Omya Korea) and 10 parts of clay (HYDROGLOSS® 90, KaMin) as the pigments. The S/B latex was used as a binder, along with some additives. The addition rate of the S/B latex was 7 pph. The coat weight was 26 g/m<sup>2</sup> for each side. After offset printing (RI-1, Akira, city, Japan) the coated papers with a black ink, a commercial folding machine (Stahlfolder Ti52, Heidelberg, Heidelberg, Germany) was used for folding. Images of the folded paper stack were taken for analysis. The fold cracked area of the paper was analyzed using Image Plus Pro software (Ver. 4.1, Media Cybernetics, Inc., Rockville, USA).

### 3. Results and discussion

#### 3.1 Characteristics of the sterically stabilized latex

The properties of the latexes used in this study are shown in Table 2-1.

Table 2-1. Properties of the latexes.

Latex	Solids (%)	pH	Average Particle Size (nm)	Viscosity (cP)	Gel content (%)	MC% of latex films
S/B	49.5	7.9	122	190	95.6	1.2
S/A	49.5	7.3	111	366	-	-
SP	35.0	7.4	70	23	98.8	5.5

The SP latex was synthesized using styrene, ethyl acrylate, butyl acrylate, acrylic acid and itaconic acid as monomers and stabilized by a protective shell. Protective shell of the SP latex contains starch and polyvinyl alcohol, which provide the steric protection of the latex dispersion. Figure 2-2 shows the TEM micrograph of SP latex particles. It clearly shows that the core polymer is surrounded by a protective layer.

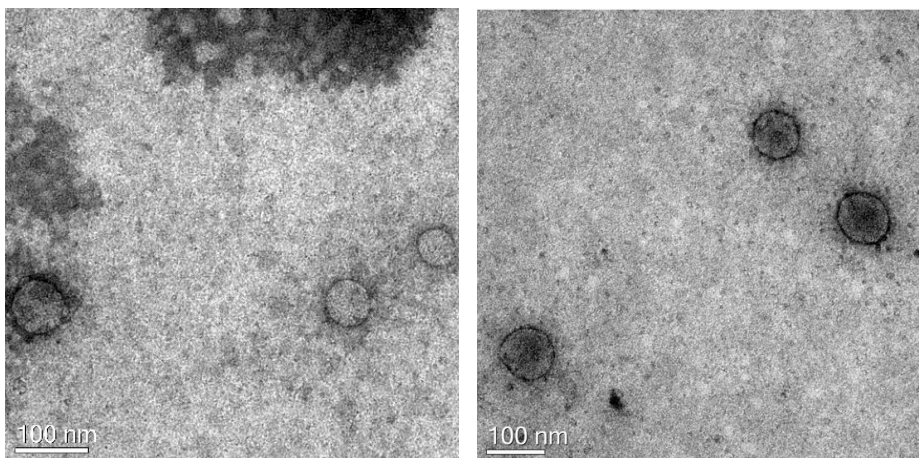


Fig. 2-2. TEM micrograph of the SP latexes.

Fig. 2-2 also shows that the SP latex particles are not uniform. This result agrees with the particle size distribution obtained by the Zetasizer (Fig. 2-3). The emulsion-polymerized latexes have more narrow size distribution than SP latex. However, all of the latex particles in Fig. 2-2 were smaller than 100 nm in diameter.

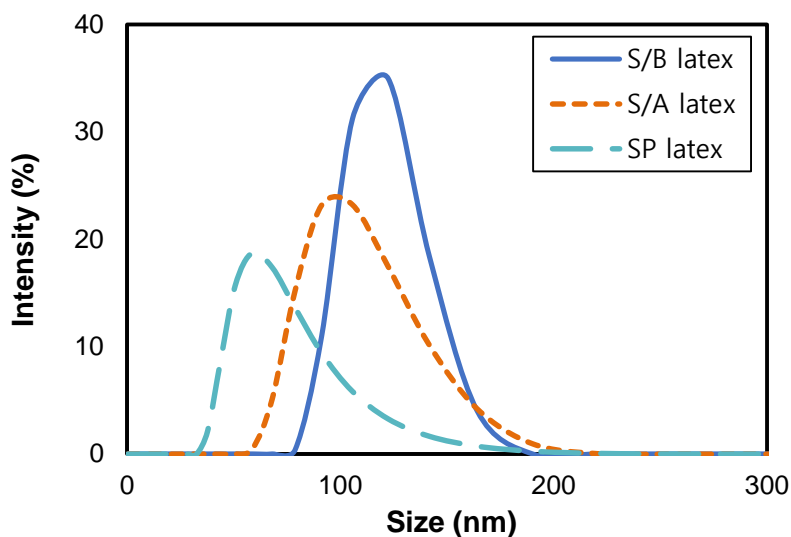


Fig. 2-3. Particle size distribution curves of S/B, S/A, and SP latexes.

FTIR spectra of the emulsion-polymerized latexes and SP latex are shown in Figure 2-4. S/B and S/A latexes were emulsion-polymerized and stabilized with surfactants. On the other hand, SP latex was stabilized with the use of a protective shell. Because both oxidized starch and PVA that were used as stabilizing agents in suspension polymerization are hydrophilic and contain a substantial amount of hydroxyl groups, the infrared spectrum of the SP latex showed a wide absorption band between  $3700$  and  $3000\text{ cm}^{-1}$  as shown in Figure 2-3.

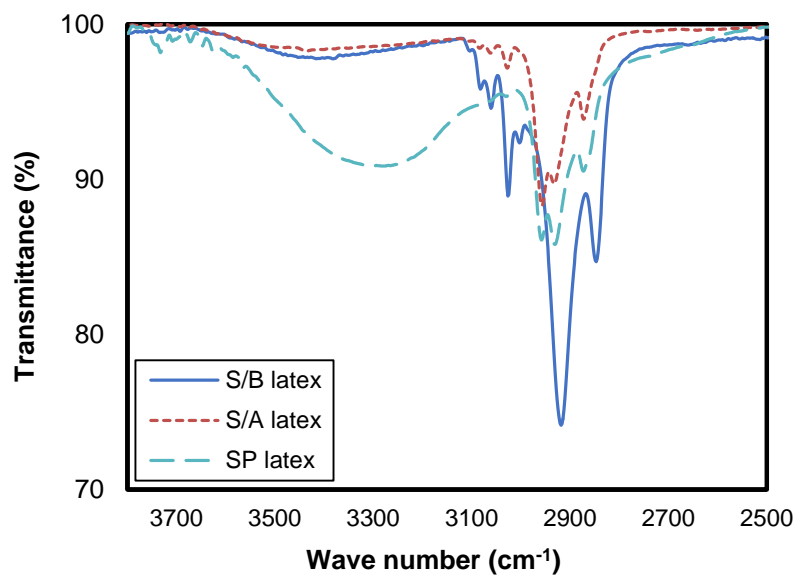


Fig. 2-4. FT-IR spectra of the latex films.

### 3.2 Surface tension and foaming tendency of latexes

The surface tension of the latexes as a function of latex concentration is depicted in Figure 2-5.

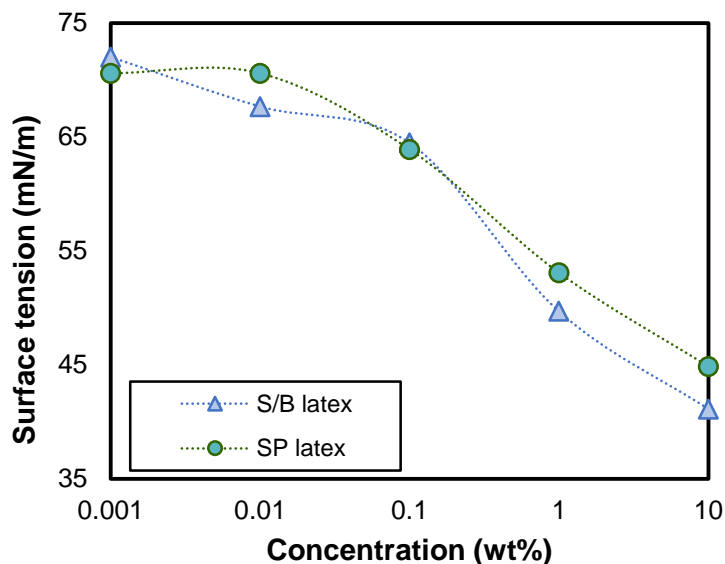


Fig. 2-5. Surface tension of latexes as a function of latex concentration.

In the case of S/B latex, the most important factor to reduce the surface tension is the surfactant because it orients itself to the air-water interface and reduces the energy required to expand the surface area of the latex for foam generation (Myers, 1999). SP latex showed a slightly higher surface tension compare to S/B latex but the surface tension reduced with a similar trend to S/B latex even though no surfactants were used in polymerization. The surface tension was decreased by the presence of oligomers or PVA, which contained both hydrophilic and hydrophobic parts and behaved like surfactant molecules. Acrylic acid oligomers that contain hydrophilic ends are known to be very effective in reducing the surface tension of water (Burczyk, 2006; Sawada, 1998). Partially hydrolyzed PVA also carries both hydrophilic and hydrophobic parts and behaves like a surfactant in water and shows surface activity at the latex-medium interface (T. Tadros, 2015). The molecular structure of partially

hydrolyzed PVA is quite different from surfactants since the hydrophilic functional groups are randomly distributed along the chain, which makes it not so effective in foam stabilization.

It is known that surfactants enhance the stability of foam by adsorbing to the surface of bubbles, thereby increasing the elasticity of the surface (Butt, H., Graf, K., Kappl, M., 2013; Shaw, 1992). The foaming-tendency evaluation showed that S/A latex generated 34 mL of foam, and S/B and SP latexes generated around 25 mL of foam after draining of 100 mL latex samples. SP latex foams, however, broke up more rapidly than those of S/B and S/A latexes. After 60 s, the foam volumes of SP latex decreased to 10 mL. In contrast, the foam generated by S/B and S/A latexes remained stable after 60 s with only minimal breakage or loss in foam volume (Table 2-2). This indicates that SP latex would be less likely to cause foaming problems during surface sizing.

Table 2-2. Foam stability of latexes.

Latex	Foam volume (mL)	
	0 s	60 s
S/B	25	24
S/A	34	22
SP	26	10

### 3.3 Chemical stability of latexes

Emulsion polymerization is a method widely used for the preparation of S/B and S/A latexes. Because surfactants with charged functional groups are used

for the stabilization of emulsion-polymerized latexes, it is possible to keep latex particles dispersed for several months. However, the stability derived from electrostatic repulsion would be lost if the latex dispersion is exposed to an environment containing counter ions, which neutralize electrostatic charges. It was shown that the stability of emulsion-polymerized latex is lost and coagulation or gelation occurs when the pH of the latex is decreased to acidic conditions. In contrast, SP latexes maintain their stability over a wide range of pH conditions because they are stabilized not by electrostatic repulsion, but through steric hindrance by the adsorbed polymers. The chemical stability of the latex particles is affected not only by the pH change, but also by the addition of polyelectrolytes.

The zeta potentials of the latexes as a function of pH were measured and are depicted in Figure 6. The emulsion-polymerized latexes were more strongly charged across the entire pH range examined. The SP latexes showed less negative zeta potentials at all pH values. Due to protonation of the carboxyl groups of the protective colloids at low pH, the isoelectric point of the SP latex approached at pH 2 as shown in Figure 2-6 (Cadena et al., 2009).



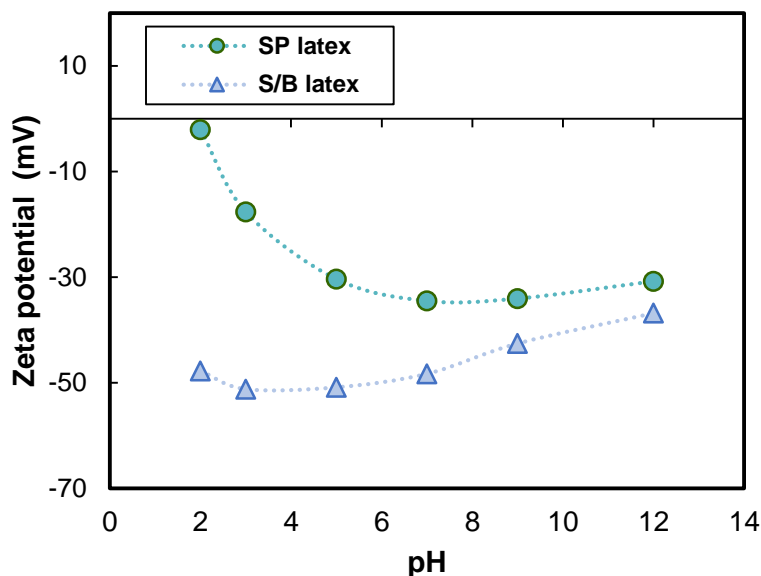


Fig. 2-6. Zeta potential of latexes as a function of pH.

The stability of the S/B and SP latexes was studied by measuring the viscosity at several pH levels (Figure 2-7). Even though the zeta potential of the S/B latex was greater than that of SP latex, it was stable only in the neutral pH range from pH 6 to 9. In acidic pH, S/B latex formed agglomerates and the dispersion became completely gelled, indicating that S/B latex lost its chemical stability in acidic conditions. In alkaline pH, the viscosity of S/B latex increased rapidly due to the electrostatic repulsion between the ionized groups, which consequently swelled the latex particles and increased the volume fraction of the dispersed phase. The viscosity decreased again at pH > 11 due to the shielding of negative charges along the polymer backbone by excess counter ions (Blackley, 1997; Tirtaatmadja et al., 1997; Ye et al., 2013). This pH sensitivity of the S/B latex may cause problems with sticky deposition during the recycling of paper (Lee and Kim, 2006). Figure 2-7 also shows that the

viscosity of SP latex is independent of pH, because the steric protection by the colloidal shells is effective over a wide pH range (Roberts and Cameron, 2002). This clearly shows that the stability of SP latexes is less influenced by pH change than that of S/B latex.

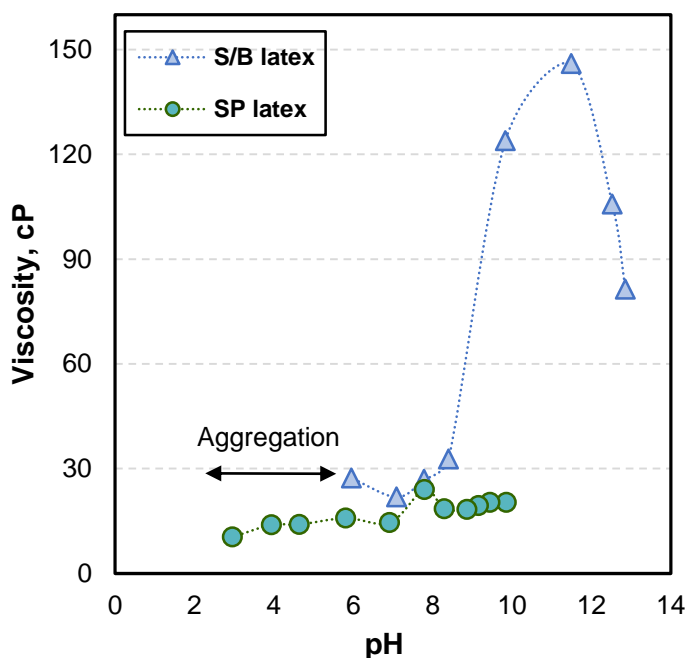


Fig. 2-7. Viscosity of latexes as a function of pH.

The viscosity of the latex dispersions as a function of shear rate is shown in Figure 2-8. SP latex showed the characteristics of a Newtonian fluid at all pH levels investigated. SP latex was slightly more viscous at higher pH, indicating some swelling of the latex core and more ionization of the protective shell under these conditions. The viscosity of S/B latex was independent of the shear rate at pH 7.1, while it was shear-dependent under alkaline conditions. S/B latex became more viscous as the pH increased to 11.5 and then less viscous again

when the pH reached 12.5, which is in very good agreement with the low-shear viscosity in Figure 2-7. The formation of temporary chemical junction networks at pH 11.5, which dissociate and re-associate dynamically, was suggested by Ye et al. (2013). At pH 12.5, the viscosity decreased due to the partial shielding of negative charge along the backbone of the polymer in the presence of excess counter ions. S/B latex showed shear thinning behavior in alkaline pH, indicating that the weak network of associating junctions was disrupted at shear values over  $10 \text{ s}^{-1}$ .

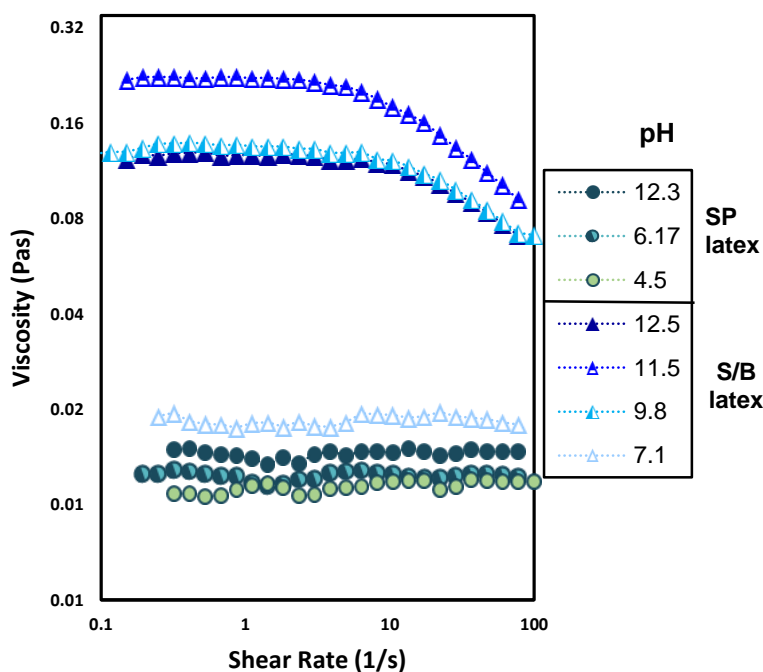


Fig. 2-8. Viscosity of S/B ( $\blacktriangle$ ) and SP ( $\bullet$ ) latexes at different pH levels as a function of shear rate.

The flocculation phenomena of the emulsion-polymerized latex have been

investigated by many research groups. Eriksson et al. (1993) have shown that latex particles are flocculated by cationic polymers that are adsorbed either through bridging between the latex particles or by charge neutralization. Feng et al. (2015) investigated the rate of flocculation of emulsion-polymerized latex particles and reported that the maximum flocculation rate was obtained immediately after the onset of mixing, and the flocculation rate gradually slowed down as adsorption progressed. They also showed that the initial rate of flocculation was minimized as the ionic strength increased.

The effect of the cationic PAM addition on the particle size and viscosity of the SP latex and S/B latexes is depicted in Figure 2-9. The addition of cationic PAM increased the viscosity of both latexes. In the case of the S/B latex, the viscosity increase was so substantial that it was not possible to measure the viscosity when the cationic PAM addition level was greater than 0.01%, which was attributed to the extensive flocculation of the latex by polymer bridging. The addition of cationic PAM to the SP latex dispersion also resulted in flocculation, but the steric stabilization of the SP latex prevented the formation of very large flocs. It has been known that steric stabilization provides the advantages of pH insensitivity and improved freeze-thaw stability (Ottewill et al. 1987).

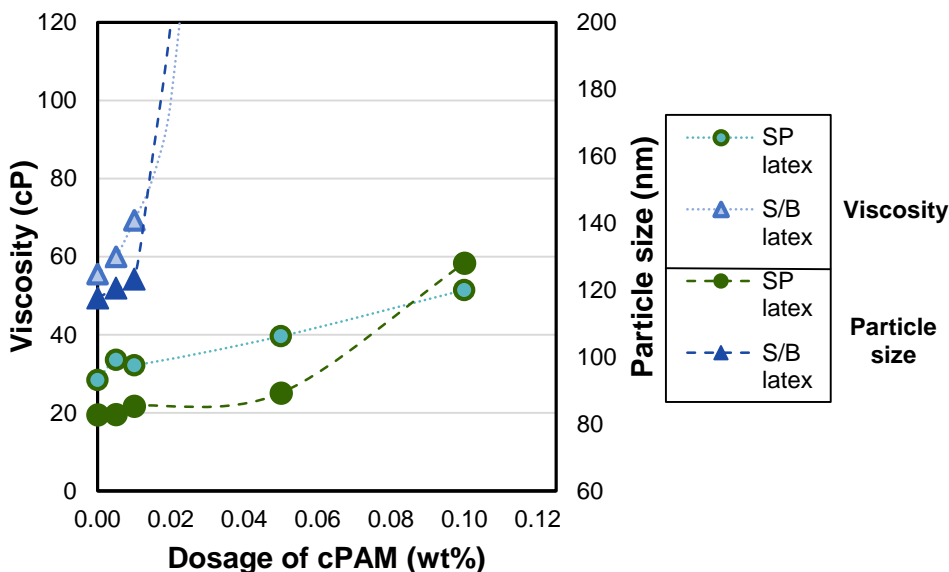


Fig. 2-9. Effect of the cationic PAM on the viscosity (open symbols) and particle size (closed symbols) of the S/B (▲) and SP (●) latexes.

The same phenomena occurred when the salt concentration increased. The effect of the salt concentration on the zeta potential of the latex is depicted in Figure 2-10. The zeta potential of the SP latex was less negative than that of the S/B and S/A latexes when there was no salt addition because the stabilization by low-charged polyelectrolytes was the dominant mechanism for the SP latex. With the addition of salt, the zeta potential decreased and approached the isoelectric point. The change in the zeta potential was more abrupt for the SP latex, which indicated that a lesser amount of counter ions is required for charge neutralization. The particle size distribution data of the S/B and S/A latexes showed that severe agglomeration of these latexes occurred at 4 M NaCl (Fig. 2-11). However, the particle size distribution curves for the SP latex showed that less agglomeration occurred (Fig. 2-12), which was because of the steric and colloidal stabilization mechanism of the SP latex. Ishikawa et al. (2005),

who investigated the effect of pH and salt concentration on the zeta potential, also showed that the total potential energy of interaction between pairs of latex particles changed by altering the salt concentration and pH and found that the steric stabilization provided greater stability for the latex. The chemical stability of the latex particles is important because the salt or polyelectrolytes contained in the base paper dissolves into the sizing solution when the hot paper web passes through the hot sizing solution or comes into contact with the surface sizing films.

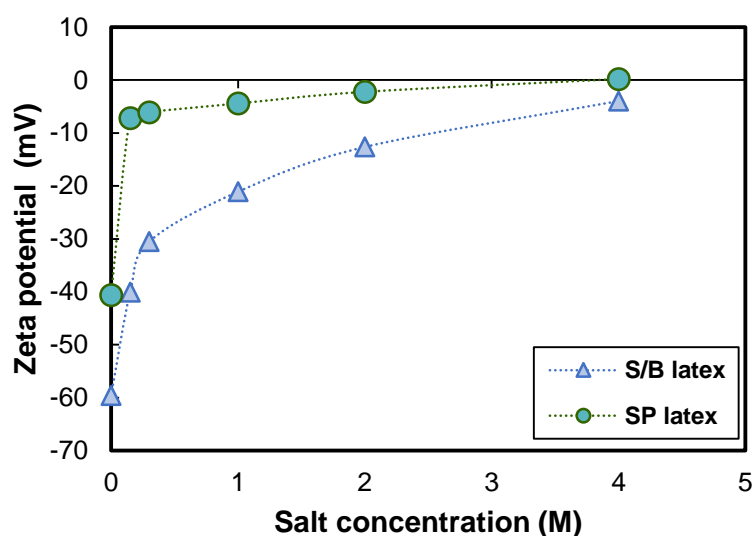


Fig. 2-10. Zeta potential of the latexes as a function of the salt concentration.

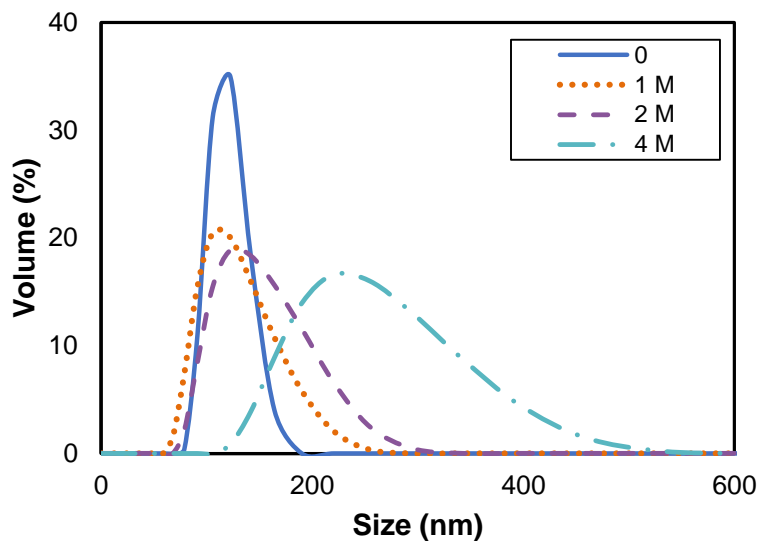


Fig. 2-11. Particle size distribution (PSD) curves for the S/B latex at four different salt concentrations.

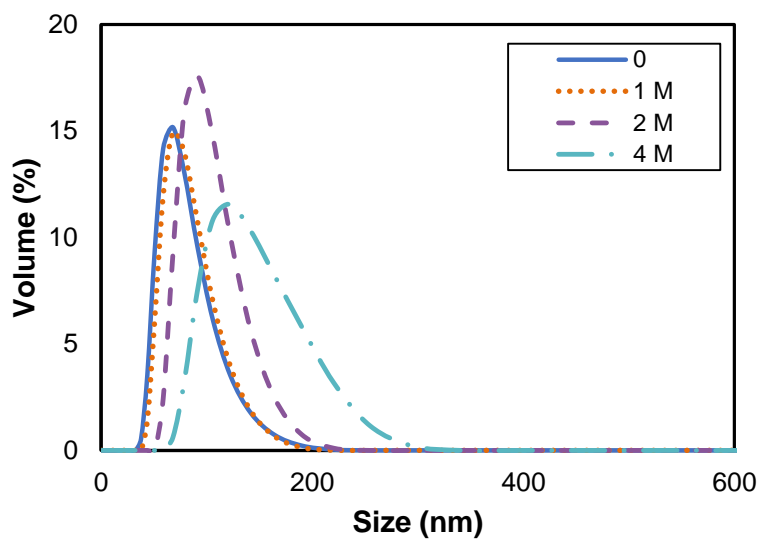
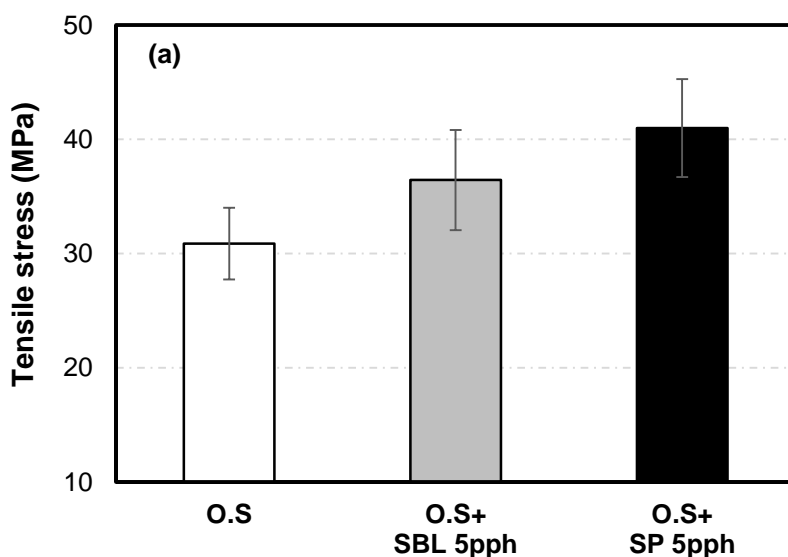


Fig. 2-12. Particle size distribution (PSD) curves for the SP latex at four different salt concentrations.

### 3.4 Tensile properties of starch films

To examine the strength and stretch properties of starch films without the influence of the base paper, films were prepared by drying the sizing solutions in petri dishes, and film properties without variability caused by the base sheet were measured. The tensile stress, elongation at break, and modulus of elasticity (MOE) of the starch films prepared with and without the latex additives are shown in Figure 2-13. The moisture content of the starch films containing 0 and 5 parts of SP latex after conditioning at was 11.2 % and 10.2 % respectively.





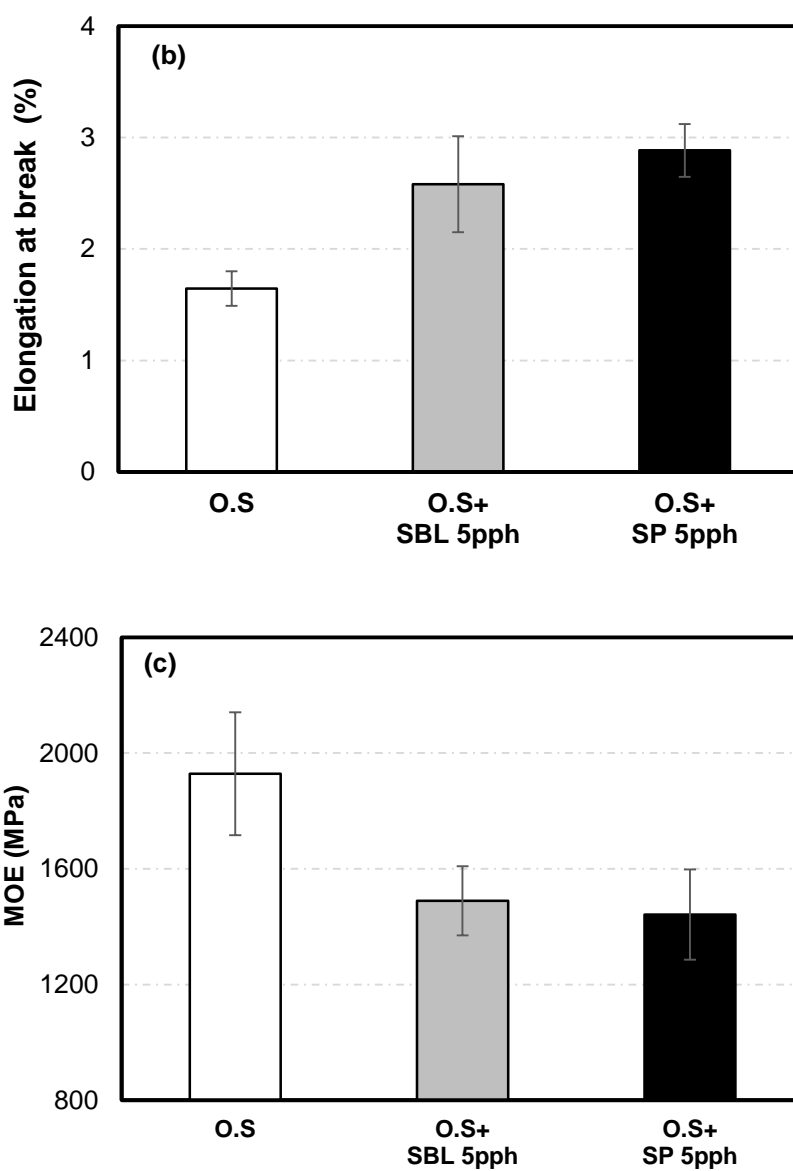
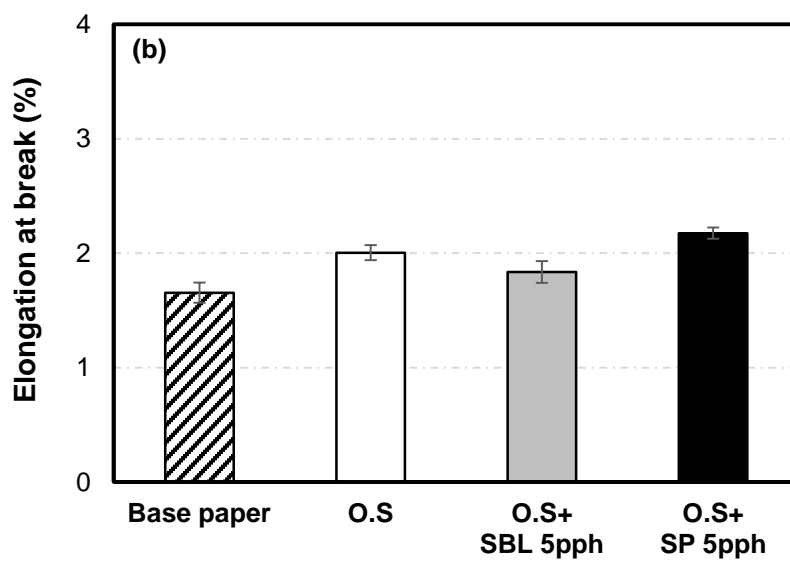
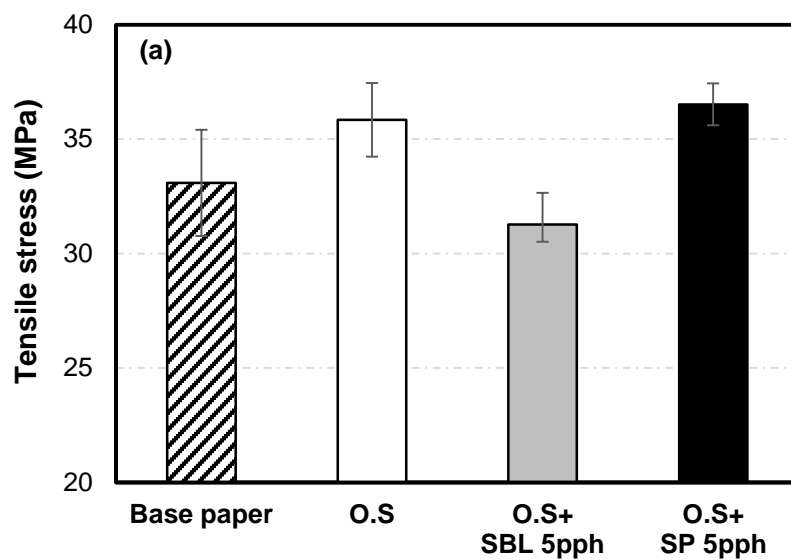


Fig. 2-13. Tensile stress (a), elongation at break (b) and MOE (c) of the starch films prepared with 5 ppH of S/B and SP latex; O.S. (oxidized starch).

Addition of 5 pph of the S/B and SP latexes resulted in higher tensile strength and elongation at break of starch films. The SP latex showed greater improvement in both the tensile strength and elongation at break. This showed that the use of SP latex would have a positive effect in improving the tensile and elongation properties of paper after surface sizing, which was attributed to the monomer composition of the SP latex. The protective shell of SP latex contains starch and PVA, which provide advantages in strength development. Oh et al. (2016) found that S/A latex has a greater extensional property than S/B latex, which is advantageous in decreasing fold cracking of coated paper.

### **3.5 Properties of surface sized papers**

To study the effect of latex addition on the paper properties, a starch solution with a solids content of 16% with and without the latex additives were prepared and applied onto a base paper using a laboratory bar coater. The pickup weight was 3.3 g/m<sup>2</sup> for all of the samples. The viscosity of the starch solutions was 30.1 cPs, and it changed to 28.0 cPs and 26.5 cPs when 5 pph of the S/B and SP latexes were added, respectively. Figure 2-14 shows the tensile stress, elongation at break, and MOE of the surface sized papers with and without the latex.



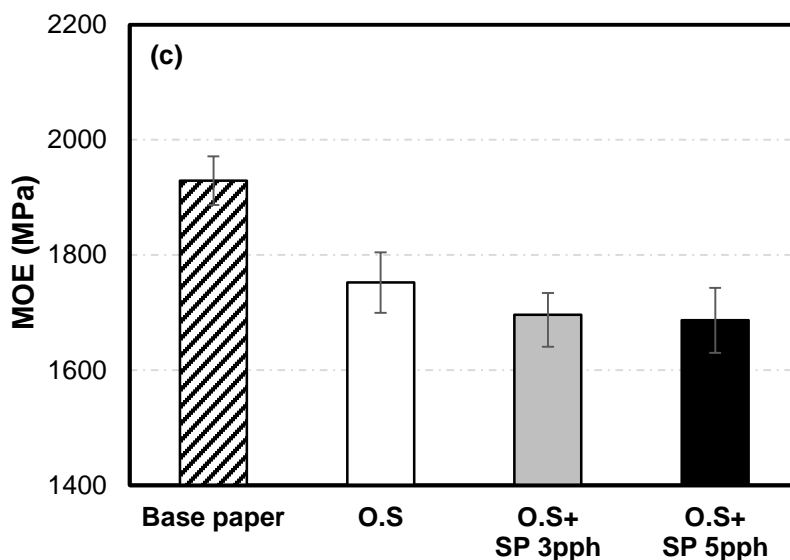


Fig. 2-14. Tensile stress (a), elongation at break (b) and MOE (c) of the base paper and sized papers with O.S. (oxidized starch) and 5 pph of the S/B and SP latex for the machine direction (MD).

Figure 2-14 shows that the tensile and elongation at break of the surface sized paper in machine direction (MD) increased after surface sizing with starch. When 5 pph of SP latex were used, the tensile stress increased further. In contrast, the addition of S/B latex decreased the tensile stress. The same trend was obtained for the elongation at break. The MOE of the sized papers decreased with the use of SP latex, which indicated that the SP latex improved the flexibility of the paper after surface sizing. Higher tensile and better extensional properties obtained because the SP latex is stabilized by a protective shell containing starch and PVA which have good compatibility with sizing solution and cellulosic fibers on the paper surface. A film of PVA is flexible and have high tensile strength (Bajpai, 2015; Miller and Klein, 1998). Therefore, the addition of PVA to starch improves the strength and flexibility of starch

products (Cinelli et al., 2006; Shogren et al., 1998). SP latex stretched more under tension due to the substitution of butadiene monomer with acrylate monomer. Increases in the tensile stress and elongation at break are highly favorable for decreasing fold cracking (K. Oh et al., 2015).

Mechanical properties of sized papers in the cross machine direction (CD) are shown in Table 2-3. Surface sizing with oxidized starch improved the tensile stress of the sized paper. In contrast to the machine direction, the addition of latexes had no noticeable effect on the tensile stress of the sized paper in the cross machine direction. When the paper is sized with oxidized starch, the elongation at break of the sized papers reduced indicating less flexibility of the sized papers. The MOE of sample sized with only oxidized starch increased revealing the stiffness of the sized papers also increased. Starch is a brittle polymer with a high glass transition temperature ( $T_g$ ) and forms a rigid and brittle film after drying (Orford et al., 1989). Addition of S/B and SP latexes to oxidized starch solution resulted in higher elongation at break and lower MOE. Compared with S/B latex, when SP latex was added to the starch solution, sized papers with a higher extension and lower elastic modulus were obtained. This showed that the use of SP latex would have a positive effect in improving the flexibility of the paper after surface sizing compared to the case of S/B latex.

Table 2-3. Properties of base paper and surface sized papers with O.S. (oxidized starch) and 5 pph of the S/B and SP latex for the cross machine direction (CD).

	Base paper	O.S.	O.S. + 5 pph S/B latex	O.S. + 5 pph SP latex
Tensile stress (MPa)	20.3	22.1	22.1	21.3
Elongation at break (%)	4.8	4.1	5.5	6
MOE (MPa)	426.6	525.6	398.8	342.6

Because the SP latex showed substantial improvement in the tensile strength and elongation at break at the 5-pph addition rate, the possibility of reducing the SP latex dosage was tested. Table 2-4 shows the tensile index, bending stiffness, and internal bond strength of the paper after surface sizing with 3 pph and 5 pph of SP latex as the surface sizing additive. Starch and PVA, which were used as protective colloids for SP latex, appeared to provide advantages in strength development. These stabilizers enhanced the mechanical properties of the sized paper by the formation of hydrogen bonds with the surface sizing starch and base paper fibers. The 3-pph dosage showed similar levels of improvement in the tensile strength and bending stiffness as at 5 pph.

Table 2-4. Properties of the surface sized paper with SP latex additive.

	Oxidized starch only		O.S. + 3 pph SP latex		O.S. + 5 pph SP latex	
	MD	CD	MD	CD	MD	CD
Tensile Index (Nm/g)	51.1	33.9	55.9	34.6	54.2	33.7
Bending Stiffness (mNm)	1.7	1.0	1.8	1.0	1.8	0.9
Internal Bond Strength (J/m <sup>2</sup> )	-	176.4	-	181.6	-	205.3
Elongation at break (%)	2.0	4.1	2.1	4.8	2.1	5.4

### 3.6 Mill trial and fold crack

The laboratory experiments showed that the addition of SP-M latex did not negatively affect the viscosity, chemical stability, and foaming. Table 2-5 shows the properties of the coating base stocks that were produced from PM1 by Moorim Paper Co. The paper was surface sized either with conventional oxidized starch or with a starch solution containing 2.9 pph of SP-M. The bulk density of the surface sized papers with and without SP-M were 1.27 cm<sup>3</sup>/g. The tensile strength and stretch increased when SP-M was used as a surface sizing additive, which decreased the stiffness in both the machine direction (MD) and cross-machine direction (CD). The internal bond strength also increased when SP-M was added to the sizing solution. This indicated that some reduction in the fold cracking may be achieved by using SP-M as a surface sizing additive.

Table 2-5. Properties of the base paper surface sized with and without SP-M latex.

Property	Oxidized Starch Only		2.9 pph of SP-M	
	MD	CD	MD	CD
Tensile Strength (kN/m)	7.93	5.57	9.10	5.38
Stretch (%)	2.54	7.95	3.55	8.06
Stiffness (g·cm)	52.5	34.7	46.9	26.1
Internal Bond Strength (J/m <sup>2</sup> )	118.6	124.9	122.7	127.3

The cross-sectional images of the papers sized with oxidized starch only and oxidized starch with 2.9 pph of SP-M latex were obtained using the microscope imaging system (Fig. 2-15). The addition of SP-M to the oxidized starch resulted in deeper penetration of the sizing solution into the base paper. This was attributed to the reduction in the viscosity of the sizing solutions with the latex addition. Deeper penetration of the sizing solution usually increases the tensile and internal bond strengths (Lipponen et al. 2003; Rajabi Abhari et al. 2017).



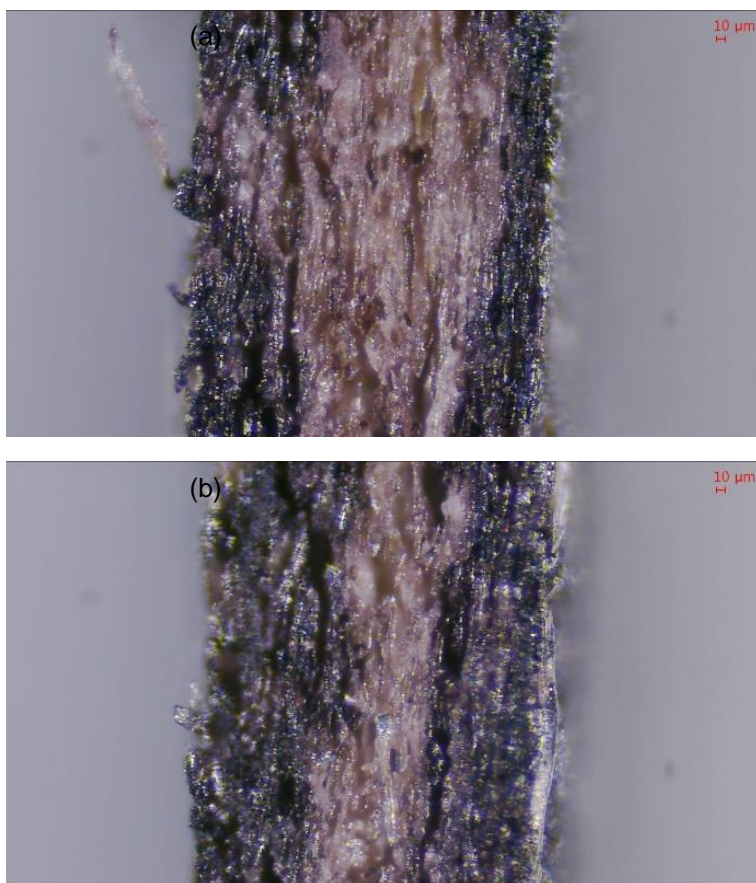


Fig. 2-15. Microscopic images obtained from the cross-section of papers sized with only oxidized starch (a) and oxidized starch containing SP-M latex (b).

The fold cracking measurement for the paper double-coated on an off-machine coater was done. The same coating color, coating condition, and coat weight were used in the trial production. The only difference was the use of SP-M latex as a surface sizing additive for the base paper. Solid printing with black ink was done on the double-coated paper using the offset printing machine, and then the folding of the printed papers using the commercial folding machine was done. Images of the folded areas were obtained, and the fold crack area was

determined. Table 2-6 shows that the trial samples, which were surface sized with 2.9 pph of SP-M latex as a surface sizing additive, showed less fold crack areas in both the MD and CD. When 2.9 pph of SP-M latex was used, the fold crack area in the MD decreased by 16% from 20.6% to 17.3%. In the case of CD folding, the reduction in the fold cracking was 27.5%.

Table 2-6. Percentage of fold crack areas and reduction percentage in the MD and CD.

Property	MD		CD	
	Control	Trial	Control	Trial
Fold Crack Area (%)	20.6	17.3	15.3	11.1
Reduction (%)	16.0		27.5	

The cross-sectional images of the folded samples were obtained and are shown in Fig. 2-16. Large coating layers were detached from the base stock surface sized with starch only. In contrast, the coating layer on the base stock surface sized with SP-M latex as an additive showed no large detachment of the coating layer. This was likely because of the improved flexibility of the starch layers on the base paper.

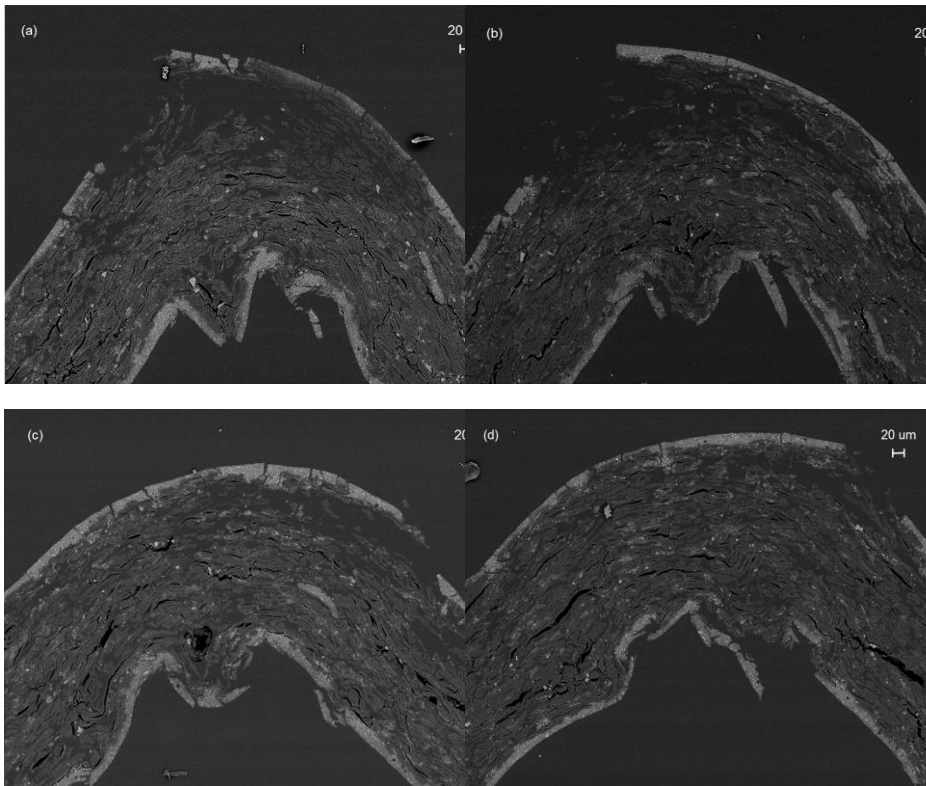


Fig. 2-16. SEM images of the fold cracked papers: (a and b) folded coated papers that were surface sized with starch only; (c and d) folded coated papers that were on the trial base stock surface sized with starch and 2.9 pph of SP-M latex.

## 4. Summary

In this research, sterically stabilized (SP) latexes were used as surface sizing additives. The physical properties of these latexes, including surface tension, foaming tendency were investigated and compared with conventional S/B and S/A latexes. It was found that, as the concentration of the SP latex increased, the surface tension reduced almost to a value similar to S/B latex. Partially hydrolyzed PVA in the protective shell of the SP latex carries both hydrophilic and hydrophobic part and increases the surface activity at the polymer-medium interface. The foaming tendency result showed that even SP latex gave similar foaming with S/B latex, the generated foams broke up more rapidly than S/B and S/A latexes. Hence it is expected use of SP latex would reduce the foaming problems during surface sizing.

The film formation and strength improvement by the surface sizing additives are important to obtain the desired effect of surface sizing. Hence starch solution with and without latexes was dried in petri dishes and the tensile strength and extensional properties of the films were measured. The result revealed that the addition of SP latex increased the tensile strength and strain while the MOE of the starch films reduced. This suggested that the use of SP latex would improve the extensional properties of sized paper.

The influence of SP latex as an additive on the mechanical properties of surface sized papers was also investigated. It was found that the SP latex improved the flexibility of sized paper compared with S/B latex, indicating the contribution of acrylate monomer in extensional properties of sized paper. The tensile strength and internal bond strength were also increased when SP latex

was used as a surface sizing additive. The protective shell of SP latex that contains starch and PVA which have good compatibility with both sizing solution and fibers in the paper, improved the formation of hydrogen bonds with starch and base paper. It is expected that a base paper with better strength and extensional properties would reduce the fold cracking tendency of the coated paper.

### **Chapter 3**

Suspension-polymerized latex as a cobinder for pigment coating- Influence on rheology of coating color and structure formation of coating layer

## 1. Introduction

Coating color, an aqueous mixture of pigments, binders, and other additives is applied on the surface of base paper to form a coating layer and to improve the optical and surface properties of paper. Porosity and void structure of the coating layer has a great influence on the optical and printing properties of the final coating (Oh et al., 2017; Tadros, 2014). Because the coating structure is strongly influenced by the components of the coating formulation and their proportions and interactions, diverse researches efforts have been made to find the influence of the coating components on coating structure. Not only the structure of dried coating layers but also the rheological properties of wet coating colors have significant effects on the quality of coated papers and coating operations. Coating technologists always try to optimize the coating formulation to improve their product quality and runnability. There are occasions, however, that the quality specification and process optimization cannot be met using conventional coating ingredients. When it is not possible to solve the quality and runnability problems using currently available ingredients, it is necessary to develop a new materials to meet the challenges.

Coating colors usually show a complicated viscoelastic behavior that affects the coating runnability, drying, and immobilization. Interaction between the components of the coating color affects the viscoelastic properties. The flocculation and microstructure formation in coating color restricts the mobility of the particles during drying and resulting in a more porous dried coating structure (Choi et al., 2015; Fadat et al., 1988; Oh et al., 2017). Suspension-polymerized latexes are sterically stabilized by protective colloids like starch, and PVA that affect the microstructure of the coating color and giving a more porous composite after drying of the coating layer.

In this study, a sterically stabilized suspension-polymerized acrylate latex (SP latex) with different amounts of an acrylic acid monomers were prepared and used as a coating cobinder. The effect of the acrylic acid monomer on physical properties such as viscosity, particle size, zeta potential of the SP latexes as a function of pH was studied. These SP latexes were used as cobinder and partially replaced with S/B latex in the coating color. The water retention and viscoelastic properties of the coating colors were evaluated to study the effect of acrylic acid on the microstructure of coating color.

The effect of SP cobinder dosage on viscoelastic properties of coating color was investigated. The sediment volume of coating color after centrifugation was also measured.

Finally, the coating colors containing different dosages of SP latex were applied on plastic film and the pore structure of coating layers was evaluated. Moreover, the surface characteristics of the coating layer were studied by FE-SEM microscopy and the optical properties of the coating layers containing SP cobinder, including opacity and brightness, were compared with that of a coating without SP cobinder.



## **2. Experimental**

### **2.1 Materials**

Three suspension-polymerized sterically stabilized latexes (SP-1, SP-2, and SP-3) were provided by SongKang Industrial Co. Styrene, methyl methacrylate, butyl acrylate, and acrylic acid monomers were used in polymerization and a protective shell containing polymeric stabilizers i.e. PVA and oxidized starch provided colloidal stability of the SP latexes. A commercial emulsion-polymerized styrene-butadiene (S/B) latex with a solids content of 50% and average particle size of 147 nm was used as a main binder (Trenseo, Korea).

Calcium carbonate and clay were used as pigments in this study. Ground calcium carbonate (GCC, Setacarb HG, Omya Korea) in slurry form and dry kaolin clay (HYDROGLOSS® 90) from KaMin were used as pigments. Poly(acrylic acid sodium salt) from Sigma-Aldrich Chemical Reagent Co., Ltd. with a molecular weight of 5100 was as a dispersing agent. HCl, and NaOH (1N) were purchased from Samchun for pH adjustment of the coating color. Deionized water was used in all the experiments. All of the chemicals and raw materials were used as received without any further modification or purification.

### **2.2 Transmission electron microscopy (TEM)**

Images of the latexes were obtained using a LIBRA 120 (Carl Zeiss) transmission electron microscope with an operation voltage of 120 kV. The latex particles were deposited on Formvar film coated grids and then the grids were exposed to a drop of uranyl acetate solution (UA) for 10 s for staining and

then washed for 1 s in two drops of DI water. The residual DI water was then removed by filter paper and the samples dried at room temperature.

### **2.3 Fourier transform infrared spectroscopy (FTIR)**

FT-IR spectra of the latexes were obtained using a Nicolet 6700 Spectrometer (Thermo Electron Corporation, USA) in attenuated total reflectance (ATR) mode in the range of 600–4000  $\text{cm}^{-1}$ . The latex film obtained after drying the latex in aluminum dishes at 70 °C was used for FTIR spectroscopy.

### **2.4 Preparation of latex dispersion at different pH**

Latex dispersions were diluted with deionized water to 38%. HCl and NaOH solutions were used to adjust the pH of the latex dispersions to 5, 7, and 9. Then the viscosity and viscoelastic properties of the latex dispersions with a solids content of 38% were determined. The latexes with a solids of 38% were diluted to a concentration of 0.1 wt.% and 0.01 wt.% with weak acid or base to pH of 5, 7, and 9 for zeta potential, and particle size measurement, respectively.

### **2.5 Preparation of coating color**

Formulation of the coating colors is shown in Table 3-1 and 3-2. The coating colors were prepared by mixing all the ingredients under vigorous stirring. The coating colors at solids contents of 65 wt.% and 62 wt.% were used for the evaluation of rheological properties of coating color and for the coating layer preparation respectively. Kaolin clay slurry was prepared by dispersing of the clay using 0.3 pph of poly(acrylic acid sodium salt), based on dry kaolin clay

in DI water. The kaolin then mixed with GCC first followed by the addition of S/B latex and SP latex (cobinder). The final pH of the coating color was adjusted to 9 using NaOH.

Table 3-1. Formulation of coating color for evaluation of the effect of acrylic acid monomer content of SP cobinder on the rheological properties of coating color.

Components		Amount (pph)
Pigment	GCC	80
	Clay	20
Binder	S/B latex	8
Cobinder	SP latexs	3
Solids content		65%
pH		9

Component amounts are written in parts per hundred (pph; by weight) based on 100 parts of pigments.

Table 3-2. Formulation of coating color for evaluation of the effect of S/B latex and SP cobinder substitution rate on coating layer preparation.

Components		1	2	3	4
Pigment	GCC	80	80	80	80
	Clay	20	20	20	20
Binder	S/B latex	11	10	8	6
Cobinder	SP latex	-	1	3	5

Component amounts are written in parts per hundred (pph; by weight) based on 100 parts of pigments.

## 2.6 Viscosity and viscoelastic measurement

Low shear viscosity of latexes and coating colors were measured at 100 rpm using a Brookfield viscometer (DV-2, USA). A stress-controlled rotational rheometer (CVO, Bohlin Instruments, USA) with a cone-plate geometry (R=40 mm, angle=4°) was used to measure the viscoelasticity of latexes and coating colors. Before those measurements, samples were pre-sheared at a shear rate of 10 s<sup>-1</sup> for 5 min, and a rest time of 10 min were applied before measurements.

## 2.7 Particle size and zeta potential evaluation

Particles size distribution (PSD) and zeta potential were measured by Zetasizer (nano-ZS, Malvern, UK). For particles size measurement, normal disposable plastic sample cells (Kartell, Italy) were used. For zeta potential measurement, specially designed disposable folded capillary cells (DTS1060, Malvern, UK) were used. An equilibrating time of 2 min was allowed before

the measurements and at least three measurements were made for each sample. Latex samples or coating colors were diluted with deionized water to 0.1 wt.% and 0.01 wt.% for zeta potential and particle size measurement, respectively.

## **2.8 Sedimentation of coating color**

The sediment volume of coating colors was measured to see the porosity of the sediment. 10 grams of sample was taken and injected into a 20 mL cylindrical plastic tube, followed by the centrifugation using a large capacity refrigerated centrifuge (Hanil scientific industrial, Korea) at 3000 G for 3h. After centrifugation, the supernatant of samples was removed and sediment volume of samples was recorded and compared.

## **2.9 Dewatering capacity analysis**

The dewatering profile of coating colors was investigated using an Åbo Akademi gravimetric water retention meter (ÅA-GWR, Kaltec scientific, USA). 10 mL of coating color was injected into a cylindrical vessel placed on a membrane (mixed cellulose ester membrane filter, pore size 0.2  $\mu\text{m}$ , Advantec, Taiwan) and blotter papers. Dewatering of the samples was performed under a pressure of 1.5 bar for 60 s.

## **2.10 Porosity of the coating layer**

The porosity of the coating composites (layer) was studied by mercury intrusion porosimetry (AutoPore IV 9500, Micromeritics Instruments Corporation). An applicator bar with a gap size of 100  $\mu\text{m}$  was used to apply

the coating color on a plastic film. The thickness of the PET film was 100  $\mu\text{m}$  and the wet coating layer was dried at ambient temperature. The thickness of the dried coating layer was about 20  $\mu\text{m}$ . Porosity and pore size distribution of the dried coating layer were studied by measuring the volume of mercury that intruded into the pores of the dried coating layer. The porosity of the sample was determined from the amount of intruded mercury. The pore size distribution from 10 to 1000 nm in diameter was obtained from the mercury intrusion porosimetry. The Washburn equation (Eq. 3-1) was used to obtain the pore diameter from the external pressure data.

$$P = \frac{-4\gamma \cos\theta}{d} \quad \text{Eq. (3-1)}$$

Where  $P$ ,  $\gamma$ ,  $\theta$  and  $d$  are the external pressure, the surface tension of mercury, contact angle and the pore diameter respectively.

## **2.11 Surface properties of coating layer**

The roughness of the coating layer was measured using a Parker Print Surface (L & W, Sweden). The coating layer surface was carried out using a field-emission scanning electron microscope (FE-SEM, AURIGA, Carl Zeiss).

## **2.12 Optical properties of coating layer**

Brightness and opacity were determined by a L&W spectrophotometer (ABB, Sweden).

### 3. Results and discussion

#### 3.1 Characteristics of the latexes

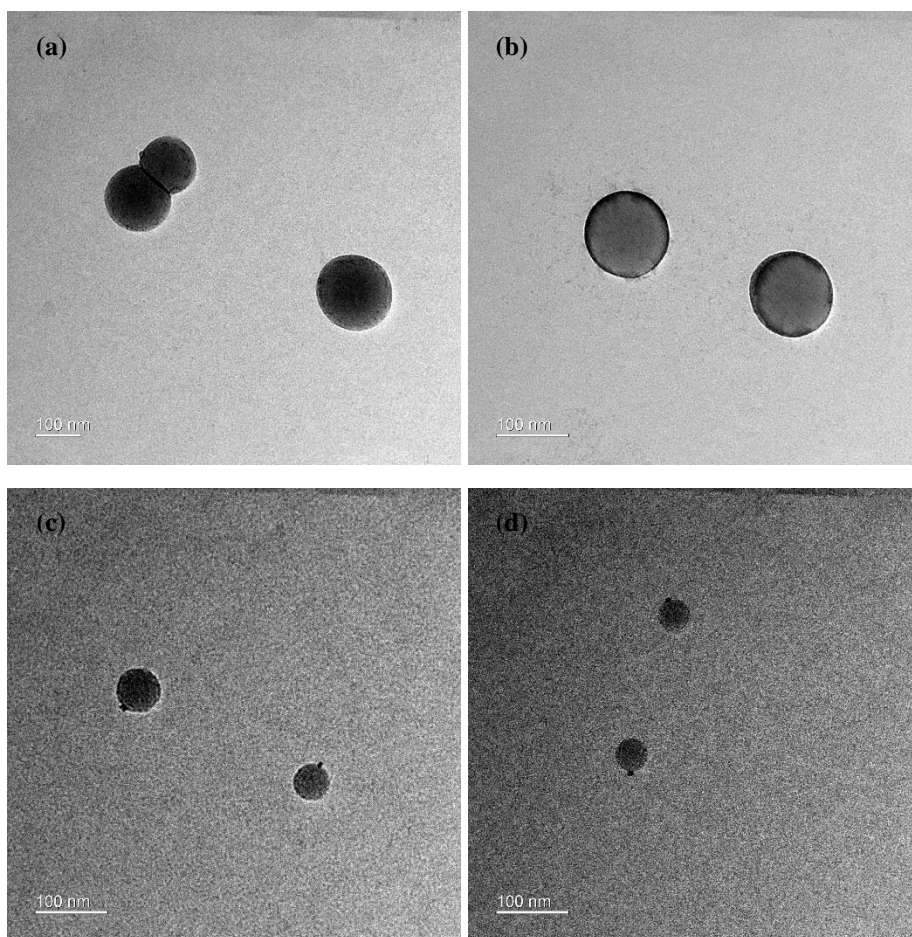
The properties of the SP latexes used for this study including solids content, pH, average particle size, viscosity, and acrylic acid content are shown in Table 3-3.

Table 3-3. Properties of the SP latexes.

Latex	Solids (%)	pH	Viscosity (cP)	Acrylic acid (%)
SP-1	48.6	6.1	136	5
SP-2	48.0	6.5	201	10
SP-3	49.1	6.5	400	15

The SP latexes were synthesized using styrene, methyl methacrylate, butyl acrylate, acrylic acid as monomers and stabilized by a protective shell. Protective shell of the SP latex contains starch and polyvinyl alcohol which provide the steric protection of the latex dispersion. The weight ratio of the protective shell and core polymer, starch/PVA ratio in the protective shell, and the amount of acrylic acid monomer affect the hydrophilicity of the SP latexes. In addition to hydrophilicity, the carboxylic groups (-COOH) of acrylic acid monomer could expand the polymer backbone by deprotonation under the alkaline conditions and influence the SP latex particle size and consequently affect the volume fraction and rheological properties of SP latex dispersion and coating color. The SP latexes having the same protective shell component but different amounts of acrylic acid monomer were used in the experiment. Figure

3-1 shows the TEM micrograph of S/B latex and SP latex particles.





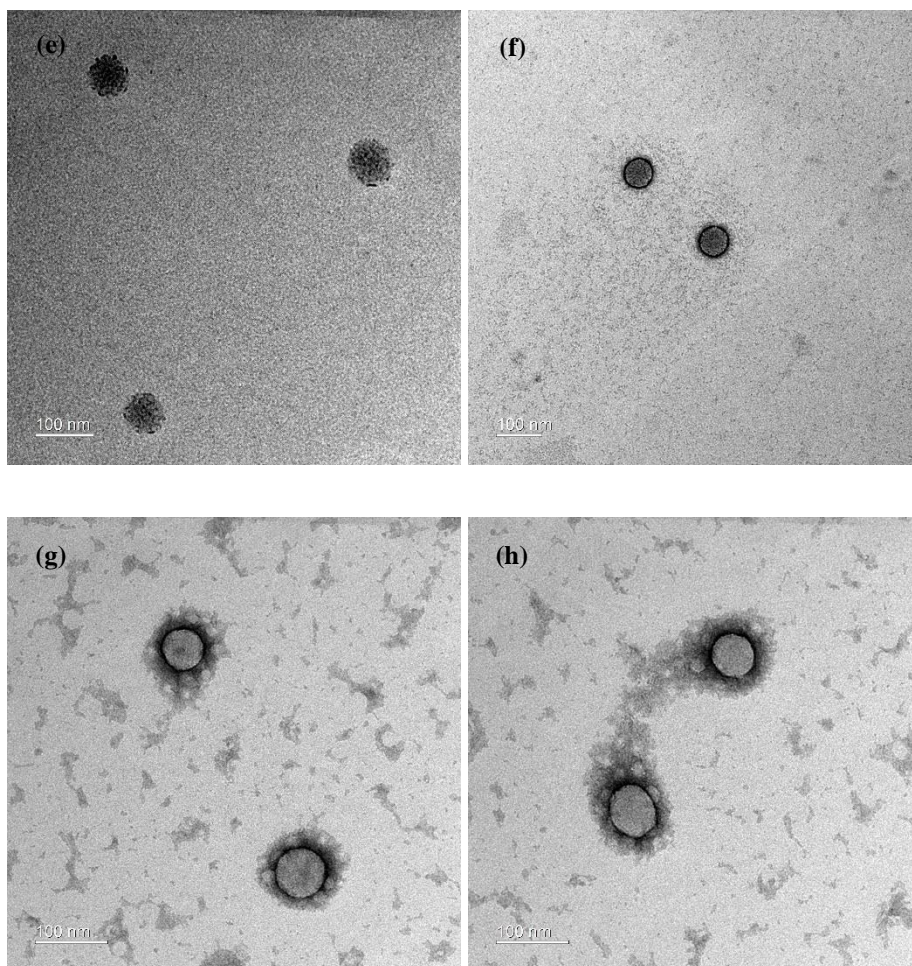


Fig. 3-1. Particle shape of S/B (a and b), SP-1 (c and d), SP-2 (e and f), and SP-3 (g and h) latexes.

FTIR spectra of the S/B and SP latexes are shown in Figure 3-2. S/B latex was emulsion-polymerized and stabilized using surfactants. On the other hand, SP latexes were stabilized with the use of the protective shell. Because both oxidized starch and PVA, which were used as polymeric stabilizers, are hydrophilic, the infrared spectrum showed a wide absorption between 3700 and

3000  $\text{cm}^{-1}$  due to the presence of hydroxyl groups as shown in Figure 3-2.

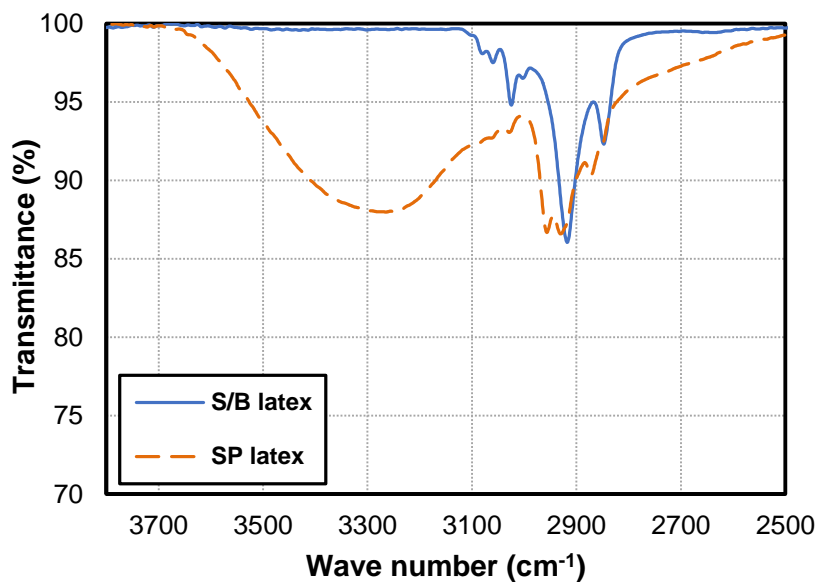


Fig. 3-2. FT-IR spectra of the latex films.

### 3.2 Viscosity and particle size distribution of SP latexes as a function of pH

Viscosity of the sterically stabilized acrylate cobinders was measured as a function of pH with a Brookfield viscometer using a spindle number of 1, 2, and 3. The result is shown in Figure 3-3.

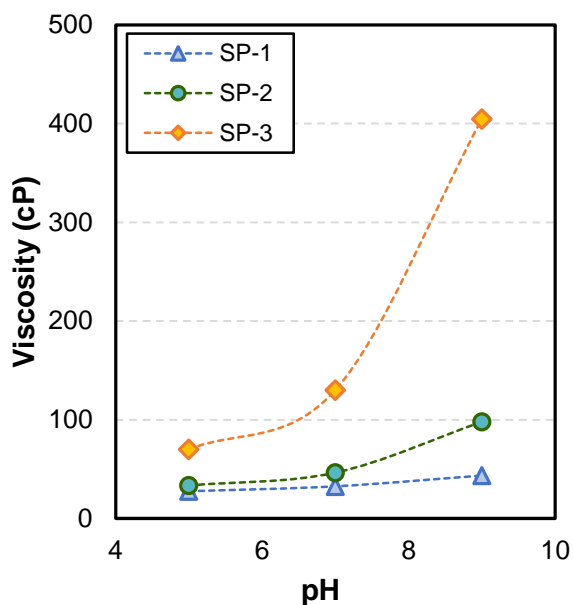


Fig. 3-3. Viscosity of the SP latexes depending on pH.

As the pH of the SP latex increased, the viscosity increased as well. The suspension-polymerized latex is sterically stabilized by polymeric stabilizers which consisted of hydrophobic and hydrophilic segments. The hydrophilic segment of starch and polyvinyl alcohol will swell or expand in water. Addition of alkali to starch solution causes a swelling or expansion of starch molecules that results in an increase in the viscosity of starch solution (Roberts & Cameron, 2002). Under the alkaline condition, starch that consists of the protective shell of the SP latex swells and increases the volume fraction of the dispersed phase and results in a higher viscosity of SP latex. Moreover, the carboxylic groups ( $-\text{COOH}$ ) of the acrylic acid are deprotonated, leading to an electrostatic repulsion which expands the polymer core of the latex. This polymer expansion results in an increase of the volume fraction of the latex, and consequently result in an increase in viscosity of the acrylate cobinder.

It was also found that when the SP latex contained more acrylic acid monomer, the viscosity increment was more pronounced as SP-3 latex at pH value of 9 showed the highest viscosity. This happened because more carboxyl groups were contained in SP-3 and they deprotonated and enhanced the repulsion of the ionized groups within a SP latex particle, which increases the electrostatic repulsion of the polymers especially at higher pH levels. However, it must be pointed out that some parts of the hydrophilic protective shell of the cobinder particles may dissolve in aqueous phase under alkaline condition and be partly responsible for the increase of viscosity.

### **3.3 Particle size distribution of SP latexes as a function of pH**

To examine whether the viscosity of SP latex dispersions was influenced by the latex particle swelling due to the deprotonation of carboxylic groups, the particle size of the latex dispersions were evaluated at different pH levels by dynamic light scattering method (DLS). Figure 3-4 shows the average particle size of the SP latexes.

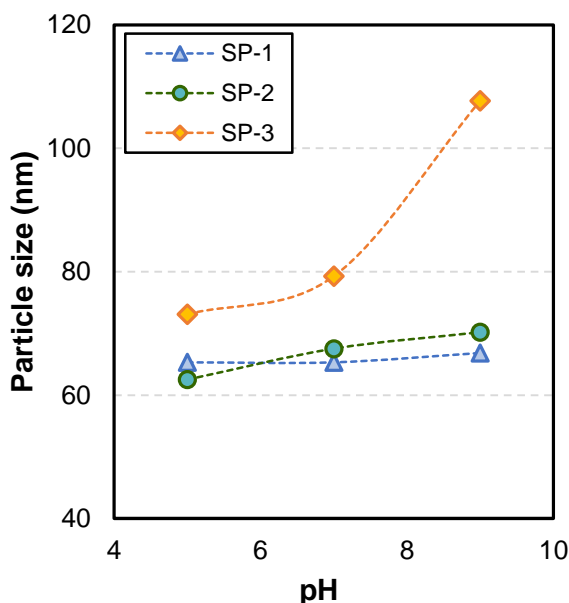
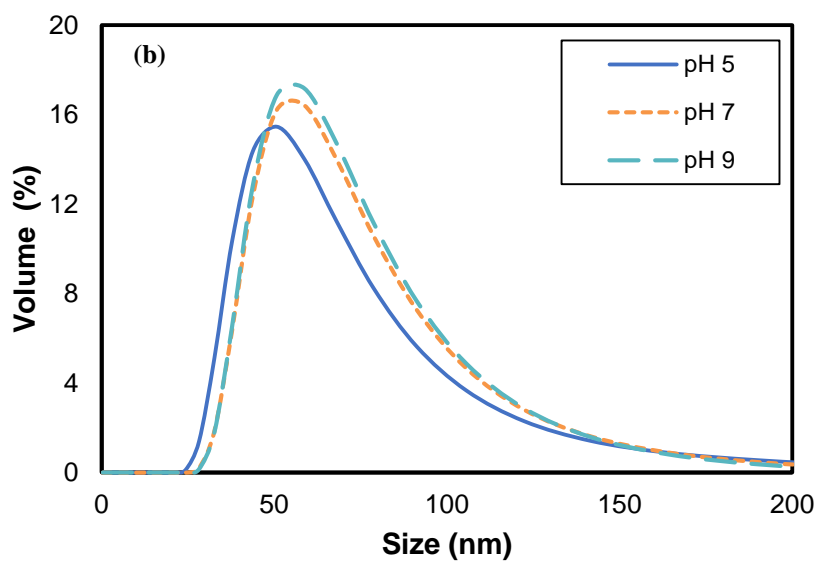
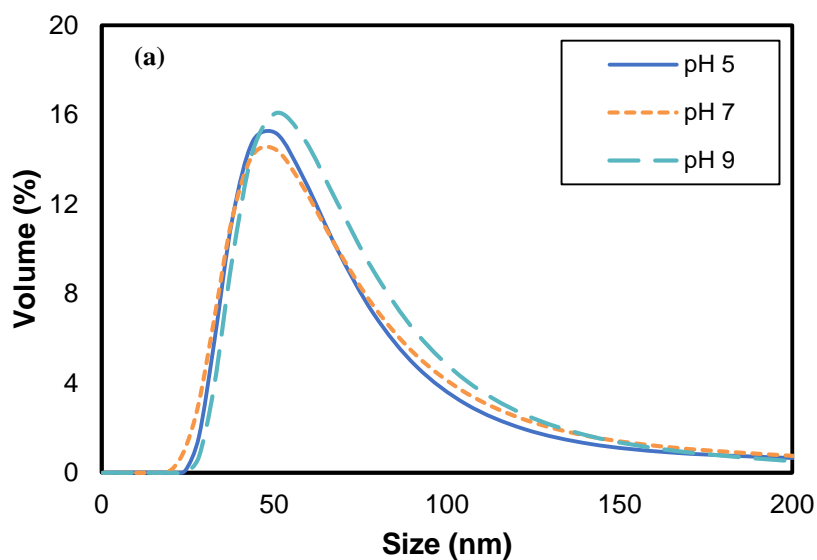


Fig. 3-4. Average particle size of the SP latexes depending on pH.

As the pH of the SP latex dispersions was increased, the average particle size increased as well. It can be explained by two reasons. Firstly, the protective shells of the SP latexes that contain starch and PVA absorb water and swell. Secondly, carboxylic groups of acrylic acid are deprotonated, which result in an electrostatic repulsion and expansion the polymer backbone. The volume fraction of the SP latexes increased as a result of the polymer expansion. It was also found that SP-3 that had a greater acrylic acid content showed higher particle size than SP-1 and SP-2. The swelling of the SP-3 was more pronounced compared with that of SP-1 and SP-2 which reveals the importance of acrylic acid in water absorption and swelling. This result agrees well with the result of viscosity shown in Fig 3-3.

As it is shown in Figure 3-5, pH influences the particle size distribution of the

SP latexes. When the pH of SP latex dispersions changed from acidic to alkaline, wider particle size distribution was obtained due to the particle swelling.



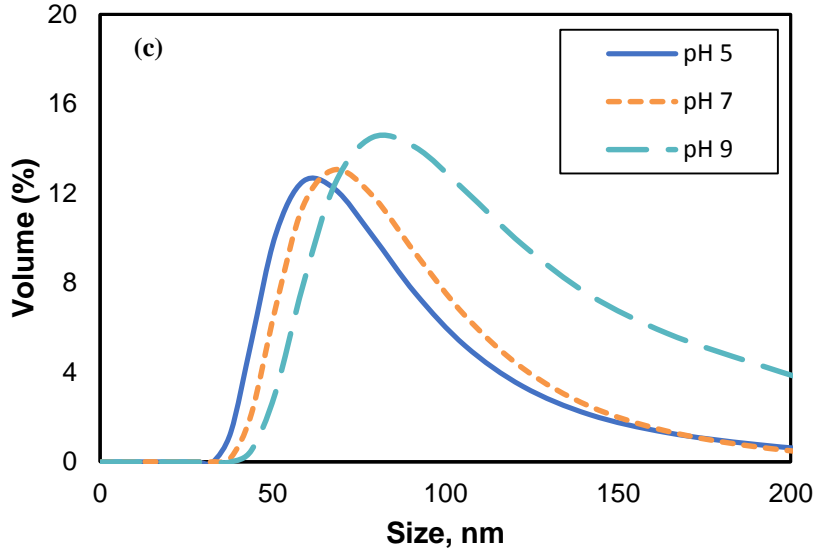


Fig. 3-5. Particle size distribution of SP-1 (a), SP-2 (b), and SP-3 (c) latexes depending on pH.

The DLS (dynamic light scattering) results showed that average particle size of the latex dispersions at pH 9 was larger than that at pH 5. The DLS or photon correlation spectroscopy measures the size of a nanoparticle when it is diffusing within a fluid dispersion. Hence the calculated size is referred to as the hydrodynamic diameter (Bhattacharjee, 2016). Hydrodynamic diameter can be derived from translational diffusion coefficient as shown in Stokes-Einstein equation (Eq.3-2)

$$d(H) = \frac{kT}{3\pi\eta D} \quad \text{Eq. (3-2)}$$

Where  $d(H)$ ,  $D$ ,  $k$ ,  $T$  and  $\eta$  are the hydrodynamic diameter, translational

diffusion coefficient, Boltzmann's constant, absolute temperature, and viscosity respectively. The hydrodynamic size is dependent on the size of nanoparticle, surface structure and charge, ionic strength of the aqueous phase of the dispersion (Bhattacharjee, 2016; Malvern Instruments, 2015).

To check the actual particle size of the SP latexes, dispersion of SP latexes were prepared at pH values of 5 and 7 and the latex particles were observed using TEM. The average particle size of SP-1 and SP-2 obtained by DLS showed that the differences in average particle size of the SP-1 and SP-2 at pH 5 and 7 were only 2 nm and 7 nm, respectively. Because of the polydispersity of the latexes, it was not easy to see the differences in size of these latexes i.e., SP-1 and SP-2, by electron microscopy. However, the electron micrograph of the SP-3 samples revealed that the size of this latex increased when the pH of the dispersion adjusted to 9 (Figure 3-6). The particle size determined using TEM, however, is not equal to the particle size in aqueous state.

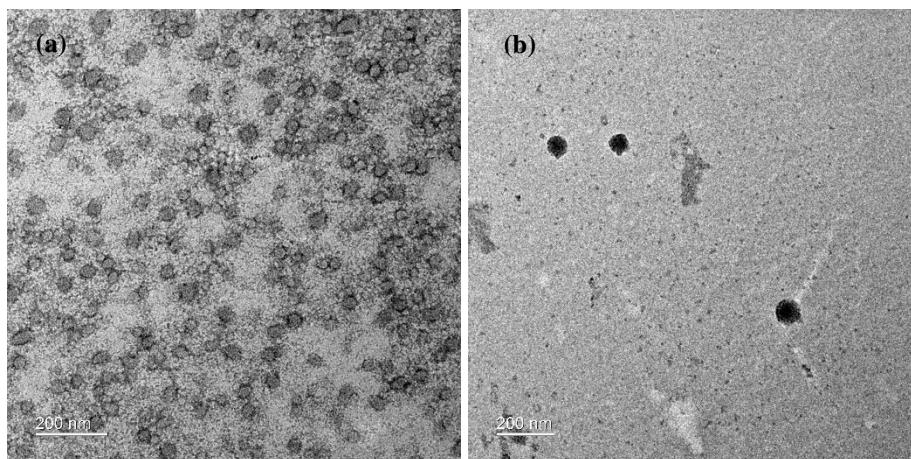


Fig. 3-6. Particle shape of SP-3 at pH of 5 (a) and 9 (b).



The average size of the SP-3 latex particles measured using Image J software pH 5 and pH 7, were 34.17 nm and 79 nm respectively. It is not surprising that the average particle size obtained from the image analysis of TEM micrograph using Image J was smaller than that of obtained from DLS method. The SP latex particles did not have a narrow particle size distribution. The DLS gives the average value after measuring plenty of SP latex particles. However, the number of particles that can be observed using TEM is limited. Furthermore, the swollen latex particles would dry and shrink under the electron beam of the TEM and UHV (ultrahigh vacuum). Moreover in the case of TEM, a projected surface area is obtained based on the amount of the incident electrons that transmit through the samples. But the DLS measures the hydrodynamic diameter that might be larger than actual size depending on the surface charge and electrical double layer (Bhattacharjee, 2016; Duracher et al., 1998).

### **3.4 Rheological properties of SP latex as a function of pH**

The viscosity of the sterically stabilized cobinders at different pH levels as a function shear rate is shown in Figure 3-7. SP latexes became more viscous as the pH of the dispersion increased. As the result reveals, the SP-1 latex shows the characteristics of a Newtonian fluid and it was not shear-dependent at all pH levels, as did the SP-2 latex. The viscosity of these latexes i.e. SP-1 and SP-2 increased at higher pH, indicating some swelling of the protective shell and polymer core of the latex. The viscosity of SP-2 was higher than SP-1 at all pH levels, and this was attributed to the higher acrylic acid content of SP-2. Carboxylic groups of acrylic acid deprotonated, leading to an electrostatic repulsion and expansion of the polymer backbone, particularly at pH 9. SP-3, however, showed shear thinning behavior and was more shear-dependent, especially under high pH condition.

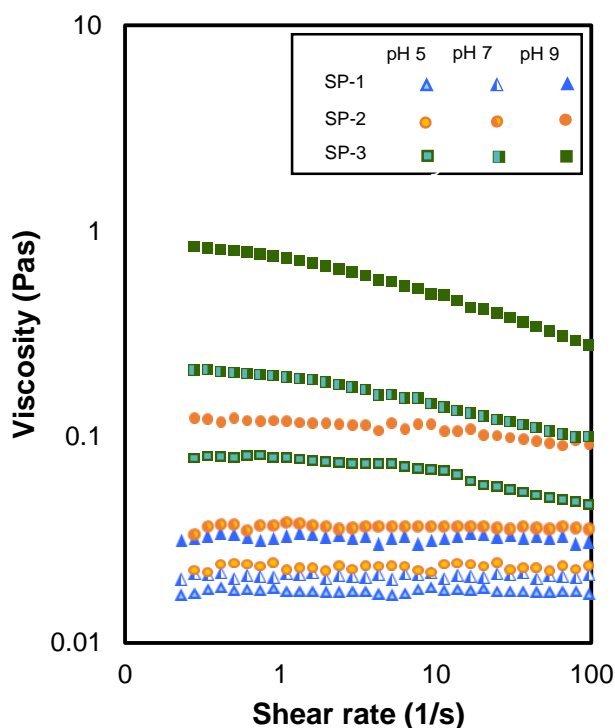


Fig. 3-7. Viscosity of SP latexes at different pH as a function of shear rate.

The acrylic acid monomers that used for polymerization increase the electrostatic repulsion in polymer chains particularly at higher pH levels. Because most of the carboxyl groups deprotonated and enhanced the electrostatic repulsion of the polymer chains within a particle. Hence the viscosity of SP-3 that had higher acrylic acid content was higher than that of SP-1 and SP-2 at any pH level.

The zeta potential of the SP latex dispersions was measured as a function of pH and depicted in Figure 3-8. The result showed that the zeta potential of SP-

3 latexes was more negative than those of SP-1 and SP-2 latexes. When the pH of SP latex increased from 5 to 9, a more negative zeta potential was obtained due to the greater ionization of the carboxyl groups. This increment was more pronounced for SP-3 which contained a greater amount of carboxyl groups. This clearly shows that more carboxyl groups deprotonated as the pH increased, which would cause electrostatic repulsion of the polymer chains that expands the polymer backbone, which increases the particle size and viscosity of the SP latexes at alkaline pH.

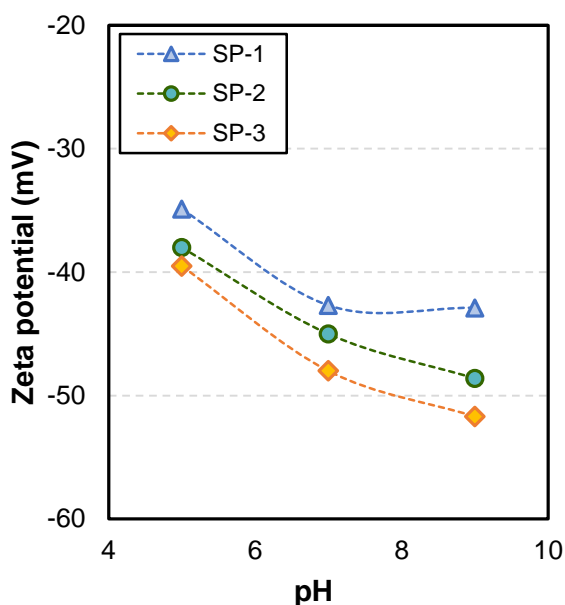


Fig. 3-8. Zeta potential of SP latexes as a function of pH.

Shear thinning behavior of the SP-3 latex is also related to the swelling of the particles. As it was shown in Figure 3-6, the particles of SP-3 latex are spherical. The carboxyl groups deprotonate under alkaline condition and this make the

latex particle swells. The swollen particles, however, easily deform when they are exposed to shear stress. Increased deformation of the SP latex particles by higher shear rate, results in an ellipsoid shape particle which have a smaller cross section in the flow direction. Hence the SP latex dispersion shows a shear thinning flow characteristic (Mezger, 2014).

Shear thinning characteristic of SP-3 latex can be also as a result of an interaction between latex particles. To examine the existence of the interaction between the latex particles, an amplitude sweep test was carried out to study the microstructure of the SP-3 latex. Storage ( $G'$ ) and loss ( $G''$ ) moduli were evaluated at a constant angular frequency (1 Hz) and changing the shear stress. The result is shown in Figure 3-9.

$G''$  was larger than  $G'$  in all pH levels for the entire shear stress range, indicating that the SP-3 latex dispersion is a viscoelastic liquid. There is no crossover point between  $G''$  and  $G'$ . However, the result revealed that as the pH increased, the yield point increased as well, indicating a viscous shear thinning behavior (shear softening) related to particle deformation.

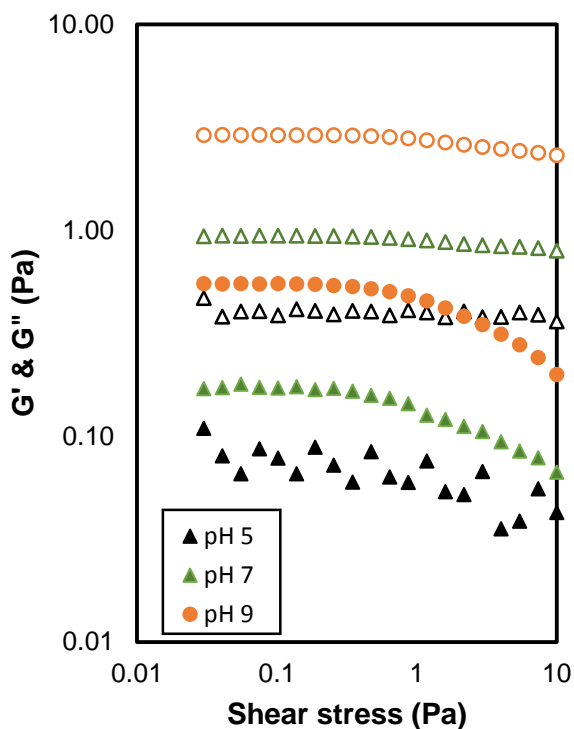


Fig. 3-9. Amplitude sweep of SP-3 latex for a range of stress (0.03-10 Pa) at a constant angular frequency (1 Hz) as a function of pH. Storage ( $G'$ ) modulus (closed symbol) and loss ( $G''$ ) modulus (open symbol).

A frequency sweep test as a function of frequency was carried out to confirm the microstructure of the latex dispersion. The result showed that (Figure 3-9) there was no crossover point between  $G''$  and  $G'$ . Loss modulus was larger than storage modulus in all pH levels, indicating the liquid like behavior is more predominant in SP-3 latex dispersion.

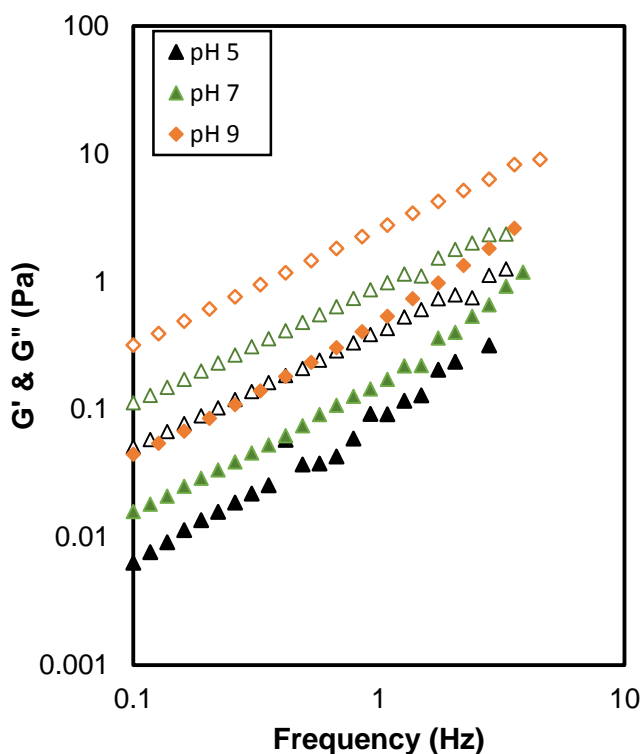


Fig. 3-10. Frequency sweep of SP-3 latex for a range of stress (0.1-10 Hz) at a constant angular frequency (1 Hz) as a function of pH. Storage ( $G'$ ) modulus (closed symbol) and loss ( $G''$ ) modulus (open symbol).

The interaction between particles of SP-3 was examined with amplitude and frequency sweep test. The results showed that loss modulus was higher than elastic modulus at all pH levels i.e. SP-3 latex showed the characteristics of a viscoelastic liquid. Hence the shear thinning behavior of the SP-3 latex would be related to deformation of the particles under applied shear.

### **3.5 Effect of SP latexes as a cobinder on rheological properties of coating color**

It was found that swelling or dissolving of the SP latexes protective shell and the ionization of the acidic groups increased the viscosity of the latexes, especially under alkaline conditions. It is expected that the addition of these sterically stabilized latexes as a cobinder to a coating color and adjusting pH value to 9, affects the flow behavior and viscosity of the coating color. In order to study the effect of the SP latex cobinder on the viscoelastic properties of the coating color, three SP latexes i.e. SP-1, SP-2, and SP-3 with an acrylic acid content of 5%, 10%, and 15 %, respectively, were used. Three parts of the main binder (S/B latex) were substituted with SP latexes. An amplitude sweep and a frequency sweep test were performed to evaluate the microstructure of the coating color.

Storage ( $G'$ ) and loss ( $G''$ ) moduli were measured as a function of shear stress at a constant angular frequency of 1 Hz. The result revealed that storage modulus was higher than loss modulus in the linear viscoelastic region indicating the coating color was a viscoelastic solid material. Substitution of S/B latex with SP cobinder, gave a greater elastic modulus than the coating color containing S/B latex only. This indicates that the coating color became more solid-like with the addition of SP latex (Figure 3-11). This effect was more pronounced when SP-3 with higher acrylic acid content was used as a cobinder. This can be attributed to the absorption of the liquid phase in the coating color by hydrophilic protective shells or carboxyl groups of the core polymer, which has the same effect on increasing the solids of the coating color.

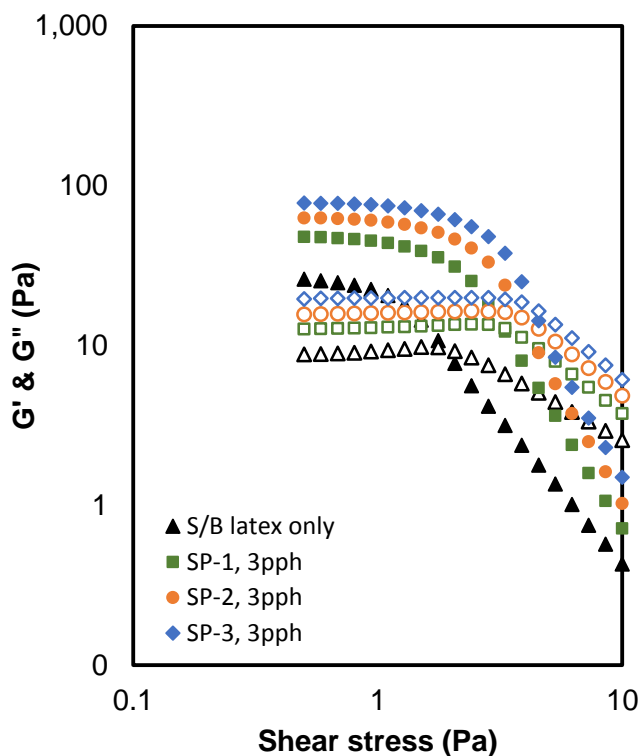


Fig. 3-11. Amplitude sweep of coating colors for a range of stress (0.03-10 Pa) at a constant angular frequency (1 Hz). Storage ( $G'$ ) modulus (closed symbol) and loss ( $G''$ ) modulus (open symbol).

The amplitude sweep result also shows that when SP latex was added to coating color the flow point of the coating color increased, showing that higher shear was needed to flow the coating color. It reveals the presence of a stronger interaction between the components of the coating color. The SP cobinder may make a network with the pigments and strength of this network is determined by the flow point (Page et al. 2002). When SP-3 i.e., the latex with higher acrylic acid content added to the system the flow point increased more indicating a higher strength of the network.



The frequency sweep test was performed to confirm the microstructure within the disperse system and results are shown in Figure 3-12. The storage and loss moduli were measured as a function of frequency. Storage modulus ( $G'$ ) was higher than the loss modulus ( $G''$ ) for all disperse systems which reveal the more solid structure of coating color. Both storage and loss moduli increased as the frequency increased showing that weakly flocculated structure was formed in disperse system. Compared with the coating color with S/B latex as a sole binder, substitution of S/B latex with SP latexes, resulted in a higher storage and loss moduli, indicating stronger interaction between coating components. Moreover, the SP-3 latex with higher acrylic acid content resulted in the formation of stronger flocculated structure in coating color.

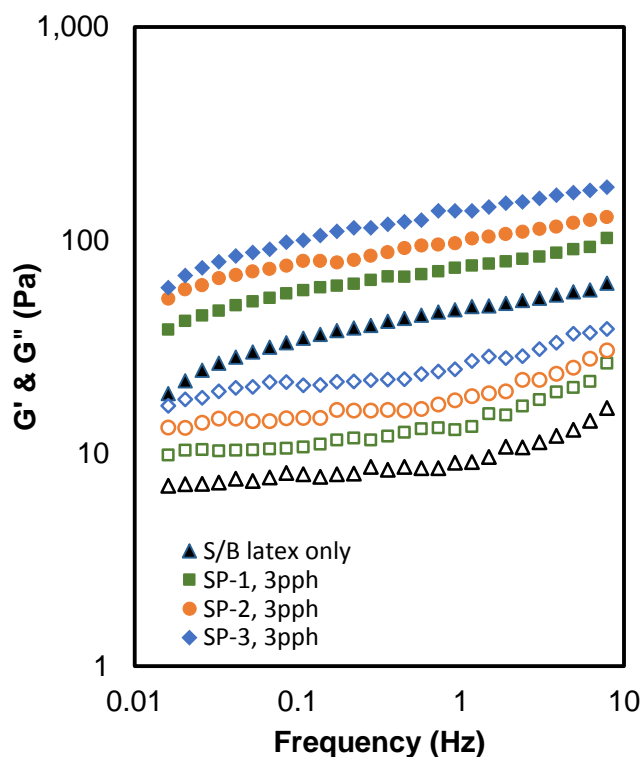


Fig. 3-12. Frequency sweep of coating colors for a range of stress (0.1-10 Hz) at a constant angular frequency (1 Hz). Storage ( $G'$ ) modulus (closed symbol) and loss ( $G''$ ) modulus (open symbol).

Complex modulus ( $G^*$ ) of the coating colors show a similar tendency compared to the storage modulus (Figure 3-13). Compared with the coating color contained only S/B latex, 3 parts of SP latexes cobinder resulted in an increased complex modulus showing more solid-like behavior of the coating colors with SP latexes. Coating color with a high acrylic acid content cobinder (SP-3) showed a higher complex moduli compared to the control and the other coating colors, indicating stronger interaction between the cobinder and

pigments.

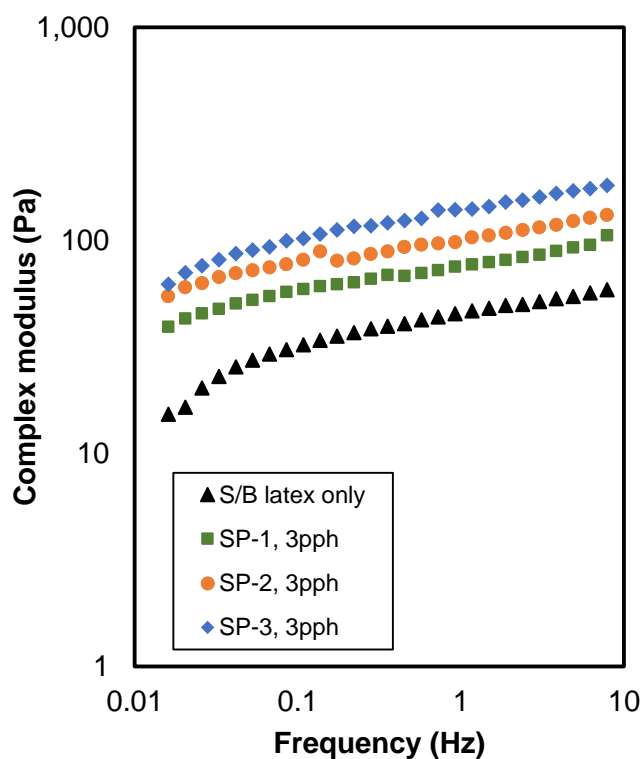


Fig. 3-13. Complex modulus ( $G^*$ ) of coating colors.

### 3.6 Zeta potential of coating color

The rheology data of the coating color revealed that substitution of S/B latex with SP cobinder increased the weak flocculation of the coating components. Hence, to study this more, the zeta potential of the coating color contained only S/B latex was measured, and compared with that of the coating colors containing SP cobinders and the result is shown in Figure 3-14.

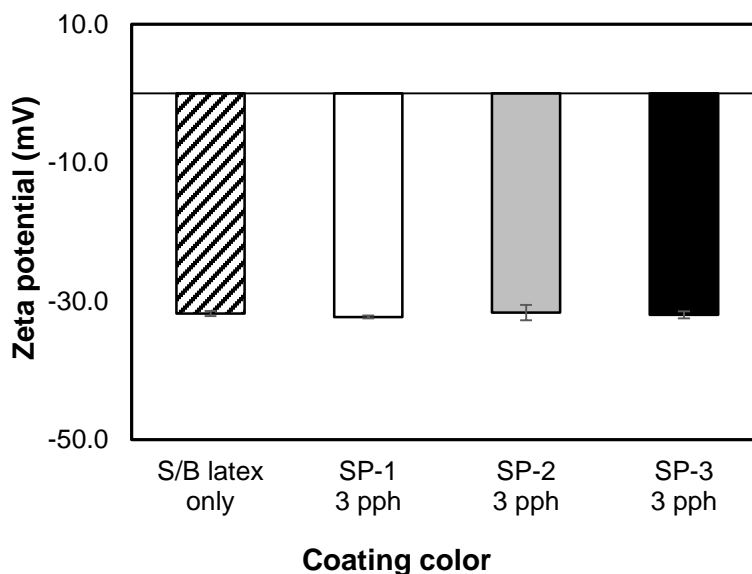


Fig. 3-14. Effect of SP latex on zeta potential of coating color.

The zeta potential of the coating color with S/B latex only as a binder was -31.8 mV. When 3 parts of the S/B latex was substituted with SP cobinders which had different acrylic acid contents, the zeta potential did not change significantly. Since the pigments i.e., GCC and clay had a negative charge, the negatively charged SP cobinders would not adsorb onto the pigment surfaces because of electrostatic repulsion. Therefore, the zeta potential of the coating colors did not change significantly.

When 3 parts of S/B latex were substituted with SP cobinder the zeta potential of the disperse phase was not affected, which showed that there was no adsorption of the cobinder on the surface of the pigments. Some part of the hydrophilic polymers which used for stabilization of the SP latexes remained in the aqueous phase of the SP latex dispersion. These polymers that are smaller

than pigment particle would move within the disperse system because of electrostatic repulsion between polymers and particles. When pigment particles approach within a diameter of the polymers, the polymers are expelled from the gap between two pigment particles. Hence the concentration of the polymers around the pigment particles is changed that leads to an osmotic pressure difference which results in an attraction between pigment particles (Xing et al., 2015; Gong et al., 2014; Edwards & Bevan, 2012). SP-3 which has a larger particle size could induce more depletion interaction between the components of coating color. A previous study by Xing and co-authors on depletion interaction of colloidal particles due to the presence of soft particles with a solid core surrounded by a soft shell showed that larger hydrodynamic diameter of the soft particles has a critical effect on depletion attraction (Xing et al., 2009).

### **3.7 Sedimentation of coating color**

In order to confirm whether the flocculation of the coating color is induced by sterically stabilized latexes, a sedimentation experiment was carried out. In this experiment, centrifugation of the coating color followed by the sediment volume measurement after decanting the supernatant were made. The result is shown in Figure 3-15. It can be seen that substitution of S/B latex with 3 parts of SP latexes gave a higher sedimentation volume, indicating that this caused by the formation of weakly flocculated structure of the coating color.

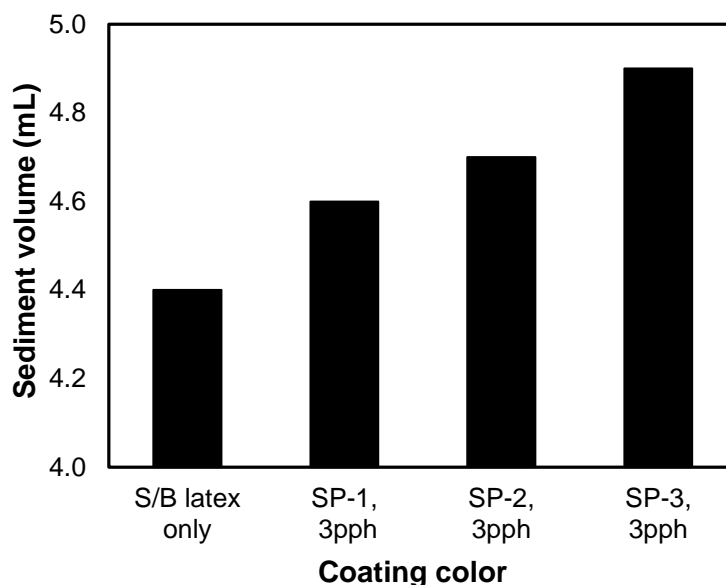


Fig. 3-15. Sediment volume of coating colors.

### 3.8 Viscosity and water retention property of coating color

Effect of the SP cobinder addition on the viscosity of coating color as a function shear rate is shown in Figure 3-16. All coating colors showed shear thinning behavior. When 3 parts of the S/B latex was substituted with SP latexes the viscosity of all the coating colors increased. Hydrophilic parts of the stabilizers absorbed the liquid phase of the disperse system, which made the coating color more solid-like. Moreover, increased interaction between coating components that accompanied the addition of SP latexes resulted in a higher viscosity of coating color compared with the coating color containing only S/B latex. As the result shows the interaction was very weak and shear rate dependent. The result also reveals that SP-3 cobinder increased the viscosity

more than 2 other SP cobinders because it contained more acrylic acid in the core polymer. This increased the interaction between pigments and water absorption, and consequently the solids of the coating color.

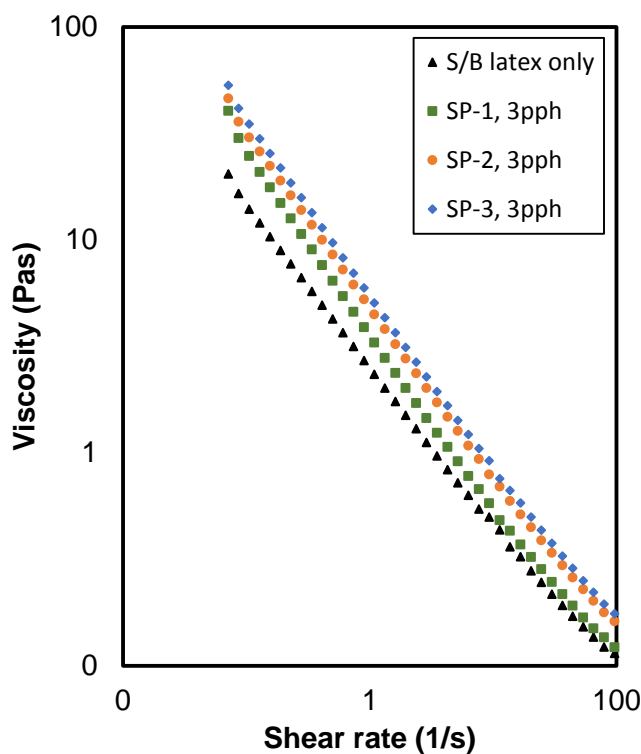


Fig. 3-16. Effect of SP latex on viscosity of coating color.

Table 3-4 shows the low shear viscosity and water retention property of the coating color with a solids content of 65% at pH 9. Addition of SP latexes increased the viscosity of the coating color. As the acrylic acid content increased the viscosity increased more.

Table 3-4. Effect of SP cobinder on viscosity and dewatering of coating color.

	S/B latex only	SP-1 3pph	SP-2 3pph	SP-3 3pph
Dewatering (g/m <sup>2</sup> )	114.9	103.5	97.0	74.6
Viscosity (cPs)	213.9	284.3	414.0	488.4

Dewatering of a coating color is influenced by the hydrophilicity and interaction of the coating components. Addition of the sterically stabilized SP latexes reduced the dewatering of the coating color i.e. increased the water retention value of the coating color. Retained water may remain in the filter cake through hydrogen bonding or just as bulk water in the formed network (Li et al., 2001). Protective shell of the SP cobinders contains hydrophilic polymers which absorbed water via hydrogen bonding and increased the water retention capacity of the coating color. It was found that higher acrylic acid content during polymerization enhanced the hydrophilicity of the cobinder and consequently increased the water retention of the coating color. Dependence of hydrophilicity of the thickener or cobinder and water holdout capacity of a disperse system were studied by different researchers (Fadat et al., 1988; Li et al., 2001). When the cobinder polymerized with higher content of acrylic acid, more hydrophilic carboxyl groups are introduced to the polymer. This could reduce the dewatering of coating color when hydrophilic SP cobinder is added to the system.

### 3.9 Effect of SP cobinder dosage on rheology of coating color

To study the effect of the dosage of SP cobinder on the properties of coating color, the SP-2 cobinder was selected and 1, 3, and 5 parts of S/B latex were



replaced with SP-2 latex.

Zeta potentials of the coating colors which contained 1, 3 and 5 parts of SP-2 latex were measured (Figure 3-17). The result showed that, substitution of SP cobinder did not change the zeta potential of the coating color, indication no adsorption of the SP latex on coating pigments was occurred.

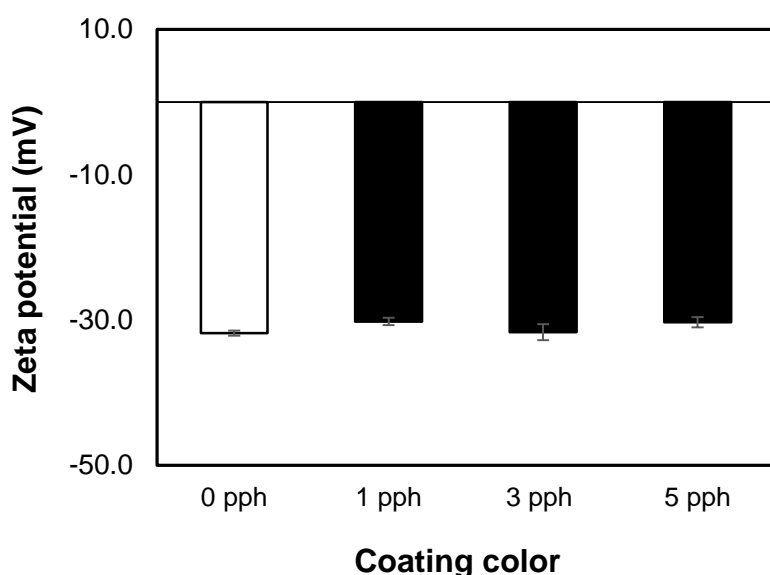


Fig. 3-17. Effect of substitution rate of SP-2 latex on zeta potential of coating color.

An amplitude sweep test was carried out to evaluate the interaction between the components of the coating color and the result is shown in Figure 3-18. It was found that substitution of SP-2 cobinder for S/B latex increased the storage modulus and flow point of coating color. When more S/B latex was replaced with SP-2 latex, stronger interaction between the components of the coating

color was obtained by depletion attraction. This change regained higher flow stress to break down the flocculated structure.

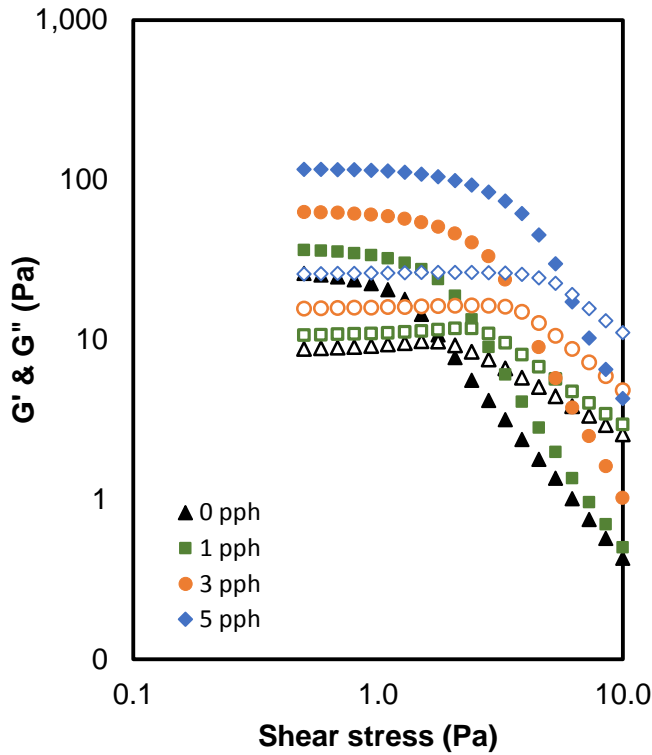


Fig. 3-18. Amplitude sweep of coating colors for a range of stress (0.03-10 Pa) at a constant angular frequency (1 Hz). Storage ( $G'$ ) modulus (closed symbol) and loss ( $G''$ ) modulus (open symbol).

The result of frequency sweep test showed that a weakly flocculated structure was built up in the coating color (Figure 3-19). Both elastic and viscous moduli increased with an increase of frequency. This confirms the formation of network and interaction between the components of coating colors. As the substitution of S/B latex with SP cobinder increased, stronger interaction was formed in the coating color due to the depletion attraction. This result is in close

agreement with a previous study on depletion interaction induced by soft particles (Xing et al., 2009).

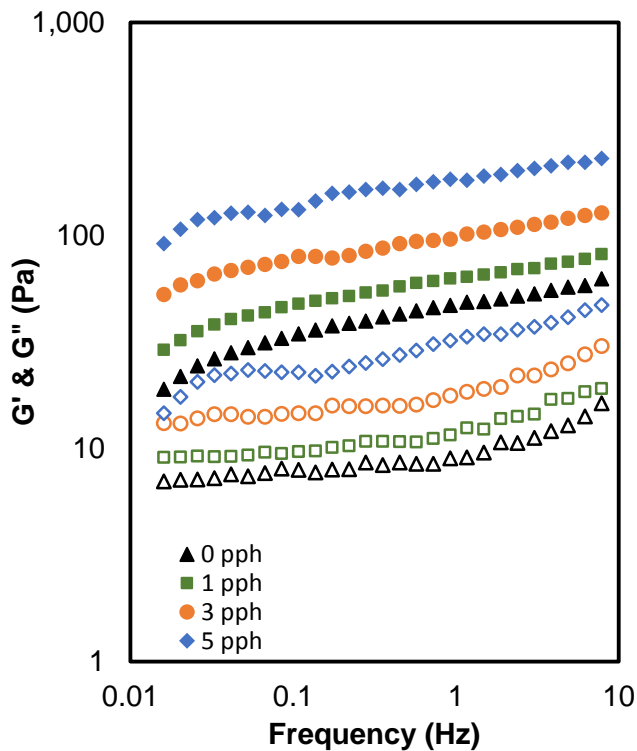


Fig. 3-19. Frequency sweep of coating colors for a range of stress (0.1-10 Hz) at a constant angular frequency (1 Hz). Storage ( $G'$ ) modulus (closed symbol) and loss ( $G''$ ) modulus (open symbol).

Figure 3-20 shows the effect of SP cobinder dosage on the complex modulus ( $G^*$ ) of the coating color. As more S/B latex was replaced with SP cobinder, higher complex modulus was obtained, which suggested more flocculation in coating color through depletion mechanism.

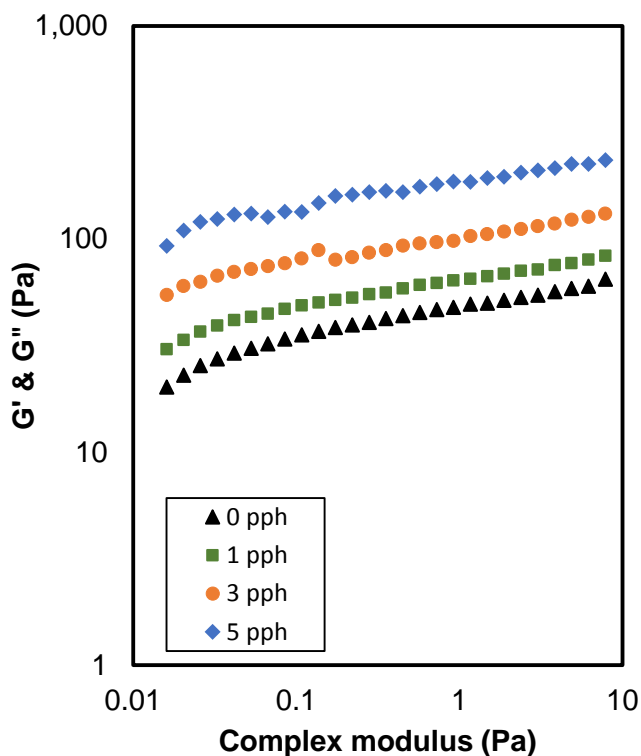


Fig. 3-20. Complex modulus ( $G^*$ ) of coating colors.

The effect of the SP cobinder dosage on the viscosity of coating colors as a function shear rate is shown in Figure 3-21. The result showed that all of the coating colors showed shear thinning behavior. As the substitution of S/B latex with SP cobinder increased, the viscosity of the disperse system increased as well. Flocculation of the coating color by the addition of SP cobinder resulted in higher viscosity. When more SP cobinder introduced to the coating color, more flocculation of the pigment particles was facilitated by depletion flocculation. Water absorption by the protective shell of the SP latex particles, made the coating color more solid-like and affect the viscosity of the coating color.

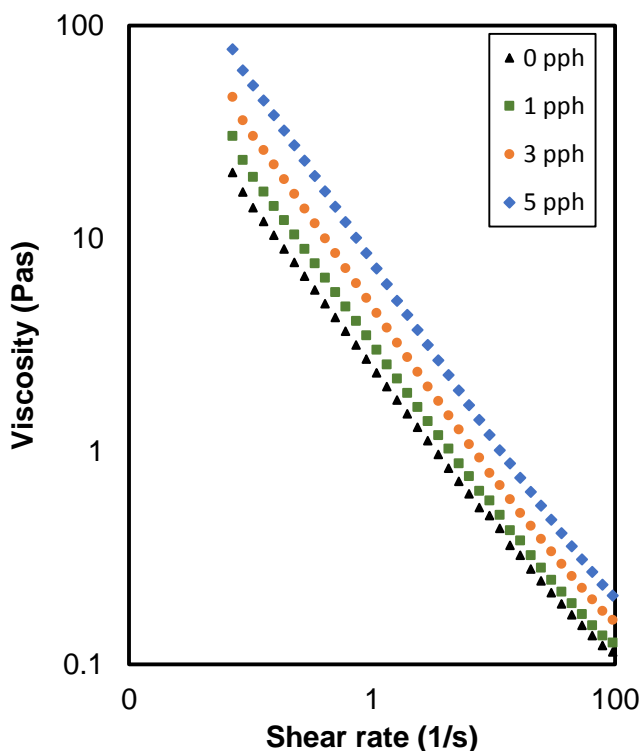


Fig. 3-21. Effect of SP latex on viscosity of coating color as a function of shear rate.

Low shear viscosity of the coating colors containing S/B latex only as a sole binder was measured and compared with those of the other coating colors which 1, 3, and 5 parts of the sterically stabilized SP-2 cobinder were substituted for S/B latex. As shown in Table 3-5, the viscosity of coating color increased when S/B latex was replaced with SP cobinder. It was also found that as the substitution amount was increased, the viscosity increased more. The protective shell of the acrylate cobinder contains hydrophilic polymers which absorbed water and affected the viscosity of the disperse system. Moreover, the hydrophilic carboxyl groups of the core polymer adsorb more water.

Dewatering of the coating color reduced when more S/B latex replaced with SP-2 latex due to hydrophilic characteristics of the latex particles.

Table 3-5. Effect of SP cobinder dosage on viscosity and dewatering of coating color.

	S/B latex only	SP-2 1pph	SP-2 3pph	SP-2 5pph
Dewatering (g/m <sup>2</sup> )	114.9	106.0	97.0	86.6
Viscosity (cPs)	213.9	246.0	414	550.8

### 3.10 Effect of cobinder dosage on sedimentation of coating color

The coating colors containing 1, 3, and 5 pph of SP-2 cobinder were centrifuged and the supernatant was discarded. The sediment volume then measured and compared with that of coating color containing only S/B latex as a sole binder. The result is shown in Figure 3-22.

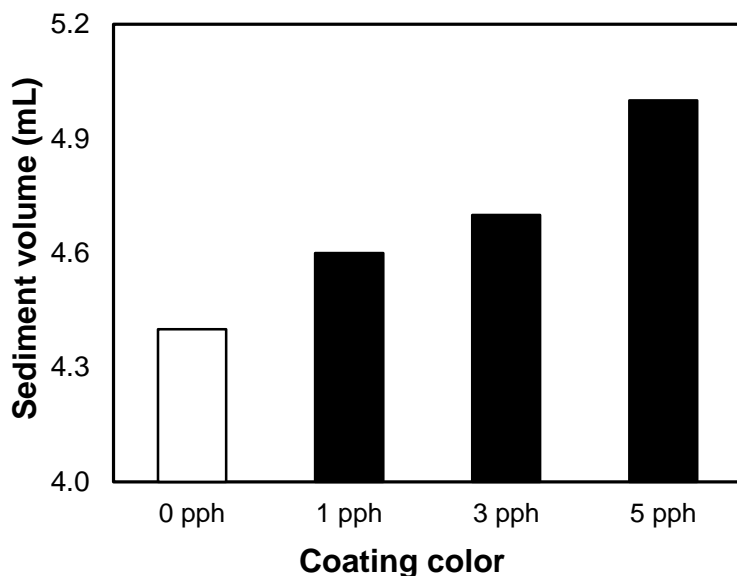


Fig. 3-22. Effect of SP cobinder dosage on sediment volume of coating color

The result shows that the coating color with S/B latex only as a binder forms a compact sediment. It was found that when S/B latex was replaced with SP-2 cobinder the sediment volume increased indicating more interaction between the coating color components.

### 3.11 Pore structure of coating color

Coating colors containing 1 and 3 pph of SP-2 latex were coated on plastic films. The porosity of dried coating layers was compared with that of the coating layer containing S/B latex only as a binder. Table 3-6 shows the total intrusion volume and porosity of the coating layer. Addition of SP latex increased the porosity of the coating layer compared with the reference coating layer. When more SB latex was substituted with SP latex, the mercury intrusion

to coating layer increased indicating that a more porous coating composite was formed. This can be explained by the flocculation of the disperse system and as the dosage of the cobinder increases, the tendency of coating color to form larger flocs and more porous coating structure after drying increased as well.

Table 3-6. Pore characteristics of coating layer.

SP latex content (pph)	Total intrusion volume (mL/g)	Porosity (%)
0	0.129	23.4
3	0.151	28.3
5	0.169	30.7

Pore size distribution and cumulative pore volume of coating layers are shown in Figures 3-23 and 3-24. The result showed that most of the pore sizes ranged from 15 to 100 nm. With the addition of SP latex to coating color, more pores between 50 to 80 nm were formed. Moreover, when S/B latex was substituted with SP cobinder, the cumulative volume was dramatically increased between 10 and 30 nm. Effect of cobinders or rheology modifiers on the flocculation of coating color which gives more porous structure was previously studied by other researchers (Choi et al., 2015; Oh et al., 2017).



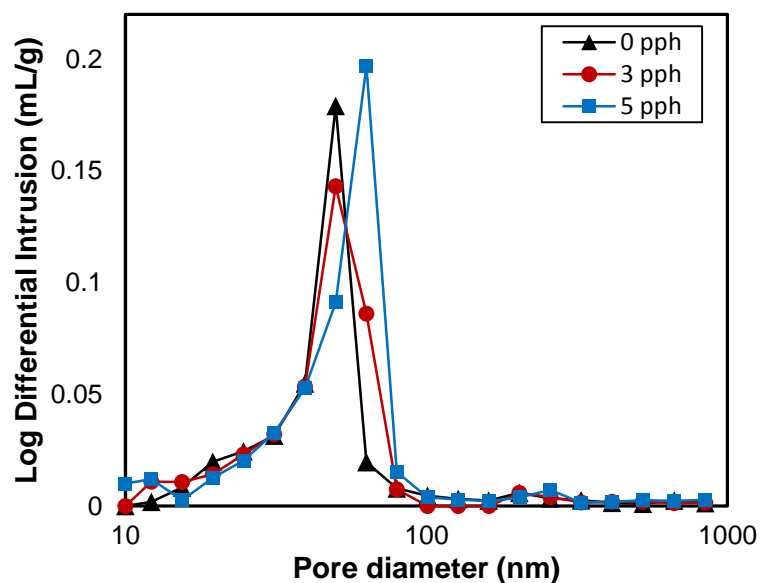


Fig. 3-23. Effect of SP cobinder on pore size distribution of the coating layer.

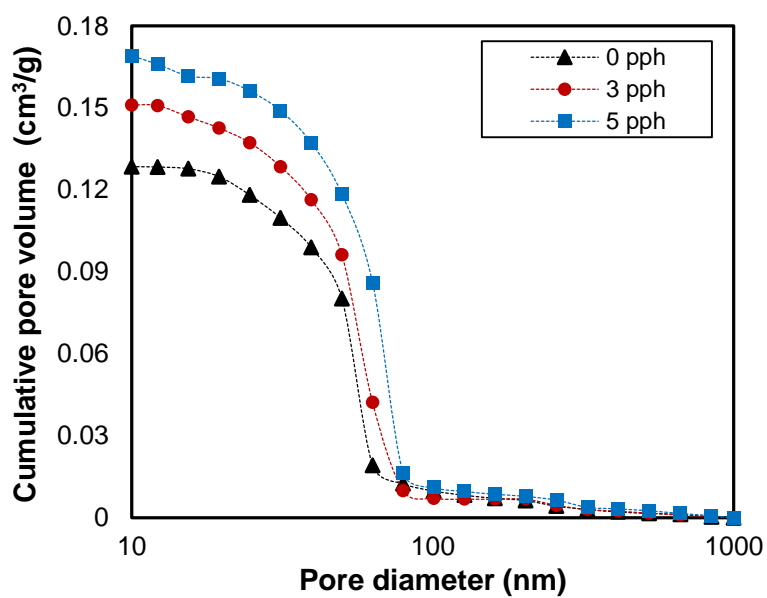


Fig. 3-24. Cumulative pore volume of dried coating layer.

### 3.12 Surface characteristics of coating layer

Effect of SP latex on the roughness of the coating layer was studied by applying the coating color on a plastic film and drying the coating layer at room temperature. The thickness of the coating layer was around 27  $\mu\text{m}$ . Figure 3-25 shows the roughness of the coating layers formed on the plastic film. It was found that the addition of the SP cobinder, increased the roughness of the coating layer. As more S/B latex was replaced with SP latex, the roughness increased more. The interaction between coating color components induced by SP latex resulted in the formation of weekly flocculated coating and consequently affected the porosity and surface roughness of the coating layer.

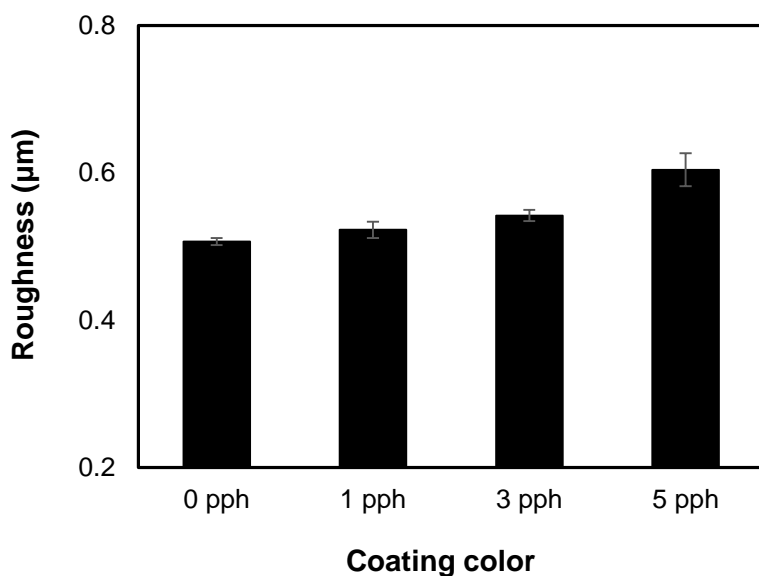
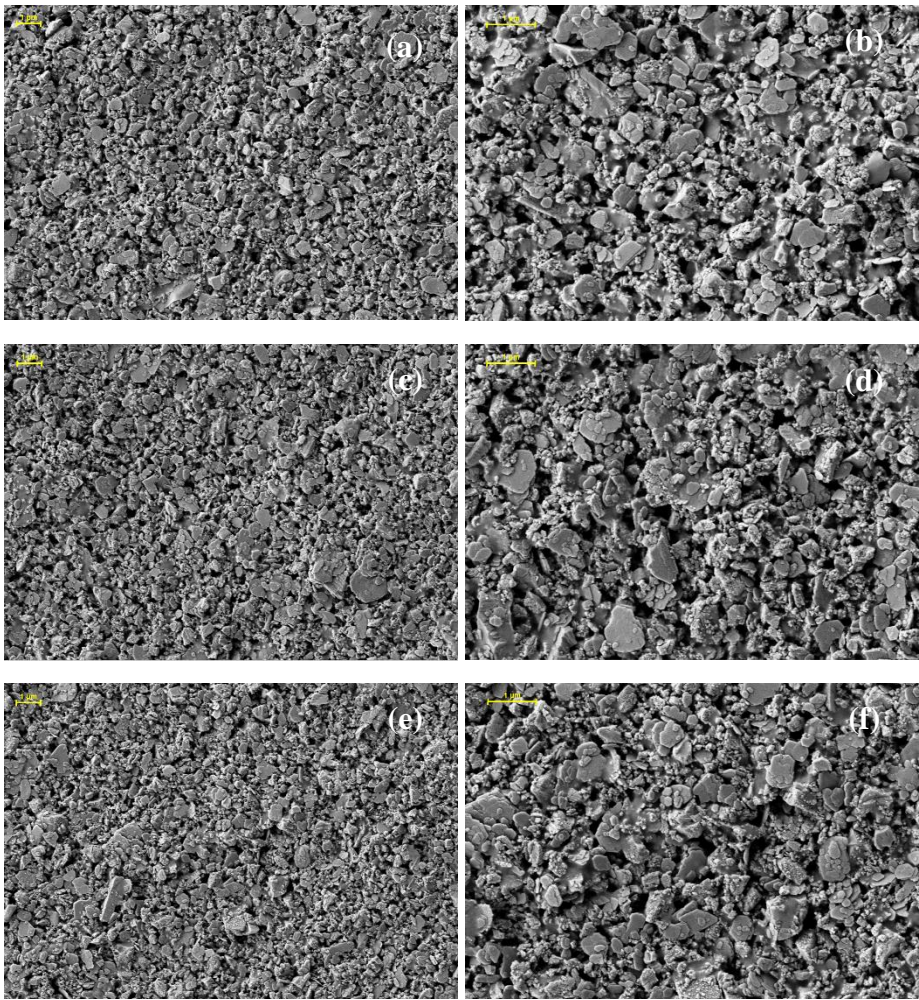


Fig. 3-25. Effect of SP cobinder dosage on roughness of coating layers.

FE-SEM micrographs from the surface of coating layers were obtained to

evaluate the effect of SP latex addition on the surface roughness of coating composites. As it is shown in Figure 3-26, when more S/B latex was substituted with SP cobinder, the surface roughness of coating layers increased.



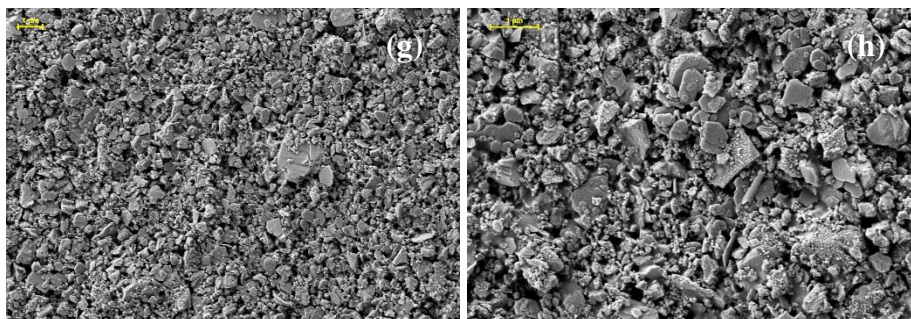


Fig. 3-26. FE-SEM images of coating layers: (a) and (b), 0 pph of SP-2; (c) and (d), 1 pph of SP-2; (e) and (f), 3 pph of SP-2; (g) and (h), 5 pph of SP-2.

### 3.13 Brightness and opacity of coating layer

Effect of the SP cobinder on brightness and opacity of the coating layers were studied and the results are shown in Figure 3-27.

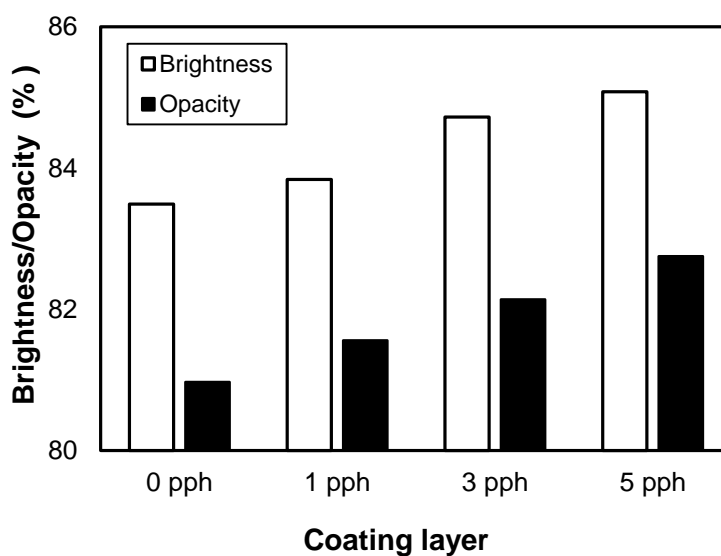


Fig. 3-27. Brightness and opacity of coating layers.

Opacity and brightness of the dried coating layer increased when S/B latex was substituted with SP cobinder indicating more light scattered within the coating layer. When SP cobinder added to the coating color, a more porous coating layer formed that resulted in more scattering of light.

#### 4. Summary

The effect of the acrylic acid monomer contents in SP latex on the viscosity, particle size, and zeta potential as a function of pH was studied. It was found that the protective shell and polymer core of the SP latex swelled under alkaline condition, which increased the volume fraction of disperse phase and resulted in viscosity increment. The SP-3 latex with 15 % acrylic acid monomer showed a higher viscosity than the other SP latexes. This was more pronounced at higher pH levels at which most of the carboxylic group deprotonated that enhanced the repulsion of the polymer chain within the particle. At alkaline pH, the latex changed to a larger particle size and more negative zeta potential. Viscoelastic properties of latexes as a function of pH were studied. The result revealed that viscose modulus was higher than the elastic modulus. The viscosity of SP-3 latex was shear-dependent.

The effect of SP cobinder on viscoelastic properties of coating color was investigated. SP cobinder containing coating color showed more elastic behavior than that of control coating color. SP cobinders resulted in depletion flocculation of coating color. Hydrophilic parts of the stabilizers absorbed the liquid phase of the disperse system and made the coating color more solid like. Moreover, weak interaction between coating components was formed when SP latexes were added, which resulted in a higher viscosity of coating color. As the result shows the interaction is very weak and shear-dependent. The result also reveals that SP-3 co-binder increased the viscosity more than two other SP cobinders because of more acrylic acid in the core polymer which increased the interaction between pigments, and water absorption and consequently the solids of the coating color.

It was also found that the addition of more SP cobinder could increase the interaction between components of coating color. Water retention property of the coating color was increased by SP cobinder addition due to the hydrophilic characteristics of the protective shells of the SP latex.

Finally, the pores structure and surface properties of the coating layer were evaluated. The results showed that flocculation of coating color influenced the porosity of the coating layer. The porosity increased when more SP latex substituted with S/B latex. More porous coating layer with higher roughness increased the light scattering and resulted in higher opacity and brightness of the coating layer.

## **Chapter 4**

Effect of suspension-polymerized cobinder on properties of coated papers



## 1. Introduction

The optical properties and surface strength of the coated paper is influenced by the properties and strength of the coating layer (Parpaillon et al., 1985). Porosity and void structure of dried coating composite, affect the light scattering and optical properties of the coating layer (Alince and Lepoutre, 1980). When a coating layer is dried, the voids between pigments are filled with latex film. Formation of a more porous coating layer is favored for better optical properties of the coated surface. In chapter three, it was shown that, when SP latex was used as a cobinder, more porous coating layer with higher opacity and brightness was formed. Mechanical properties of a coating layer, however, is affected by its porosity. A more porous coating layer deteriorates the mechanical properties by reducing the strength and stiffness of the coating layer. The strength of the coating layer, is of concern during converting processes like folding and printing (Lepoutre & Hiraharu, 1989). A strong coating layer with high extensional properties that is well adhered to the base sheet is favorable during converting and printing operations (Lepoutre and Rigdahl, 1989).

Pigments and binders as the major components of the coating color and have a critical effect on the mechanical properties of the dried coating layer. It was found that clay-based coatings layer is more porous and fragile compared to  $\text{CaCO}_3$  coating (Lepoutre & Hiraharu, 1989). A latex binder with a low glass transition temperature increases the stretch of the pigment coating layer (Okomori et al. 2001; Oh et al. 2015). Coating layer containing styrene-acrylate (S/A) latex has a greater extensional property than a layer containing styrene-butadiene (S/B) latex (Oh et al. 2016).

In this study, a sterically stabilized suspension-polymerized acrylate latex (SP

latex) was used as a cobinder for paper coating. The influence of SP latex on porosity, surface and optical properties of the coated papers were studied. The effect of SP latex on the strength and extensional properties of the coating layer was investigated. In addition, the influence of SP latex on strength and elongation of coated paper was evaluated. The fold crack area and dry pick area were measured using an image processing method.

## 2. Experimental

### 2.1 Materials

A suspension-polymerized latex (SP latex) was provided by SongKang Industrial Co. Styrene, butyl acrylate, and acrylic acid monomers were used for polymerization and a protective shell containing oxidized starch and PVA provided colloidal stability of the SP latex. A commercial emulsion-polymerized styrene-butadiene (S/B) latex with a solids content of 50% and average particle size of 147 nm was used as a main binder (Trenseo, Korea). To check the effect of acrylate monomers on tensile properties of the coating layer, a styrene acrylate (S/A) latex with a solids content of 50% and average particle size of 129 nm was also used (SA1801, LG Chemical, Korea).

Calcium carbonate and clay were used as pigment in this study. Ground calcium carbonate (GCC, Setacarb HG, Omya Korea) was prepared in slurry form and dry kaolin clay (HYDROGLOSS® 90) was prepared from KaMin. Poly(acrylic acid sodium salt) with a molecular weight of 5100 g/mol was used as a dispersing agent. Polyvinyl alcohol (POVAL, Korea) with a degree of hydrolysis of 98-99.5 % and a molecular weight of 75000-80000 g/mol, and oxidized starch purchased from Kuraray (Japan) were used. NaOH (1N) used for pH adjustment of coating color was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Deionized water used through all the experiments. All of the chemicals and raw materials were used as received without any further modification or purification. Surface sized papers with a basis weight of 78 g/m<sup>2</sup> and 198 g/m<sup>2</sup> from Moorim paper (Jinju, Korea) were used as the base paper for paper coating.

## **2.2 Transmission electron microscopy (TEM)**

Images of the latexes were obtained using a LIBRA 120 (Carl Zeiss) transmission electron microscope with an operation voltage of 120 kV. The latex particles were deposited on Formvar film coated grids and then the grids were exposed to a drop of uranyl acetate solution (UA) for 10 s for staining and then washed for 1 s in two drops of DI water. The residual DI water was then removed by filter paper and the samples dried in room temperature.

## **2.3 Fourier transform infrared spectroscopy (FTIR)**

FT-IR spectra of the latexes were obtained using a Nicolet 6700 Spectrometer (Thermo Electron Corporation, USA) in attenuated total reflectance (ATR) mode in the range of 600-4000  $\text{cm}^{-1}$ . The latex dispersions dried in aluminum dishes at 70 °C.

## **2.4 Pore size distribution of coated paper**

Effect of SP latex as a cobinder on the pore size distribution of coated paper was studied by mercury intrusion porosimetry (AutoPore IV 9500, Micromeritics Instruments Corporation). To do this, the volume of mercury that intruded into the pores of the coated paper was measured. The pore size was investigated within a range of 10 to 1000 nm.

## **2.5 Surface properties of coated paper**

The gloss, roughness of the coated paper were measured using a gloss meter (L&W, Sweden) and a Parker Print Surface (L & W, Sweden) respectively. Micrograph of the coated paper surface was carried out using a field-emission scanning electron microscope (FE-SEM, AURIGA, Carl Zeiss).

## **2.6 Optical properties of coated paper**

Brightness and opacity were determined by a L&W ELREPHO spectrophotometer (ABB, Sweden).

## **2.7 Ink absorption ratio of coated paper**

The ink absorption ratio of the coated paper was evaluated according to SCAN-P 70:09 (2008). The paper was printed with Croda ink (Batch No VUU2 3RDU LOT #7847168, Film Group, Luxembourg, Luxembourg) using an applicator bar with a gap size of 50  $\mu\text{m}$ . The absorption time was 2 min. The ink absorption was calculated based on the brightness before and after ink absorption (Eq. 4-1).

$$\text{Ink absorption ratio (\%)} = (R_{\infty} - R_s) / R_{\infty} * 100 \quad (\text{Eq. 4-1})$$

Where  $R_{\infty}$  and  $R_s$  are the brightness before and after ink absorption.

## **2.8 Properties of latex films**

Latex particles are usually dispersed by electrostatic or steric repulsion force derived from the surfactants or polymeric stabilizers. During drying, the individual particles get close to each other and coalesce to make a continuous film (Sheetz, 1965; Steward et al., 2000; Winnik, 1997). The binding power of latex and ability of latex to make a film with desirable extensional properties are related to the chemistry and elasticity of the polymer (Bacquet and Isoard, 1997). Hence this study was conducted to prepare films of S/B and SP latexes and their mixtures aimed to evaluate the tensile properties of the latex films. The moisture content of the conditioned latex films at a constant temperature of 23 °C and a relative humidity of 50% and the gel content of the latex films were also calculated.

### **2.8.1 Gel content of the latexes**

The gel content of S/B latex and SP latex films were measured. The films were prepared by drying the latex dispersions in aluminum dishes at a temperature of 60 °C. To calculate the gel content of the latexes, 0.3-0.4 g of the films of latexes were soaked in toluene (Duksan, Korea) for 24 h in plastic tubes. Then the tubes were shaken for 60 s to disperse the precipitated latex on the bottom followed by passing the solution through a wire mesh with 150 µm openings. The percent of the dried latex remaining on the mesh compared with the original latex amount was used for the gel content calculation.

### **2.8.2 Moisture content of the latexes**

The prepared latex films were conditioned at a constant temperature of 23 °C and a relative humidity of 50% for 96 h and the moisture content of the films were calculated.

### **2.8.3 Latex film preparation for tensile measurement**

Different materials were tried as a substrate for latex film formation and finally, a glass substrate was used. As it is shown in Figure 4-1, 6 layers of adhesive tapes were attached to two sides of the glass substrate to make a latex film with a thickness of 120  $\mu\text{m}$  after drying. The latex dispersions were applied on the glass substrate using an automatic bar coater (GIST Co. Ltd., Korea).

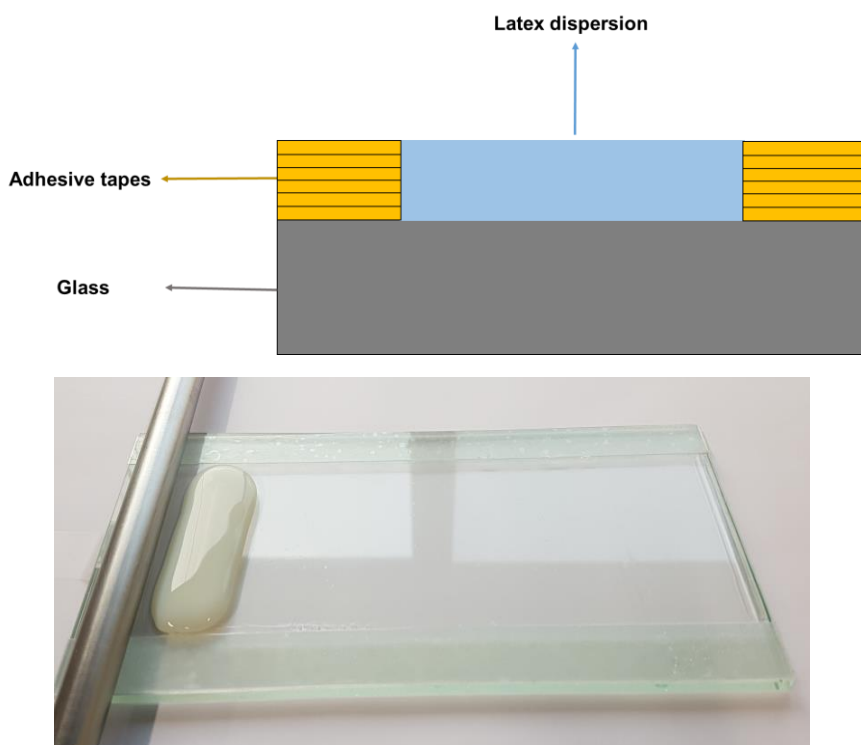


Fig. 4-1. Preparation of latex film samples.

S/B latex and SP latex dispersions and a mixture of the S/B and SP latex at different ratios were used to prepare latex films. Table 4-1 shows the different latex dispersions for latex film preparation.



Table 4-1. Formulation of latex dispersions for film preparation.

Latex	Proportion (pph)					
	1	2	3	4	5	6
S/B	100	95	90	80	70	-
S/P	-	5	10	20	30	100

The latex films were dried in a conventional oven at a temperature of 120 °C for 10 minutes. Then the samples peeled off carefully from the glass substrates. Figure 4-2 shows the dried latex films.

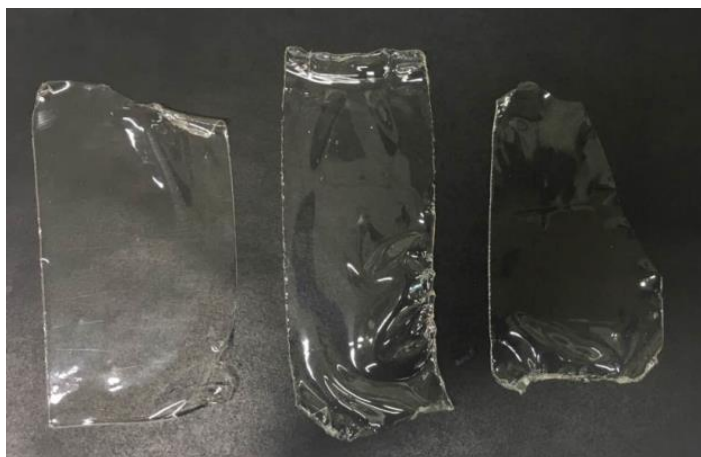


Fig. 4-2. Latex films after drying.

#### **2.8.4 Tensile properties of latex films**

Latex films were conditioned for at least 24 h at a constant temperature of 23 °C and a relative humidity of 50%. Tensile strength was measured using a Universal Testing Machine, Instron 5943 (Instron Int. Ltd., USA). The width and length of the samples were 12 mm and greater than 40 mm, respectively. The span length for the tensile testing was 20 mm. The latex films containing S/B latex and different dosages of SP latexes were tested with a crosshead speed of 2 mm/min. At least 11 samples without any deformation or defects were prepared for tensile testing.

### **2.9 Tensile properties of coating layers**

#### **2.9.1 Coating color preparation**

To study the effect of SP cobinder on tensile properties of the coating layer, coating colors containing only S/B latex as a sole binder or with 1, 3, and 5 parts of SP cobinder were prepared and used for coating layer preparation. The coating colors were prepared by mixing all the ingredients under vigorous stirring with a solids content of 62 wt%. Kaolin clay slurry was prepared by pre-dispersion of clay using 0.3 parts of poly(acrylic acid sodium salt), based on dry kaolin clay in DI water. The kaolin then mixed with GCC first followed by the addition of S/B latex and SP cobinders. The final pH of the coating color was adjusted to 9 using NaOH. The formulation of coating colors is shown in Table 4-2.

Table 4-2. Formulations of coating color.

Components		1	2	3	4
Pigment	Setacarb HG	80	80	80	80
	Clay	20	20	20	20
Binder	S/B latex	11	10	8	6
Co-binder	SP latex	-	1	3	5

Component amounts are written in parts per hundred (pph; by weight) based on 100 parts of pigments

### 2.9.2 Preparation of coating layer

A polyester film with a thickness of 30  $\mu\text{m}$  was used as a substrate for coating layer preparation. Double-coating was applied to obtain a thick coating layer with a dry coat weight of 75  $\text{g}/\text{m}^2$  using an automatic bar coater (GIST Co. Ltd., Korea). After applying the first coating layer, it was dried in a hot-air drying oven at 120  $^{\circ}\text{C}$  for 2 min. Then the second coating was applied and dried at room temperature for 12 h. The dried coating layer on plastic films was conditioned for more than 24 h at a constant temperature of 23  $^{\circ}\text{C}$  and a relative humidity of 50%. Dry coating layers with a thickness of 50  $\mu\text{m}$  were carefully detached from the plastic films. The moisture content of the coating layers was also measured after conditioning.

### 2.9.3 Effect of SP latex on tensile strength of coating layers

Tensile strength was measured using a Universal Testing Machine, Instron 5943 (Instron Int. Ltd., USA). The width and length of the samples were 12 mm and greater than 50 mm, respectively. Figure 4-3 shows the samples prepared for tensile measurement. At least 16 samples without any crack or defects were prepared for tensile testing.



Fig. 4-3. Coating layer samples for tensile measurement.

The span length for the tensile testing was 30 mm. The coating layers were tested with a crosshead speed of 3 mm/min.

#### **2.9.4 Effect of acrylate monomers, starch, and PVA on tensile strength of coating layers**

In another set of experiment, the effect of acrylate monomers of latex and starch and PVA as cobinders on tensile properties of the coating layer were examined. For this study, a coating color contained 11 parts of S/B latex as a sole binder, and another coating color consisted of 8 parts of S/B latex and 3 parts of SP cobinder were prepared as reference coating colors. A coating color contained S/A latex only as a binder was prepared to investigate the effect of acrylate monomers on tensile strength and elongation of coating layers. The core polymer/protective shell weight ratio of the SP latex was 60/40. The protective shell contained starch and PVA and their weight ratio was 3:1. Hence coating colors contained 9.8 parts of S/B latex and 1.2 parts of starch and/or PVA were prepared. The tensile strength of these coating layers was determined to study the effect of starch and PVA on the tensile strength of coating layer. Formulation of coating colors is shown in Table 4-3.

Table 4-3. Formulations of coating color for the evaluation of the effect acrylate monomers of latex, starch, and PVA on tensile strength of coating layer.

Components		1	2	3	4
Pigment	Setacarb HG	80	80	80	80
	Clay	20	20	20	20
Binder	S/B latex	11	-	9.8	6
	S/A latex	-	11	-	-
Additives	Starch	-	-	1.2	0.9
	PVA	-	-	-	0.3

\*Component amounts are written in parts per hundred (pph; by weight) based on 100 parts of pigments.

## 2.10 Paper coating

### 2.10.1 Single coating

A coating color containing S/B latex as a sole binder was prepared as a control coating color. To investigate the influence of SP latex on the mechanical properties of coated paper and fold crack resistance, coating colors containing different dosages of SP latex were prepared. Table 4-4 shows the formulation of coating colors.

Table 4-4. Formulations of coating color.

Components (pph)		1	2	3	4
Pigment	Setacarb HG	80	80	80	80
	Clay	20	20	20	20
Binder	S/B latex	11	10	8	6
Co-binder	SP latex	-	1	3	5

Papers with a basis weight of 78 g/m<sup>2</sup> and 198 g/m<sup>2</sup> were single coated using a laboratory bar coater (GIST Co. Ltd., Korea). The coated papers were dried in a hot-air oven for 2 min at 120 °C. Coated papers with a coat weight of 28 g/m<sup>2</sup> conditioned at a temperature of 23 °C and a relative humidity of 50% for 24 h.

### 2.10.2 Double coating

To study the effect of SP latex in the pre and top coating color on fold crack resistance, the base papers were double coated and the SP latex was replaced with starch and S/B latex in pre-coating and top-coating color. Table 4-5 and Table 4-6 show the formulation of pre and top coating colors. One part of optical brightening agent (OBA) was used for all the pre-coating colors. 1 pph, 0.5 pph, and 0.05 pph of OBA, lubricant, and insolubilizer were used for top coating colors respectively. Different combinations of pre-coating and top-coating were applied to obtain the double coated papers. 14.5 g/m<sup>2</sup> and 15.5 g/m<sup>2</sup> of coating color were applied for pre-coating and top-coating respectively. Table 4-7 shows the applied combinations for pre and top-coating.

Table 4-5. Formulations of pre-coating color.

Components (pph)		A	B	C	D
Pigment	Hydrocarb 60	100	100	100	100
Binder	S/B latex	6	4	6	6
	Starch	6	6	3	3
	SP latex	-	2	3	1

Table 4-6. Formulations of top-coating color.

Components (pph)		E	F
Pigment	Hydrocarb 60	80	80
	Setacarb HG	20	20
Binder	S/B latex	10	8
	SP latex	-	2



Table 4-7. Combinations of pre and top-coating colors for double coating.

Coating combination	Pre-coating	Top-coating
1	A	E
2	A	F
3	B	E
4	B	F
5	C	E
6	D	E

### 2.10.3 Coating on two sides of paper

Since during folding process, the outer layer of paper is subjected to tension and the inner layer undergoes a compressive stress (Alam et al., 2009; Guyot et al., 1992; Oh et al., 2016; Sim et al., 2012) in another set of experiment top side and bottom side of the base paper were coated. S/B latex was substituted with SP latex in coating color and applied on the top side or bottom of the base paper and the crack area was evaluated after folding. Table 4-8 and 4-9 show the coating color formulation and conditions of the coating.

Table 4-8. Formulations of coating color.

Components (pph)		A	B
Pigment	Setacarb HG	80	80
	Clay	20	20
Binder	S/B latex	11	8
Co-binder	SP latex	-	3

Table 4-9. Combinations of coating on top and bottom sides of the paper.

Coating combination	Top side	Bottom side
1	A	A
2	A	B
3	B	A
4	B	B

## 2.11 Mechanical properties of coated paper

The coated papers were conditioned at a temperature of 23 °C and a relative humidity of 50% for at least 24h. The conditioned papers were calendered using a laboratory soft-nip calender (2 times) at a temperature of 23 °C and the nip pressure of 130 kgf/cm. The tensile strength of coated papers was determined according to TAPPI standard (T 1009 om-92).

## 2.12 Crack area evaluation

To evaluate the effect of SP latex on fold crack resistance coated papers, the calendered papers were printed with black off-set ink (UT-8). The ink was well mixed and diluted using a solvent (paint thinner) with a ratio of 1:2. The prepared ink then applied on the surface of coated paper using a hand roller. The printed papers were dried for 3 days at 23 °C and 50% RH. The dried coated papers were cut with dimensions of 25 mm × 40 mm. The samples were pre-folded using a ruler and then the loosely folded coated paper was folded with a constant pressure of 2 bar for 1 s using AA-GWR (Gravimetric water retention meter), which is used for measuring the dewatering capacity of coating color. Figure 4-4 shows how the coated papers were folded by AA-GWR.

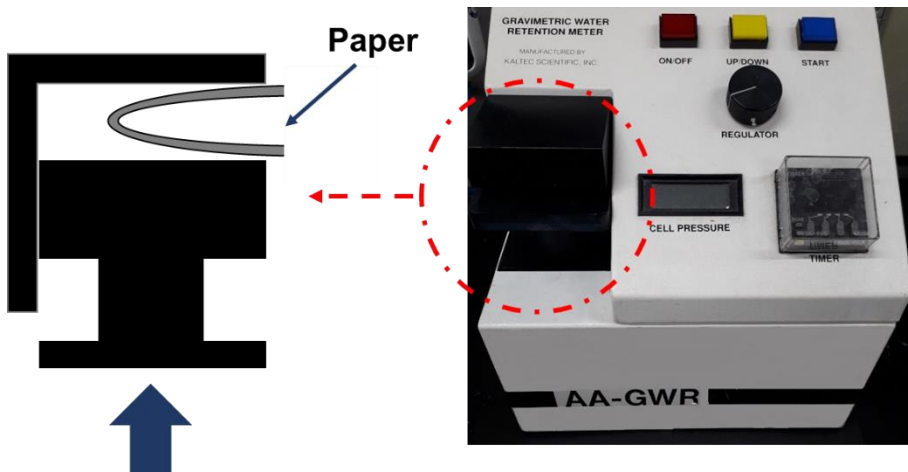


Fig. 4-4. Folding of coated papers using AA-GWR.

Because of anisotropic characteristics of paper, the direction of folding affects the stress and elongation development during paper folding (Oh et al., 2016; Pál et al., 2017). Hence, as shown in Figure 4-5, during folding the

direction of the fold was considered and the coated papers were folded in alignment with fibers orientation (MD fold) and perpendicular to the fiber orientation (CD fold).

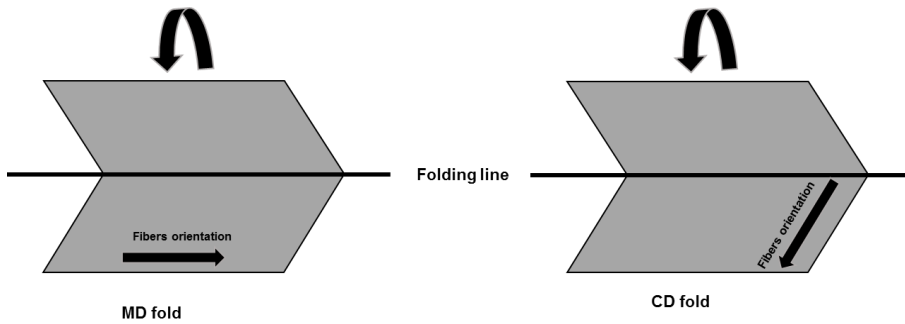


Fig. 4-5. Definition of MD and CD foldings.

The folded area of the papers then scanned by a scanner (Epson Perfection V370 photo) with a resolution of 1200 dpi, to obtain the images for fold crack evaluation. A sample holder with the inner angle of 30 degrees used for scanning of the folded area of papers (Sim et al., 2012). The image of the folding line was extracted from the scanned image and converted to a binary image by Photoshop software (Adobe Photoshop, Ver. 19. 1. 6). Then the cracked area was evaluated by an image processing software (Image Pro-Plus). Figure 4-6 shows the process of scanning and image processing. For each condition, 10 papers were folded and used for image processing and fold crack area measurement.

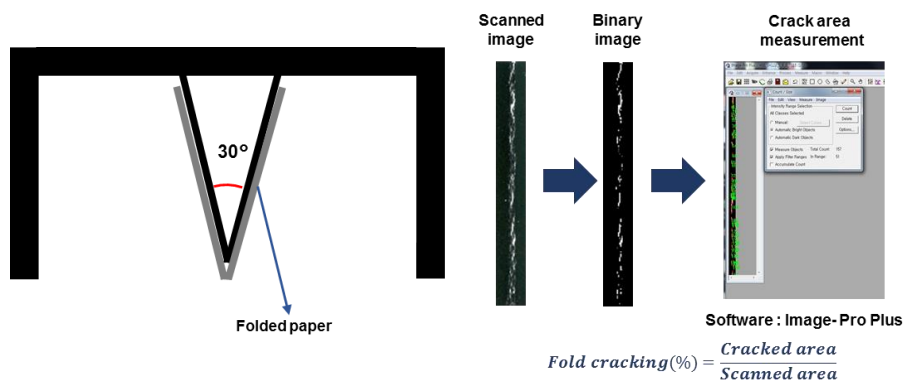


Fig. 4-6. Scanning and image processing of folded area.

## 2.13 Cross section images using FE-SEM

The folded papers were fixed on sample clips (Multiclips, Struers) then the samples were embedded in epoxy resin (Epofix resin, Struers). The samples cured for 48 h in a humidity room (23 °C, RH 50%). A polishing machine (LaboPol-5, Struers) was used for sample grinding and polishing. Silicon carbide grinding paper (SiC papers) #800, #1200, #2400, #4000, and 3 µm and 1 µm diamond particles were used to prepare samples with a smooth surface. Figure 4-7 shows how 4 folded papers embedded in epoxy resin.



Fig. 4-7. Folded paper for electron microscopy.

#### **2.14 Dry pick strength**

The dry pick strength was evaluated using a RI printer device (AKIRA, IHI machinery, Japan). For this measurement, the paper with a grammage of 198 g/m<sup>2</sup> was used as base stock. Coating color containing ground calcium carbonate as a pigment and 6 parts of S/B latex and 6 parts of starch was used as the pre-coating color. A coating color containing 10 parts of S/B latex was prepared as control top-coating color. To investigate the effect of SP latex as cobinder in top coating layer on dry pick strength of coated paper, 2 parts of S/B latex was substituted with SP latex and the base papers were double coated. The formulation of coating colors is shown in Table 4-10. The paper samples were taken into contact with a role which was coated with 0.4 g of a standard red ink with a tack value of 15. The printed samples then brought into contact with a set-off paper. The set-off paper then scanned and the obtained images

were converted into binary images using the Photoshop software (Adobe Photoshop, Ver. 19. 1. 6). The picked area then was calculated by image processing using Image J software (v1. 51 k.).

Table 4-10. Formulation of coating colors.

Components (pph)		Pre-coating color	Top-coating color	
			Control	Trial
Pigment	Hydrocarb 60	100	80	80
	Setacarb HG	-	20	20
Binder	S/B latex	6	10	8
	Starch	6	-	-
	SP latex	-	-	2

### 3. Results and discussions

#### 3.1 Characteristics of the latexes

The properties of the SP and S/B latexes used for this study are shown in Table 4-11.

Table 4-11. Properties of the latexes.

Latex	Solids (%)	pH	Viscosity (cP)	Particle size (nm)	Gel content (%)	MC% of latex films
S/B	50.0	7.9	364	147	96.7	1.2
SP	48.9	6.6	194	90.3	99.6	4.4

The SP latexes was synthesized using styrene, butyl acrylate, acrylic acid as monomers and stabilized by a protective shell. Starch and polyvinyl alcohol used during polymerization to provide the steric protection of the SP latex dispersion. Figure 4-8 shows the TEM micrograph of the SP latex particles. It clearly shows that the core polymer is surrounded by a protective layer.



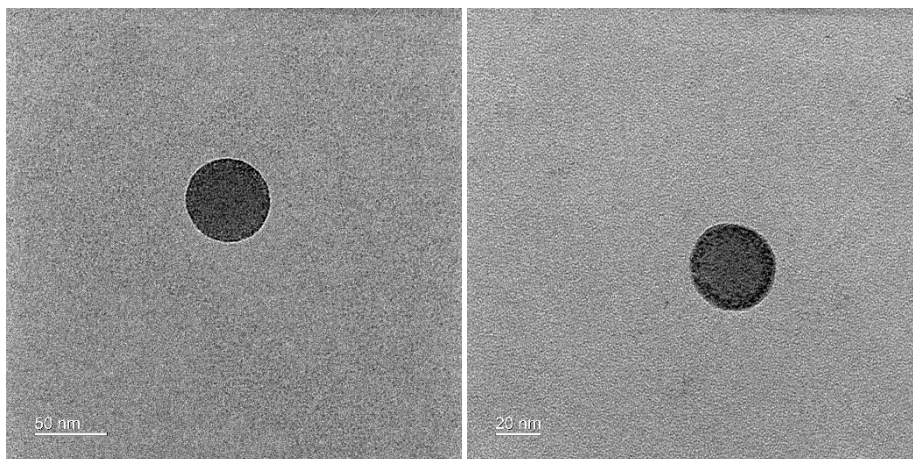


Fig. 4-8. TEM micrograph of SP latex particles.

FTIR spectra of the S/B and SP latexes are shown in Figure 4-9. SP latexes were stabilized with the use of a protective shell containing oxidized starch and PVA, which are hydrophilic. The infrared spectrum showed a wide absorption associated with hydroxyl groups between  $3700$  and  $3000\text{ cm}^{-1}$  (Figure 4-9).

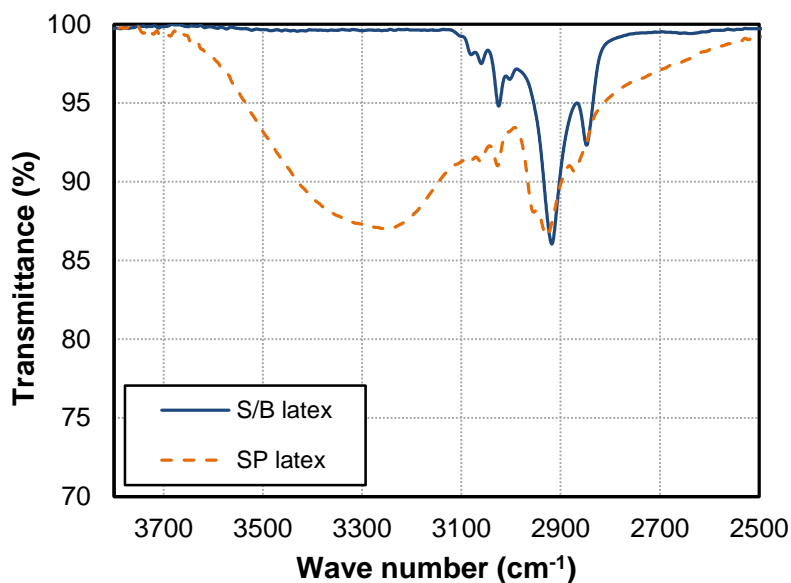


Fig. 4-9. FT-IR spectra of the latex films.

### 3.2 Pore size distribution of coated paper

The pore size distribution of the coated papers is shown in figure 4-10. The result shows that when more S/B latex was substituted with SP latex, the porosity increased especially those with a diameter of 50 to 80 nm.

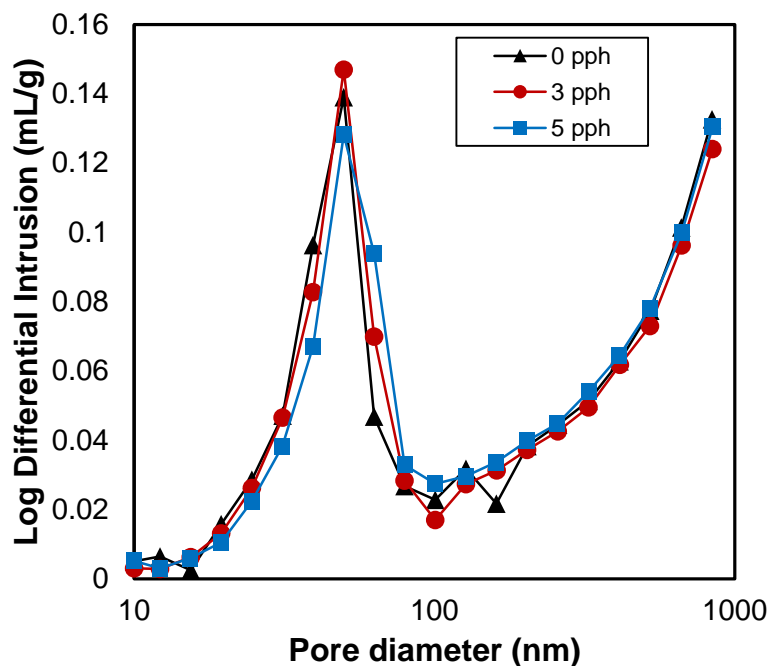


Fig. 4-10. Pore size distribution of the coated paper.

### 3.3 Surface properties of coated paper

Effect of SP latex on the gloss and roughness of the coated paper are shown in figure 4.11. The roughness of the coated paper gradually increased with an increase of SP latex addition. The gloss of the coated paper containing only S/B latex as binder was slightly higher, which can be explained by lower roughness of the coated paper. Interaction between coating color components induced by SP latex resulted in formation of weekly flocculated structure in coating color (as shown in chapter 3) and a more surface roughness of the coated paper.

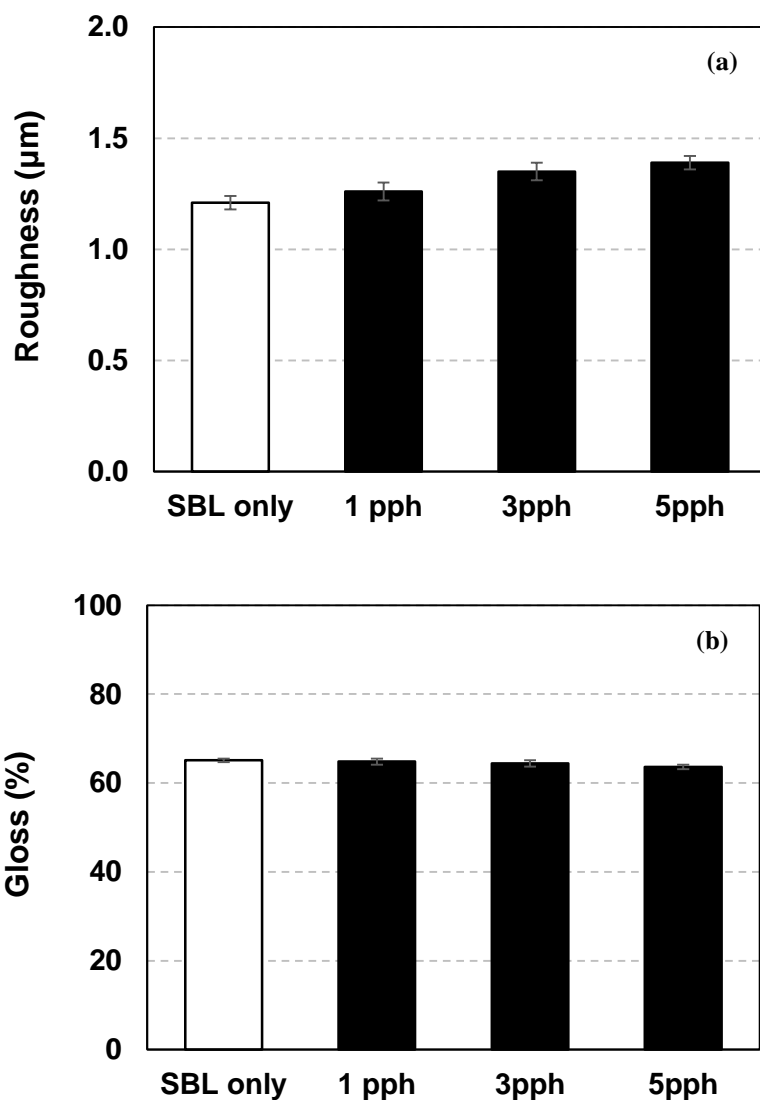


Fig. 4-11. Effect of SP latex on roughness (a) and gloss (b) of the coated paper.

The surface of the coated papers was studied using microscopy. The scanning electron micrographs of the coated papers (Fig. 4-12) reveal that the addition of SP latex enhanced the surface roughness of the coated papers.

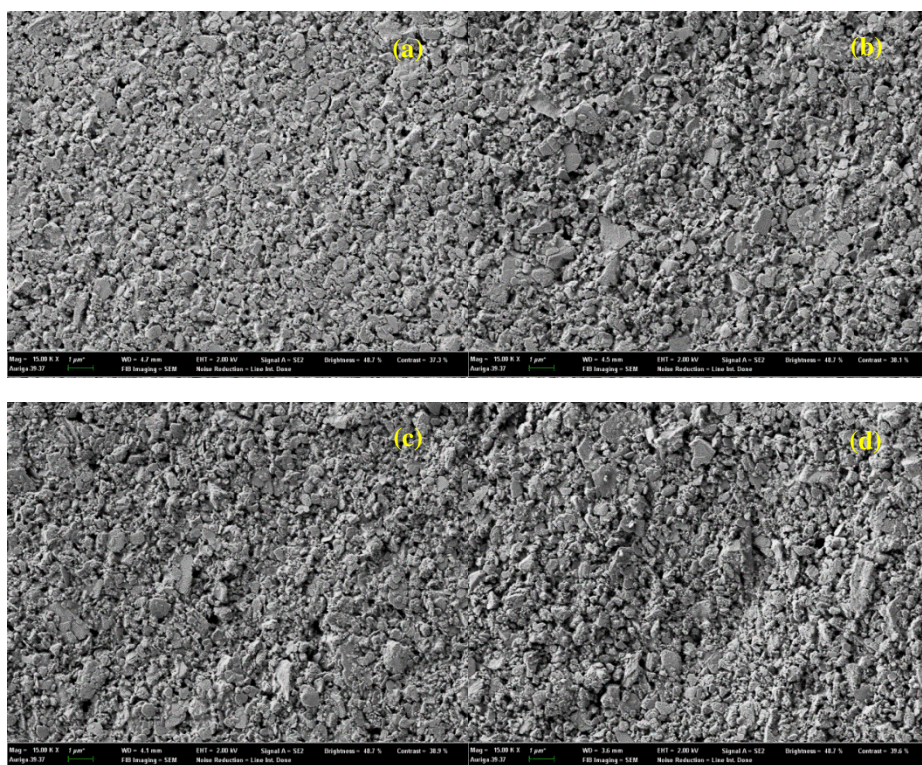


Fig. 4-12. FE-SEM micrographs of the surface of coated paper: (a), 0 pph of SP latex; (b), 1 pph of SP latex; (c), 3 pph of SP latex; and (d), 5 pph of SP latex.

### 3.4 Optical properties of the coated paper

Effect of SP latex on the opacity and brightness of the coated paper are shown in figure 4.13. The result shows that, although when S/B latex was replaced with SP latex, the porosity and roughness of the coated paper slightly increased, but the opacity and brightness of coated paper were not affected much.

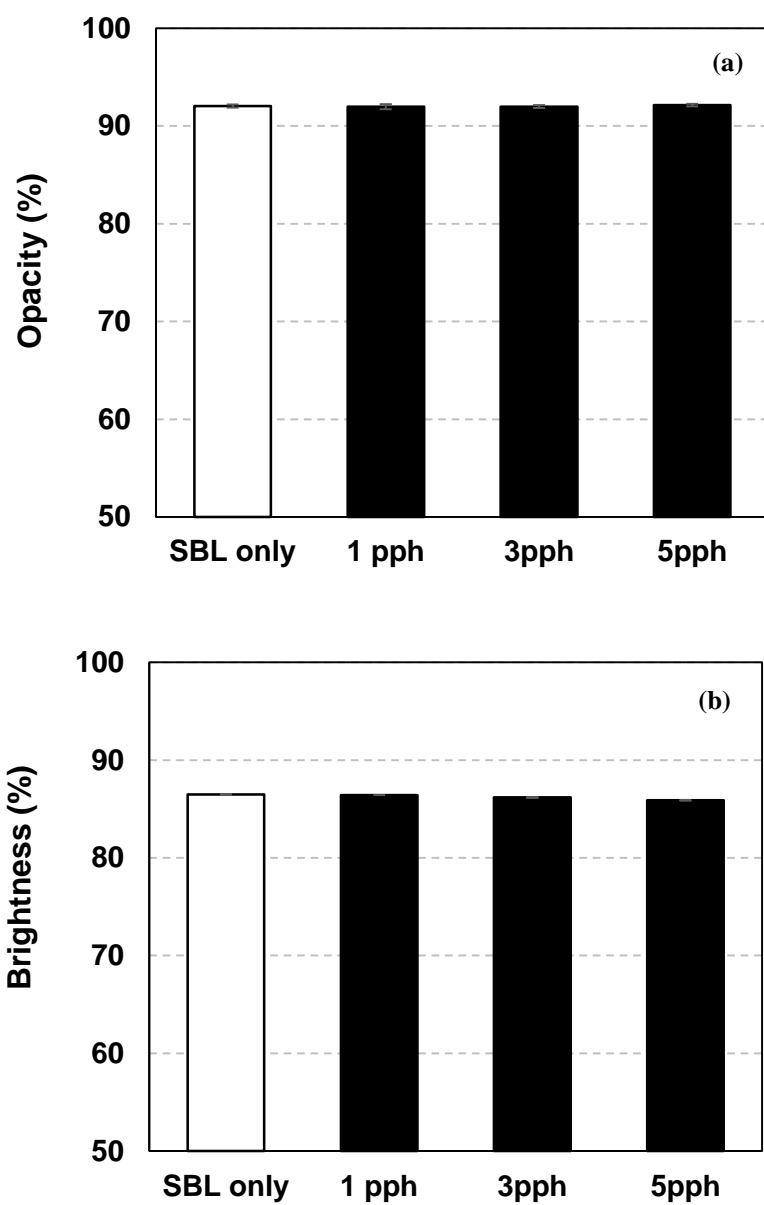


Fig. 4-13. Effect of SP latex on opacity (a) and brightness (b) of the coated paper.

### 3.5 Ink absorption ratio of the coated paper

The ink absorption ratio of the coated papers is depicted in Figure 4-14. When 1 part of S/B latex was replaced with SP latex, the ink absorption ratio slightly decreased. However, when more SP latex was added, the ink absorption ration increased as well. This can be attributed to the higher porosity and roughness of the coated paper as a result of SP latex addition.

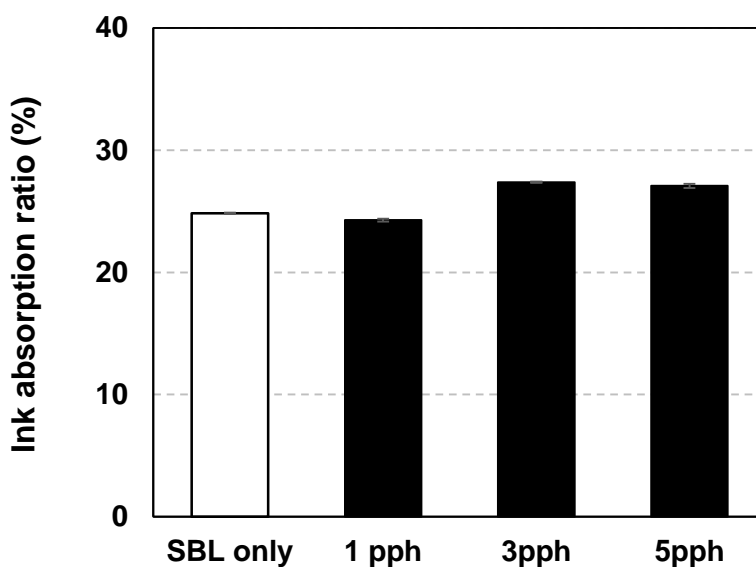


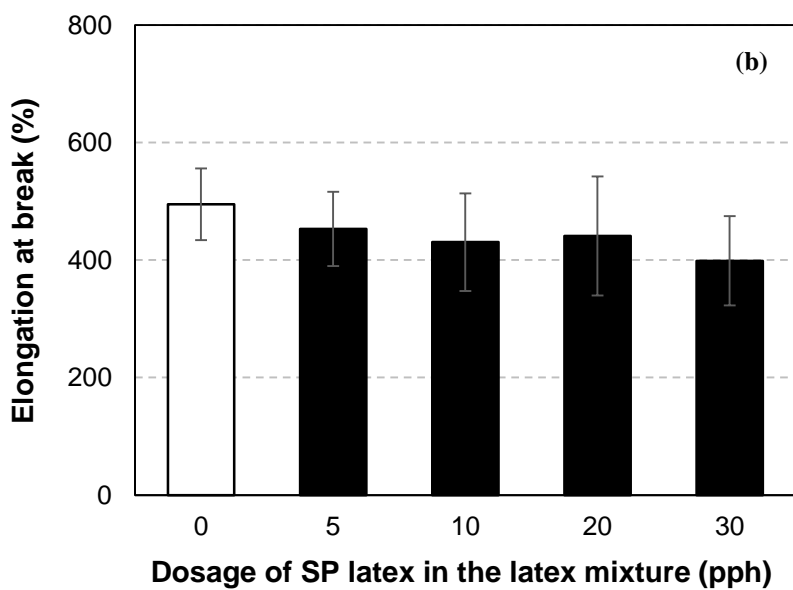
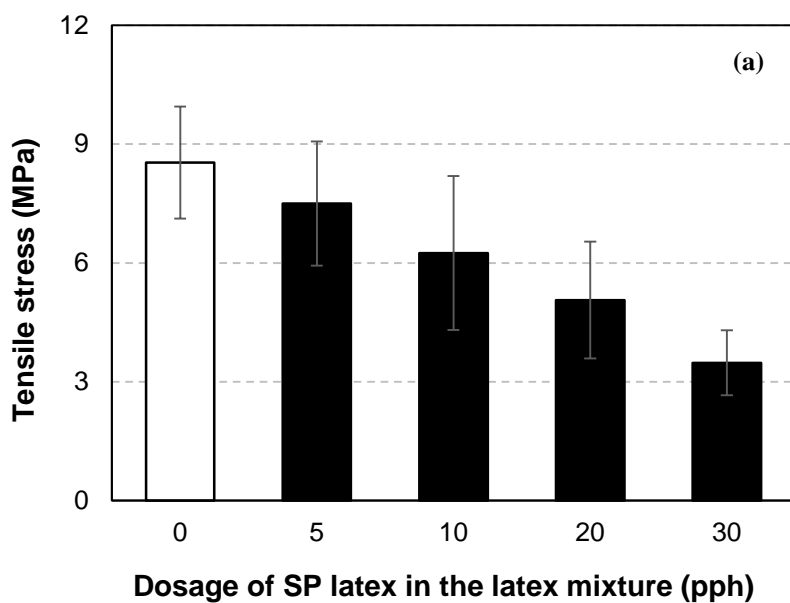
Fig. 4-14. Ink absorption ratio of the coated paper

### 3.6 Tensile properties of latex film

S/B and SP latexes and dispersions contained different amounts of S/B and SP latexes were coated on the glass substrate. After drying in an oven for 10

minutes, the coating was detached carefully and used for tensile measurement. The protective shell of SP latex particle consisted of starch and PVA gave a rigid film after drying, which was too brittle to detach without damage from the glass substrate. Figure 4-15 shows, the tensile properties of the latex films. Replacement of S/B latex with S/P latex could reduce the tensile strength of the generated latex film. As more S/B latex was substituted with SP latex, tensile stress reduced more. The same trend was observed for the elongation at break and MOE. SP and S/B latexes have a different drying behavior. SP latex has a hydrophilic shell consisted of starch and PVA and consequently different drying behavior compared to S/B latex. Hence during drying of the applied blend of the latexes on the glass substrate, SP latex may move with the water molecules to the surface of the polymer blend and phase separation of the latexes might occur likely which resulted in inferior tensile properties compared to the S/B latex only film. This result is in agreement with that of some previous studies which reported a phase separation and reduced mechanical properties, when the mixed latexes, have different drying rates or when a film of incompatible polymer blends is formed (Feng et al., 1995; Mahapram & Poompradub, 2011; Sheu et al., 1990).





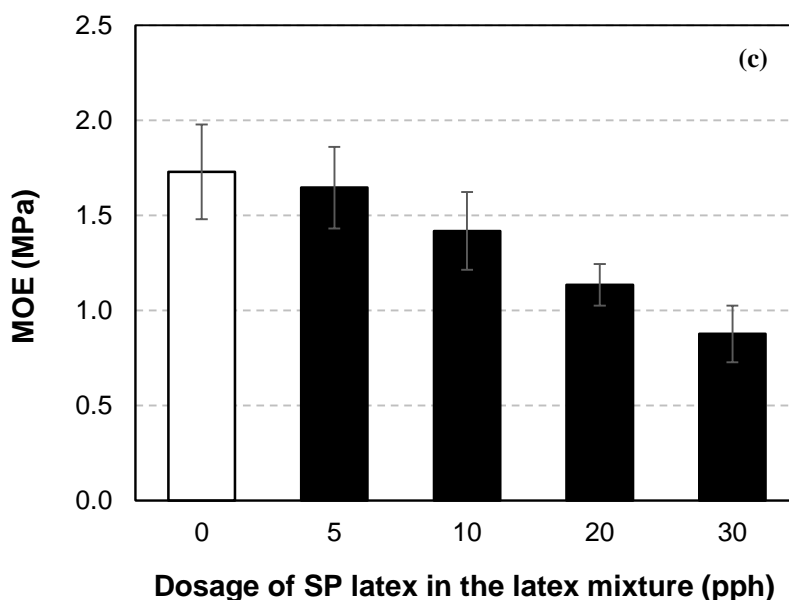
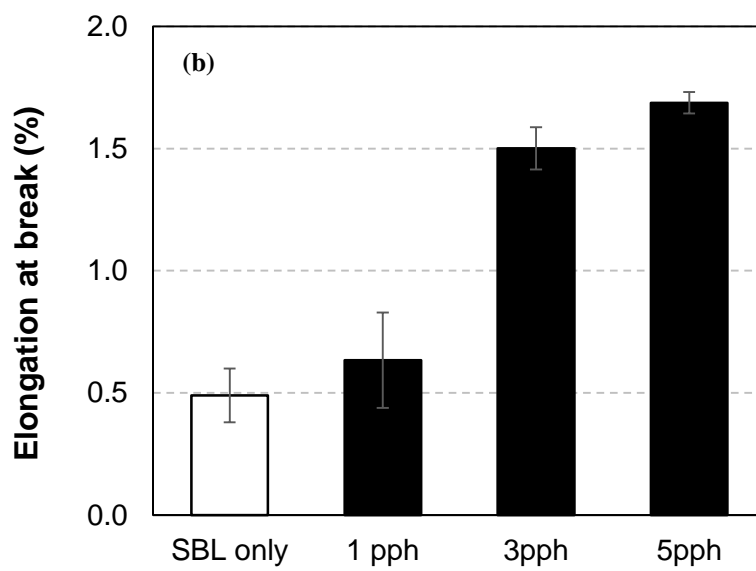
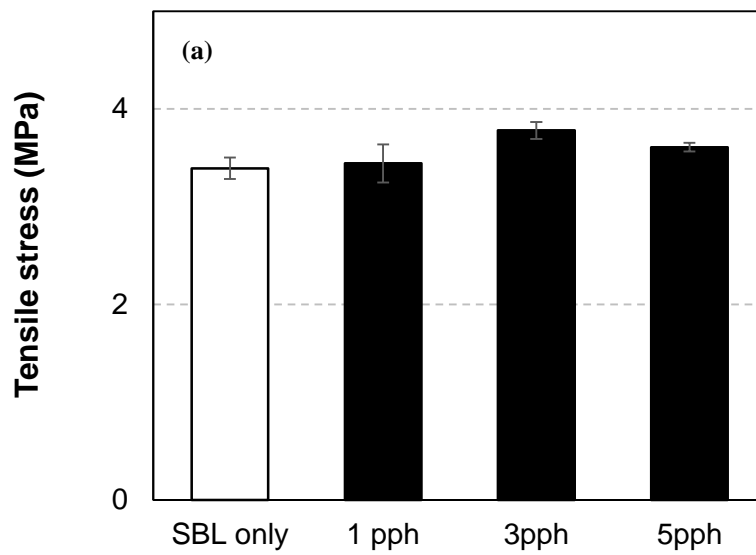


Fig. 4-15. Tensile stress (a), elongation at break (b) and MOE (c) of the latex films prepared with different substitution rates of S/B with SP latex.

### 3.7 Tensile properties of coating layer

Mechanical properties of a coating layer that influence the fold crack resistance of coated paper are affected by coating color composition especially by the type of binder (Husband et al., 2006; 2009; Oh et al., 2016; Okomori et al., 2001). To examine the effect of SP cobinder on the strength and stretch properties of coating layer without the influence of the base paper, coating layers were applied on plastic films were detached after drying. Figure 4-16 shows the tensile stress, elongation at break, and MOE of the starch films prepared with and without the latex additive.



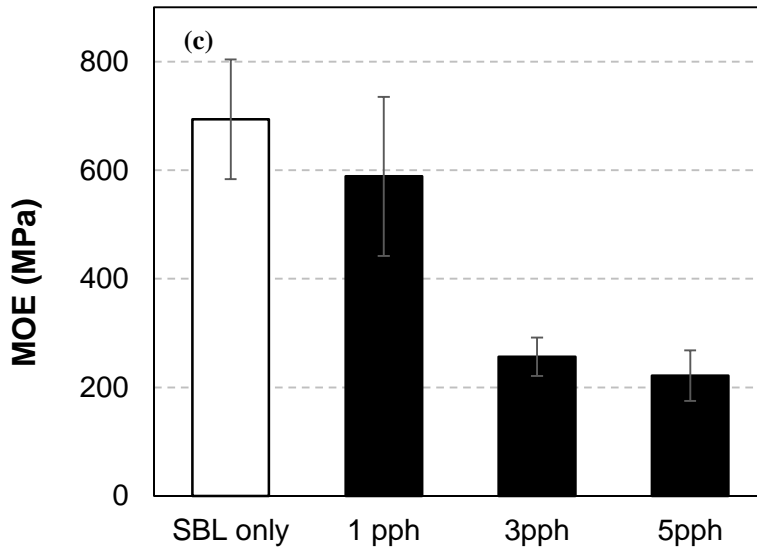
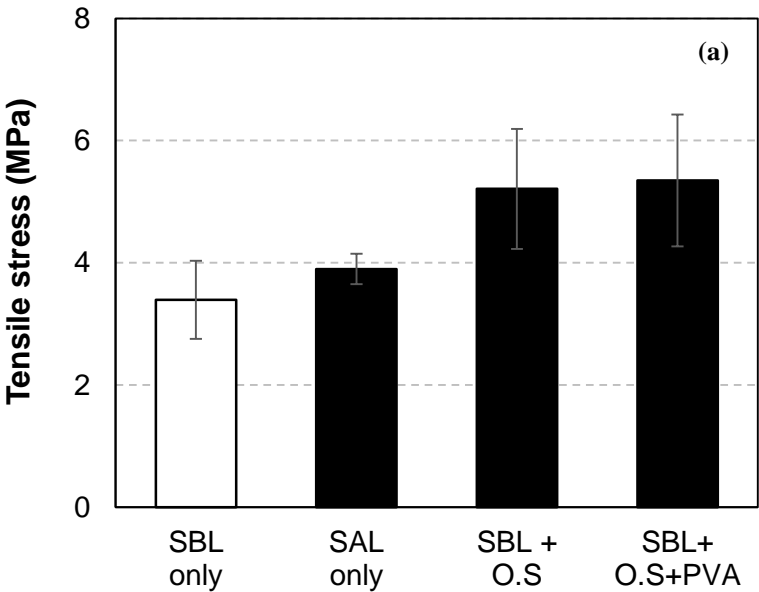


Fig. 4-16. Tensile stress (a), elongation at break (b) and MOE (c) of the coating layers prepared with different substitution rates of S/B with SP latex.

The result showed that the tensile strength of the coating layers was improved when S/B latex was substituted with SP latex indicating the used SP latex contained coating gave a stronger layer. This may be explained by reinforcement of the coating layer by starch and PVA. Replacement of 1 pph of the S/B latex with SP latex resulted in higher elongation at break of the coating layers. When more S/B latex was substituted with SP cobinder, the elongation at break significantly increased. When S/B latex was replaced with SP cobinder, the MOE of the coating layers reduced, indicating a less stiff coating composite with better elasticity was formed. It was attributed to the substitution of butadiene monomer with acrylate monomer in the coating layer. Higher strain and lower elastic modulus shows better extensional properties as a result of SP latex addition to coating color which was attributed to the monomer composition of SP latex ( Oh et al., 2015). This suggests that use of SP latex

would have a positive effect in fold cracking of coated papers. The protective shell of SP latex contains starch and PVA, which provide advantages in strength development. Oh et al. (2016) found that S/A latex has a greater extensional property than S/B latex, which is advantageous in decreasing fold cracking of coated paper. The moisture content of the coating conditioning in humidity room humidity was around 1 %.

To confirm this, in another set of experiment effect of S/A latex as a sole binder and substitution of S/B latex with oxidized starch or/and PVA as co-binders on tensile properties of coating layer were examined (Tabel 4-3 shows the coating color formulation). Due to a very high viscosity of coating color as a result of substitution of S/B latex with PVA, it was unable to make a coating color with 1.2 parts of PVA so the co-binder level kept 1.2 pph and coating colors containing 1.2 pph of oxidized starch and 0.9 oxidizes starch and 0.3 pph PVA were used for coating layer preparation. The result is shown in Figure 4-17.



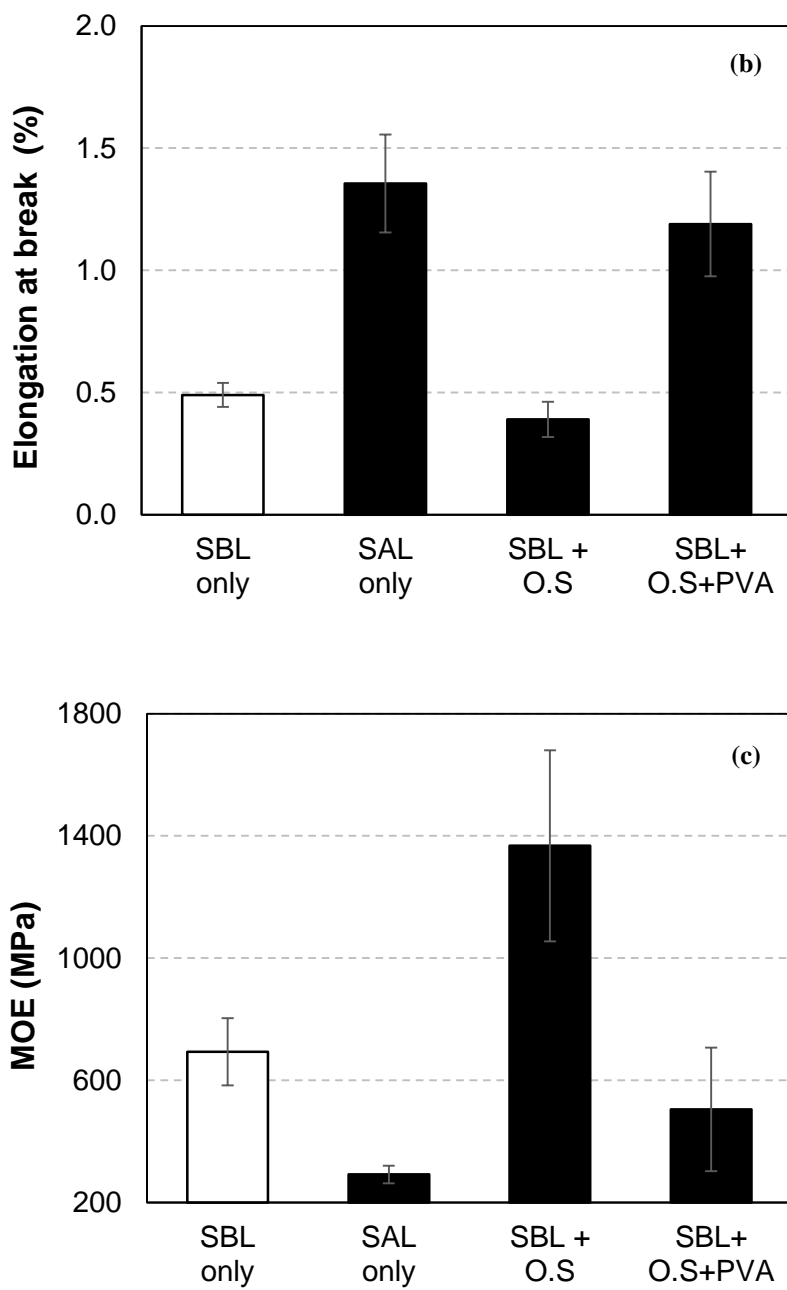


Fig. 4-17. Effect of S/A latex, oxidized starch and PVA on tensile stress (a),

elongation at break (b) and MOE (c) of the coating layers.

When S/A latex was used as a sole binder, tensile stress of coating layer slightly increased. On the other hand the elongation at break significantly increased and MOE of coating layers decreased. This can be attributed to the lower cross-linking degree of S/A latex compared with S/B latex which gives higher extensional properties to the coating layer. Effect of S/A latex on tensile properties of the coating layer was studied by Oh et al., (2016) and it was suggested that lower gel content of S/A latexes was favorable for extensional properties of the coating layer and consequently fold crack reduction.

The result also showed that the addition of oxidized starch and PVA to coating color could contribute to strength development of coating layer. When 1.2 pph of oxidized starch was used as a binder, the elongation at break reduced, while the MOE increased dramatically. This result agrees well with the previous studies that showed the addition of starch could reduce the elongation of a coating layer and increase the modulus of elasticity (Oh et al., 2015; Okomori et al., 2001; Rioux et al., 2011).

### **3.8 Tensile properties of coated paper**

The tensile properties of latex films and coating layers (part 3.2 and 3.3 in this chapter) showed that the use of SP latex as a co-binder negatively affect the tensile and strength properties of latex film. However, it could reinforce the coating layer and result in the formation of a strong coating composite with high elongation. A coating layer with high tensile strength and extensional

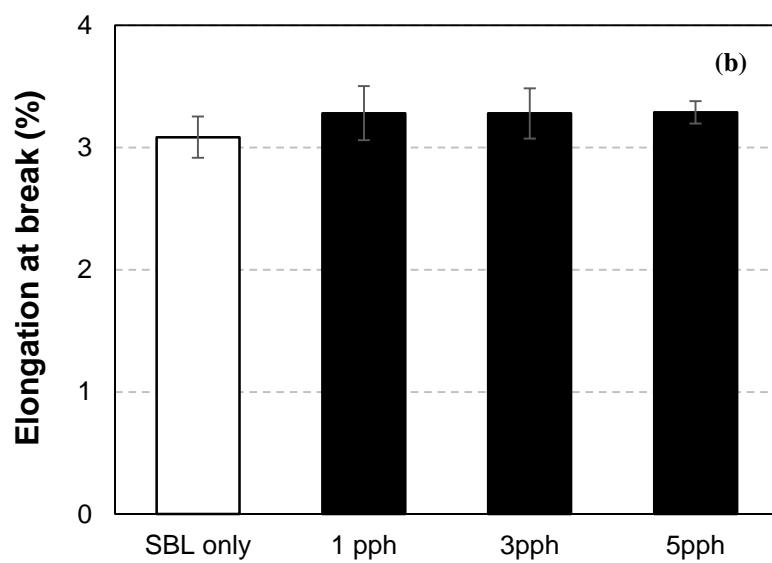
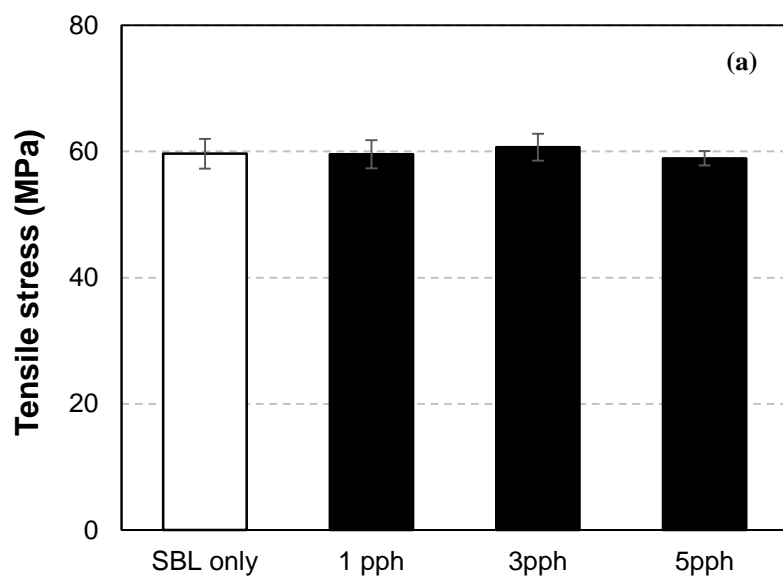
properties, and low MOE would be favorable for crack reduction. Besides the extensional properties of the coating layer, the elastic modulus and stiffness of coated paper affect the fold crack resistance of coated paper as the fold crack tendency reduces with a decrease of coated paper stiffness (Alam et al., 2009; Salminen et al. 2008a; 2008b). Hence the tensile properties of coated papers including the tensile stress, elongation at break and MOE for single and double coating were evaluated.

### **3.8.1 Tensile properties of single coated paper**

To test the effect of SP latex on the mechanical properties of paper, coating colors containing different substitution rate of S/B latex with SP cobinder were prepared and applied on base papers. The coat weight was 28 g/m<sup>2</sup>. To evaluate the effect of SP latex with minimum influence of the base paper, a paper with a grammage of 78 g/m<sup>2</sup> was used as a substrate. This allowed to reduce the variability caused by the base sheet when the mechanical properties of coated paper were measured.

Figure 4-18 shows the tensile stress, elongation at break and MOE of the coated papers in the machine direction (MD). Substitution of S/B latex with SP latex, did not significantly affect the tensile strength of the coated papers. However, it increased elongation at break of the coated papers and the MOE reduced as a result. It was attributed to the substitution of butadiene monomer with acrylate monomer. This indicated that SP latex can improve the flexibility of the coated paper with a consequent favorable effect on fold cracking.





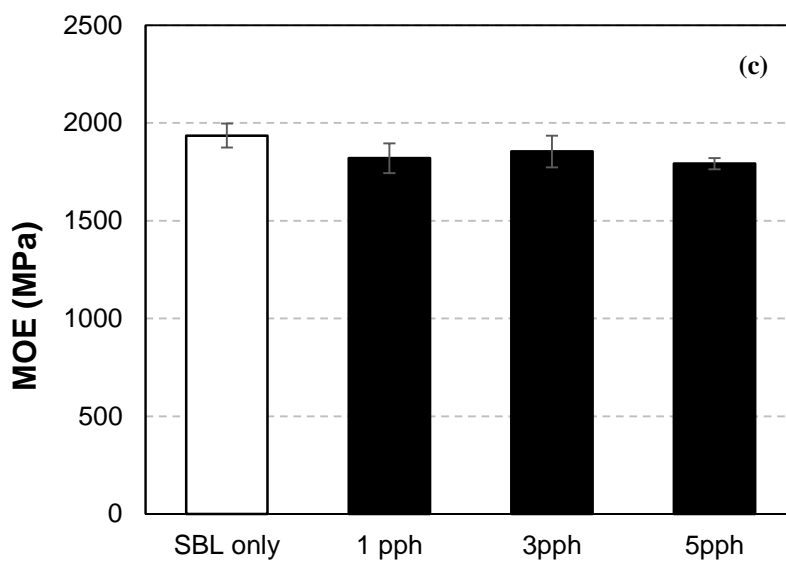


Fig. 4-18. Tensile stress (a), elongation at break (b) and MOE (c) of the single coated papers for the machine direction (MD).

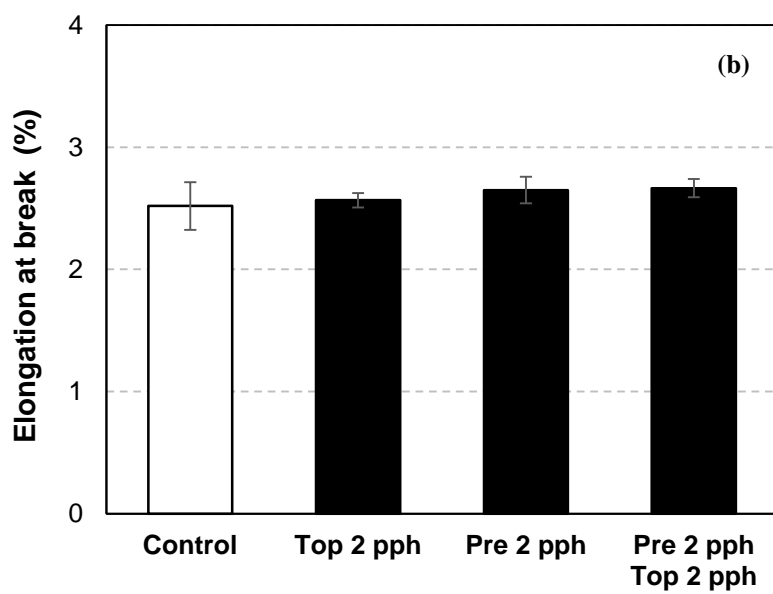
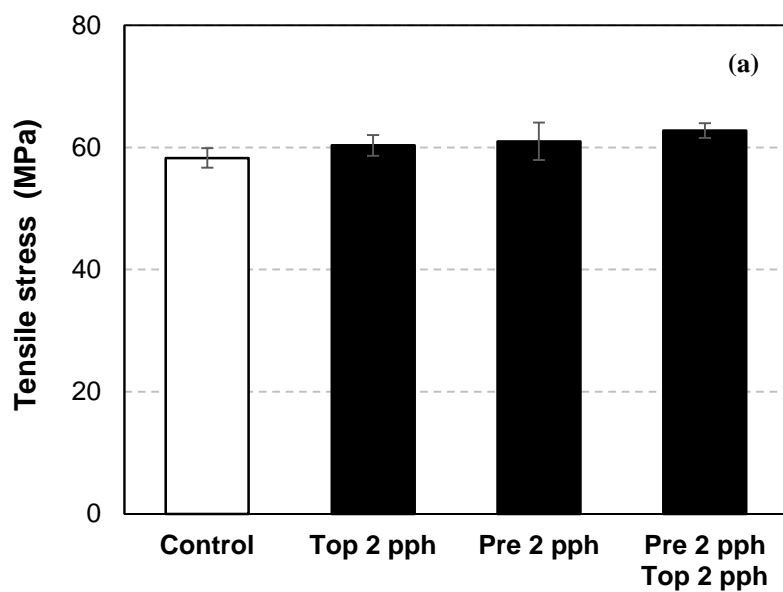
Table 4-12 shows the tensile properties of coated papers in the cross machine direction. A similar trend was observed for the tensile stress, elongation at break and MOE as in the machine direction.

Table 4-12. Tensile properties of coated papers for the cross machine direction (CD).

	S/B latex only	SP latex 1 pph	SP latex 3 pph	SP latex 5 pph
Tensile stress (MPa)	26.5	26.3	25.6	25.8
Elongation at break (%)	5.4	6.4	6.4	5.8
Elastic modulus (MPa)	489.7	414.1	399.1	444.1

### 3.8.2 Tensile properties of double coated paper

The tensile properties of double coated papers with a basis weight of 78 g/m<sup>2</sup> and a total coat weight of 30 g/m<sup>2</sup> were measured. 2 pph of S/B latex was replaced with SP latex in the top and/or pre-coating layer and the tensile properties of the coated papers were evaluated. The results are shown in Figure 4-19. It was found that the presence of SP latex in pre and top coating could slightly improve the extensional properties of coated papers. SP latex contains acrylate monomers which give better extensional properties to the coating layer. Higher tensile stress and elongation at break are favorable for decreasing fold crack.



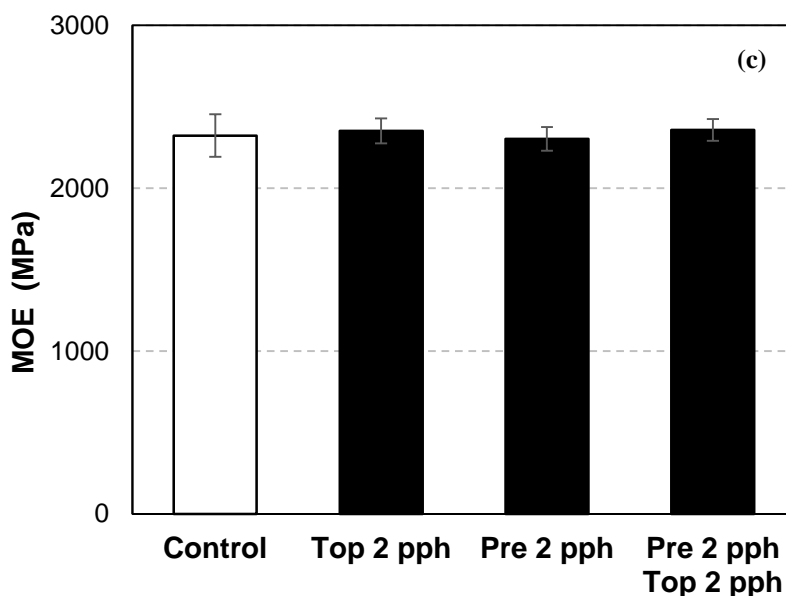


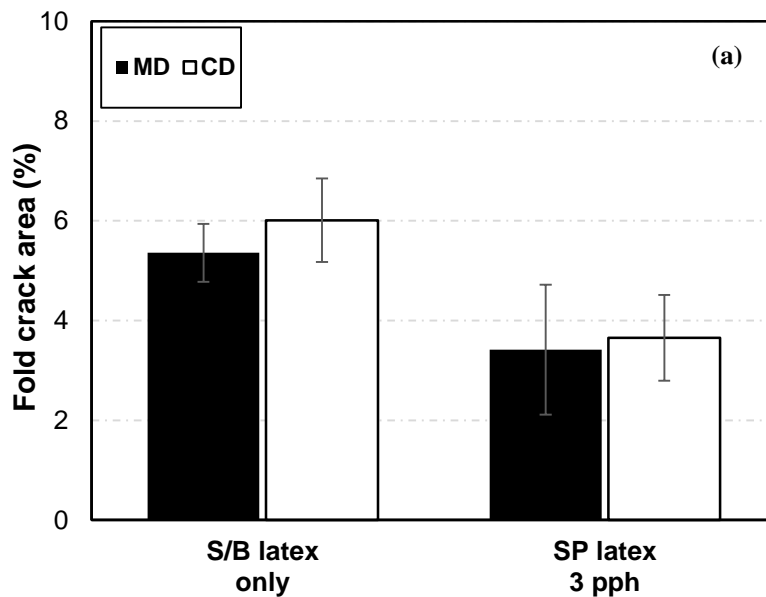
Fig. 4-19. Tensile stress (a), elongation at break (b) and MOE (c) of the double coated papers for the machine direction (MD).

### 3.9 Fold crack evaluation

Evaluation of the tensile properties of coating layer and coated papers showed that, extensional properties of the coating layer and coated papers improved when S/B latex was substituted with SP cobinder. This suggests that SP latex has a potential to increase fold crack resistance of the coated papers. To examine this, single and double coated low basis weight and high basis weight papers were folded in MD and CD direction and the effect of SP latex on fold crack tendency was evaluated.

### 3.9.1 Fold crack evaluation of single coated paper

Figure 4-20 shows the average crack area of the single coated papers. When 3 pph of S/B latex was substituted with SP latex, the fold crack area was reduced for low and high grammage base papers. Higher crack area obtained for the papers with a grammage of 198 g/m<sup>2</sup> than the papers with a grammage of 78 g/m<sup>2</sup>. The CD folding resulted in a slightly larger crack area than MD folding. These results agree with that of the previous study by Oh et al. (2016).



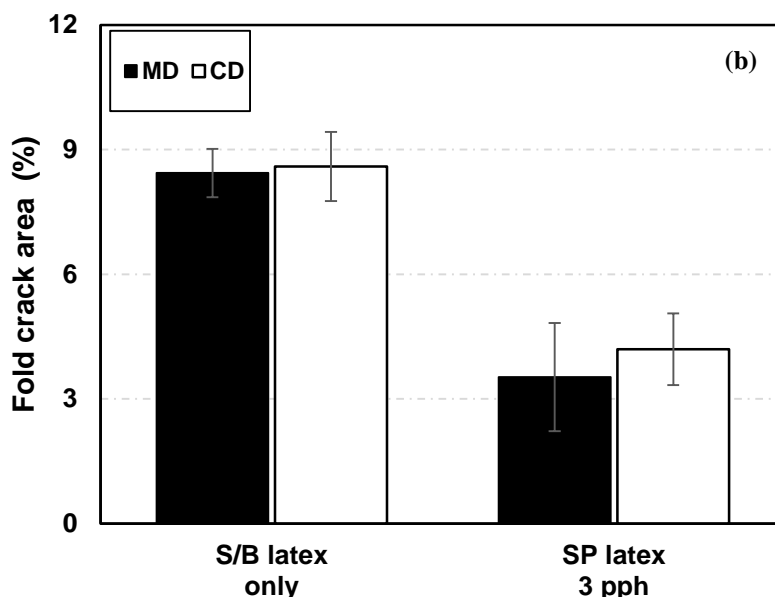


Fig. 4-20. Average crack area for MD and CD fold. (a) grammage of base paper: 78 g/m<sup>2</sup>, (b) grammage of base paper: 198 g/m<sup>2</sup>.

The cross-sectional images of the folded samples were obtained and are shown in Fig. 4-21, 4-22 and 4-23. Large coating layers were detached from the base stock when S/B latex was used as a sole binder. In contrast, the coating layer containing SP latex as a cobinder showed no large detachment of the coating layer. This was likely due to the improved flexibility of the coating layers. It is clear that a paper with a higher grammage gives larger fold cracks. The difference between MD and CD fold cracks was not very clear for a paper with low basis weight, in contrast, the images of high grammage paper that showed larger cracks in CD folding.

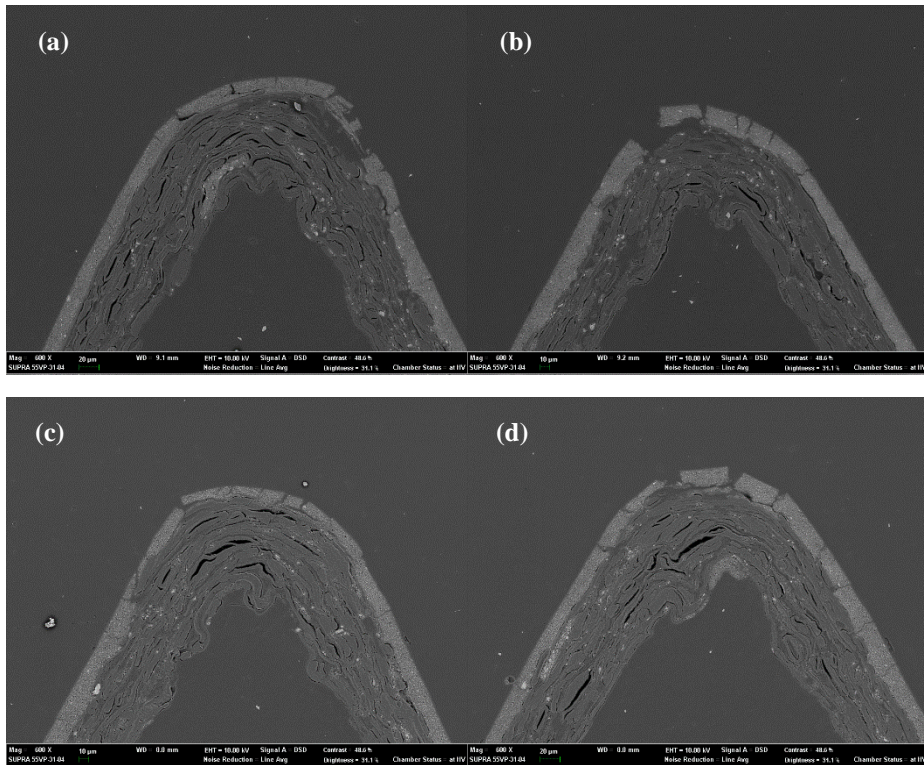


Fig. 4-21. Cross-sectional images of the folded paper in CD. S/B latex only used as a binder in image (a) and (b), while SP latex was used as a cobinder for paper coating in image (c) and (d). Base paper: 78 g/m<sup>2</sup>.



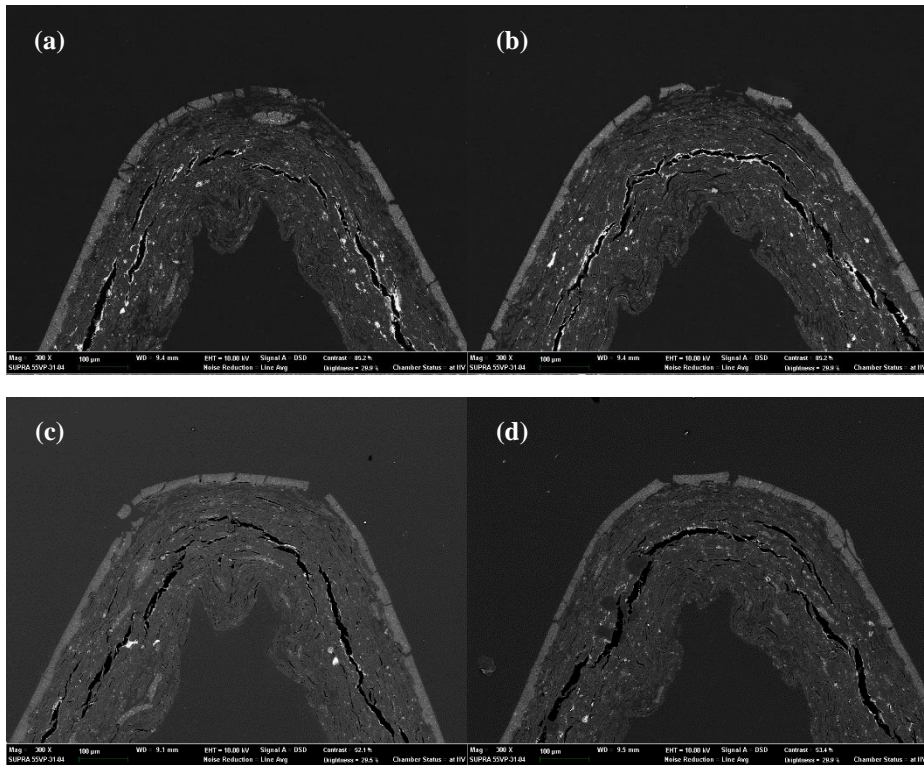


Fig. 4-22. Cross-sectional images of the folded paper in MD. S/B latex only used as a binder in image (a) and (b), while SP latex was used as a cobinder for paper coating in image (c) and (d). Base paper: 198 g/m<sup>2</sup>.

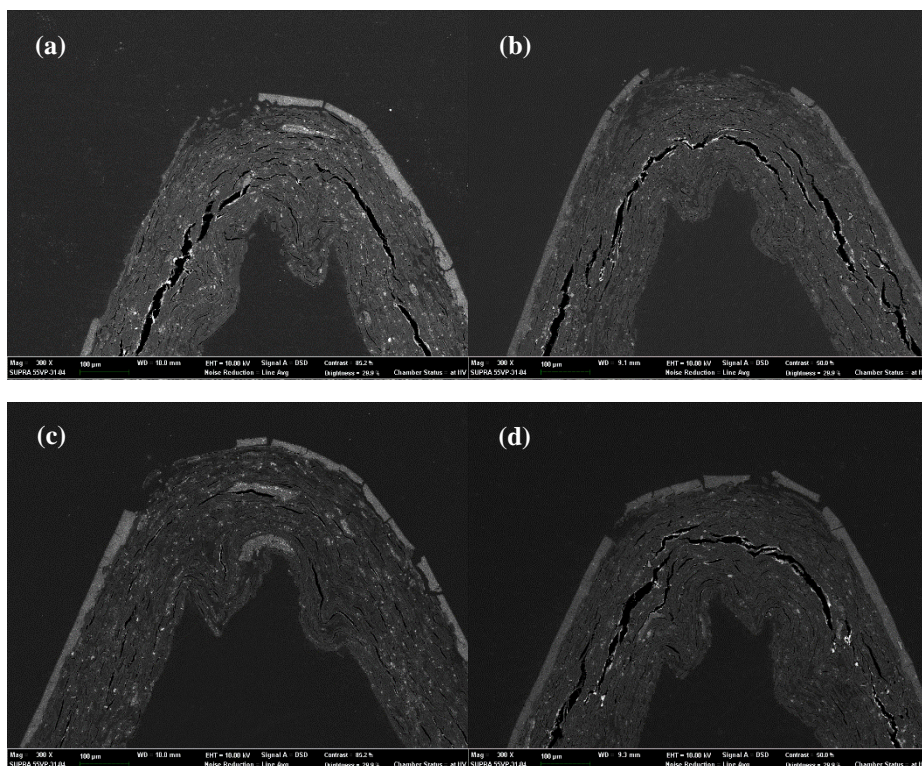
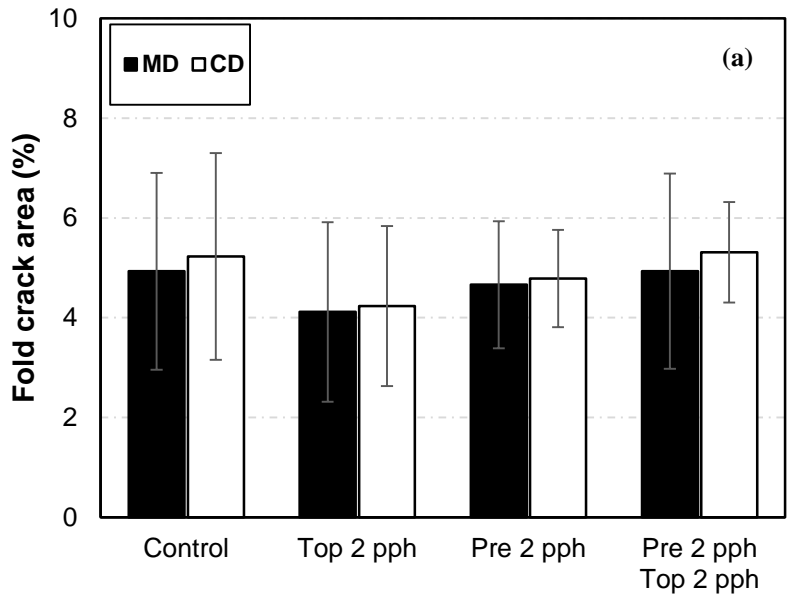


Fig. 4-23. Cross-sectional images of the folded paper in CD. S/B latex only used as a binder in image (a) and (b), while SP latex was used as a cobinder for paper coating in image (c) and (d). Base paper: 198 g/m<sup>2</sup>.

### 3.9.2 Fold crack evaluation of double coated paper

Effect of SP latex on fold cracking behavior of a double coated paper was investigated. Presence of SP latex in the top and pre-coating layer and substitution of SP latex with S/B latex and starch were evaluated. Figure 4-24 shows the average crack area of folded papers when S/B latex was replaced with 2 parts of SP latex in the top and pre-coating layer. It was found that when S/B latex was substituted with SP latex in the top and pre-coating layers, the

crack was reduced for MD and CD fold. SP latex contains acrylate monomers which give better extensional properties to the coating layer. It was also reported by Oh et al. (2016) that S/A latex has a greater extensional property than S/B latex, which is advantageous in decreasing fold cracking of coated paper. Addition SP latex to top-coating layer was more effective to increase fold crack resistance. Higher grammage base paper gave greater fold crack areas because thicker paper caused greater strain development in the coating layer. The CD folding resulted in a slightly larger crack area than MD folding.



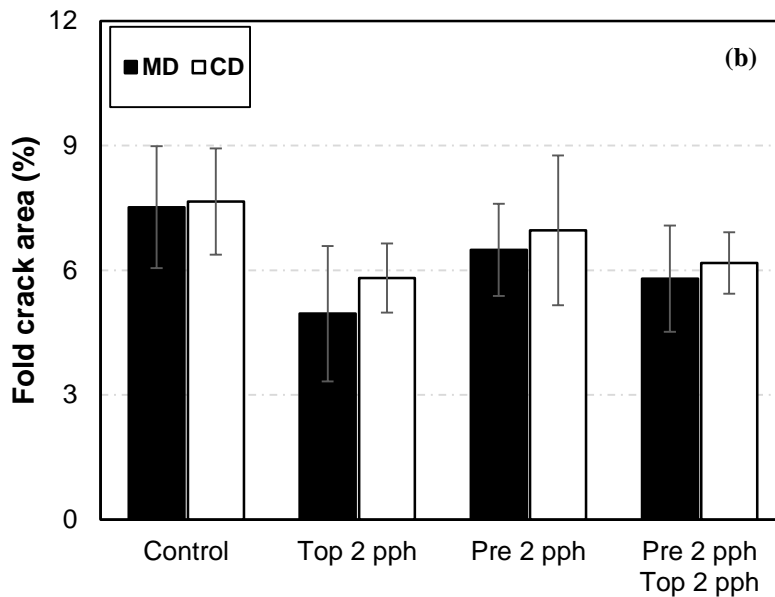
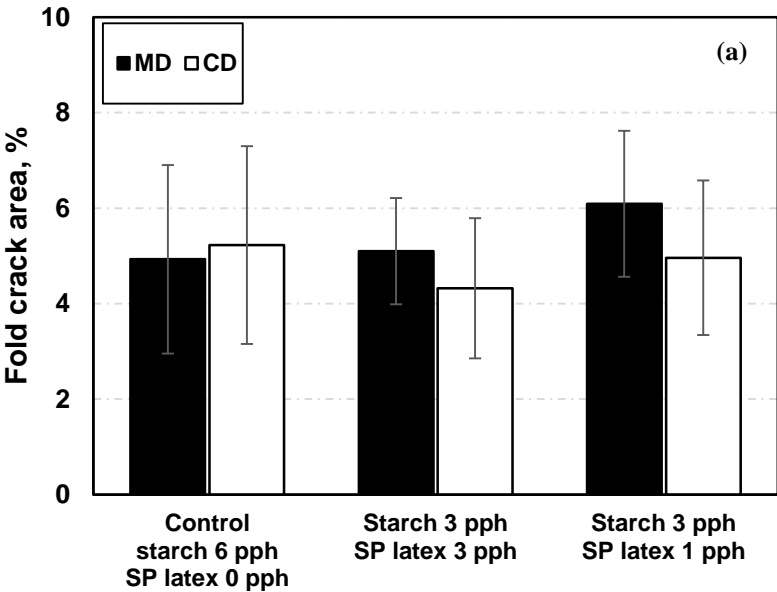


Fig. 4-24. Crack area when S/B latex was replaced with SP latex in pre and to coating for MD and CD fold. (a) grammage of base paper: 78 g/m<sup>2</sup>, (b) grammage of base paper: 198 g/m<sup>2</sup>.

Figure 4-25 shows the crack area after paper folding when starch was replaced with SP latex in the pre-coating layer. For the base paper with a grammage of 78 g/m<sup>2</sup>, when 3 parts of starch was replaced with SP latex, the crack area for MD fold was not affected. However, smaller crack area was obtained in the CD fold. In the case of base paper with a grammage of 198g/m<sup>2</sup>, the crack area in MD and CD reduced. It shows the starch in the coating layer tends to increase the fold crack area. This result agrees with that of Oh et al. (2015), which reported the negative effect of starch in the pre-coating layer on fold crack resistance of coated paper.

In another case, the total binder content in pre-coating layer reduced, as 3 parts of starch in the pre-coating layer was replaced with 1 part of SP latex. This resulted in the appearance of a larger crack area for MD and CD fold when a base paper with a grammage of 78 g/m<sup>2</sup> or 198 g/m<sup>2</sup> was used. This shows the importance of total binder content of pre-coating layer which for providing the coating layer strength.



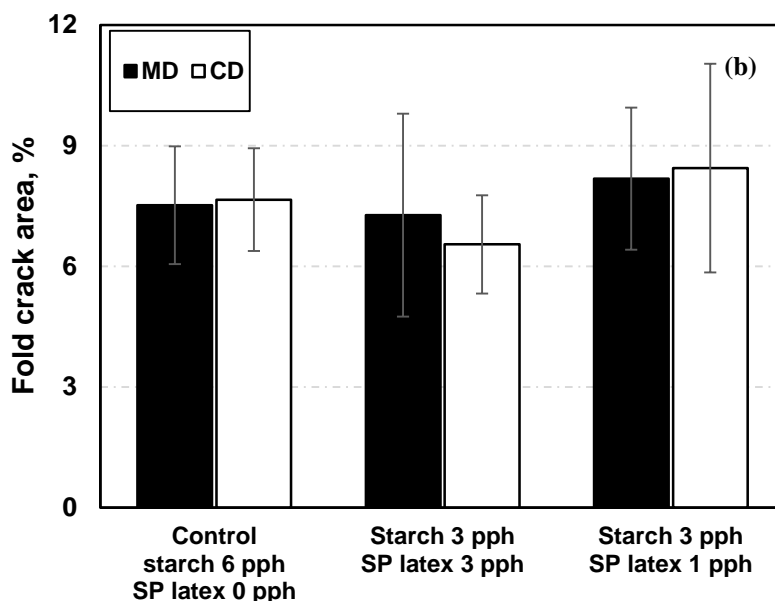


Fig. 4-25. Crack area when starch was replaced with SP latex in pre-coating for MD and CD fold. (a) grammage of base paper: 78 g/m<sup>2</sup>, (b) grammage of base paper: 198 g/m<sup>2</sup>.

### 3.9.3 Fold crack evaluation of two sides coated paper

The outer and inner layers of paper are subjected to tension and compressive stress respectively top side and bottom side of the base paper were coated and the effect of SP latex on coating layer was investigated and the result is shown in Figure 4.26. When both top and bottom sides of the paper were coated with the control coating color, the lowest MD fold crack was obtained. In the case of CD folding, application of SP latex in top and bottom coating layer resulted in less crack area.

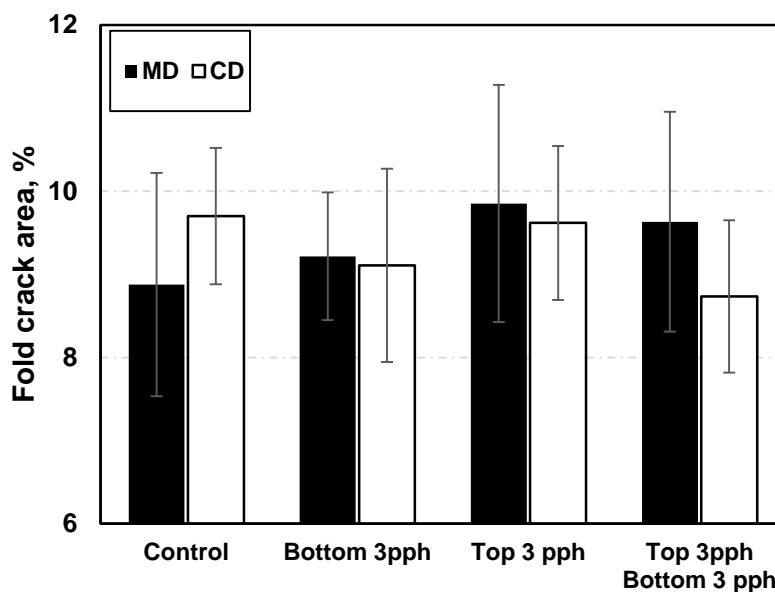


Fig. 4-26. Crack area of two sides coated paper for MD and CD fold. Grammage of base paper: 198 g/m<sup>2</sup>.

### 3.10 Dry pick strength

The effect of SP latex in top coating layer on dry pick strength of double coated paper was investigated using RI printer. The printed samples then brought into contact with a set-off paper. The set-off paper then scanned and the obtained images were converted into binary images using Photoshop software. The original and binary images are shown in figure 4-27.

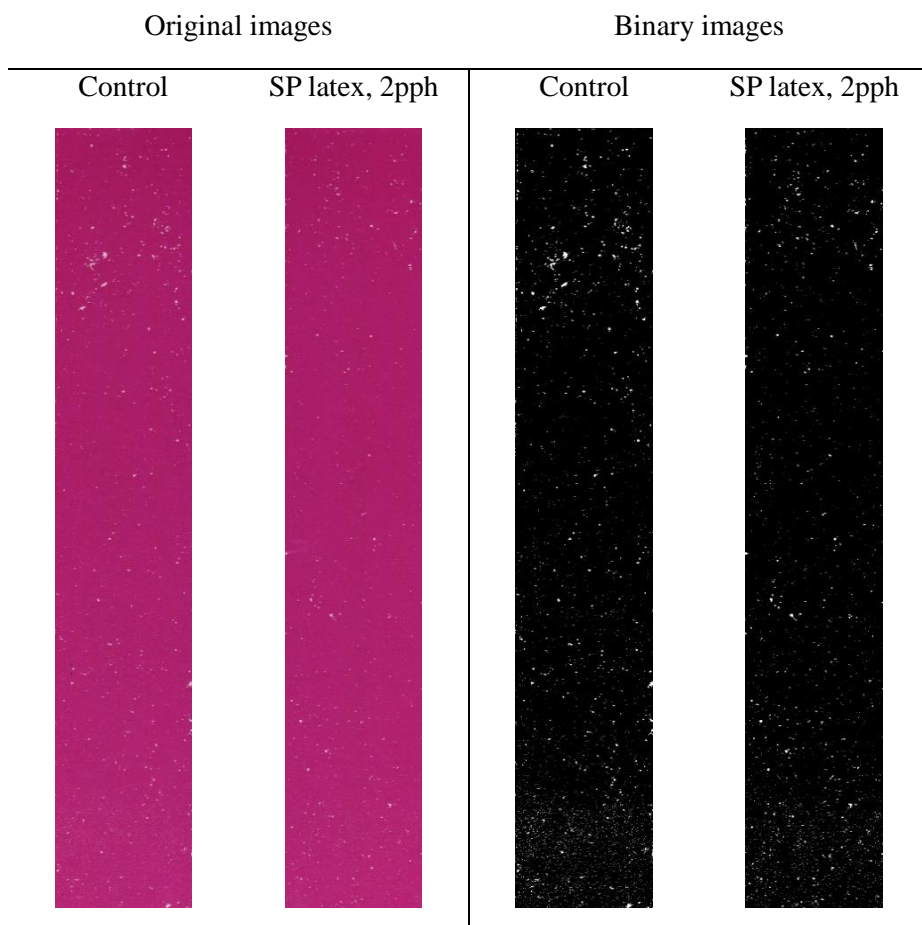


Fig. 4-27. Scanned and binary images of the coated paper after picking.

The images show clearly that application of the SP latex as cobinder could enhance the dry-pick resistance of the coated paper. This is attributed to the formation of a coating layer with higher strength and extensional properties. The picked area then was calculated by image processing and picked area values of 4.8% and 3.1% was obtained for control and trial samples. The smaller particle size of the SP latex contributed to the development of higher binding force and acrylate monomers of the latex improved the strain of the



coating layer. This result suggests that SP latex could improve dry pick strength of the coated paper.

#### 4. Summary

Fold cracking of coated paper is highly dependent on the properties of the coating layer. The coating composition including pigments and binders affect the properties of the coating layer. A latex with a good extensional property could improve the flexibility of the coating layer and result in a less crack area after folding of coated paper. It was attributed to the substitution of butadiene monomer with acrylate monomer.

The pore size distribution and surface properties of the coated papers was evaluated. The results revealed that substitution of S/B latex with SP latex influenced the porosity of the coated paper. The porosity increased when more SP latex replaced with S/B latex. It was also found that a coated paper with higher roughness and ink absorption ratio was obtained, while the gloss, brightness, and opacity of the coated paper was almost remained at a similar level to the control samples.

The influence of SP latex on the extensional properties of coating layer was investigated. The result showed that the addition of SP latex improved the tensile strength and elongation at break of the coating layers. Acrylate monomer of the SP latex resulted in better extensional properties of the coating layer.

The effect of SP latex addition on the tensile properties of coated paper was also investigated. When S/B latex was replaced with SP co-binder, the tensile stress and elongation at break of coated papers were increased while MOE of coated papers reduced. As the SP latex dosage was increased in the coating layer, the extensional properties of the coated papers enhanced. Higher tensile

stress and elongation of coated paper are highly favorable for decreasing the fold crack.

The influence of SP latex on the fold cracking of single coated paper was investigated. To examine this a base paper with a grammage of 78 g/m<sup>2</sup> or 198 g/m<sup>2</sup> was coated with coating colors with or without SP latex as cobinder. The result showed that addition of SP latex to coating layer could reduce the fold crack area for MD and CD fold.

2 parts of S/B latex was replaced with SP latex in the top and pre-coating layer. The result revealed that the presence of SP latex in the top and pre-coating layer, is favorable for fold crack reduction. Moreover, when 3 parts of starch in pre-coating color was replaced with SP latex, the fold crack area slightly reduced for MD and CD fold, indicating the influence of starch on the rigidity of coating layer.

Finally, the effect of SP latex on dry pick strength of the coated paper was investigated and the result suggested that SP latex had a potential of improving the dry pick resistance of the coated paper.

## **Chapter 5**

Overall conclusions and remarks

Fold cracking of coated paper is highly dependent on strength and elastic properties of the base material and extensional properties and strength of the coating layer. In this study application of sterically stabilized (SP) latexes were used as an additive for surface sizing and paper coating. SP latexes polymerized with acrylate monomers which improve the extensional properties of the starch film or coating layer. Moreover, SP latexes were stabilized with a protective shell, containing starch and PVA that have high compatibility with the starch solution or coating color components.

The physical properties of these latexes, including surface tension, foaming tendency were investigated and compared with conventional emulsion-polymerized latexes. Emulsion-polymerized latexes contained surfactants which orient themselves in the air-water interface and increase the stability of the latex foam. Surface activity of the SP latex is dependent on the protective shell that carries both hydrophilic and hydrophobic part. The foaming tendency result showed that even SP latex gave similar foaming with S/B latex, both the generated foams broke up more rapidly than S/B and S/A latexes. Hence it is expected use of SP latex would reduce the foaming problems during surface sizing.

The film formation of surface sizing agents is important to obtain the desired effect of surface sizing. Thereby, the tensile strength, elongation at break and MOE of the oxidized starch films with and without latexes were evaluated. The result showed that extensional properties of the starch films improved when SP latex was added to the starch solution. Compared with starch films containing S/B latex, higher tensile stress and elongation at break and a lower MOE obtained, when SP latex was added to the starch solution. Acrylate monomers in the SP latex, enhanced the tensile and elongation properties of the starch film.

This showed that the SP latex would have a positive effect in improving the extensional properties to of surface sized paper.

The starch solution without or with 3 parts of S/B and SP latexes were prepared and applied onto the paper surface. The results suggested that an improvement in the tensile strength and extensional property could be achieved with the use of latex as a surface sizing additive. This improvement was more pronounced for the SP latex compared with the S/B latex indicating the contribution of acrylate monomer in extensional properties of sized paper. In addition, the bending stiffness and internal bond strength of the sized papers with 0, 3, and 5 pph of SP latex was measured. The tensile strength and stretch increased when SP latex was used as a surface sizing additive, which decreased the stiffness in both the machine direction (MD) and cross-machine direction (CD). The internal bond strength also increased when SP latex was added to the sizing solution. It was indicated that the use of SP latex would provide an opportunity to reduce the fold cracking after coating. The 3-pph dosage showed similar levels of improvement in the tensile strength and bending stiffness as at 5 pph.

Physical properties of three SP latexes with a similar shell component, shell/core ratio and different content of acrylic acid monomer, including viscosity, particle size, and zeta potential as a function of pH was studied. The dynamic light scattering result showed that the average particle size of the SP latexes increased as pH increased from 5 to 9. It was attributed to the protective shell of the latex which swells under alkaline condition. The viscosity of the latexes was also measured and the result showed that the viscosity of the latexes increased as the pH increased. When the protective shell of the latexes swelled under alkaline condition, the volume fraction of the disperse phase increased

which resulted in higher viscosity. Acrylic acid monomers were also deprotonated in alkaline condition and increased the viscosity by electrostatic repulsion in the polymer backbone. The result also showed that as the acrylic acid content of the SP latex increased, the viscosity increased more at the alkaline condition. Because most of the carboxyl groups were deprotonated and enhanced the repulsion of the ionized groups within a particle under alkaline condition. Hence the viscosity of SP-3 with higher acrylic acid content was greater than that of SP-1 and SP-2. This was confirmed with a more negative zeta potential of the latex particles at pH 9, especially for SP-3 which reveals more carboxylic groups deprotonated under alkaline pH.

Viscoelastic properties of latexes as a function of pH were also studied. The result revealed that viscose modulus was higher than the elastic modulus, indicating no solid structure and interactions between particles. The viscosity of SP-3 latex, however, was shear-dependent. Deformation of the latex particles as a result of applied shear would result in shear thinning behavior of SP-3 latex.

The effect of SP latex as a cobinder on viscoelastic properties of coating color was investigated. An amplitude sweep test was carried out to study the microstructure of the coating color. The addition of SP latex to the coating color increased the elastic and viscose moduli. The elastic modulus was higher than viscose modulus in the linear viscoelastic region. It was found that when SP co-binder substituted with S/B latex the critical stress at which the structure was destroyed increased indicating a stronger interaction between coating color components was formed. Frequency sweep test was also carried out and the result confirmed weakly flocculated structure was built up in coating color. Both elastic and viscous moduli increased with an increase of frequency that shows the formation of network and flocculation structure in coating colors.

Hydrophilic polymers of the protective shell along with carboxylic groups of the acrylate in SP co-binder resulted in a weakly flocculated structure in coating color. More substitution of S/B latex with SP co-binder resulted in higher storage modulus that indicates more interaction of the coating color. The zeta potential of the coating color was measured and it was found that the addition of SP latex had no influence on zeta potential, suggesting no adsorption of the SP latexes on pigment particles. Hence interaction between coating components was induced by depletion flocculation of coating color

The viscosity of coating color as a function of shear rate increased when S/B latex was replaced with SP latex. Hydrophilic parts of the stabilizers absorbed the liquid phase of the disperse system and made the coating color more solid like. Moreover, weak interaction between coating components as a result of the SP latexes resulted in a higher viscosity of coating color compared with the coating color containing only S/B latex. Water retention property of the coating color was increased by SP cobinder addition due to the hydrophilic characteristics of the protective shells of the SP latex.

The porosity of the coating layers was measured and it was found that flocculation of the coating color by SP latex resulted in the formation of a more porous coating layer. The results also showed that the formation of a more porous coating layer increased the light scattering and resulted in higher opacity and brightness of the dried coating.

The influence of SP latex dosage on tensile strength and stretch of the coating layer was studied. The result revealed that, as the SP latex dosage was increased in the coating layer, the extensional properties of the coating layer enhanced. Higher tensile stress and elongation are highly favorable for decreasing the fold



crack. The effect of SP latex on tensile properties of coated paper was investigated. The result showed that, when S/B latex was replaced with SP co-binder, the tensile stress and elongation at break of coated papers were increased while MOE of coated papers reduced, indicating a coating color with more flexibility was formed.

The influence of SP latex on fold cracking of coated papers was examined. A base paper with a grammage of 78 g/m<sup>2</sup> or 198 g/m<sup>2</sup> was coated with coating colors with or without SP latex as cobinder. The result showed that addition of SP latex to coating layer could reduce the fold crack area for MD and CD fold. It was likely attributed to the monomer composition of the SP latex. Effect of SP latex on fold cracking of double coated paper was also studied. S/B latex was replaced with SP latex in the top and pre-coating layer. The result revealed that the presence of SP latex in top and pre-coating layer, is favorable for fold crack reduction. Moreover, when 3 parts of starch in pre-coating color was replaced with SP latex, the fold crack area slightly reduced for MD and CD fold, indicating the influence of starch on the rigidity of coating layer.

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