การตกแต่งกันยับผ้าฝ้ายโดยปราศจากฟอร์มัลดีไฮด์ด้วยโคพอลิเมอร์ของกรดอะคริลิกและกรดมาลิอิก

นางสาว อุษา ฐานะสุนทรฤกษ์

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NON-FORMALDEHYDE DURABLE PRESS FINISHING OF COTTON FABRIC USING ACRYLIC ACID / MALEIC ACID COPOLYMER

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Applied Polymer Science and Textile Technology
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นางสาวอุษา ฐานะสุนทรฤกษ์ : การตกแต่งกันยับผ้าฝ้ายโดยปราศจากฟอร์มัลดีไฮด์ด้วยโคพอลิเมอร์ของกรดอะคริลิกและกรดมาลิอิก. (NON-FORMALDEHYDE DURABLE PRESS FINISHING OF COTTON FABRIC USING ACRYLIC ACID / MALEIC ACID COPOLYMER) อ. ที่ปรึกษา : รศ. ดร. วีระศักดิ์ อุดมกิจเดชา, อ. ที่ปรึกษาร่วม : นางพิศมัย ลิขิตบรรณกร; 130 หน้า. ISBN 974-347-079-4.

การตกแต่งผ้าฝ้ายให้มีสมบัติกันยับสามารถทำได้โดยการใช้โคพอลิเมอร์ของกรดอะคริลิก (AA)และกรดมาลิอิก(MA) ทำหน้าที่เป็นสารตกแต่งกันยับแบบปราศจากฟอร์มัลดีไฮด์ร่วมกับโซเดียมไฮโปฟอสไฟต์ซึ่งเป็นตัวเร่งปฏิกิริยาโดยวิธีจุ่มน้ำยา-อบแห้ง-อบผนึก ในการศึกษาขั้นต้นจะเลือกระบบในการตกแต่งกันยับที่เหมาะสมระหว่างระบบ AA/MA และ ระบบ MA/AA รวมทั้งอุณหภูมิและเวลาที่เหมาะสมในการอบผนึก หลังจากนั้นจะศึกษาผลของภาวะการอบผนึก มอนอเมอร์ และตัวเร่งปฏิกิริยาต่อองศาการคืนตัวต่อรอยยับ ความแข็งแรง และความขาวของผ้าที่ผ่านการตกแต่งกันยับแล้ว และใช้เทคนิคอินฟราเรดสเปกโทรสโกปี (FT-IR) ในการยืนยันการเกิดหมู่เอสเทอร์ในผืนผ้าที่ผ่านการตกแต่งกันยับแล้ว นอกจากนี้ยังใช้เทคนิคคาร์บอน 13 นิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี (^{13}C NMR) และเทคนิคเจลเพอร์มิเอชันโครมาโทกราฟี (GPC) ในการหาโครงสร้างและน้ำหนักโมเลกุลของโคพอลิเมอร์ ตามลำดับ

จากการทดลองพบว่าการตกแต่งผ้าฝ้ายโดยใช้เรซินในระบบ AA/MA ที่อัตราส่วนโมล 1:0.5 และ1:1 โดยใช้กรดอะคริลิก 12% และตัวเร่งปฏิกิริยา 12% ภายใต้ภาวะอบผนึกที่อุณหภูมิ 160 °C เป็นเวลา 3 นาที สามารถทำให้ผ้าฝ้าย 100% มีองศาการคืนตัวต่อรอยยับและความขาวของผ้าที่ผ่านการตกแต่งด้วยเรซินใกล้เคียงกับผลที่ได้จากผ้าที่ผ่านการตกแต่งด้วย DMDHEU ขณะที่ความแข็งแรงของผ้าต่ำกว่าเล็กน้อย

ภาควิชา วัสดุศาสตร์ ลายมือชื่อนิสิต.....................................

สาขาวิชา วิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ลายมือชื่ออาจารย์ที่ปรึกษา......................

ปีการศึกษา 2543 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.................

##b2552123 : MAJOR APPLIED POLMER SCIENCE AND TEXTILE TECHNOLOGY
KEY WORD : DURABLE PRESS / FINISHING / NON-FORMALDEHYDE / UNSATURATED CARBOXYLIC ACID

USA THANASOONTHORNROEK: NON-FORMALDEHYDE DURABLE PRESS FINISHING OF COTTON FABRIC USING ACRYLIC ACID / MALEIC ACID COPOLYMER. THESIS ADVISOR: ASSOC.PROF. DR. WERASAK UDOMKICHDECHA, THESIS CO-ADVISOR PISSAMAI LIKITBANAKORN, 130pp. ISBN 974-347-079-4.

The wrinkle recovery property of finished cotton fabric was imparted using acrylic acid (AA) / maleic acid (MA) copolymer as a crosslinking agent with sodium hypophosphite as a catalyst by pad-dry-cure method. Preliminary study was conducted to select suitable treatment system between AA/MA system and MA/AA system including suitable temperature and curing time. After that, effects of curing conditions, monomers and catalyst on dry wrinkle recovery angle, tensile strength and whiteness of the finished fabrics were examined. FT-IR spectroscopy was used to identify the presence of ester groups to confirm the ester crosslinking reaction occurred in the treated fabric. Moreover, structure and molecular weight of the copolymer were characterized using NMR and GPC analysis, respectively.

The resin treatments with AA/MA system at 1:0.5 and 1:1 mole ratios using 12%AA and 12%catalyst under the curing condition at 160 °C for 3 min were found to be the effective DP finishing for 100% cotton fabric. The results of dry wrinkle recovery angle and whiteness index of the resin finished fabrics could be compared to those of the finished fabrics treated with DMDHEU. However, tensile strength retention property of the resin finished fabrics were found slightly lower.

Departmant of Materials Science Student Signature…………………
Field of study Applied Polymer Science and Textile Technology Advisor's Signature…………………
Academic Year 2000 Co-advisor's Signature……………

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TABLE OF CONTENTS

Page

Chapter

Page

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

Figure Page

Figure Page

LIST OF ABBREVIATIONS

AA	acrylic acid
^{0}C	degree Celsius
cm^{-1}	unit of wavenumbers
%CV	percent of coefficient of variation
DMDHEU	dimethylol dihydroxyethylene urea
DWRA	dry wrinkle recovery angle
^{0}F	degree Fahrenheit
g	gram
in.	inch
kgf	kilogram force
l	liter
MA	maleic acid
min	minute
mm	millimeter
nm	nanometer
%owb	percent on weight of bath
%owf	percent on weight of fiber
%owm	percent on weight of monomer
ppm	part per million
%RH	percent of relative humidity

CHAPTER I

Introduction

Cotton fabrics have the ideal properties for clothing over other fabrics such as comfortability, moisture absorbance, good ventilation, soft, non-irritant and cool to touch. As these properties, cellulose fibers still play an important part in worldwide manufactured fiber production even though synthetic fiber production appears to steadily increase between 1978 to 1998 as illustrated in Figure 1.1 (1). Introduction, cellulose fiber production tends to increase continuously in Asia although the production decreases apparently in other region among the same period as shown in Figure 1.2 (1).

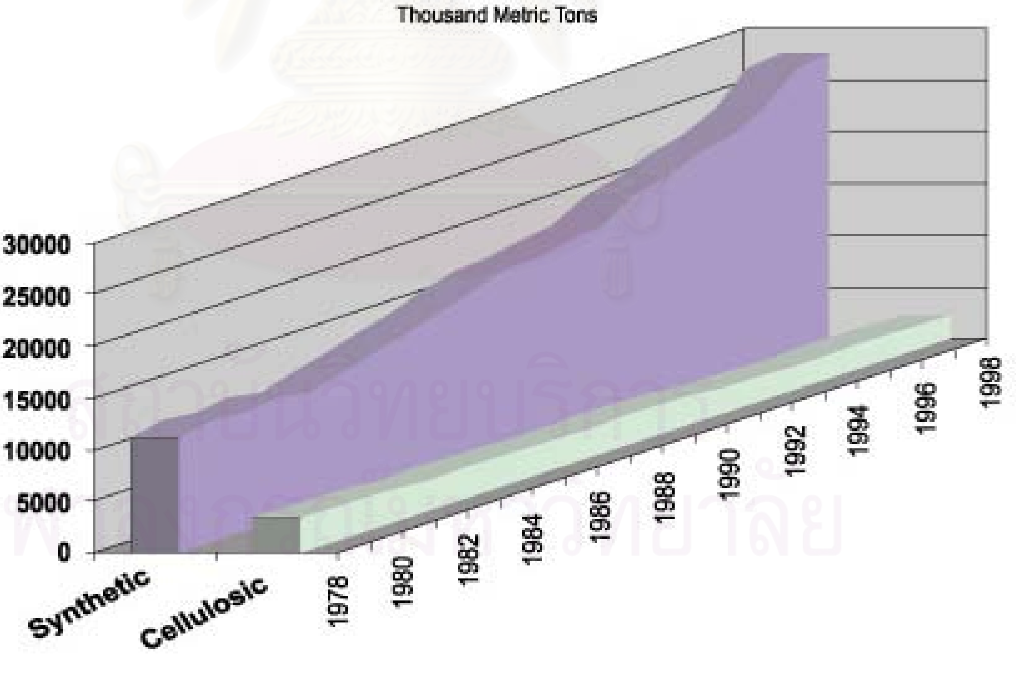


Figure 1.1 Worldwide manufactured fiber synthetic production vs. cellulosic production (1).

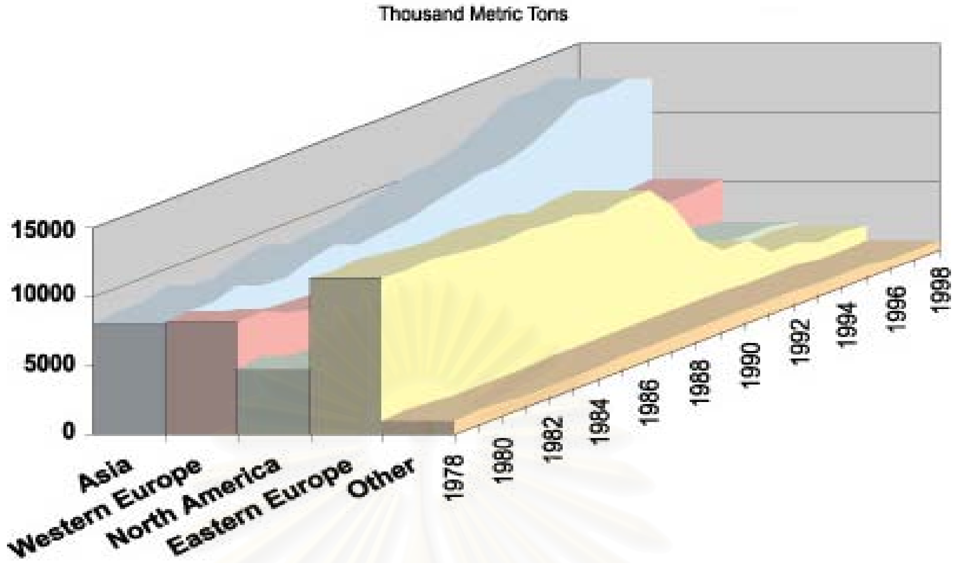


Figure 1.2 Worldwide cellulosic fiber production by region (1).

Although the cotton fabric provides good properties in wearing, it has a big problem in wrinkle easily. Consequently, long-time ironing is required for cotton fabric before use. Due to the advances in textile technology, this wrinkle problem can be overcome by using organic chemicals to impart wrinkle resistant properties of cotton fabric. The other way to improve the wrinkle is to blend the cotton fibers with the synthetic fibers such as polyester fibers but the blended fabric will not have good moisture absorbance and less comfort compared with those of cotton fabric. Therefore, numerous chemicals have been highly interested to impart wrinkle property to the cotton fabric. The introduction of chemical bond between adjacent cellulosic polymer chains in amorphous regions when the fabrics was in desired shape was the basic way to bring about a good resistance in wrinkle. Hydroxyl groups of cellulose fiber can react with any functional groups of the organic chemical in the presence of suitable catalyst under appropriate conditions to form chemical crosslinking inside the cellulose fiber structure.

The early chemical agents used for crosslinking with cellulose were focused on formaldehyde and formaldehyde derivatives. These reactants could help improving dimensional stability and wrinkle recovery properties of cellulosic fabric by forming the ether bonds. At this moment, the most widely used finishing agent is dimethyloldihydroxy ethyleneurea (DMDHEU). The cotton fabric finished with DMDHEU will have a good wrinkle resistance, good durable press properties and good whiteness; however, fabric treated with DMDHEU still has the tendency to release formaldehyde during processing and storage. As we have known, formaldehyde is recognized as a carcinogen for animals, and it causes irritation to human being.

Nowadays, people realize the toxic of formaldehyde release, and try to limit the amount of formaldehyde release as low as possible or close to zero from the finished cotton fabric with DMDHEU. To obtain the zero of formaldehyde release from the finished fabric is impossible if the cotton fabric is still finished with DMDHEU. Consequently, developing formaldehyde-free crosslinking agents instead of DMDHEU has become an interesting issue in the textile finishing. Polycarboxylic acids in conjunction with alkali metal salts of phosphorous-containing inorganic acids are the most promising to provide zero formaldehyde release on the finished fabric. 1,2,3,4-butanetetracarboxylic acid (BTCA) and tricarboxylic acid (TCA) are the most effective crosslinking agent among the polycarboxylic acids. The high cost of BTCA and TCA is a problem to replace DMDHEU as a durable press finish agent instead of DMDHEU in the textile finishing. Citric acid (CA) is the other polycarboxylic acid that provides good crosslinking network inside the cellulose structure but it causes yellowing on the treated fabric.

Generally, the finished fabric treated with any durable press agent have a good wrinkle recovery, but the strength will be decreased almost 40 percent compared with that of untreated fabric. It was assumed that the excess of the degree of crosslinking with cellulose chain might be the cause. Therefore, unsaturated mono- or dicarboxylic acids, which can form long chain polycarboxylic acids by polymerization, have become the new alternative to use as a new durable press finishing agent. Some previous studies (2,3) found that 100% cotton fabric treated with two unsaturated dicarboxylic acids, maleic acid and itaconic acid, as the copolymer possessed high level of wrinkle resistant properties nearly BTCA. In addition, tensile strength retention of treated fabric was improved slightly.

The objective of this research was to find out the suitable conditions to finish the cotton fabric using acrylic acid, unsaturated monocarboxylic acid, and maleic acid, unsaturated dicarboxylic acid. The suitable condition could be achieved by varying concentration and mole ratio of monomers, by varying concentration of catalyst, and by varying temperature and time of curing. The effects of crosslinking agent, catalyst and curing conditions on finished fabric properties such as wrinkle recovery angle, tensile strength and whiteness were examined and compared with those properties of the fabric treated with DMDHEU. Additionally, reactive and basic dyeability on the resin finished fabrics were conducted including washing and light fastness. The presence of ester groups was identified by FT-IR spectroscopy to confirm the ester crosslinking reaction happening in the treated fabrics. Furthermore, structure and molecular weight of the copolymer were characterized using NMR and GPC analysis, respectively.

CHAPTER II

Literature Survey

2.1 Cotton Fiber

Cotton is classified as a natural cellulosic fiber. It was widely used before 3000 BC in the Indus Valley, now modern Pakistan. Nowadays, it still plays an important role in textile industry. The fiber is a single cell, which grows out of the seed as a hollow cylindrical tube. The quality of cotton depends on its length, strength, fineness, and maturity. Other factors affecting its quality are color and leaf residue. Raw cotton is creamy white in color, while the purified cotton fiber is pure white, tasteless and odorless, highly absorbent, very smooth and soft, non-irritant and cool because the purified cotton is passed scouring and bleaching process.

2.1.1 Chemical Nature of Cellulose

Cellulose is a carbohydrate substance containing the elements of carbon (44.4%), hydrogen (6.2%), and oxygen (49.4%). Normally, cellulose is a long chain molecule or a liner polymer. It consists of several thousand 1,4-β -anhydroglucose units joined together by an oxygen atom in the same plane. It seems like a sugar molecule but cellulose is not soluble in water because of its immense molecular size and well orderly structures of the polymolecule. Two glucose units combine first to form cellobiose, which is a repeating unit of cellulose. Then many cellobiose units combine to form the cellulose. The number of anhydroglucose units in the cellulose molecule is referred to as the degree of polymerization. Generally, a typical degree of polymerization for a native cellulosic fiber is about 10,000.

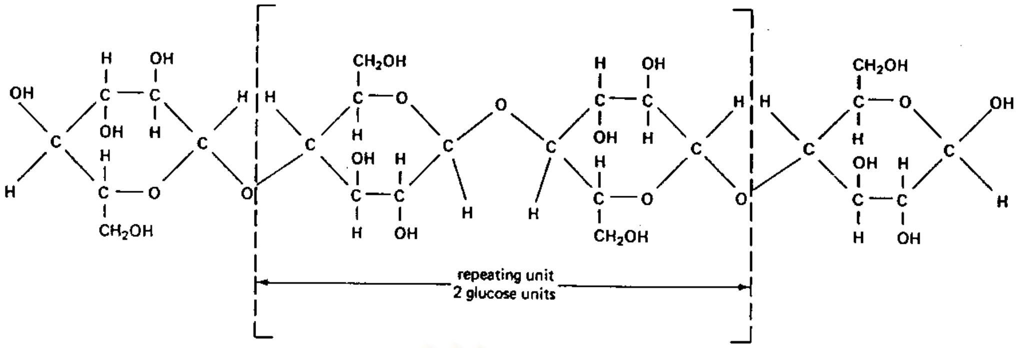


Figure 2.1 Diagram of cellulose molecule [(2)].

2.1.2 Fiber Composition

2.1.2.1 Macrostructure

Cotton fiber is a single elongated cell that is flat, twisted, and ribbonlike with a wide inner core. It is about 0.3 to 5.5 cm in length with having color in range from white to yellow: white, light-spotted, spotted, tinged and yellow.

Figure 2.2 Scanning electron micrographs of raw cotton fibers [(3)].

The fiber is composed of an outer cuticle (skin), covered with a protective waxlike coating, a primary wall, a secondary wall, and a central hollow or lumen with residues of protoplasm. The lumen is the main canal providing nourishment conveys during the growth of cellulose fiber. The secondary wall is the flesh of the fiber consisted of many layers of cellulose. Each cellulose layer is consisted of bundles of cellulose chains known as fibrils. Naturally, fibrils are spirally arranged in the same direction, by the way, these spirals may be reversed in different direction. That is a major factor in the convolutions, elastic recovery, and elongation of the fiber. The primary wall is also found to consist of a lattice network of fibrils packed more tightly than in the secondary wall. These compact layers support the cuticle, which makes abrasion resistance to cotton, and with it, stiffen and strengthen the fiber. In addition, there is a small amount of slippage between the layer of primary and secondary walls resulted in elasticity and flexibility.

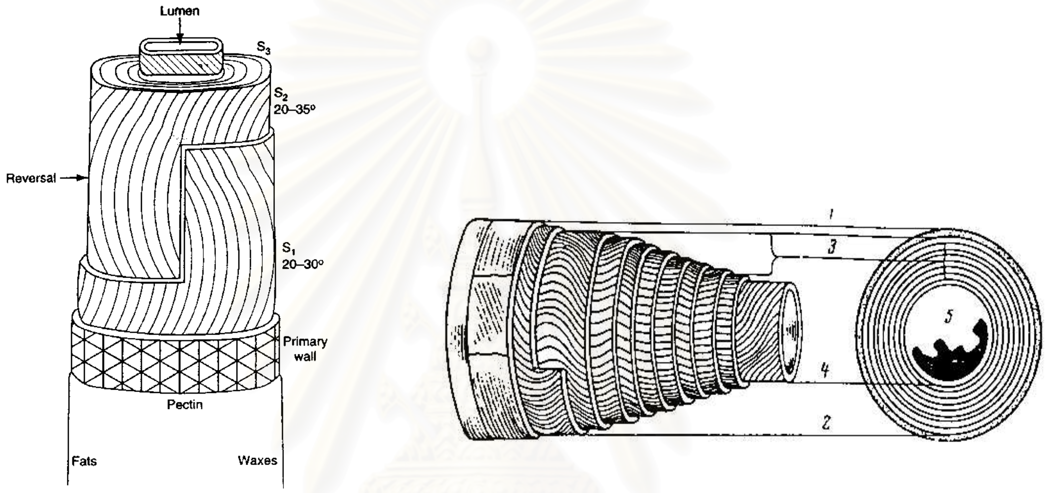


Figure 2.3 Morphological structure of a cotton fiber structure (4).

1- primary wall; 2-outer layer of secondary wall; 3-central part of secondary wall; 4-inner wall layer; 5-lumen with remnants of protoplasm

2.1.2.2 Microstructure

In term of microstructure, cotton fiber is composed of about 90% cellulose and about 6% moisture; the remainder consists of natural impurities. Like all cellulose fibers, cotton contains carbon, hydrogen, and oxygen including hydroxyl (OH) groups. The chemically reactive groups or hydroxyl units in adjacent edges closed to cellulose chains can be formed hydrogen bonding which arranges a number of cellulose molecules in parallel direction. These order structures called crystalline regions are approximately to 85-95%, which help to stabilize the structure. Whereas, unordered areas surrounding crystalline regions are known as amorphous regions. Various chemical treatments may undergo substitution reaction with the chemically reactive groups in the amorphous regions in application of some dyestuffs and finishes.

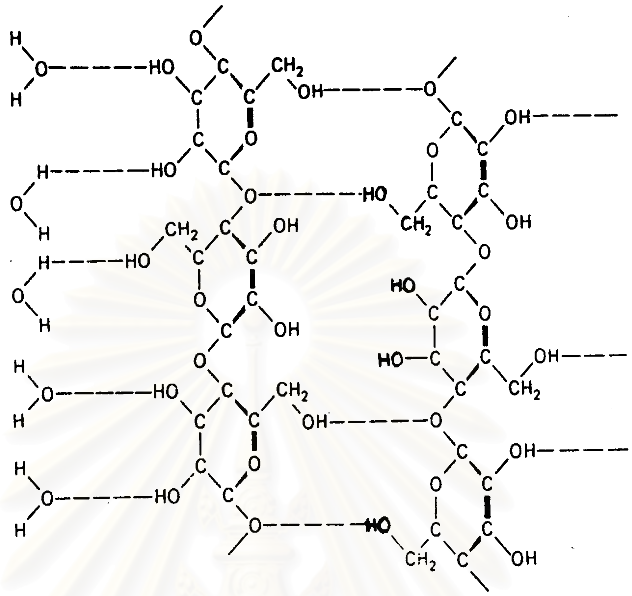


Figure 2.4 Hydrogen bonding between cellulose chains (5).

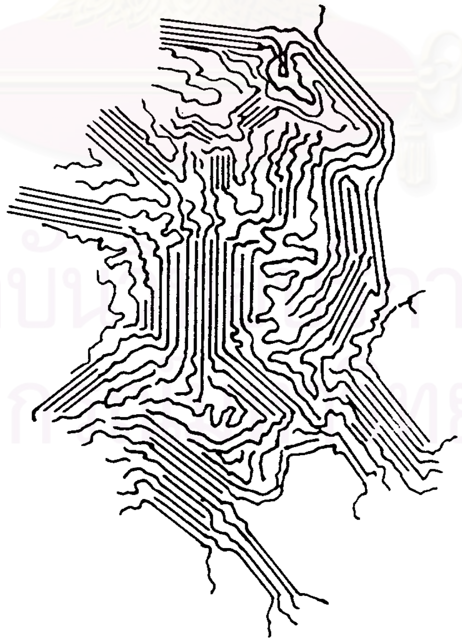


Figure 2.5 Model showing crystalline and amorphous regions in cellulose (6).

2.1.3 Fiber Properties

The properties of cotton fiber are listed in Table 2.1

Table 2.1 Properties of cotton (5).

Molecular Structure	Cellulose
Macroscopic Features	
Length:	0.3 to 5.5 cm.
Cross-section:	Kidney-shaped.
Color:	Generally white, may be cream-colored.
Light reflection:	Low luster, dull appearance.
Physical Properties	
Tenacity (g/den):	3.0 to 5.0 (dry), 3.6 to 6.0 (wet)
Stretch and elasticity:	3 to 7% elongation at break. At 2% elongation recovery is 70%
Resiliency:	Low.
Abrasion resistance:	Fair to good.
Dimensional stability:	Fabrics may shrink during laundering.
Moisture regain:	8.5%
Specific gravity:	1.54
Chemical Properties	
Effects of bleaches:	Highly resistant to all bleaches.
Acids and alkalies:	Highly resistant to alkalies. Strong acids and hot dilute acids will cause disintegration.
Organic solvents:	Resistant to most organic solvents.
Sunlight and heat:	Withstands high temperatures well. Prolonged exposure to light will cause yellowing due to oxidation.
Resistance to stains:	Poor resistant to water-born stains.
Dyeability:	Good affinity for dyes. Dyed with direct, vat, and basic dye.
Biological Properties	
Effects of fungi and molds:	Highly susceptible to attack by mildew.
Effect of insects:	Starched cottons are attacked by silverfish.
Flammability Behavior	Burns rapidly. Smoldering red after glow.
Electrical and thermal Conductivity	Good heat conductor.

2.1.4 Appearance

The color of cotton fibers may vary from almost pure white to dirty gray, but it can be improved by scouring and bleaching process. The luster of cotton is low unless the cotton fibers are passed the process of mercerization.

2.1.5 Comfort

Particularly, cotton has ability to absorb moisture because it contains hydroxyl groups, which are polar groups. The good moisture absorption and softness of cotton fibers have made these fibers more favorable to be used in modern apparel and modern domestic items than other fibers.

2.1.6 Care

Most cotton fabrics can be laundered and dried with home laundering equipment. There is no negative effect on the fiber with most detergents. Cotton fabrics wrinkle easily and do not recovery well from wrinkling because of its low elasticity and poor resiliency, yet special treatments can solve this problem. By the way, cotton fabric can be ironed easily at medium to medium-high temperature setting if it requires ironing.

2.2 Concept of Cellulose Crosslinking

After World War II, with the evident of nylon and polyester fabrics that are naturally resilient, there was interesting in making cotton fabrics smooth drying and dimensionally stability (7). In order to understand why cotton is not resilient, one has to consider its morphology. Due to the characteristic of the cellulosic fibers that cellulose chains have only hydrogen bonds and Van der Waals forces between them, so the cellulosic fabrics appear to crease or wrinkle easily.

The concept of crosslinking between cellulose chains within the fiber has now become the accepted theory. Generally, it is believed that the increase in elastic recovery of the fiber is brought about by the crosslinking reaction between adjacent cellulose chains. The hydrogen bonds and Van der Waals forces between cellulosic chains are not sufficient to prevent slippage of adjacent cellulose chains. When the untreated cotton fiber is extended or deformed under wrinkling or laundering because the H-bond and van der Waals forces are weak and not strong enough to pull the chain backs after laundering. This causes the wrinkle on untreated cotton fabric. Therefore, cellulose must be chemically treated to introduce additional linkages between adjacent cellulose molecules in the amorphous regions, as illustrated in Figure 2.6. As a result, the stress-induced slippage of polymer chains can be forbidden with stable covalent crosslinks.

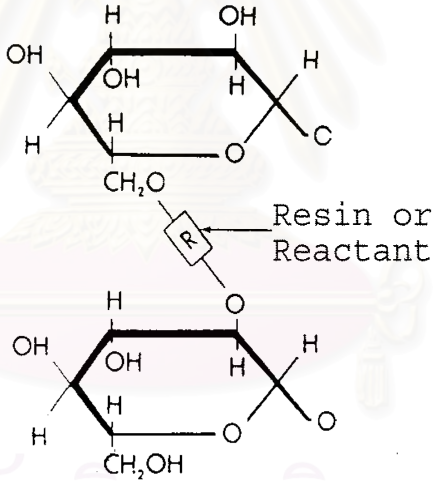


Figure 2.6 Resin crosslink (8).

The important factors of the formation interchain linkages are the availability and reactivity of hydroxyl groups at C-2, C-3, and C-6 positions of the anhydroglucose units along the molecular chains. The order of reactivity of the three OH groups is C-6>C-2>C-3. However, the reaction can be accomplished only with hydroxyl groups in the amorphous or accessible regions of the fiber. The crosslinking condition is controlled by the presence of exotic substances, such as additives, dyes or colorants and contaminants. The amount of moisture in the fiber during the reaction period is also considered. Besides, the chemical structure, the solubility and the concentrations of the crosslinking agent must be included to achieve good performance to fabrics.

2.3 Wrinkle-Resistant Finishing Process

Wrinkle-resistant finishing process is the technique to improve recovery from wrinkles by applying the finishing agents through the fabric. Various processes are provided for supporting the variety of fabrics. The differences between each process arise from the different temperature, curing time and moisture content of fabrics during curing (9).

2.3.1 Pad-Dry-Cure Process

The fabric, in this process, is immersed in the finishing solution containing crosslinking agent and catalyst. After that, it is squeezed through a padder containing 2 rollers to gain 80-100% wet pick-up and dried at 85-100 °C. The dry fabric is then cured at the high temperature at a certain time depending on what kind of reactant or resin used in the finishing process. Additionally, the fabric is usually stretched on the stenter in the drying and curing stages in order to control the dimension of the fabric, which is necessary to obtain smooth appearance property.

2.3.2 Mild Cure Process

This process has one step, which is performed on fabrics containing the crosslinking agent and a strongly acid catalyst by padding through the padder. Without prior drying, the treated fabric is cured at 120 °C for a short time. Thus, the optimum moisture content is reduced to 3-5% from initial moisture level after padding. For the last step of the process, the fabric is neutralized with sodium carbonate solution.

2.3.3 Moist Cure Process

In this process, the finishing solution contains crosslinking agent and a very strong acid catalyst. The fabrics are immersed in the solution and then dried to maintain specific moisture content of about 6-12%. After that, the fabrics are then batched in a polyethylene film for 12-24 hours at room temperature to prevent changing of moisture content. During the batched, the crosslinking reaction will gradually occur. Finally, the treated fabrics are neutralized with sodium carbonate and washed. Nevertheless, this process is more suitable for cotton woven fabric than weft-knitted fabrics. The fabric degradation by cellulose hydrolysis may be increased because of the long reaction time. Some cross-linking agents, such as urea formaldehyde, cannot be used in this process because the precipitation of pad bath solution due to the polymerization of crosslinking agent will occur as soon as the strong acid catalyst is added.

2.3.4 Wet Cure Process

Like the moist cure process, the fabric is passed throughout the finishing solution containing crosslinking agent and catalyst. On the contrary, the pre-drying step is omitted before batching. The treated fabric is then wrapped in polyethylene film to prevent loss of moisture. The following stages are batching and rotating for 24 hours before neutralizing and drying the treated fabric.

2.3.5 Wet-Fix Process

This is a dual-step process consisting of initial reaction at room temperature and continuing with the curing step after the resin deposition. Firstly, the fabric is padded with crosslinking agent in acid condition and then batched for 12-24 hours. Secondly, catalyst such as magnesium chloride is added to reactivate the reaction inside the batched fabric by re-immersing and re-padding the treated fabric. Finally, the treated fabric is dried at 60 °C for 4 min and cured at 160 °C for 4 min.

2.4 The Development of Durable Press Finishing of Cotton Fabrics

Among various finishing processes on fabrics, durable press finishing was consumer demand for easy care textile. The fabrics and garments with some or all cellulosic composition are treated with a reactant or resin composition to impart smoothness and prevention of wrinkles in wearing and after laundering. The properties are usually measured in term of durable press (DP) rating and wrinkle recovery angle (WRA). Durable press performance can be described by other terms such as wrinkle free, wrinkle resistant, crease resistant, permanent press, non-iron, wash and wear and easy care.

Historically, durable press finishing started with the work of Eschalier in 1907. In his work, Cellulosic materials, depolymerized cellulose and specifically regenerated cellulose were treated with formaldehyde under acidic condition to improve strength in the dry and especially in the wet state because the regenerated cellulose or rayon has the low wet strength (10). In addition, it was easy tearing, easy shrinkage and easy distortion. There were many processes to conduct the polymerization or condensation reaction of regenerated cellulose with formaldehyde in solution, dry or gaseous state with acid catalysts. In 1926, the treatment of fabrics with formaldehyde-containing reactant to provide dimensional stability and recovery from wrinkling was carried out, which included the finishing of rayon fabrics with water soluble-urea or phenol-formaldehyde resins. The finishing process providing dimensional stability and recovery from wrinkling became more common practice during the 1930’s and 1940’s. Later, the urea-formaldehyde resins were used commonly for applying on cotton fabric to give those properties. Blends of polyester and cotton were also treated with resin to provide wrinkle resistant and better strength and resistance to wear. The resin used not only urea-formaldehyde resin but water soluble reaction products of formaldehyde with triazine, triazone, uron, ethyleneurea, propyleneurea, imidazolidinone and carbamates also (11).

2.5 Types of Formaldehyde Reactants(11)

2.5.1 Urea-Formaldehyde

The first important chemical providing wrinkle resistance to cellulosic fabrics was the reaction product of urea and formaldehyde. The urea-formaldehyde was prepared by reaction of a mixture of mono- and dimethylolurea as shown in Figure 2.7. It has been observed that the finish agent was degraded by chlorine bleach, hydrolyzed in acid media, and tended to release large amounts of free formaldehyde.

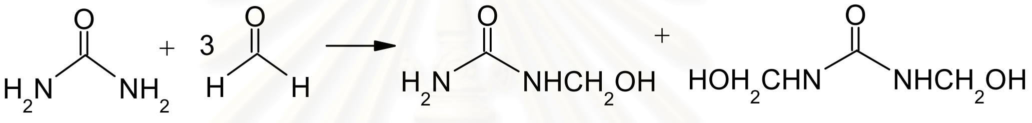
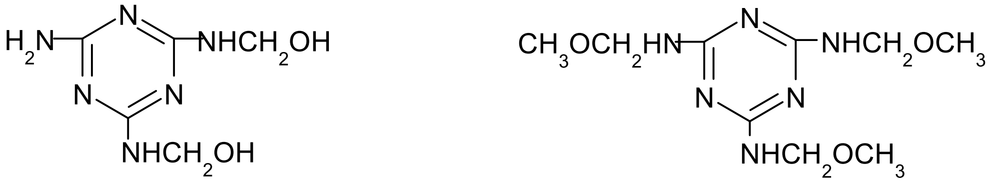


Figure 2.7 Preparation of Urea-Formaldehyde (11).

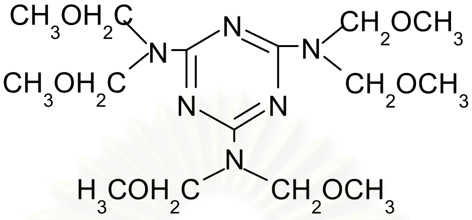
2.5.2 Triazine or Melamine Reactants

The next reactants were triazine- or melamine-formaldehyde products. There are three main products of this group applied to fabrics, such as dimethylolmelamine, trimethylmelamine and hexamethoxymethylmelamine. They are still used in textile industry because of lack of chlorine-retention problem. But white fabric finished with these resins becomes yellow during bleaching.



Dimethylolmelamine

Trimethoxymethylmelamine



Hexamethoxymethylmelamine

Figure 2.8 Structure of Triazine- or Melamine-formaldehyde products (11).

2.5.3 Uron-Formaldehyde Reactant

Uron-formaldehyde was another commercially important reactant. It can be prepared by the reaction of 1 mole of urea with approximately 4 moles of formaldehyde and then followed by reaction with methanol to form N,N'-dimethoxymethyluron. This product can provide fairly good durability to laundering but it is likely to retain chlorine.

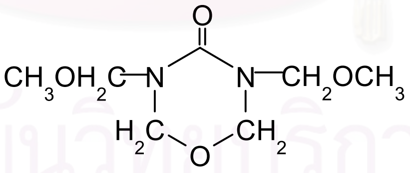


Figure 2.9 N,N'-dimethoxymethyluron (11).

2.5.4 Triazone-Formaldehyde

The use of Triazone-formaldehyde has extremely decreased since 1960's. According to Figure 2.10, the dimethyloltriazone was produced by the reaction between one molecule of the triazone and two molecules of formaldehyde. The R group was usually a short chain, such as methyl or ethyl.

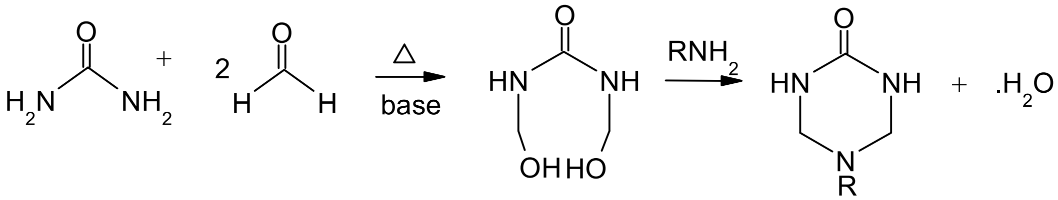


Figure 2.10 Formation of Triazone-Formaldehyde [(11)].

2.5.5 Cyclic Urea-Formaldehyde

The most important chemicals used to date are cyclic urea-formaldehyde products. Five of the main products are dimethylolethyleneurea (DMEU), dimethylolpropyleneurea (DMPU), monomethylol or dimethylol-4-hydroxy (methoxy)-5,5-dimethylpropylenurea and dimethyloldihydroxyethyleneurea (DMDHEU).

DMEU was the largest amount consumes for the cellulose reactant in the 1950’s. However, its use has sharply declined in recent years because it has a limit in durability to commercial laundering. Urea is reacted with ethylenediamine to form ethyleneurea, which is then reacted with formaldehyde to give dimethylolated derivative.

DMPU also has limited durability to commercial laundering because it is sensitive to acid hydrolysis. It is made by reaction of propylenediamine with urea and then followed by methylation.

The monomethylol- and dimethylol-4-hydroxy (methoxy)-5,5-dimethypropyleneurea products were found to be better resistant to hydrolysis and lower formaldehyde release compared with those of DMPU. The ring hydroxy (methoxy) group of these compounds can react with the hydroxy groups of cellulose at elevated temperatures in addition to the methylol groups.

DMDHEU is the most important formaldehyde reactant used at present for durable press fabrics. Because the fabrics treated with DMDHEU have good resistance to acid hydrolysis, low chlorine retention and low formaldehyde release. It is formed by reaction of one molecule of urea with one molecule of glyoxal and then followed by reaction with two molecules of formaldehyde. The methylol groups attached to nitrogen not only can react with the hydroxyl groups of cellulose to form an ether at elevated temperatures, but the two OH groups attached to the ring carbon can react with cellulose as well. This reactant is often related to a glyoxal type reactant. Moreover, the methylation of DMDHEU can provide a product, which has less formaldehyde release. Consequently, this product has been widely used in raising amounts to impart durable press fabrics even though the treated fabrics may loss its mechanical properties.

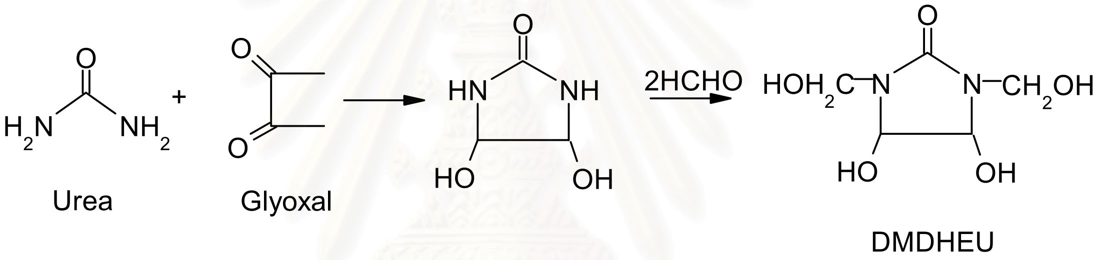
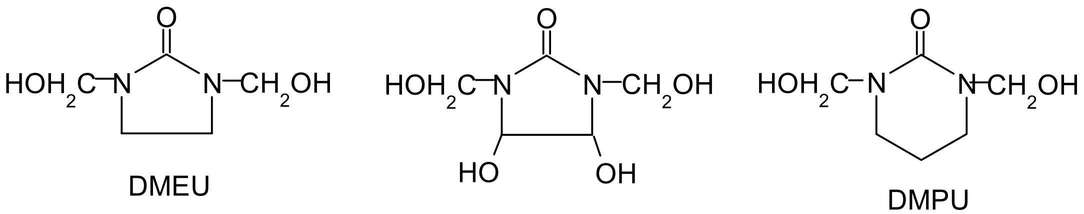


Figure 2.11 Formation of DMDHEU (11).

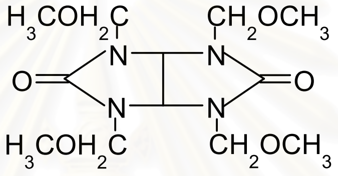
Tetramethoxymethylglyoxaldiurine is another urea-formaldehyde product that has good resistance to hydrolysis and has low formaldehyde release. This product can be produced by the reaction of two molecules of urea with one molecule of glyoxal and then followed by reaction with four molecules of formaldehyde. The outcome of the reaction provides the methylated product.



DMEU DMDHEU DMPU

Monomethylol-4-hydroxy(methoxy)-
5,5-dimethylpropylene urea

Monomethylol-4-hydroxy(methoxy)-
5,5-dimethylpropylene urea

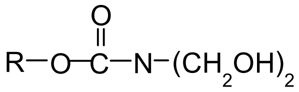


Tetramethoxymethyl glyoxaldiurea

Figure 2.12 Cyclic urea-formaldehyde reactants (11).

2.5.6 Methylol Carbamates

The methylol carbamates may be methyl, ethyl, hydroxyethyl, methoxyethyl, isopropyl or isobutyl for the R groups. The general structure of methylol carbamates is illustrated in Figure 2.13. The first application of methylol carbamates to fabrics was the methyl and ethyl carbamates. The methylol carbamates have good resistance to chlorine and to hydrolysis, and do not yellow white treated fabrics. Nevertheless, ethyl carbamate was found to be a carcinogen resulting in dramatically decrease of using this product. Although, these two carbamates have free formaldehyde content, the formaldehyde release from finished fabrics is not so high.



$$R-O-\overset{O}{\overset{\|}{C}}-N-(CH_2OH)_2$$

Figure 2.13 Methylol carbamate (11).

The effective reaction of formaldehyde reactants with cellulosic fabrics depends on a number of factors as shown below (12).

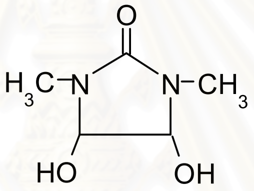
1. The reactant composition
2. The nature and amount of the catalyst
3. The time and temperature of cure
4. Impurities in the formaldehyde reactant
5. The condition of the fabric
6. The additives in the impregnating bath

In fact, each of those reactants has its own interesting properties in imparting wrinkle resistance to fabrics. The properties required for a wrinkle resistant finish can be generally classified as follow (13):

1. Dry and wet crease resistance
2. Good dimensional stability
3. Little loss in physical properties (i.e., tensile and abrasion)
4. Compatibility with other finishing agents (e.g., water-repellent, softeners, optical brightening agent)
5. Minimum effect on handle
6. Little effect on dye or print shade or the light fastness of the dye
7. Little effect on rubbing fastness of dyed or printed fabric
8. No effect on the whiteness of the fabric
9. Possible low formaldehyde release
10. Good environmental condition both in the application of the resin and in the final making up of the fabric when finished
11. Ease of application and low cost add-on factor in both chemical and application cost.

However, these formaldehyde reactants contain significant levels of free formaldehyde (CH_2O), which is not only present in the reactants but is also release from treated fabrics into the surrounding environment of air, liquid, or even skin (14). Consequently, the health risk associated with formaldehyde emission has caused increasing concern in worldwide. Due to formaldehyde was recognized as probable human carcinogen (14,15,16). Finding ideal formaldehyde-free crosslinking agents for cotton has become a focus of the textile industry.

In an attempt to seek formaldehyde-free finishes, DHDMI or 4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone has been state to be the attractive finishes. Similarly to DMDHEU, it is the adduct of urea and glyoxal with 1,3-methyl substituents. Unfortunately, DHDMI, as a bifunctional crosslinking agent, is far less effective than DMDHEU and requires high resin add-on levels. It is also expensive because it needs to be purified enough to elude discoloration of fabric (17). Therefore, it is not widely used in the industry.



DHDMI

Figure 2.14 4,5-dihydroxy-1,3-dimethyl-2-imidazolidinone (17).

To sum up, those resins mentioned above can be categorized into five types depending upon free formaldehyde contents as shown in Table 2.2 (18).

Table 2.2 Development of cellulose crosslinking agents.

Formaldehyde	Crossliking agent type
High-2000 ppm	Phenol-formaldehyde Methylolmelamine Dimethylolurea
Reduced-500 ppm	Dimethylol ethylene urea Dimethylol dihydroxyethylene urea
Low	Dimethylol dihydroxyethylene urea (DMDHEU)
50-300 ppm	Methylated or glycolated with or without a scarvenger
Free-0 ppm	Dihydroxy dimethylimidazolodinone (DHDMI) Polycarboxylic acids

2.6 Polycarboxylic Acids Used As Durable Press Finishes

Alternative to the formaldehyde or N-methylol agents, which form ether or acetal crosslinkages by reaction with hydroxyl groups of cellulose, Polycarboxylic acids have been identified as proper crosslinking agents with ester type linkages to impart wrinkle resistance property of the finished fabrics.

An advantage of using polycarboxylic acids is that they neither contain nor release formaldehyde. So, a number of polycarboxylic acids have recently been developed as the cellulosic crosslinking agent. These acids react with hydroxyl groups of cellulose to form ester-type crosslinks connecting adjacent cellulose chains in a 3-dimensional network inside the cotton fibers (19,20,21).

It is widely accepted that such polycarboxylic acids esterify with cotton at high temperature in the presence of alkali metal salts of phosphorus containing inorganic acids by forming cyclic anhydrides as cellulosic reactive intermediates (22,23). This phenomenon is known as cyclic anhydride mechanism. In the presence of heat, a molecule of water is lost from adjacent, non-sterically hindered carboxylic acid groups to form a cyclic anhydride and in the presence of catalyst, the anhydride reacts with cellulose to form an ester and regenerate break one carboxylic acid group (24). As illustrated in Figure 2.15, pairs of neighboring carboxyl group will form an anhydride ring and then esterify with a hydroxyl group of cellulose. Consequently, at least three carboxyl groups must exist in each acid molecule to provide the effective crosslinking network (25,26).

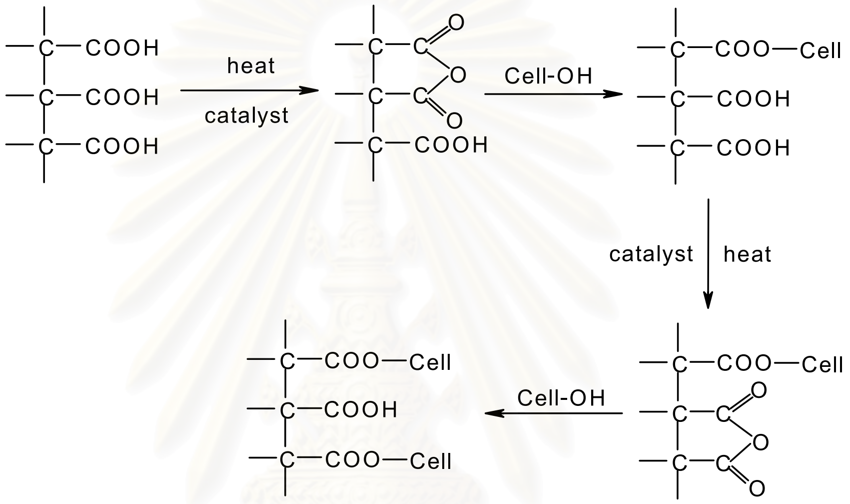


Figure 2.15 Schematic of cyclic anhydride mechanism (19).

Many types of polycarboxylic acids are in use, such as straight chain, aromatic, saturated and unsaturated (27). In the case of a saturated system, at least three carboxylic acid groups are required to accomplish crosslinking of the cellulose (28). For unsaturated system, at least two carboxylic acid groups in an α, β –unsaturated system are required. Molecules containing more carboxylic acid group; however, may bring about better effects of crosslinking. Besides, these carboxylic acid groups have to be separated from one another by at least two carbon atoms but not more than three carbon atoms. For aromatic acids, the positions of the acid groups must be ortho, and a cis-orientation must be present in unsaturated polycarboxylic acids (29).

Most of the research has concentrated in tri- and tetracarboxylic acids, especially citric acid (CA) and 1,2,3,4-butanetetracarboxylic acid (BTCA).

2.6.1 Tricarboxylic Acids

Propane tricarboxylic acid (tricarballylic acid), propene tricarboxylic acid (aconitic acid) and citric acid, a hydroxy acid, were investigated (24). It was found that the order of effectiveness of these acids is tricarballylic acid > aconitic acid > citric acid. Aconitic acid, on the other hand, produced severe yellowing to treated fabric. Tricarballylic acid provided high initial performance on the finished fabrics such as wrinkle resistant property, but the laundering durability was less than with BTCA finished fabric (23).

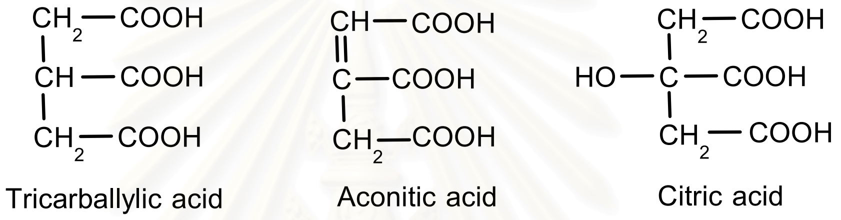


Figure 2.16 Structure of tricarballylic acid, aconitic acid and citric acid (24).

Citric acid has encouraged itself to be an interesting agent because it is low cost, proven lack of toxicity and ready availability. The most suitable concentration of citric acid found to impart durable press properties to fabrics was at 7% and the most effective catalyst with citric acid was sodium hypophosphite (17,30). The best mole ratios to be used were 1:1.5 (30) and 1:2 (17). The influence of curing temperature on fabric properties was also investigated by varying the temperature and curing time. The fabric treated with CA at high temperature and short curing time will cause less whiteness index and better DP rating of the finished fabric that those of finished fabric treated with CA at low temperature and long time. But when low temperature and long curing time was used, whiteness indices of finished fabric was generally higher and durable press ratings of finished fabric was lower than those from high temperature curing (30). The appropriate curing condition for fabric treated with CA was at 160 °C for 90 sec (17). However, it caused fabric yellowing during curing at elevated temperatures that can be explained by the formation of unsaturated polycarboxylic acids attributed to aconitic acid produced during the curing process (24,31). This problem can be reduced by using proper catalyst such as sodium hypophosphite (17,26,30). Nevertheless, whiteness index of the finished fabric treated with CA is not as good as that of the finished fabric treated with DMDHEU.

Adding specific hydroxyalkyl amine or quaternary ammonium salts to the pad bath of CA can improve whiteness index of the finished fabric better than that of the finished fabric treated with DMDHEU while good durable press properties of the finished fabric remain the same. The highly effective additives are triethanolammonium salts or tetrakis (hydroxy-ethyammonium) salts. In addition, these additives allow reduction of the amount use of expensive hypophosphite catalyst by at least 50%(32). Many studies were continued to find other appropriate additives, which increase the whiteness retained during formaldehyde-free durable press finishing of cotton fabric with citric acid. The effect of three tertiary alkanolamine compounds such as triethanolamine (TEA), triisopropanolamine (TPA), and N-methyldiethanolamine (MDA) were compared (33). All of them were found to be effective additives in the enhancement of fabric whiteness. Generally, tertiary alkanolamine seemed to be able to improve strength and abrasion resistance of the treated fabrics but it caused somewhat decreased wrinkle resistance (34).

Poly (ethylene glycol) with molecular weight of 400 could enhance the whiteness of the finished fabric and particularly affected level of DP rating and WRA. Additionally, boric acid also improved the whiteness index but it lowered the DP rating and WRA (33).

Whiteness and strength properties tended to decrease as citric acid concentration increased. However, this discoloration was caused by mostly from the unreacted finish residues on the fabric, so the aftertreatment procedure such as washing can recover the whiteness thereof (30). Moreover, durability of the citric acid finish to laundering was not as great as that of DMDHEU- or BTCA- based finishes, but is equal to that of DHDMI, and in some cases is greater than that of DHDMI. As a result, the use of citric acid as an extender for the more expensive BTCA seemed to be attractive.

2.6.2 Tetracarboxylic acids

Among a number of polycarboxylic acids used as crosslinking agents for cellulose, BTCA appeared to be the most promising reactant. Many advantages were taken into account, such as level of smooth drying properties, durability to laundering, fabric strength retention, low reagent volatility and absence of odor.

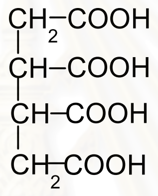


Figure 2.17 Structure of BTCA (35).

The key to successful use of BTCA in finishing cotton for durable press is to use appropriate class of esterification catalysts. Although weak bases have some catalytic effect in durable press finishing with BTCA, a number of alkali metal salts of phosphorus-containing mineral acids show considerably greater activity as catalysts and curing agents (36). The most effective catalyst currently known is sodium hypophosphite monohydrate ($NaH_2PO_2.H_2O$), and 3.3-6.5% concentration of it has generally been used in BTCA or citric acid finishing (23,37).

Performance properties of BTCA/ $NaH_2PO_2.H_2O$ finished fabric after 30 home laundering washing has DP smoothness performance equal to that of DMDHEU finished fabrics. The tensile, tear and abrasion test results were better for BTCA finished fabrics. Particularly, the abrasion resistance of the BTCA finished fabrics was significantly better than the DMDHEU finished fabrics (37).

Normally, the durability to laundering of BTCA finished fabric depended on the activity of the curing catalyst. It was found that the DP rating remained at or above 3.5 for 80 laundering cycles when used sodium hypophosphite as catalyst. However, condition of application was also the major factor concerning the increase of the performance life of BTCA finishes. Machine wash and tumble dry cycles at wash temperature (50-55 °C) and alkalinity (pH 9.8) was suitable for home laundering. Besides, curing temperature and time were important factors governing the durability of repeated laundering, and the greatest durability to laundering could be obtained if the finished fabric was cured at 210-215 °C (410-419 °F) for 15 or 20 seconds. In addition, high speed fabric finishing with BTCA/ $NaH_2PO_2.H_2O$ could be accomplished in less than 15 seconds at these temperature (23).

Although sodium hypophosphite has high curing activity, it has high cost and tendency to cause shade changes in fabric dyed with sulfur dyes as well as certain reactive dyes. Moreover, the phosphorus compounds are likely to serve as nutrients to algae to growth when waste solutions of phosphorus-containing compounds are discharged into steams and lakes (38).

Consequently, further progress was made in developing nonphosphorus containing catalyst, co-catalyst and crosslinking modifiers for use in polycarboxylic acid finishing. Because the reaction of BTCA with cotton in the presence of $NaH_2PO_2.H_2O$ depended on diffusion and penetration of reactant and catalyst into cellulose fiber so highly polar solvent was used to assist the required diffusion and penetration. Tertiary alkanolamines and N,N'-disubstituted amides were highly polar solvents capable of making and breaking hydrogen bonds in hydroxylic polymers such as cellulose. They acted as penetrants and carriers to speed diffusion of BTCA and $NaH_2PO_2.H_2O$ into the cellulose fiber. In addition, they increase DP performance and laundering durability without additional fabric strength loss (39).

As a curing additive, triethanolamine (TEA) was more effective than N-methyldiethanolamine in improving DP ratings. It was believed that TEA could increase the average length and degree of branching of the crosslinking by forming a 3-dimensional network with BTCA in the course of forming an amine-BTCA-cellulose terpolymer (39). Furthermore, TEA was found to improve the abrasion resistance of treated fabrics but slightly lower DP performance (40). And in order to improve the flex abrasion resistance in BTCA finished fabric, TEA was considerably more effective than polyols such as glycerol or pentaerythritol (36). Similarly, small amount of polyethoxylate quaternary ammonium salt was also added to baths containing BTCA or DMDHEU to improve the abrasion resistance of both BTCA and DMDHEU treated fabrics (40).

The use of sodium bromide as a co-catalyst with $NaH_2PO_2.H_2O$ in BTCA finishing permitted a 75% decrease in the concentration of the phosphorus derived catalyst but unable to improve the strength and abrasion resistance retained. Sodium chloride had a smaller effect than the sodium bromide as co-catalyst (36).

Moreover, alkali metal salts of various acid were developed to be alternative to use as a catalyst. The sodium salt of α-hydroxy polycarboxylic acid such as malic, tartaric or citric acid could serve as direct replacements for $NaH_2PO_2.H_2O$ or other phosphorus compounds as curing catalyst for BTCA (36,38).

Mono- or disodium salts of unsaturated acids, such as fumaric acid, maleic acid and itaconic acid, were effective catalysts to replace $NaH_2PO_2.H_2O$ for the reaction of BTCA and cellulose. The improvement was considerable in both DP rating and WRA of treated fabric. Moreover, retention of stoll flex abrasion resistance was substantially increased (39).

The sodium salts of saturated carboxylic acids, such as formic acid, oxalic acid, malonic acid, succinic acid, glutaric acid and adipic acid were also examined. They were generally more effective than sodium carbonate, but they were less effective than $NaH_2PO_2.H_2O$ for improving smooth drying appearance of the treated fabric in the presence of BTCA (39).

A three-component catalyst containing triethanolamine, malic acid and $NaH_2PO_2.H_2O$ was proved to increase the breaking strength, tearing strength and flex abrasion resistance of cotton fabric treated with BTCA while the mole ratio of TEA: (BTCA + malic acid) was in the range of 0.90-1.00. Flex abrasion resistance of the treated fabric was equaled to the value of untreated fabric, and was nearly double that DMDHEU-finished fabric at the same level of DP performance. BTCA was believed to esterify hydroxyl groups of triethanolamine and of malic acid as well as cellulose to produce a graft copolymer of cellulose having a more open and flexible three-dimensional molecular network than those obtained in crosslinking cotton with BTCA or DMDHEU by conventional catalysts.

Trisodium citrate (TSC) and a combination of sodium oxalate (SOX) and sodium formate (SF) were also used as catalysts in durable press finishing with BTCA. The results showed that the fabric finished with BTCA using these catalyst performed good wrinkle resistance properties. However, TSC is far safer and much more acceptable environmentally than SOX or SF (36).

2.6.3 Mixed Polycarboxylic Acids

According to high cost of the tetrafunctional agents, such as BTCA and cyclopentanetetracarboxylic acid (CPTA), further research based on mixing tetrafunctional agents with citric acid, an inexpensive tricarboxylic acid, was progressed.

The α-hydroxyl group of citric acid interferes the effectiveness of this acid used as an effective cellulose crosslinking agent. Adding small amounts of polycarboxylic acids that do not contain hydroxyl groups in their molecular structure considerably increase the performance of citric acid. These additives, hypothetically, esterify some α-hydroxyl groups of the citric acids to yield dimeric, trimeric and perhaps higher polycarboxylic acids which could be used as effective durable press finishing agents.

The mixture of citric acid and BTCA or PCA (1,2,3-propanetricarboxylic acid) was proved more effective for imparting smooth drying properties than those from citric acid alone. It is hypothesized that adding BTCA or PCA may esterify the α-hydroxyl group of citric acid during the first stage of the heat cure to yield more carboxylic groups than system with CA alone. A continuation of this reaction with still other citric acid molecules could lead to a dendritic polymer having a great many carboxyl groups which could be able to form numerous ester linkages to cellulose. Figure 2.18 showed the nature of one possible intermediate for the reaction of BTCA with α-hydroxyl groups of two citric acid molecules to yield higher polycarboxylic acids. However, this mixed finish imparted the yellowing problem to the finished fabric (35).

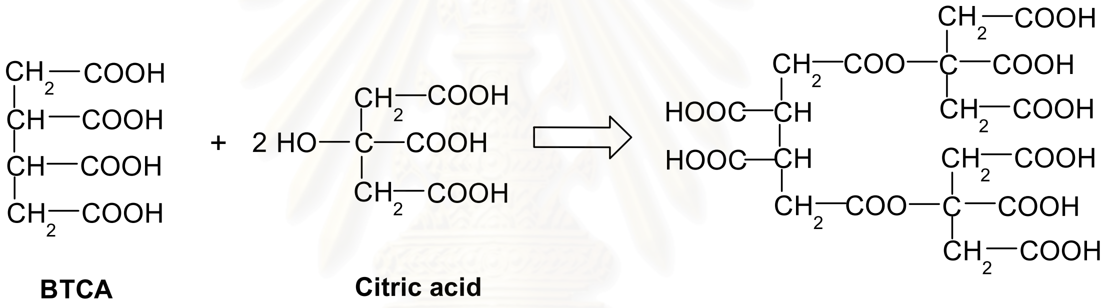


Figure 2.18 The reaction of BTCA with α-hydroxyl groups of two citric acid molecules (35).

Tartaric acid having α-hydroxyl groups is another effective additive for citric acid durable press formulation. Carboxyl groups of citric acid could conceivably esterified the secondary hydroxyls of tartaric acid during the cure to yield higher polycarboxylic acids (35). On the other hand, the possibility of tartaric and citric acid could form a 1:1 alternating copolymer *in situ* in cotton by esterification of the two secondary hydroxyl groups of each tartaric acid molecule by carboxyl groups of citric acid molecules during the heat cure was considered to be used as a crosslinking agent (41). The results found that the 1:1 mole ratio of tartaric acid and citric acid provided higher appearance DP ratings, increased WRA and improved whiteness of fabric.

5-7% citric acid in the presence of various corrective additives and time of storage in air at 40-55% relative humidity were found to be useful to increase the whiteness of cotton finished fabric. The presence of tartaric acid, 1-hydroxyethane-1, 1-diphosphinic acid, or boric acid as additives could enhance the whiteness as well. The first two of these additives enhanced DP performance, whereas boric acid decreased DP performance. In addition, a subsequent rinsing process increased the whiteness also (41).

In spite of the fact that methyl hydrogen silicone is a fabric softener, it could be applied as a mixture with finishing agent to convey better DP performance, greater wrinkle resistance, and better final whiteness index than those obtained from low-density polyethylene (41). The addition of small amounts of phosphoric acid, phosphorous acid, or 1-hydroxyethane-1, 1-diphosphonic acid (HEDPA) in the citric formation with no BTCA present also increased the effectiveness of citric acid. Similarly, Maleic and malic acids imparted a good level of DP performance and wrinkle resistance when they were applied to fabric with moderate amounts of BTCA and using sodium hypophosphite as the catalyst. Malic acid finishes, particularly, have the advantage that they lead to high degree of fabric whiteness (35).

The combination of CA and a terpolymer of maleic acid, acrylic acid, and vinyl alcohol (TPMA) were recently elaborated as a non formaldehyde durable press finishing system (42,43). This system was applied to garment finishing on booth laboratory and industrial production scales and compared with the traditional DMDHEU systems. The DP rating, WRA, mechanical strength, and abrasion resistance of the garment finished with this system were comparable to those treated with the conventional DMDHEU systems. Nonetheless, tensile strength of slacks finished with TPMA/CA system was lower than those finished with DMDHEU (42). Furthermore, the performance of TPMA/CA as a non formaldehyde durable press finish system applied to cotton fabrics was also evaluate and compared with a low formaldehyde DMDHEU. The cotton fabrics treated with TPMA/CA showed durable press performance and mechanical properties better than those treated with low formaldehyde DMDHEU. In addition, ethyleneglycol (2%) was added to one of the TPMA/CA formulation and it was found that the addition of ethyleneglycol improved fabric whiteness whereas it reduced wrinkle resistance.

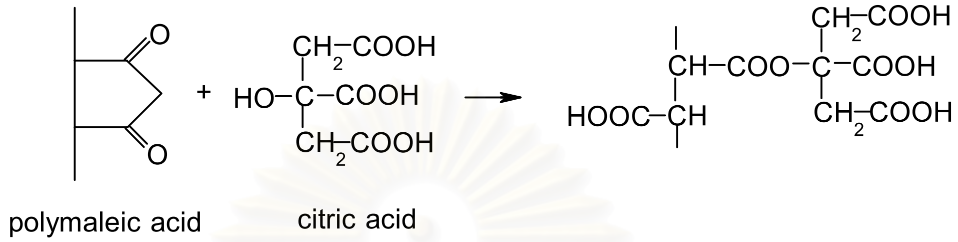


Figure 2.19 Reaction of the anhydride of PMA and TPMA with CA on cotton fabric under curing conditions (43).

2.6.4 Unsaturated Carboxylic Acids

As previous research, most polycarboxylic acids providing acceptable smooth-drying properties to cotton fabrics have small molecular structure, which can penetrate through cellulose fiber producing three-dimensional crosslinking. Although a high level of resiliency and stability of the finishes to machine laundering was obtained, these finishes still caused a considerable decrease in strength and abrasion resistance to the treated fabrics (26,28).

Therefore, a polymerization-crosslinking (PC) treatment has been developed to alleviate these disadvantages. It was believed that retention of mechanical properties was better with the deposition of polymerizing resins within the interior of wet swollen fibers, and subsequent formation of longer, flexible crosslinks of cellulose through the functional groups in the resins (44). To achieve smooth-drying properties of finished fabrics, unsaturated carboxylic acids were another attractive choice as crosslinking agents. These acids should have at least two carboxylic acid groups in the adjacent carbon atoms and have double bond existing in their molecules. The radical polymerization could polymerize unsaturated acid in the presence of peroxide initiator to yield long chain polycarboxylic acids capable of undergoing an esterification reaction with cotton cellulose.

Olefinically unsaturated dicarboxylic acids, maleic acid (MA) and itaconic acid (IA) has recently been introduced to use as copolymer crosslinking agent for cellulose by using them with the combination of potassium persulfate ($K_2S_2O_8$) and $NaH_2PO_2.H_2O$ as a free radical initiator and an esterification catalyst, respectively (44). Because their homopolymerization rate are expected to be low due to steric effects in MA and allylic radical formation in IA, copolymer system of MA and IA would be more effective than MA alone. Further explanation was that maleic acid can be copolymerized *in situ* in the cotton fabric with itaconic acid to form tetra, hexa- and higher functional polycarboxylic acids in drying step of pad-dry-cure application.

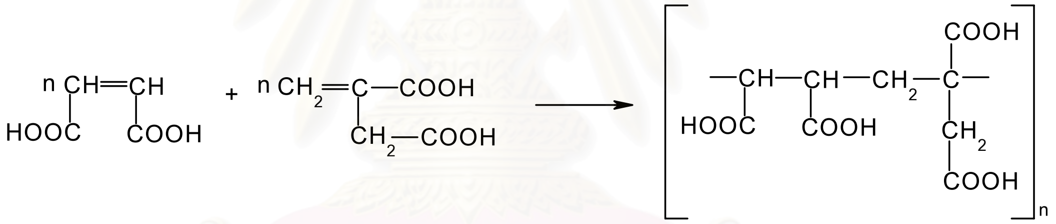


Figure 2.20 Structure of Maleic Acid / Itaconic copolymer formed *in situ* (19).

According to Table 2.3, the system of a 1:1 mole ratio of MA and IA with $NaH_2PO_2.H_2O$ at 1:1 or 1:3 mole ratio of monomer and catalyst was the most effective. The DP ratings were comparable with that of fabric treated with conventional DMDHEU, although WRA were likely to be slightly low. Stoll flex abrasion resistance of treated fabrics, in particular, were higher than that of the untreated control. Whereas the higher monomer concentration increased in both DP rating and WRA to a degree comparable to those of the DMDHEU treated fabric but unusually higher-retention in tearing strength and stoll flex abrasion resistance as demonstrated in Table 2.4

Table 2.3 Performance properties of 100% cotton fabric twill treated with MA/IA [a] (44)

Monomer, Mole ratio	Acid-cat Mole ratio[b]	Add-on[c], %	DP rating	WRA Degree (w+f)	TS, %[d]		BS[e], %	SFA[f], %	BL[g], cm
					W	f			
Untreated	-	-	1.5	171	100	100	100	100	3.7
DMDHEU-treated[h]	-	4.0	4.5	278	55	59	45	18	3.0
MA	1:1	9.1	3.5	219	67	73	56	99	2.9
MA/IA(2:1)	1:1	9.6	4.0	254	78	82	56	196	2.5
MA/IA(1:1)	3:1	7.4	4.0	233	82	91	64	323	2.7
	2:1	7.7	3.5	242	93	86	73	269	3.0
	1:1	11.6	4.4	268	76	90	49	214	2.7
	1:1.33	10.8	4.4	256	79	90	57	226	2.7
MA/IA(1:2)	1:1	10.8	4.0	258	68	87	67	131	2.7

[a] Treating bath: 12% monomers, 1.5%owm $K_2S_2O_8$, $NaH_2PO_2.H_2O$,1%softener,and 0.1% Triton X-100. Dry: 100°C/10 minutes. Cure: 180°C/2 minutes. Wash and tumble dry. [b] Molar ratio between monomer and $NaH_2PO_2.H_2O$. [c] Add-on(%)={(weight after treatment and washing-initial weight)/initial weight}x100. [d] Tearing strength retention(wrap and fill). [e] Breaking strength retention. [f] Stoll flex abration. [g] BL:Bending length. [h] Treatment bath:12%DMDHEU,1.5% $Zn(NO_3)_2.6H_2O$, 1%softener, and 0.1% Triton X-100. Dry:100°C/5 minutes. Cure:165°C/3 minutes. wash and tumble dry.

Table 2.4 Effects of the PC treatment on 100% cotton twill (MA/IA, 1:1) [a] (44)

Monomer conc., %owb (curing°C/min)	Add-on, %	DP Rating	WRA (w+f)	TS, %		BS, %	SFA, %	BL, cm	WI[b]	Cuene Insol., %	% Acetyl	-COOH Content (mequi/100g sample)	ΔE Basic Blue9
				w	F								
6.2%	5.2	3.7	242	85	98	62	221	2.7	46.7	6.4	0.1744	31.3	74.6
8.9%	8.4	4.0	271	83	97	59	148	2.5	47.0	22.4	0.1946	55.8	74.7
12%(160/3.5)	11.4	4.2	272	62	89	58	143	2.5	44.7	-	0.4545	35.8	75.0
12%(170/2)	11.3	4.0	273	70	88	60	158	2.5	49.7	-	0.3010	45.1	74.9
12%(180/2)	11.6	4.4	268	76	90	49	214	2.7	49.0	53.3	0.6416	76.1	74.5
12%(190/2)	11.3	4.4	283	51	78	58	133	2.4	30.3	-	0.3946	40.6	74.8
15.6%	3.5	4.5	290	46	82	54	81	2.5	45.5	58.0	0.9120	69.3	75.3
DMDHEU-treated									48.3	94.5	-	-	42.2
Untreated									56.3	2.7	-	5.7	54.8

[a] Treatment bath: monomers, 1.5% owm $K_2S_2O_8$, 8.8% $NaH_2PO_2.H_2O$., 1% softener, and 0.1% Triton X-100. Dry:100°C/10 minutes. Cure:180°C/2 minutes, unless otherwise specified. The abbreviations are same as before. [b] Before washing

However, loss of breaking strength in this PC treatment was considerable, even though the loss was less than with DMDHEU. This may result from insufficient diffusion or migration of monomers into fiber during drying stage, so that deposition of polymer was just below or at the fiber surface. To examine this assumption, treated fabric was dried with basic blue 9. It was found that these treated fabrics showed considerable affinity for basic blue 9. In addition, the effects of some treatment parameters such as monomer concentration, initiators, pH and additives were also examined (45). It was found that monomer concentration of 9% or more was necessary to obtain DP rating and WRA comparable with those of the fabric treated with DMDHEU. And among various free radical initiators, potassium persulfate and sodium persulfate brought about the most desirable performance properties to treated fabric. Especially, the fabric treated with potassium persulfate resulted in higher DP rating and WRA compared with the fabrics treated with the fabrics treated with other initiators.

Influence of pH of the treating bath revealed that add-on decreased continuously with increase pH up to 4 and zero add-on was obtained at pH 6 and above. The zero add-on indicated that esterification reaction did not occur and the oligomers / polymers appeared to be removed by washing.

Addition of TEA as an additive in the copolymerization could noticeable improve strength retention, stoll flex abrasion resistance and whiteness index. But with a compensating decrease in DP rating and WRA. Other hydroxyl-containing additives such as 3-butene-1,4-diol, poly(vinyl alcohol) and poly(ethylene glycol) were likely to slightly increase strength retention. Similarly, slight improvement in DP rating and WRA was obtained with addition of tricarboxylic acid such as aconitic acid and citric acid, but severe yellowing of the treated fabric was remarkable. Moreover, BTCA was also added to imparted DP rating and WRA, but stoll flex abrasion resistance significantly decreased.

CHAPTER III

Experimental Procedures

3.1 Scope

1. The 100% cotton fabric was desized, scoured, bleached and mercerized, and then finished with various concentrations of durable press finishing agent by pad-dry-cure method.

2. Acrylic acid and maleic acid were mixed and then used as a crosslinking agent in this study. Potassium persulfate is an initiator for polymerization of acrylic acid and maleic acid, sodium hypophosphite was chosen as catalyst.

3. The fabric was treated with the mixture of MA and AA under various conditions. The various conditions were adjusted by varying mole ratios and concentrations of acrylic acid and maleic acid, by varying concentrations of catalyst and by varying temperature and time of curing.

4. The treated fabrics, which were finished with DMDHEU and with the crosslinking agents, were tested their physical properties, such as dry wrinkle recovery angle (DWRA), CIE whiteness index and tensile strength.

5. The untreated fabric was dyed with reactive dye and then finished with the selected mixture of the crosslinking agents. In addition, the resin treated fabric having best properties was selected to be dyed with reactive and basic dyes. Then washing fastness and light fastness were determined as well.

6. FT-IR spectroscopic method was used to identify the esterification reaction occurring in the treated fabric and the selected mixtures of the crosslinking agents were characterized by NMR and GPC analysis.

3.2 Materials

The desized, scoured, bleached and mercerized 100%cotton fabric supplied by Thanapaisarn R.O.P. is a 96x36 plain weave and 6 oz/yd^2 cotton weight.

3.3 Chemicals

The chemicals used in these experiments were laboratory reagent grade.

3.3.1 Crosslinking Agents

3.3.1.1 Maleic Acid ($C_4H_4O_4$) (46)

Molecular weight : 116.07

Properties : colorless crystals, repulsive astringent taste, faint odor, soluble in water, alcohol and acetone, very slightly soluble in benzene; d 1.59, mp 130-131°C. At temperatures slightly higher than its melting point, it is converted partly to fumaric acid.

3.3.1.2 Acrylic Acid ($C_3H_4O_2$) (46)

Molecular weight : 76.02

Properties : colorless liquid; acrid odor. Polymerize readily. Miscible with water, alcohol and ether; bp 140.9 °C; mp 12.1 °C; d 1.052, vap press 3.1 mm Hg.

3.3.1.3 Arkofix NDF

Arkofix NDF was used as a control of finishing agent in this study. The properties of cotton fabrics treated with the Arkofix NDF were compared with those of fabrics treated with mixture of MA and AA. It is slightly yellowish transparent aqueous solution of a derivative of dimethylol-4,5-dihydroxy-ethylene urea (DMDHEU).

It is recommended for low formaldehyde type resin finishing for white and coloured textiles composed of cellulosic fibers.

3.3.2 Initiator

Potassium Persulfate ($K_2S_2O_8$) (46)
Molecular weight : 270.32
Properties : white crystals, soluble in water, insoluble in alcohol, d 2.477, mp decomposes bolow 100 °C

3.3.3 Catalyst

3.3.3.1 Sodium Hypophosphite Monohydrate ($NaH_2PO_2.H_2O$) (46)

Molecular weight : 87.97
Properties : Colorless, pearly, crystalline plates or white granular powder; saline taste. Soluble in water, partially soluble in alcohol.

3.3.3.2 Katalysator PS-U

It is the tradename of special catalyst for Arkofix NDF to achieve effective crosslinking of cellulose fibers.

3.3.4 Dyestuffs

3.4.1 Reactive Blue CA

Levafix® Blue CA gran was provided by Dystar.

3.4.2 Basic Blue

Astrazon® Blue BG 200% was provided by Dystar.

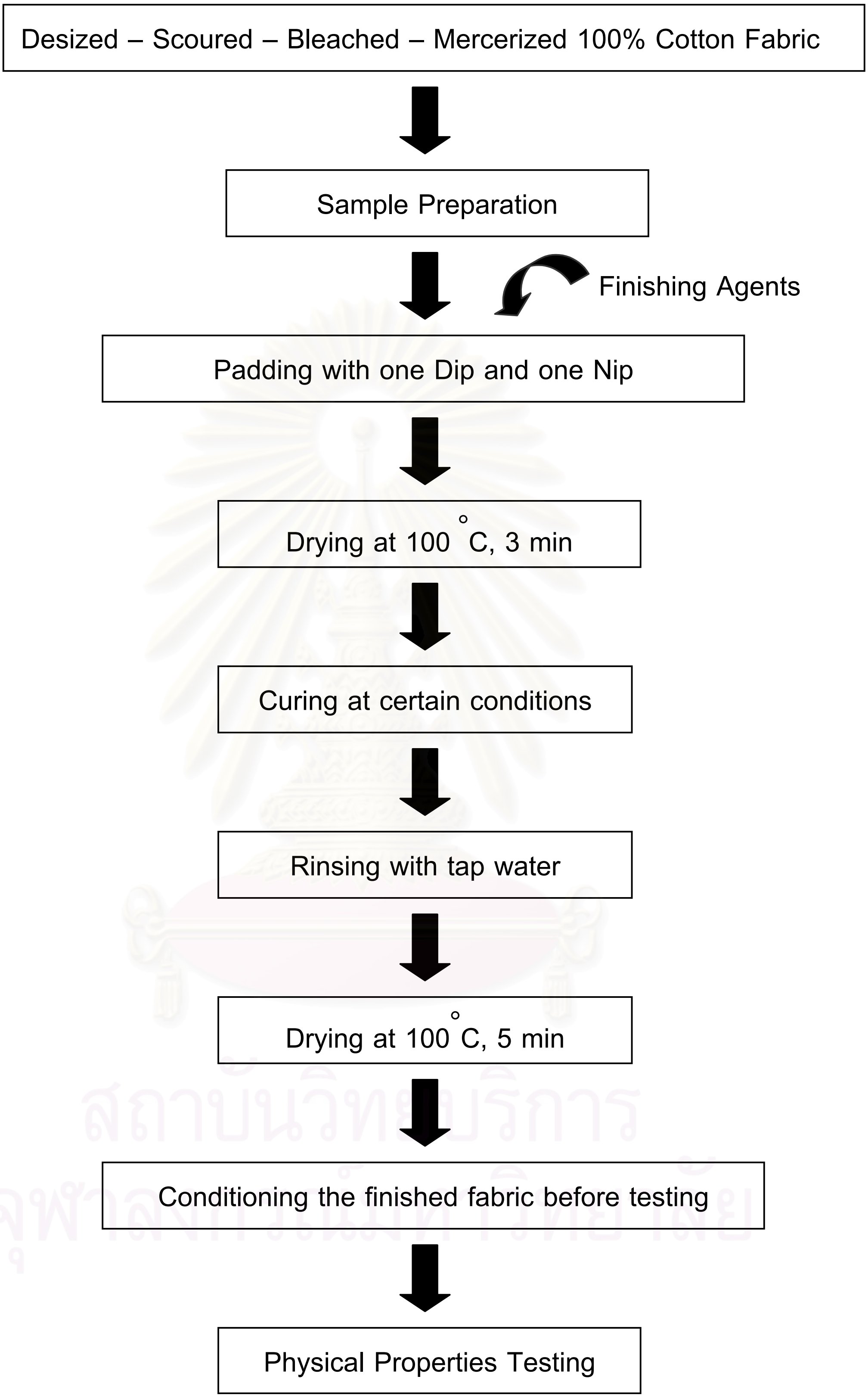


Figure 3.1 Flow chart of durable press finishing procedures.

3.4 Equipments

3.4.1 Laboratory padder

3.4.2 Dryer (Minidryer)

3.4.3 Wrinkle Recovery Tester

3.4.4 Reflectance Spectrophotometer (Spectraflash 500)

3.4.5 Tensile strength tester (Instron Universal Tester)

3.4.6 Infrared heated dyeing machine (Nuance)

3.4.7 Washing Tester (Launder-O-meter)

3.4.8 Light fastness Tester (Fade-O-meter)

3.4.9 Fourier Transform Infrared Spectrometer (FT-IR)

3.4.10 Nuclear Magnetic Resonance Spectrometer (NMR)

3.4.11 Gel Permeation Chromatographic equipment (GPC)

3.4.12 Glasswares

3.5 General Procedures for Durable Press Finishing Treatment

3.5.1 Sample Preparation

The remaining starch on the fabric was checked by using iodine solution testing and then the fabric was cut into a small specimen of 30x30 cm for using in a step of finishing.

3.5.2 Padding

The specimens were immerged in finishing agents and padded with one dip and one nip on a laboratory mangle to obtain 80-90% wet pick-up.

3.5.3 Drying

After the padding step, the specimen was fixed on the frame and dried at 100 °C for 3 min in the minidryer.

3.5.4 Curing

The dry fabrics were cured at different curing conditions by varying the time and temperature of curing in the same minidryer.

3.5.5 Rinsing

After curing step, the specimen was rinsed with tap water for 2 minutes and then dried at 100 °C for 5 minutes in the minidryer.

3.6 General Procedures for Testing of Treated Fabrics

3.6.1 Dry Wrinkle Recovery Angle Test

Dry wrinkle recovery angle (DWRA) of finished cotton fabric was evaluated by following AATCC Test Method 66 (47).

The dry wrinkle recovery angle property is the ability of the fabric to recover its flat position from folded position. Dry wrinkle recovery angle of a specimen is a sum of dry wrinkle recovery angle of specimen in warp and weft directions of the fabric. As a consequence, the maximum of wrinkle recovery angle of each direction is 180 degrees, while zero degree indicates no recovery from creasing.

3.6.1.1 Apparatus:

1) Wrinkle Recovery Tester composes of disk and protractor jointed coaxially together on a vertical support, thus their rotations on a horizontal axis are allowed.

2) Clamp is adjacent to the face of the disk for supporting the specimen holder

3) Specimen holder consists of two superimposed metal leaves, which have the same width of 16 mm and the different lengths of those two metal are 18 and

23 mm jointed together at one end. So the other end can be opened for inserting the specimen.

4) Transparent Plastic Press comprises of two superimposed leaves of equal length and width, approximately 95 mm and 20 mm respectively, and fixed together at one end.

5) A 500 g weight is placed on the press platform to impart regular pressure over the area.

6) A stop watch

3.6.1.2 Test specimens:

1) Test specimens from samples of fabric must be free from wrinkles.

2) Samples were cut into twelve specimens, six from warp direction and the other six from filling direction. The size of each specimen is 15x40 mm. Each warp and filling specimens should be taken from different yarns.

3) The warp direction specimens are divided into 2 groups. Three from them are folded face-to-face and the others are folded back-to-back for testing wrinkle recovery angle.

3.6.1.3 Conditioning

The specimens were conditioned at 65±2 %RH, 21±1°C (70±2 °F) for at least 24 hours. And they must be flat and free from wrinkles.

3.6.1.4 Procedure:

1) Each conditioned specimen was inserted into the specimen holder at one end under the 18mm mark directly and folded the other end on the top of the shorter leaf.

2) The holder and specimen were inserted into spread jaws of plastic press. Then, a load of 500 g was gently applied to press-holder combination.

3) After 5 min ± 5 sec, the load was removed. The press-holder and the specimen holder were lifted and inserted the end of the specimen holder into the mount

on the face of the tester. Then, the press-holder was removed rapidly. It's necessary to try to avoid touching upon the specimen leg.

4) During its recovery period, the dangling specimen leg aligned with the vertical guide line was kept to omit gravitation effects.

5) Exactly 5 min ± 5 sec after removing the load (10 min after the load application).

3.6.1.5 Report

Average all wrap readings and all filling readings were reported as a sum if the difference between the average of face-to-face and average of back-to-back is not greater than 15 degrees. If the difference is greater than 15 degree, those two averages were report separately.

3.6.2 Tensile Strength Test

Tensile strength of finished cotton fabric was tested following ASTM Method D 5035 (48).

The Instron Universal Tester (Model 5583) was used for testing this property. This Instron is type E (constant-rate-of-extension: CRE). It was operated at a cross-head speed of 300 ± 10 mm/min (12 ± 5 in./min). The distance between the clamps (gage length) was set at 75 ± 1 mm (3 ± 0.05 in.).

Each sample was cut into five specimens from the warp direction and eight specimens from the filling direction. It is preferable to space the specimens along a diagonal of the fabric in order to get different warp and filling yarns in each specimen, the specimen size is 25 mm (1 in.) plus 20 yarns for raveling in width and at least 150 mm (6 in.) in length. The length of specimen should be accurately parallel to the direction of testing and force application.

An approximately even number of yarns are raveled from each side of the specimen to gain the required testing width, 25 mm. Besides, the specimen must be under conditioning at 65 ± 2 %RH, 21 + 1 °C (70 + 2 °F) for at least 6 hours before testing. Then, the specimen was clamped at the central position of the holder in the tensile testing machine, and the alignment of specimen should be parallel as possible as to the line direction of force application. A force was applied to the specimen until it broke and the breaking load was read. The mean tensile strength value of all warp direction and of all filling direction were reported as kgf.

3.6.3 Whiteness

Whiteness of the fabric was measured followed AATCC Test Method 110(49). This test method provides to indicate how white the textile is. A reflectance spectrophotometer or colorimeter is used for measuring the reflectance. The reflectance will be converted to CIE tristimulus values. The whiteness is calculated from formulae based on the CIE chromaticity co-ordinates.

3.6.3.1 Apparatus

A reflectance spectrophotometer is able to calculate CIE tristimulus values with D 65/10°. In addition, this instrument can automatically calculate whiteness index.

3.6.3.2 Test Sample

Each sample must be free of dirt and crease, and its size must be large enough to cover the aperture of the instrument.

3.6.3.3 Procedure

Firstly, the spectrophotometer spectraflash 500 instrument was calibrated before testing as the equipment’s direction . Next, the sample was fold until it is opaque. Then, three reading of reflectance were taken and average to one measurement of whiteness index. Specimens were 90° rotated during measurement procedure.

3.6.3.4 Calculating and Interpretation

For illuminant D 65 and 10° observer, the whiteness index can be calculated by this equation.

$$W_{10} = Y_{10} + 800\,(x_{n,10} - x_{10}) + 1700\,(y_{n,10} - y_{10})$$

Where:

W_{10} = whiteness index

Y_{10} = CIE tristimulus value Y of the sample

x_{10}, y_{10} = chromaticity co-ordinates of the sample

$x_{n,10}$, $y_{n,10}$ = chromaticity co-ordinate of perfect diffuser

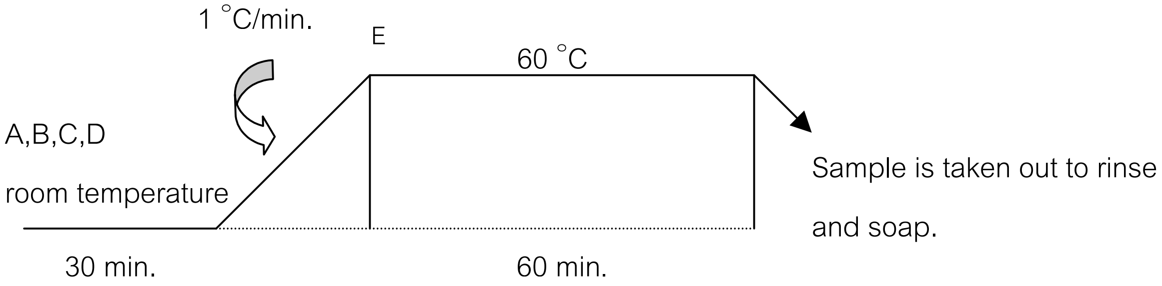
($X_{n,10}$=0.3158, $y_{n,10}$= 0.3310)

Generally, the higher the value of W, the greater the whiteness.

3.6.4 Dyeing of Reactive Dye on the Fabric

General dyeing procedure

Unfinished and resin finished fabrics were dyed using reactive dye (Levafix® Blue CA gran) in Infrared heated dyeing machine (NUANCE) at liquor ratio of 30:1. The dyebath was composed of 3%owf reactive dye, 50 g/l NaCl, 15 g/l Na_2CO_3 and 1 g/l wetting agent. All dyeing except Na_2CO_3 were commenced at room temperature and held for 30 minutes. The temperature was raised to 60 °C by the rate 1°C/min. Na_2CO_3 was added when temperature reached 60 °C, and continued dyeing at this temperature was taken for 60 min. The dyed fabric was then taken out and rinsed through in running tap water. Then, rinsed fabrics were soaped off in the boiling solution containing nonionic surfactant. The dyeing process diagram of reactive dye may be illustrated in Figure 3.2.



Where A = cotton fabric

B = Reactive dye 3%owf

C = NaCl 50 g/l

D = wetting agent 1 g/l

E = Na_2CO_3 15 g/l

Figure 3.2 The dyeing process diagram of reactive dye.

3.6.5 Dyeing of basic dye on the fabric

Unfinished and resin finished fabrics were dyed using basic dye (Astrazon® Blue 200%) in Infrared heated dyeing machine (NUANCE) at liquor ratio of 30:1. The suitable pH of dyeing for fabric dyestuff is 4-4.5, so that the buffer system containing acetic and sodium acetate was used.

Where A = cotton fabric

B = Basic dye 3%owf

C = acetic acid(30%) 4%owf

D = sodium acetate 2%owf

E = wetting agent 1 g/l

Figure 3.3 The process diagram of Astrazon® Blue 200% used in this task.

The starting process of basic dyeing was to add 4% owb of 30% acetic acid, 2%owb of sodium acetate and 1g/l of wetting agent in the dye bath. Secondly, the dyed bath was heated to 50°C and then the fabric were put into the solution for 5 minutes. The 3% owf basic dye was dissolved with boiled water before it was added into the solution. The dyeing temperature was raised to the boil at rate of 3°C/min and held at this temp for 60 minutes. After that, the temperature was cooled down to 60°C at rate of 3°C/min. Finally, the fabric was taken out and rinsed through tap water before soaping-off with the boiling solution containing nonionic surfactant. The process diagram of Astrazon® Blue 200% is shown in Figure 3.3.

3.6.6 Determination of washing fastness

The ISO 105 C03 color fastness to wash (50) is designed to determine the effect of washing only on the color fastness of the textile. In the principle, a dyed specimen and a piece of white cotton cloth were sewed together and put in a soaping solution. The specimen is mechanically agitated under specified conditions of time and temperature in a soaping solution, then rinsed and dried. The change in color of the specimen and the staining on the whiteness cotton cloth are evaluated with the grey scales.

Test procedure

A 40 mm x100 mm of dyed specimen was sewed with the same side of white cotton cloth. The tested specimen was placed in the beaker and added the certain amount of soap solution at the liquor of 50:1 containing 5 g/l of standard soap and 5 g/l of anhydrous sodium carbonate in distilled water. The soaping solution was heated to 60 °C before putting the specimen in the soap solution for 30 min. After the end of this stage, the tested specimen was removed, rinsed in through tap water and running water for 10 minutes, and squeezed out the excess water. The dyed specimen and the white cotton cloth were separated and dried under ambient condition.

3.6.7 Determination of light fastness

The ISO 105-B02 color fastness (51) was used to determine the resistance of light fastness of the colored under the artificial light of xenon arc, which is artificial light source representative of natural daylight. The light fastness of dye is usually assessed against a set of standard dyeing.

In the test, a dyed fabric is exposed to artificial light source under prescribed conditions, along with a set of dyed blue wool as references. The light fastness rating corresponds to the number of blue reference showing a contrast equal to that of the test dyed sample (visual contrast between exposed and unexposed parts of the specimen).

3.6.8 Fourier Transform Infrared (FT-IR) Spectroscopy

Infrared spectroscopy is a classical molecular spectroscopic method used for identifying organic dyes, textile fibers, polymer and blends. In this study, it was used to confirm the evidence of cellulose crosslinking through esterification reaction between carboxyl groups in MA/AA copolymer and cellulose hydroxyl groups. It is based on the interaction of infrared radiation with molecular dipole moments in the sample. When molecules are stimulated from ground vibrational state to higher vibrational state by interaction with emission of electromagnetic radiation of the appropriate frequency. In phase, the vibrations are enhanced and the energy was transfered from the incident radiation to the molecule. The spectral transitions are detected by scanning through the frequency, the vibration frequency are shown to be characteristic of particular functional groups in molecules.

The basic components of a fourier transform infrared (FT-IR) spectrometer consists of the infrared light source, the interferometer, the sample chamber and the IR detector. The infrared light source passes into the interferometer, which has two mirrors, the transmitting and reflectance are combined at the beamsplitter where they produce interference effects. The beam is then passed through the sample and the signal "interferogram" will be generated at the detector. The infrared spectrum is calculated through fourier transformation of this data.

The method of sample preparation used in this experiment is pressed-disc technique. Treated fabrics were separated into yarns and cut into powder before mixing with potassium bromide. Then the mixtures were pressed into translucent discs. The spectra of the prepared discs were obtained on a Perkin Elmer system 2000 FT-IR spectrometer. Resolution for all the spectra presented was 4 cm^{-1}. The number of scan was 16. All the spectra were transferred to the computer for further analysis and plotting by spectrum for windows software.

3.7 General Procedure for Characterization of AA/MA copolymer

3.7.1 ^{13}C-NMR Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is an important method for materials characterization and for the study of polymer structure-property relationships. The NMR signals in virtually all-modern NMR spectrometers are obtained by a combination of pulsed NMR and fourier transformation. Common tools for all NMR spectrometers are a high field magnetic, a source of radio frequency (rf), and a computer.

In the absence of rf pulses, the nuclear magnetic moments tend to align with magnetic field. The application of rf pulses rotates the magnetisation into the xy plane, where it rotates, or precesses, at a rate that depends on the magnetic environment. This rotation is detected as the oscillating signal known as a free induction decay and converted into a frequency spectrum by fourier transformation.

3.7.2 Gel -Permeation Chromatography (GPC)

This technique is also called Sized-exclusion chromatography (SEC). That is capable of characterizing very high-molecular-weight film and fiber polymers up to 10^6 molecular weight, thermoset resins of molecular weight 10^3 and 10^4, oligomers or pre-polymers in which only a few monomer units are jointed, and finally simple molecules present in commercial polymers in the form of additives. It has the ability for separation and quantitation. In addition, it also offers considerable potential to determine molecular sized (weight) and molecular weight distributions.

Conventional liquid chromatographic equipment is normally used for GPC. A dilute polymer solution is injected into the solvent stream, which then flows through a column or series of columns, packed with material of narrow particle size and controlled pore size, the pore size being comparable to the size of molecules to be separated. The solvent molecules pass through and allow the packing media, carrying the polymer molecules with them, where possible. The smaller molecules are able to pass through most of the pores and so have a relatively long flow path through the column. Whereas the larger polymer molecule are excluded from all but the largest of pores and hence elude first. In this experiment, Equipment mode PL-GPC 110 was used with NaOH as an solvent. The detector used is the differential refractometer (DRI).

CHAPTER IV

Results and Discussions

4.1 Fabric Preparation for Wrinkle Resistant Finishing

The desized, scoured, bleached and mercerized, plain woven cotton fabric was firstly tested by iodine solution to ensure that the fabric has been pretreated completely before it was used in finishing process. No starch was detected on the fabric after testing with iodine solution because the yellow color of iodine solution did not turn to blue color which indicates a presence of starch. Therefore, this cotton fabric can be used in the finishing process.

4.2 Fabric properties treated with Arkofix NDF

In order to make a comparison with commercial DMDHEU finished fabric, Arkofix NDF is the commercial name of DMDHEU finishing agent for cotton fabric. Katalysator PS-U is a commercial name of catalyst for Arkofix NDF. The finishing formula used in the study was 100 g/l of Arkofix and 30 g/l of catalysator PSU. The fabric was padded with one dip and one nip at about 80%wet pick-up. The padded fabric was dried at 100 °C for 3 min and cured at 160°C for 3 min. Then, it was rinsed and dried at 100°C for 5 min before testing. The testing properties of untreated cotton fabric and cotton fabric treated with Arkofix NDF shown in Table 4.1

Table 4.1 Properties of cotton fabric treated with Arkofix NDF.

Treatment on cotton fabric	Properties				
	DWRA (degree,w+f)	Tensile strength(kgf)		Strength loss %(w+f)	CIE Whiteness Index
		Warp(w)	Filling(f)		
untreated	166	49.087	25.749	0	52.8
Arkofix(control)	233	32.161	15.304	36.57	51.6

4.3 Preliminary study for selecting the AA/MA system or MA/AA system

4.3.1 Comparison of AA/MA system and MA/AA system

The two monomers used in this work were acrylic acid (AA) and maleic acid (MA). From the hypothesis, the both unsaturated acids can copolymerize by radical polymerization in the presence of suitable initiator such as potassium persulfate under high temperature to form polycarboxylic acid. The copolymer can react with the hydroxyl groups of cellulose chain in the presence of appropriate catalyst such as sodium hypophosphite in order to from crosslinking network to impart wrinkle resistant property for the fabric. However, whiteness and tensile strength properties of the treated fabric may be deteriorated by the reaction. Evaluation of wrinkle resistant property was carried out by measuring the dry wrinkle recovery angle (DWRA). The higher dry wrinkle recovery angle value means that the treated fabric is more resistant to wrinkle.

To select an appropriate copolymer system between AA/MA system and MA/AA system, the ratios of both monomers were varied by fixing one monomer concentration constantly and varying the other by mole ratio and vice versa. For the AA/MA system, the concentration of AA was fixed, while concentrations of MA were varied. Four different mole ratios of AA/MA system were 1 to 0, 1 to 0.2, 1 to 0.5 and 1 to 1. The MA/AA system was similar to AA/MA system but the concentration of MA was constant and the concentrations of AA were varied instead at the same way as in the AA/MA system. The fabric treated with the both systems under different conditions were measured fabric properties given in Table 4.2.

The results in Table 4.2, Figures 4.1 and 4.2 indicate that DWRA of finished fabrics under different curing conditions in both systems were likely to increase while the total mole ratio increase. It could be noticeable that pure MA imparted better wrinkle resistant property to fabrics than pure AA could. However, fabrics finished with pure MA showed higher strength loss than those finished with pure AA.

Table 4.2 Effects of AA/MA system (a) and MA/AA system (b) under different curing conditions on fabric properties.

AA/MA ratio	DWRA (degree,w+f)			%Strength loss			CIE Whiteness Index		
	180°C1 min	180°C2 min	160°C3 min	180°C1 min	180°C2 min	160°C3 min	180°C1 min	180°C2 min	160°C3 min
1:0	179	192	182	23.41	31.01	27.93	41.4	45.7	46.0
1:0.2	183	217	193	33.70	38.70	32.72	45.6	44.9	47.5
1:0.5	201	230	209	40.42	42.55	42.66	45.8	42.7	47.1
1:1	198	237	217	37.68	46.39	42.13	46.1	42.6	44.1
MA/AA ratio									
1:0	195	201	194	54.72	51.73	48.62	48.5	43.1	48.8
1:0.2	205	205	199	48.37	51.92	48.23	47.7	43.5	46.9
1:0.5	198	208	203	43.81	48.90	42.75	47.1	41.7	47.2
1:1	196	216	210	41.12	46.64	40.10	46.8	41.4	47.0
DMDHEU	-		233	-		36.57	-		51.6
untreated	166			0			52.8		

[a] Treating bath :12%owb AA, 2%owm $K_2S_2O_8$, 7%owm $NaH_2PO_2.H_2O$. [b] Treating bath :12%owb MA, 2%owm $K_2S_2O_8$, 7%owm $NaH_2PO_2.H_2O$.

5 replicates of breaking strength in warp direction within 7%CV and 8 replicates of breaking strength in filling direction within 9%CV.

6 replicates of DWRA in both warp and filling directions within 6%CV.

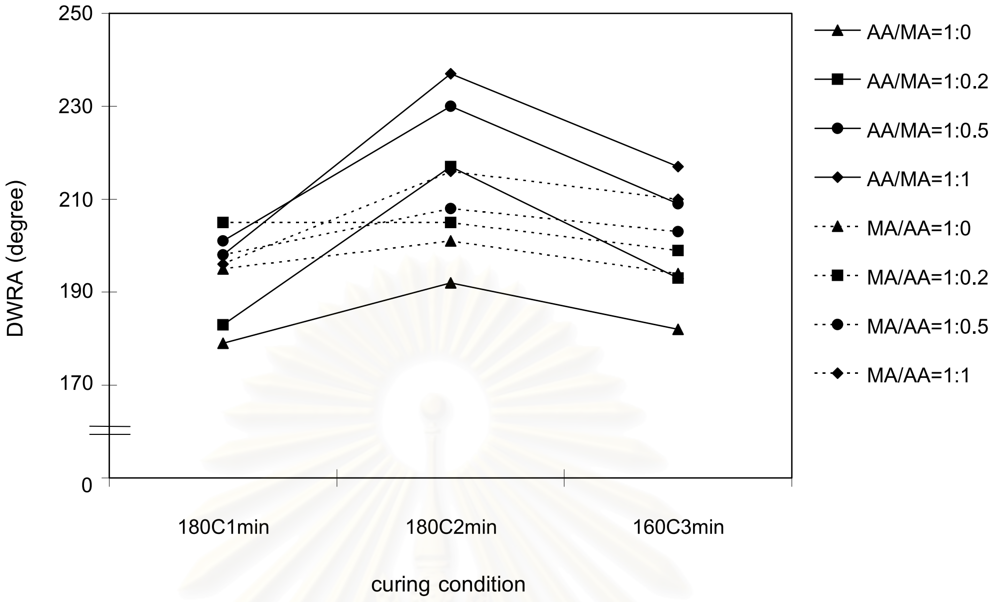


Figure 4.1 DWRA of finished fabrics treated with AA/MA and MA/AA system.

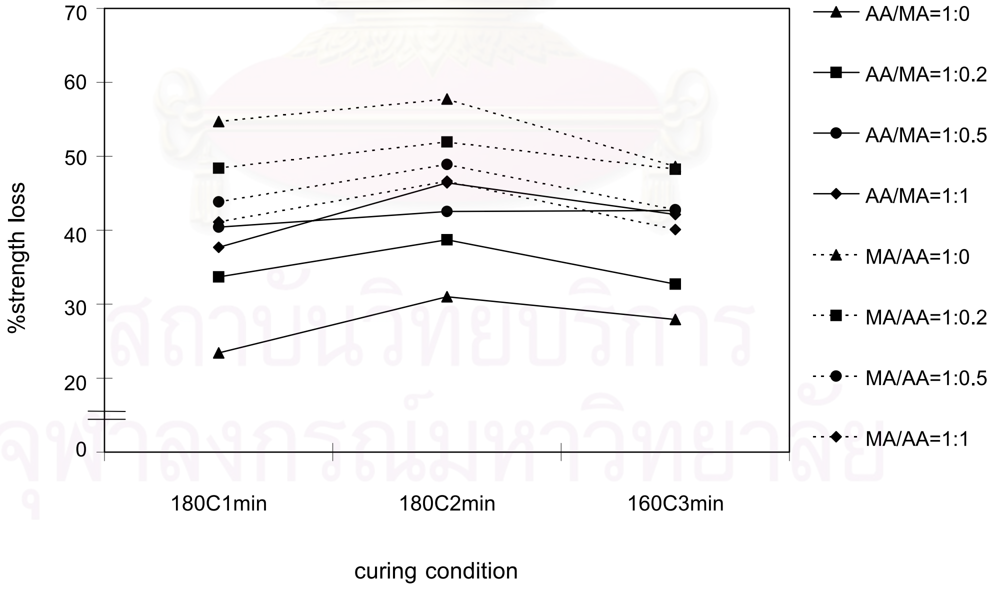


Figure 4.2 %strength loss of finished fabrics treated with AA/MA and MA/AA system.

Moreover, strength loss of finished fabrics treated with AA/MA system increased gradually when the amount of MA increased. On the other hand, strength loss of finished fabrics treated with MA/AA system decreased when the amount of AA in the system increased. The trend of strength loss in both systems under three different curing conditions was the same. Additionally, it was noticeable that AA caused slightly yellowing on finished fabric while MA did not cause that problem. And MA brought better wrinkle resistance to fabric than AA could; however, serious problem of MA was that the finished fabric had very high strength loss.

As these results, it could be concluded that MA/AA system brought about slightly better wrinkle resistant properties to treated fabrics than AA/MA system did while strength loss of finished fabrics treated with MA/AA system was higher than those of finished fabrics treated with AA/MA system. Whiteness index of the fabrics treated with both systems was comparable and seemed to decrease with the addition of AA. Therefore, the AA/MA system was selected for further experiments.

4.3.2 Comparison of three different curing conditions

Curing condition also played an important role in finished fabric properties in those three testing properties. Curing condition consisted of time and temperature of curing. The good combination of time and temperature of curing such as high temperature-short time or low temperature-long time. The experiment was carried out by varying curing temperature and curing time in three conditions: 180°C for 1 min, 180 °C for 2 min and 160°C for 3 min. The fabric was finished with both AA/MA system and MA/AA system using 12% owb AA in AA/MA system and 12% owb MA in MA/AA system, 2% owm potassium persulfate was used as an initiator and 7% owm sodium hypophosphite as a catalyst. The padding step, each of the treated fabrics was dried at 100°C for 3 min and cured at different curing conditions. Then, they were rinsed and dried at 100°C for 5 min. Finally, dry wrinkle recovery angle (DWRA), tensile strength and whiteness were evaluated. The properties of finished fabrics under different curing conditions were also shown in Table 4.2, Figures 4.1 and 4.2.

Results from Table 4.2, Figures 4.1 and 4.2 showed that best wrinkle recovery property of the finished fabrics treated with the mixture of AA/MA and MA/AA solutions can be achieved by curing under 180°C for 2 min. This condition; however, brought about worst strength loss and whiteness index on the finished fabrics as well. Whereas curing condition at 180°C for 1 min was the best condition to retain fabric strength in finished fabrics treated with the mixture of AA/MA system. Additionally, DWRA and %strength loss of finished fabrics treated with both mixture solutions and cured at 160°C for 3 min were similar to those of finished fabrics cured at 180°C for 1min. For comparison to those properties obtained from DMDHEU finished fabrics, it could be concluded that DWRA and whiteness of all finished fabrics were lower than those of DMDHEU finished fabric except for DWRA of finished fabrics treated with AA/MA system and cured at 180°C for 2 min. The only property that can be comparable to that of DMDHEU finished fabric was tensile strength.

The conditions of 180°C for 1 min and 160°C for 3 min were selected for further experiments. Even though DWRA of finished fabric cured under these conditions was not as good as that of finished fabrics cured under 180°C for 2 min, it was believed that further experiments could improved DWRA by adjusting other factor such as concentration of monomers and amount of catalyst.

To sum up, AA/MA system was selected because strength loss of finished fabrics treated with this system was markedly lower than that of finished fabrics treated with MA/AA system. Whereas DWRA of finished fabrics treated with both systems was similar. The selected curing conditions were 180°C for 1 min and 160°C for 3 min.

The further experiments were to study the effect of the concentration of the mixture of AA/MA, and amount of catalyst used on the tested properties of the finished fabrics under selected curing conditions. The fabrics were treated with 8%owb, 10%owb, and 12%owb AA, and the mole ratio of AA/MA equal to 1 to 0, 1 to 0.2, 1 to 0.5 and 1 to 1 based on the pure concentration of AA. Each treating bath contained AA or MA as monomers and 2%owm potassium persulphate as an initiator. Amount of sodium hypophosphite as a catalyst was varied, such as 7%owm, 9%owm and 12%owm. The finished fabrics were cured at 180°C for 1 min or 160°C for 3 min.

4.4 Effects of curing conditions, monomers and catalyst on DWRA

4.4.1 Effect of different curing conditions on DWRA

The DWRA of the finished fabrics treated with each condition mentioned above were concluded in Table 4.3. The results in Table 4.3, Figures 4.3, 4.4 and 4.5 indicate that the superior DWRA was achieved when fabrics were cured at 160°C for 3 minutes and it was obviously observed when mole ratio of AA to MA was increased to 1 to 0.5 and 1 to 1.

In order to select appropriate curing condition, it was believed that treatment under curing at 160°C for 3 min considerably resulted in more efficiency of curing than those from 180°C for 1 min.

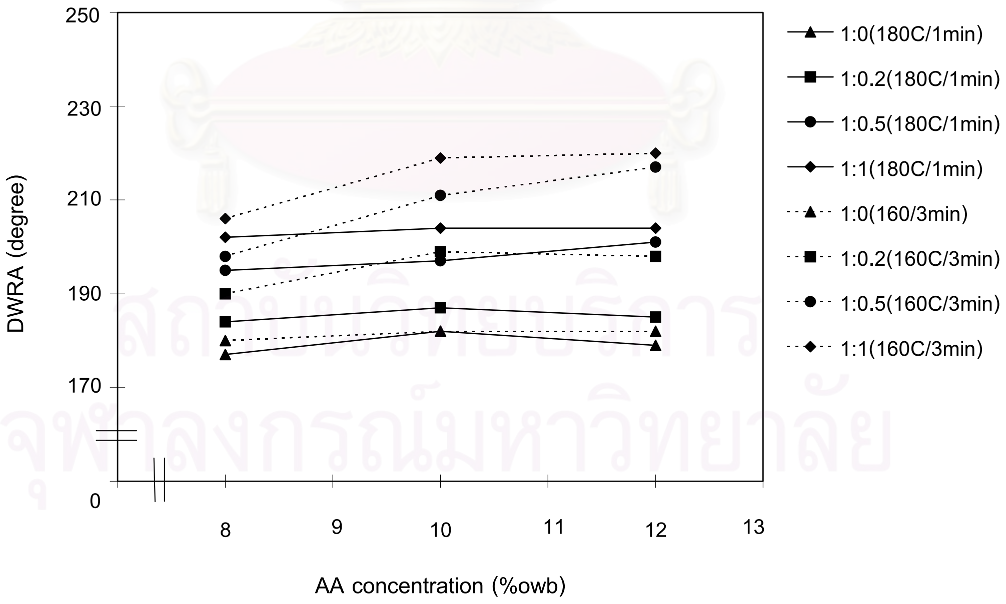


Figure 4.3 Effects of curing conditions and monomers on DWRA of the finished fabrics from treatment with AA/MA system at 7%owm catalyst.

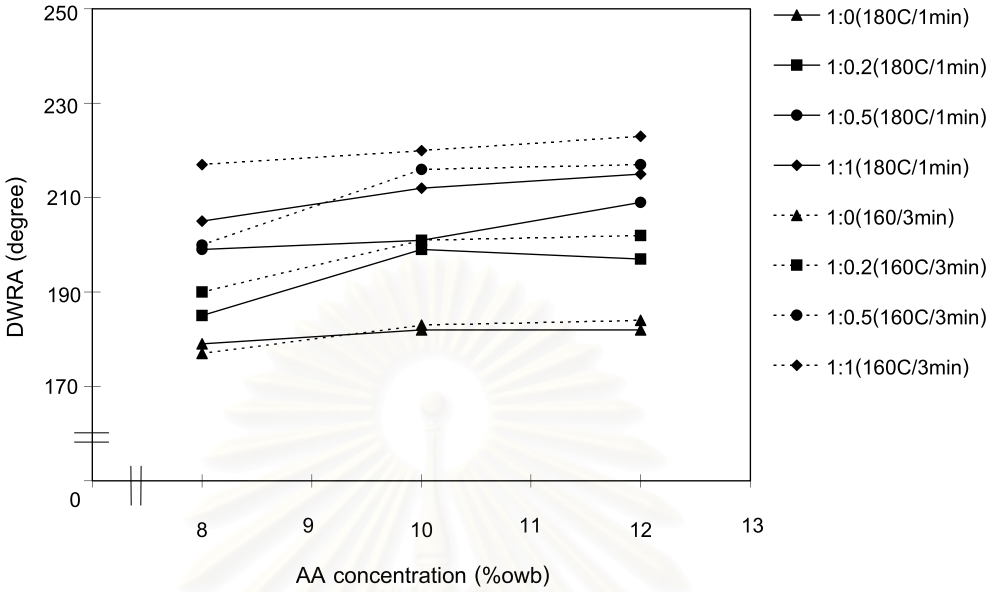


Figure 4.4 Effects of curing conditions and monomers on DWRA of the finished fabrics from treatment with AA/MA system at 9%owm catalyst.

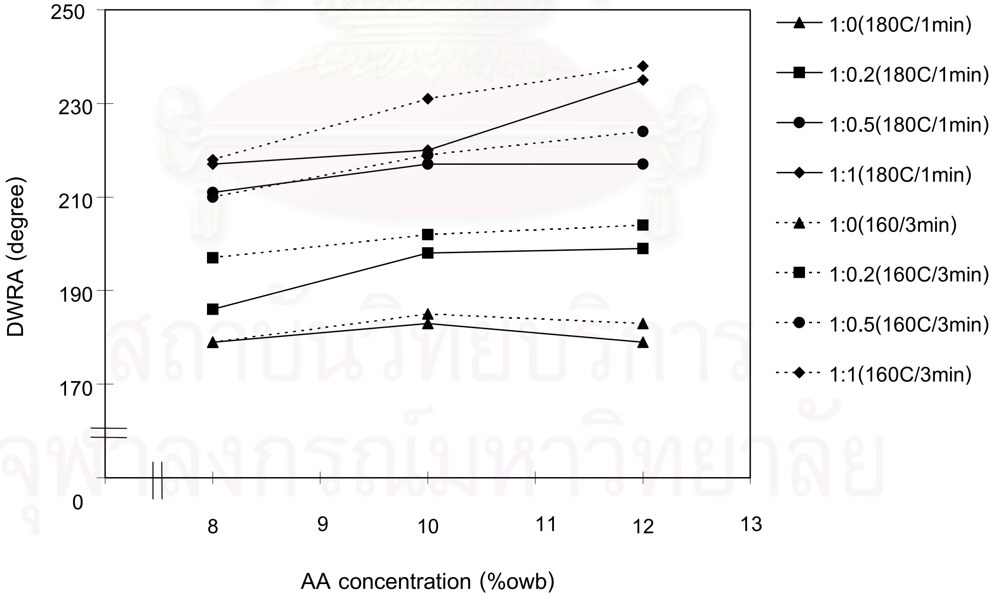


Figure 4.5 Effects of curing conditions and monomers on DWRA of the finished fabrics from treatment with AA/MA system at 12%owm catalyst.

Table 4.3 DWRA of the finished fabrics from the treatments of the mixture of AA/MA.

AA conc.	AA/MA ratio	DWRA (w+f, degree)					
		7% catalyst		9% catalyst		12% catalyst	
		180°C 1 min	160°C 3 min	180°C 1 min	160°C 3 min	180°C 1 min	160°C 3 min
8%	1:0	177	180	179	177	179	179
	1:0.2	184	190	185	190	186	197
	1:0.5	195	198	199	200	211	210
	1:1	202	206	205	217	217	218
10%	1:0	182	182	182	183	183	185
	1:0.2	187	199	199	201	198	202
	1:0.5	197	211	201	216	216	219
	1:1	204	219	212	220	220	231
12%	1:0	179	182	182	184	179	183
	1:0.2	185	198	197	202	199	204
	1:0.5	201	217	209	217	217	224
	1:1	204	220	215	223	235	238
DMDHEU		233					
Unfinished		166					

6 replicates of DWRA in both warp and filling directions within 5%CV.

4.4.2 Effects of different concentrations and mole ratios of monomers on DWRA

From Table 4.3, Figures 4.3, 4.4 and 4.5, DWRA of the finished fabrics were slightly better when AA concentration was increased or when mole ratio of monomers was increased, especially at the mole ratio of AA/MA equal to 1 to 0.5 and 1 to 1. Although wrinkle recovery values of the finished fabrics from all conditions were higher than that of unfinished fabric, the DWRA of many finished fabrics were still lower than that of DMDHEU finished fabric. However, the DWRA of finished fabrics treated with 10%owb AA at mole ratio of AA/MA equal to 1 to 1 and with 12%owb AA at the same mole ratio under curing condition at 160°C for 3 min were comparable with that of finished fabrics treated with DMDHEU. Additionally, the best improvement of DWRA was obtained from the treatment containing 12%owb AA at mole ratio of AA/MA equal to 1 to 1 and 12%owm catalyst under curing condition at 160°C for 3 min.

4.4.3 Effect of amount of catalyst on DWRA

Catalyst was another important factor for imparting desired properties to fabric, because the suitable amount of catalyst could bring about the effective crosslinking reaction between active groups of resins and cellulose chains.

As seen in Figures 4.6, 4.7 and 4.8, wrinkle resistant property of fabric is proportional to the concentration of catalyst as assumed at the beginning. When concentration of catalyst was increased, it was gradually increased in wrinkle resistant property of fabric finished with 1 to 1 mole ratio of AA and MA. Nevertheless, concentration of catalyst did not affect DWRA of finished fabrics treated with pure AA at different concentrations. This may be caused by AA itself was not a good crosslinking agent. It does not have three carboxylic acid groups in the adjacent carbon atoms capable for supporting effective cyclic anhydride mechanism, so crosslinking reaction would not be accomplished. Thus, DWRA of finished fabrics treated with pure AA was likely to be stable although how much of amount of catalyst was used.

As previous assumption, catalyst had an important role in producing effective crosslinking reaction between resin and cotton fabric. Since the carboxyl groups of resin, which penetrated through cotton fibers, can react with hydroxyl groups of cellulose chain in 3-dimension, resulting in progression of crosslinking reaction. Therefore, it was necessary to have enough amount of catalyst to support the reaction.

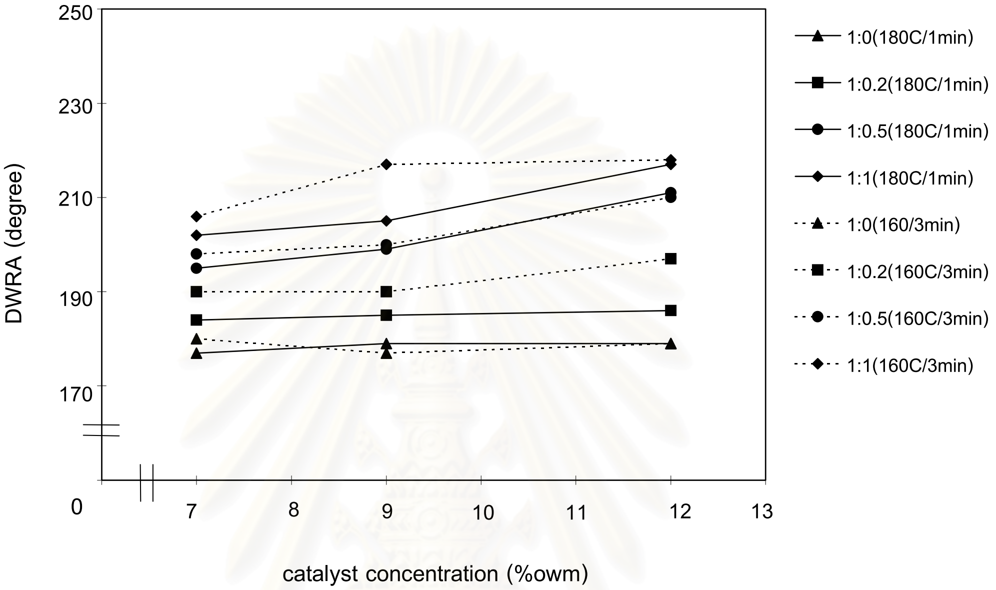


Figure 4.6 Effect of amount of catalyst on DWRA at 8%owb AA.

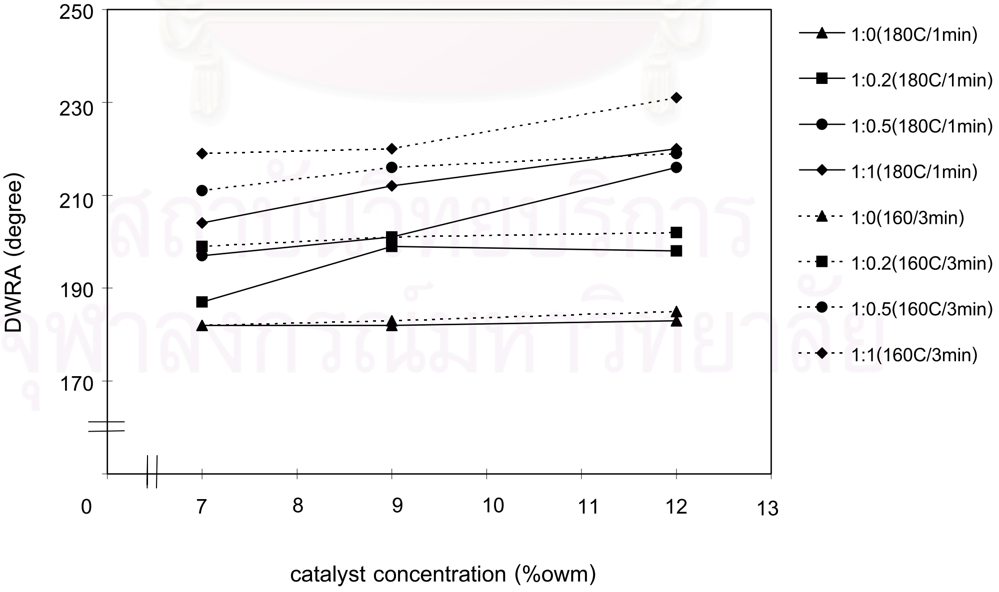


Figure 4.7 Effect of amount of catalyst on DWRA at 10%owb AA.

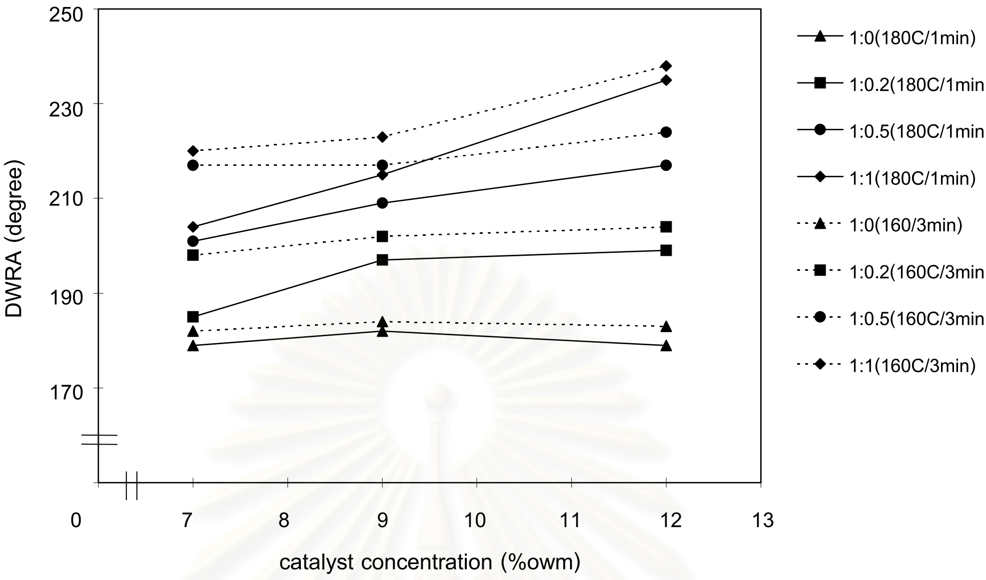


Figure 4.8 Effect of amount of catalyst on DWRA at 12%owb AA.

4.5 Effects of curing conditions, monomers and catalyst on fabric strength

4.5.1 Effects of different curing conditions on fabric strength

Tensile strength of finished fabrics were reported in %strength loss. According to the results in Table 4.4, Figures 4.9, 4.10 and 4.11, %strength loss of finished fabrics cured under conditions 180°C for 1 min and 160°C for 3 min were not significantly different. The trend of strength loss of finished fabrics treated with both curing condition was the same while the strength loss of finished fabrics cured under condition 180°C for 1 min were likely to be lower than that of finished fabrics cured at 160°C for 3 min.

Table 4.4 %strength loss of the finished fabrics from the treatments of the mixture of AA/MA.

AA conc.	AA/MA ratio	%strength loss					
		7% catalyst		9% catalyst		12% catalyst	
		180°C 1 min	160°C 3 min	180°C 1 min	160°C 3 min	180°C 1 min	160°C 3 min
8%	1:0	11.75	12.41	12.25	12.36	9.00	11.4
	1:0.2	27.85	31.78	27.78	29.59	25.46	28.17
	1:0.5	35.74	37.16	33.23	34.33	31.82	31.20
	1:1	38.33	39.11	35.55	36.34	33.74	34.23
10%	1:0	17.47	17.30	17.33	17.16	15.45	16.96
	1:0.2	32.52	35.69	31.20	34.27	30.46	30.67
	1:0.5	38.40	40.62	38.25	39.15	37.56	36.92
	1:1	41.18	42.03	40.60	41.04	39.65	40.24
12%	1:0	23.41	27.93	16.90	19.81	15.91	18.18
	1:0.2	33.70	35.75	31.67	34.38	31.64	32.85
	1:0.5	40.42	42.66	38.32	40.96	36.83	40.86
	1:1	38.33	42.13	38.76	40.47	38.62	39.84
DMDHEU		36.57					
Unfinished		0					

5 replicates of breaking strength in warp direction within7%CV and 8 replicates of breaking strength in filling direction within 7%CV.

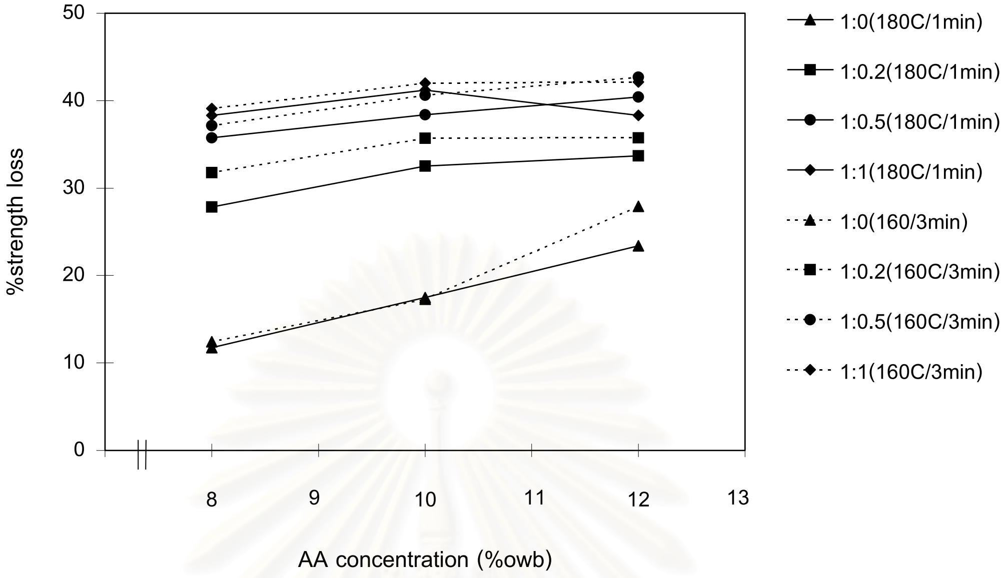


Figure 4.9 %strength loss of the finished fabrics from the treatments of the mixture of AA/MA at 7%owm catalyst.

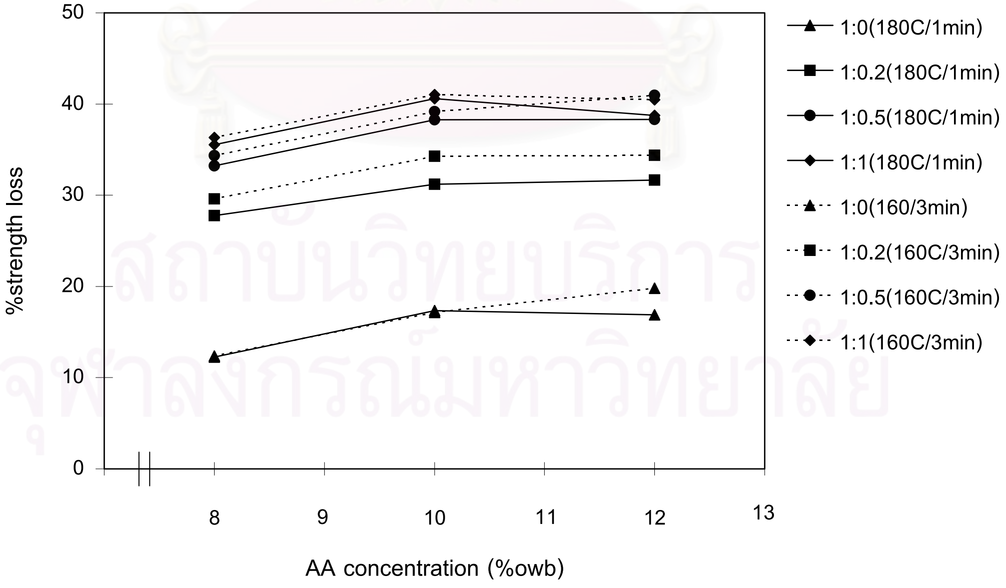


Figure 4.10 %strength loss of the finished fabrics from the treatments of the mixture of AA/MA at 9%owm catalyst.

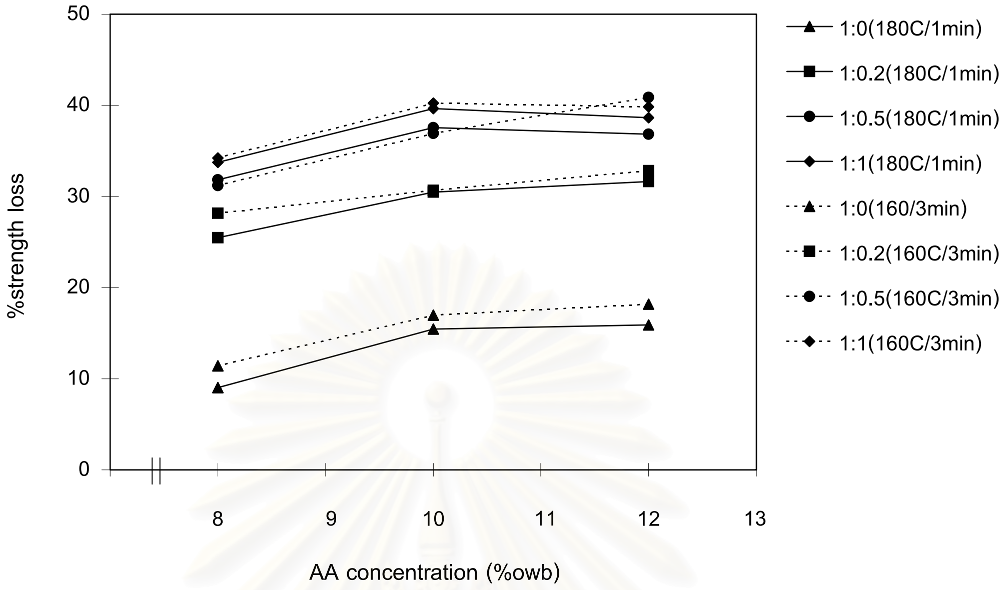


Figure 4.11 %strength loss of the finished fabrics from the treatments of the mixture of AA/MA at 12%owm catalyst.

4.5.2 <u>Effects of different concentrations and mole ratios of monomers on fabric strength</u>

The influences of concentrations and ratios of monomers on %strength loss in Table 4.4, Figures 4.9, 4.10 and 4.11 demonstrate that %strength loss of finished fabrics were increased when AA concentrations and mole ratio of monomers increased. Nevertheless, those of finished fabrics treated with mole ratio of AA/MA equal to 1 to 0 and 1 to 0.2 were still lower than that of DMDHEU finished fabric. In fact, cotton fibers can be completely dissolved in 70% sulfuric acid. AA and MA are also acids, therefore they can damage the strength of cotton fabrics as well.

4.5.3 Effect of amount of catalyst on fabric strength

From Figures 4.12, 4.13 and 4.14, increasing catalyst concentrations had a tendency to decrease %strength loss in finished fabrics treated with all systems.

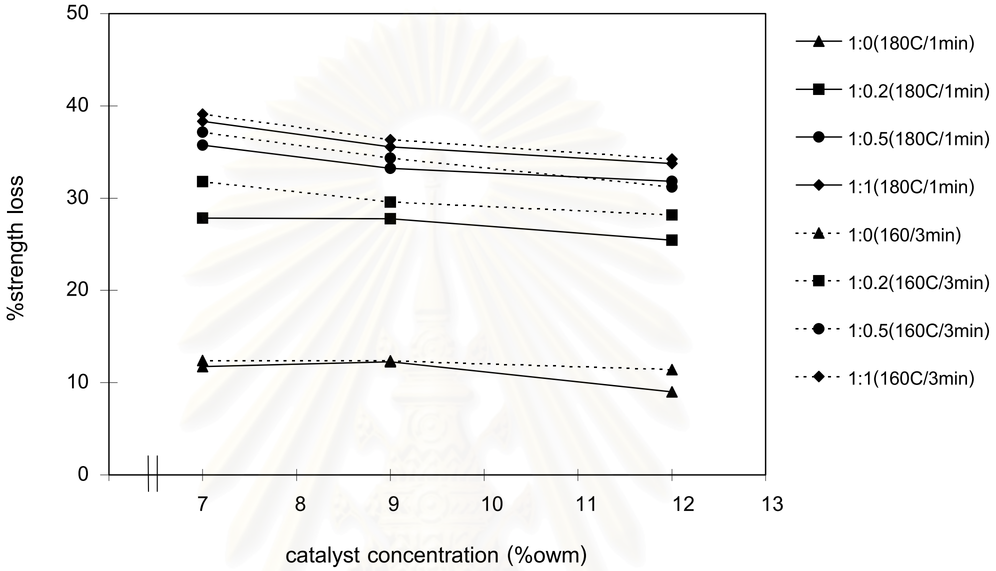


Figure 4.12 Effect of amount of catalyst on fabric strength at 8%owb AA.

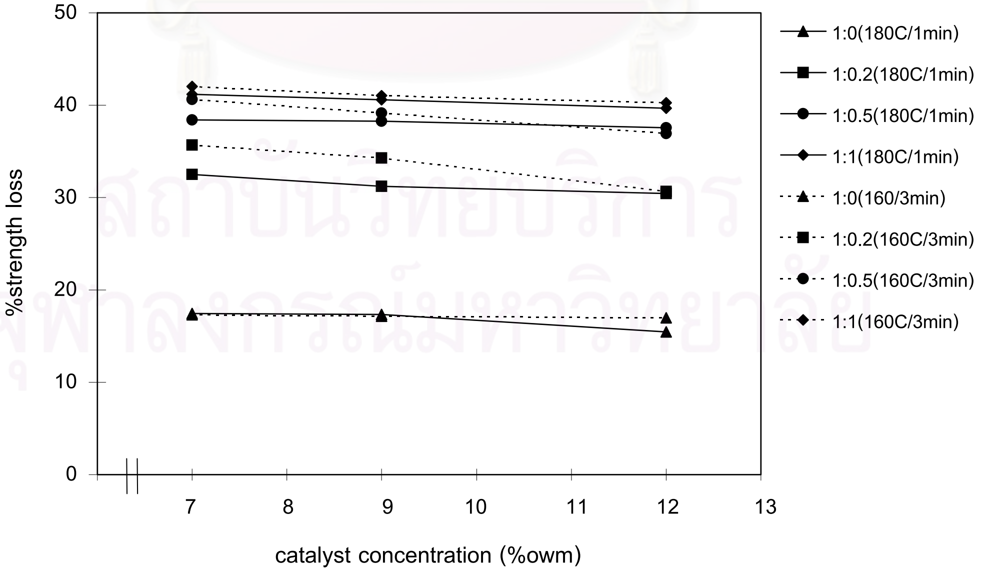


Figure 4.13 Effect of amount of catalyst on fabric strength at 10%owb AA.

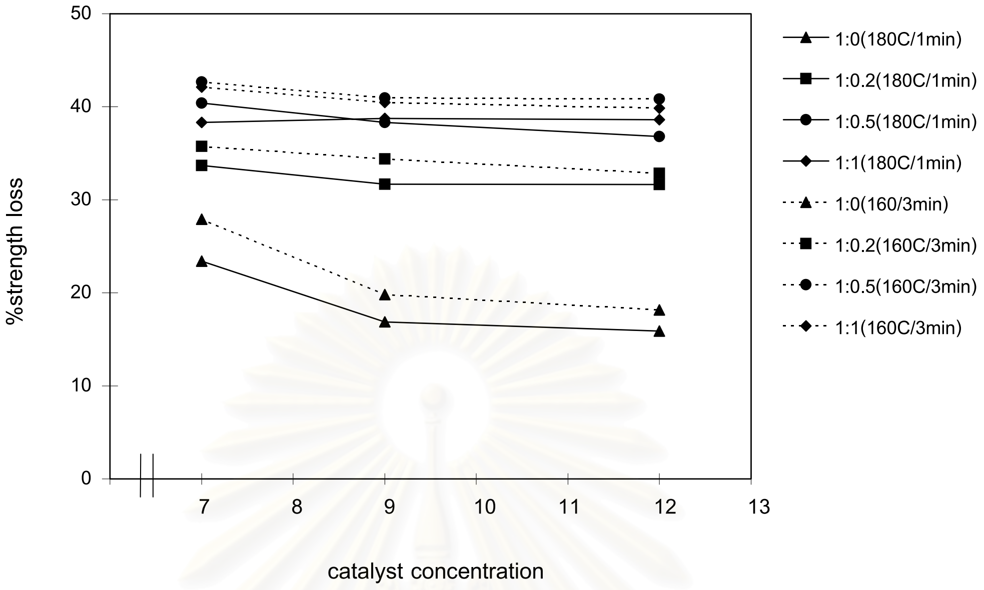


Figure 4.14 Effect of amount of catalyst on fabric strength at 12%owb AA.

According to these results, it could be imply that catalyst can support crosslinking reaction between resin and cotton fabric. Therefore, the opportunity of fabric strength damaged by resin was decreased.

4.6 Effects of curing conditions, monomers and catalyst on whiteness index

4.6.1 Effects of different curing conditions on whiteness index

Generally, the fabrics started to get yellowish when the finished fabrics were treated under high temperature condition, the influences of both selected curing conditions on whiteness of finished fabrics were shown in Table 4.5.

Whiteness of each finished fabric was worse than that of unfinished fabric. However, when the finished fabrics were cured at 180°C for 1 min, the whiteness of the finished fabrics was higher than that of the finished fabrics were cured at 160°C for 3 min.

Table 4.5 Whiteness Index of the finished fabrics from the treatments of the mixture of AA/MA

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AA conc.	AA/MA ratio	CIE Whiteness Index					
		7% catalyst		9% catalyst		12% catalyst	
		180°C 1 min	160°C 3 min	180°C 1 min	160°C 3 min	180°C 1 min	160°C 3 min
8%	1:0	50.0	46.9	49.9	48.7	46.9	49.8
	1:0.2	52.0	49.8	51.6	50.5	51.2	50.6
	1:0.5	51.2	50.4	51.7	51.4	51.4	51.1
	1:1	47.9	46.6	47.9	48.0	48.8	46.3
10%	1:0	48.0	45.5	48.4	47.1	48.5	47.4
	1:0.2	49.4	46.7	50.4	48.4	50.7	50.1
	1:0.5	51.6	49.6	50.5	49.9	50.8	49.5
	1:1	46.6	42.2	47.2	44.2	47.1	44.1
12%	1:0	41.4	46.0	43.2	45.2	49.8	48.0
	1:0.2	45.6	47.5	47.9	45.6	51.4	49.9
	1:0.5	45.8	47.1	47.2	47.1	49.7	50.4
	1:1	46.1	44.1	46.9	43.2	45.7	46.1
DMDHEU		51.6					
Unfinished		52.8					

4.6.2 Effects of different concentrations and mole ratios of monomers on whiteness

Whiteness, another important property of finished fabrics listed in Table 4.5 indicates that AA caused yellowing in the finished fabrics. The adding of small amount of MA could alleviate the yellowing. Adding the MA in the system which has the mole ratio of AA/MA equal to 1 to 1 decreased the whiteness of the finished fabrics as lower than that of finished fabrics treated with all pure AA allowed. However, there is slightly difference among all systems, which is hardly noticeable with naked eyes.

4.6.3 Effect of amount of catalyst on whiteness

Results of amount catalyst affecting on whiteness of fabrics listed in Table 4.5 display that when amount of catalyst was increased, the superior whiteness index was achieved. This may be resulted from the fact that sodium hypophosphite is an oxidizing agent, which can discolor the finished fabrics. Finally, it could be concluded that the more increase of amount of catalyst the more increase of tested properties, such as DWRA, fabric strength and whiteness.

Based on these experimental data, the compromise properties showed in the treatment of 12%owbAA, mole ratio of AA/MA equal to 1 to 0.5 and 1 to 1 using 12%owm catalyst under curing at 160°C for 3 min. However, the best compromise properties appeared to peak at the treatment of 12%owbAA, mole ratio of AA/MA equal to 1 to 1 and 12%owm catalyst under curing at 160°C for 3 min. This treatment condition was selected for treating the fabric to be used in further study of an effect of dyeing.

4.7 Dyeability on durable press finished fabric

4.7.1 Dyeability of rective dye

Two sets of dyeing experiments were conducted by the same procedure and chemicals. Firstly, untreated cotton fabric was dyed with 3%owf Levafix® Blue CA gran at liquor ratio of 30:1. After dyeing step, the dyed fabric was rinsed through a running tap water to remove unreacted dyed before soaping the dyed fabric in boiling solution containing nonionic surfactant. Secondly, resin finished fabric was dyed in the same procedure. The different results of the color yield in both fabrics were optically observed. The color of unfinished fabric was strong deep blue while the color of resin finished fabric was just fairy blue color. Unfortunately, the dyed uptake of resin finished fabric was not uniform. These results may imply that reactive groups of reactive dyed did not react effectively with hydroxyl groups of cellulose chains in resin finished fabric. Similar to Andrews and Morrell (24), they claimed that dye sites of polycarboxylic finished fabric are locked by crosslinking, the more highly crosslinked a fabric is, the less dye receptivity it has. Nevertheless, dyeing condition may be another case.

In actually, reactive dye is usually applied to fabric under alkaline condition. The dyeing condition, therefore, may be disturbed by acidic condition possessed in resin finished fabric. In addition, the acidic resin may cause damage to structure of cellulose resulting in failure to adsorb dye.

The results as mention above obtained from the fabric treated with resin and then dyed with the reactive dye. The next step was to study the effect of resin on the dyed fabric. The cotton fabric was dyed with reactive dye and treated with the resin treatment as mention above. After the dyed fabric was treated with resin, there was noticeable change in color of fabric. The color strength of dyed fabric after treatment was lower than that of untreated fabric. Due to acidic condition of finishing solution, it was believed that fixed dye in fabric was able to be hydrolyzed.

4.7.2 Basic Dyeability

According to Welch and Andrews (28), the anionic nature of polycarboxylic acid treated fabrics is known by their affinity to basic dye. Andrews and Morrell (24) stated that cationic dye is an indicator for the extent of crosslinking network in the finished fabric because the cationic dye produces a positive stain on the finished fabric. In order to examine the crosslinking network, resin finished fabric and blank were dyed with 3%owf Astrzon ® Blue 200% at liquor ratio of 30:1. The dyed fabric, then, were rinsed through running tap water to remove unfixed dye.

As assumed, the resin finished fabric had an affinity for basic dye, whereas regular cotton fabric did not. However, dye uptake of resin finished fabric was not uniform and dye fixation was seriously poor. Consequently, washing fastness and light fastness test were not conducted.

4.8 The washing fastness test of resin finished fabric dyed with reactive dye

The unfinished fabric and resin finished fabrics before and after dyed with reactive dye were subjected to wash fastness test (ISO 105-C03). Color change after washing was compared with standard grey scale level; the higher the level number the better the washing fastness properties. The results, in Table 4.6, demonstrate that the staining of the adjacent fabrics and the change in color of all fabrics after washing, except the resin finished fabric after dyeing, were compared and equal to number 5 on grey scale. The number 5 on grey scale means that the dye-fiber bond of the dyed fabric was resisted to washing. Because there were no change in color after washing and there were no staining on the adjacent fabric. However, the change in color of resin finished fabric after dyeing was compared and equal to number 2 on grey scale. The color strength of the resin finished fabric after dyeing observed after washing was higher than that observed before washing. It was believed that the acidic condition of the resin finished fabric after dyeing was neutralized under alkali condition of soaping solution.

Table 4.6 Washing fastness test of reactive dyed fabrics.

Kind of fabrics	Washing Fastness (rating) of reactive dyed fabrics					
	Unfinished fabric		Resin finished fabric after dyeing		Resin finished fabric before dyeing	
	Color staining	Color change	Color staining	Color change	Color staining	Color change
Acetate	5	5	5	2	5	5
Cotton	5		5		5	
Nylon	5		5		5	
Silk	5		5		5	
Acrylic	5		5		5	
Wool	5		5		5	

4.9 <u>The light fastness test of resin finished fabric dyed with reactive dye</u>

Light fastness test followed by ISO 105 B-02 was also conducted on all fabrics dyed with reactive dye. The light fastness rating of all fabrics were compared to number 5, which the light fastness rating corresponded to the number of blue reference showing a contrast equal to that of the dyed fabric (visual contrast between exposed and unexposed parts of the specimen). Therefore, it can imply that the dyed fabrics were in good performance to light fastness.

Table 4.7 Light fastness test of reactive dyed fabrics.

Reactive dyed fabrics	Light fastness (rating)
Unfinished fabric	5
Resin finished fabric after dyeing	5
Resin finished fabric before dyeing	5

To sum up, it was believed that hydroxyl groups of cellulose chain in cotton fabric were not completely crosslinked with polycarboxylic acids finishing. The results of reactive dyeability could be enough to support that.

4.10 Results of FT-IR Analysis

In order to confirm the evidence of cellulose crosslinking through esterification reactions between carboxyl groups in AA/MA system and cellulose hydroxyl groups, Fourier transform infrared spectroscopy was used. The fabrics were treated with different solutions containing AA and MA as a crosslinking agent, potassium persulfate as an initiator and sodium hypophosphite as a catalyst. The spectra of finished fabrics were received.

4.10.1 Effect of monomers ratios

The effects of monomers ratios on the ester cross-linking of cotton were inspected. The cotton fabrics were treated with solutions containing 12%AA and MA in different mole ratios of AA to MA such as 1 to 0, 1 to 0.2, 1 to 0.5 and 1 to 1, respectively. The padded fabrics were dried at 100°C for 3 min, cured at 160°C for 3 min and rinsed before being dried at 100°C for 5 min.

As shown in Figure 4.15, the ester carbonyl band at 1725.11 cm^{-1} was clearly observed on finished fabrics while the untreated fabric had slight peak in this area. The 1374 cm^{-1} and 1431 cm^{-1} bands dealt with the bending vibration mode of hydrocarbon structure in cellulose molecule (17). It is also observed that the intensity of the ester carboxyl band increased as the mole ratios of AA and MA increase.

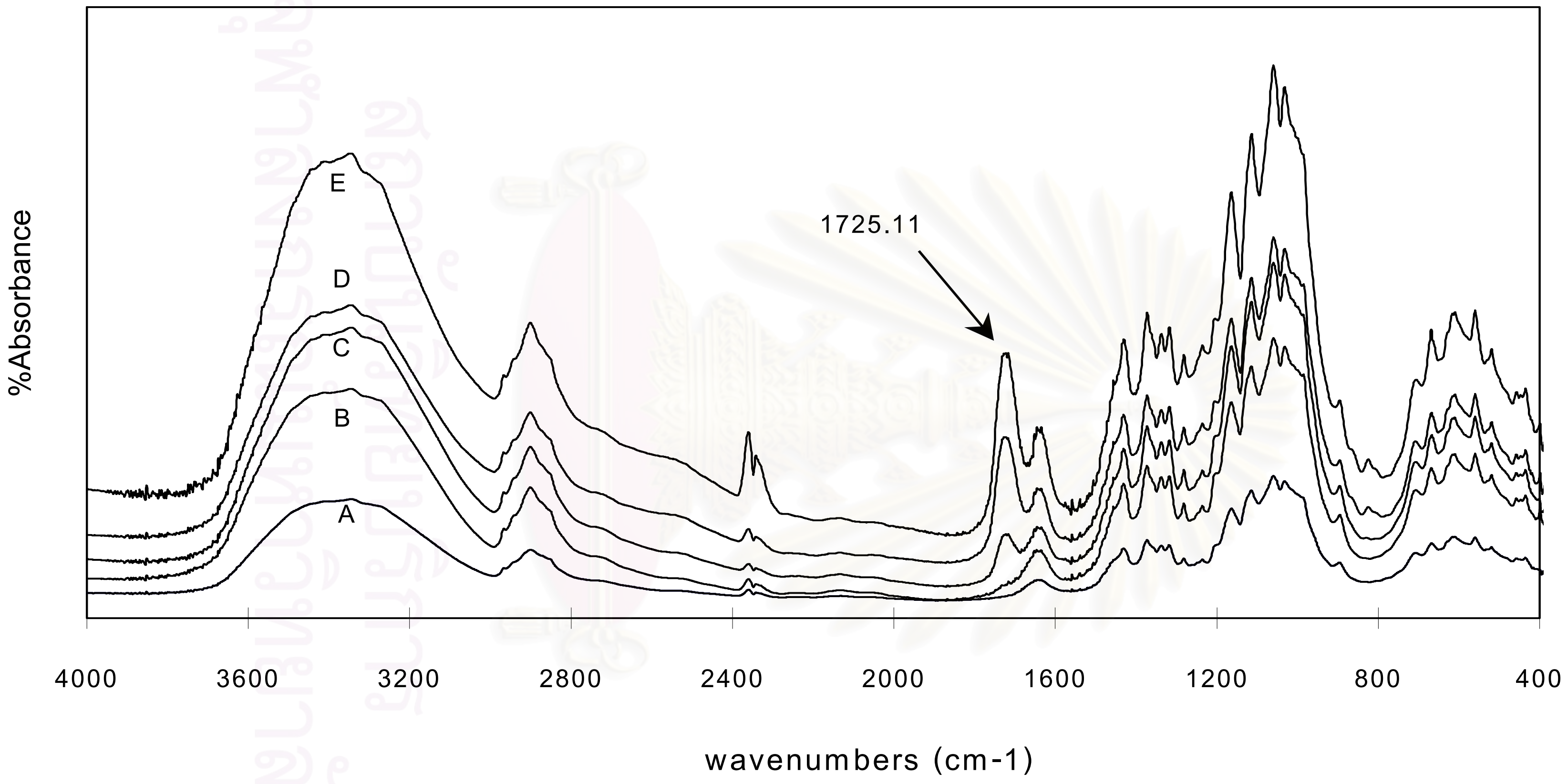


Figure 4.15 FT-IR of untreated cotton fabric and of cotton fabric treated with different mole ratios of AA and MA.

A=untreated, B=1:0(AA/MA), C=1:0.2(AA/MA), D=1:0.5(AA/MA), E=1:1(AA/MA)

4.10.2 Characterization of the intermolecular ester crosslinking of cotton fabrics

Generally, the carbonyls in the fabric could form in three patterns after esterification reaction occurred between polycarboxylic acids and cellulose molecules. They were intermolecular ester linkage, carboxyl and carboxylate (Figure 4.16), which the intensity of carbonyl band at 1725.11 cm^{-1} may composed of the overlapping between ester carbonyl and carboxyl bands.

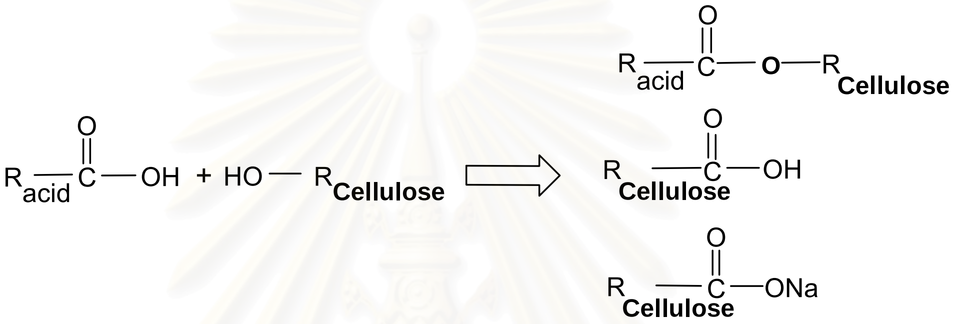


Figure 4.16 Three forms of product exist in the treatment of finished fabrics. (17)

Consequently, the fabric was prepared by treating with 12%AA at 1:1mole ratio of AA and MA as finishing agent, 2%potassium persulfate and 7%sodium hypophosphite as an initiator and catalyst. Then, the finished fabric was impregnated in distilled water with stirring for 5 min at room temperature, next the finished fabric was treated with a 0.1 N NaOH solution for 5 min, and rinsed with distilled water again. It was noticed that the converting from carboxyl to carboxylate by sodium hydroxide, the 1575.62 cm^{-1} band intensity was increased while the 1725.11 cm^{-1} band intensity was decreased as shown in Figure 4.17.

After that, the old finished fabric was treated with 0.1 N hydrochloric acid in the same procedure. As a consequence, the 1575.62 cm^{-1} band completely disappears since the carbonyl of carboxylate and the carboxyl, including ester carbonyl bands overlapped at 1725.11 cm^{-1}. So, the total quantity of the ester groups in the finished fabrics can be determined by measuring the 1725.11 cm^{-1} band intensity.

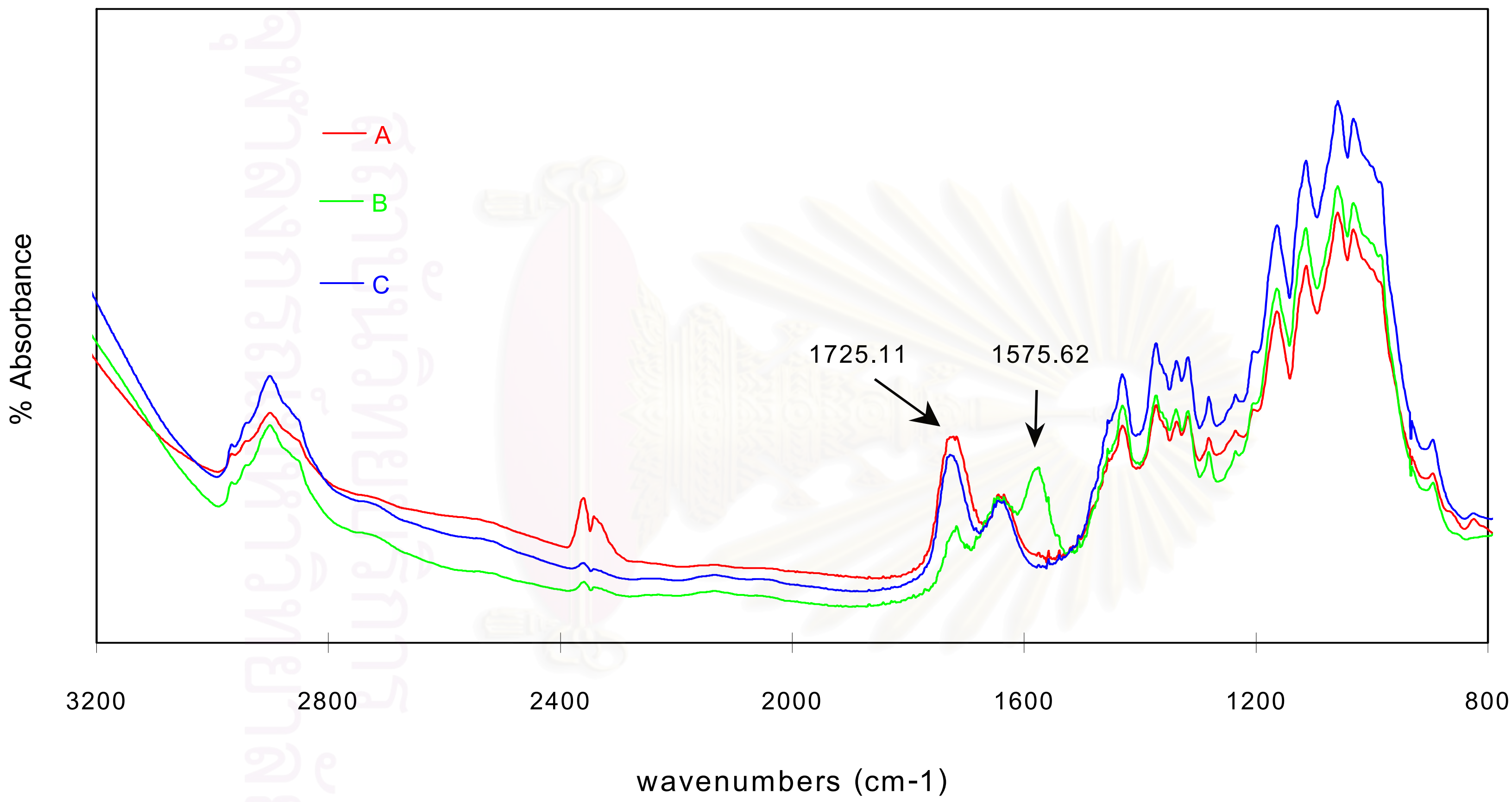


Figure 4.17 Infrared spectra of cotton fabrics finished with 1:1 mole ratio of AA/MA and cured at 160°C for 3 min.

A= resin treated B= resin treated with 0.1 N NaOH solution C= resin treated with 0.1 N HCl solution

However, the existing of ester groups in the finished fabrics is not only the ester crosslinkages but also the ester groups between cellulose and single bonded acid molecules. Thus the effectiveness of the acid as a crosslinking agent in cotton fabric can not be represented by using 1725.11 cm $^{-1}$ ester carbonyl band alone.

The intensity ratio of carbonyl band is more useful to evaluate the effectiveness of the acid. Increasing intensity ratio of the carbonyl band (ester/carboxylate) signifies an increase in the average number of ester groups formed per each acid molecule (52).

4.11 Results of characterization of AA/MA copolymer

4.11.1 Result of Carbon-13 Nuclear Magnetic Resonance Spectroscopic Studies

The ^{13}C NMR Spectroscopy was also used to characterize the products of polymerization reaction of MA and AA. Four samples from AA/MA system with 12%AA in D_2O were characterized. They were the different mole ratios of AA/MA, such as1 to 0, 1 to 0.2, 1 to 0.5 and 1 to 1, and 2% $K_2S_2O_8$ was used as an initiator. Before being characterized, they were preheated at 100°C for 5 min and then heated at 160°C for 3 min. The ^{13}C NMR spectra of these samples are shown in Figures 4.20, 4.21, 4.22 and 4.23.

In addition, pure monomers of MA and AA were also characterized by ^{13}C NMR spectroscopy for comparing with that obtained from the four samples. The ^{13}C NMR spectra of both monomers in D_2O are shown in Figure 4.18 and Figure 4.19.

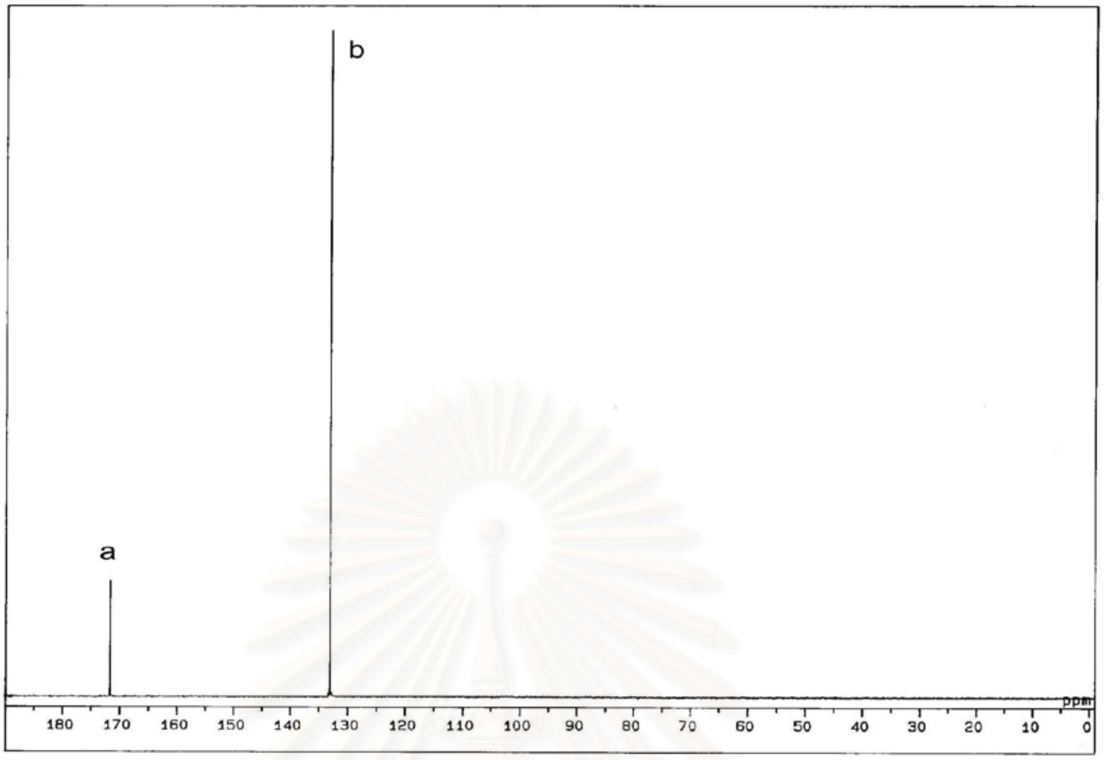


Figure 4.18 ^{13}C NMR spectrum of maleic acid in D_2O.

(full size spectrum can be seen in Figure A1)

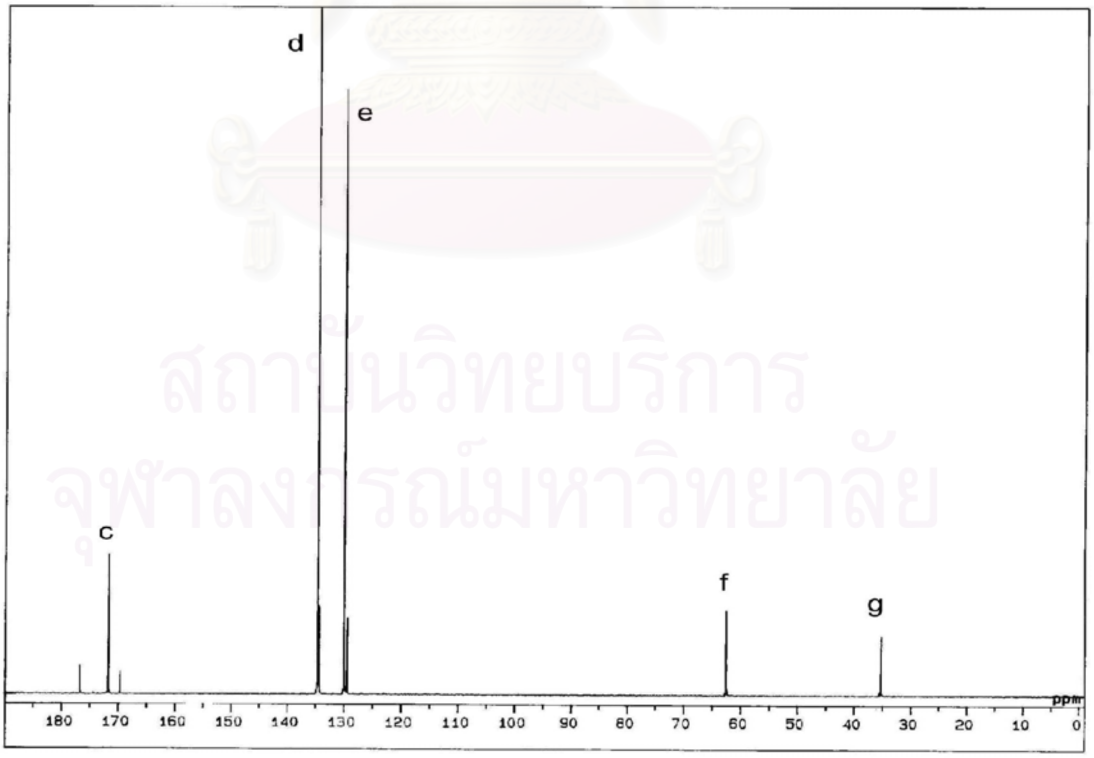
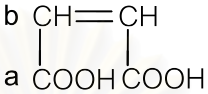
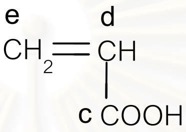


Figure 4.19 ^{13}C NMR spectrum of acrylic acid in D_2O.

(full size spectrum can be seen in Figure A2)

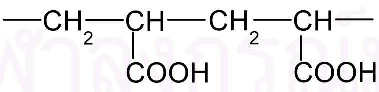
From Figure 4.18 and Figure 4.19, it can be determined for each carbon in Table 4.8 below.

Table 4.8 Peak assignments of acrylic acid and maleic acid.

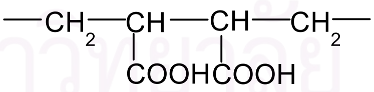
Monomer	Structure	Peak Assignments
Maleic acid	 $\overset{b}{}\underset{a\,COOH}{CH}=\underset{COOH}{CH}$	a = 171.619 b = 132.893
Acrylic acid	 $\overset{e}{CH_2}=\underset{c\,COOH}{\overset{d}{CH}}$	c = 171.701 d = 134.489 e = 129.850

However, there were undesirable signals (signal f and signal g) in the ^{13}C NMR spectrum of acrylic acid. We suspected that acrylic acid was also self polymerized.

According to Figure 4.20, the chemical shift values of poly(acrylic acid) are assigned to signals h, f, i and g. The signal h (181.227 ppm) corresponds to the carboxyl carbon (-COOH) of poly(acrylic acid) and the signal f (63.502 ppm) is assigned to methine carbon (-CHCOOH) of poly(acrylic acid) (53). The methylene carbon (CH_2) was observed at 44.254 ppm (signal i). Moreover, resonated peaks between 35.929-37.410 ppm (signal g) were due to the methine carbon. This might be caused by the different arrangement of monomer; head-to-tail or head-to head replacement.


$-CH_2-\underset{COOH}{CH}-CH_2-\underset{COOH}{CH}-$

head-to-tail


$-CH_2-\underset{COOH}{CH}-\underset{COOH}{CH}-CH_2-$

head-to-head

The carbon signals of acrylic acid monomer were also observed at 134.489 ppm (signal d) and 129.850 ppm (signal e). However, signal c (171.701) of acrylic acid was not observed. It was supposed that this signal was not strong enough.

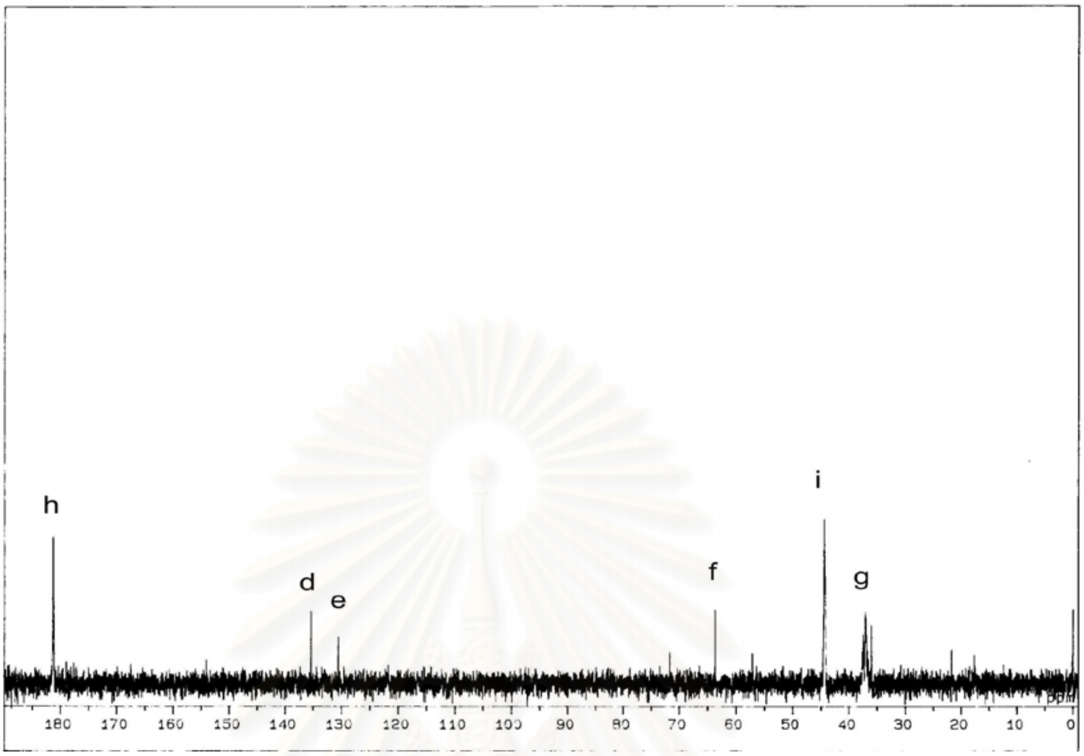


Figure 4.20 ^{13}C NMR spectrum of AA/MA with mole ratio 1to 0 in D_2O.

(full size spectrum can be seen in Figure A3)

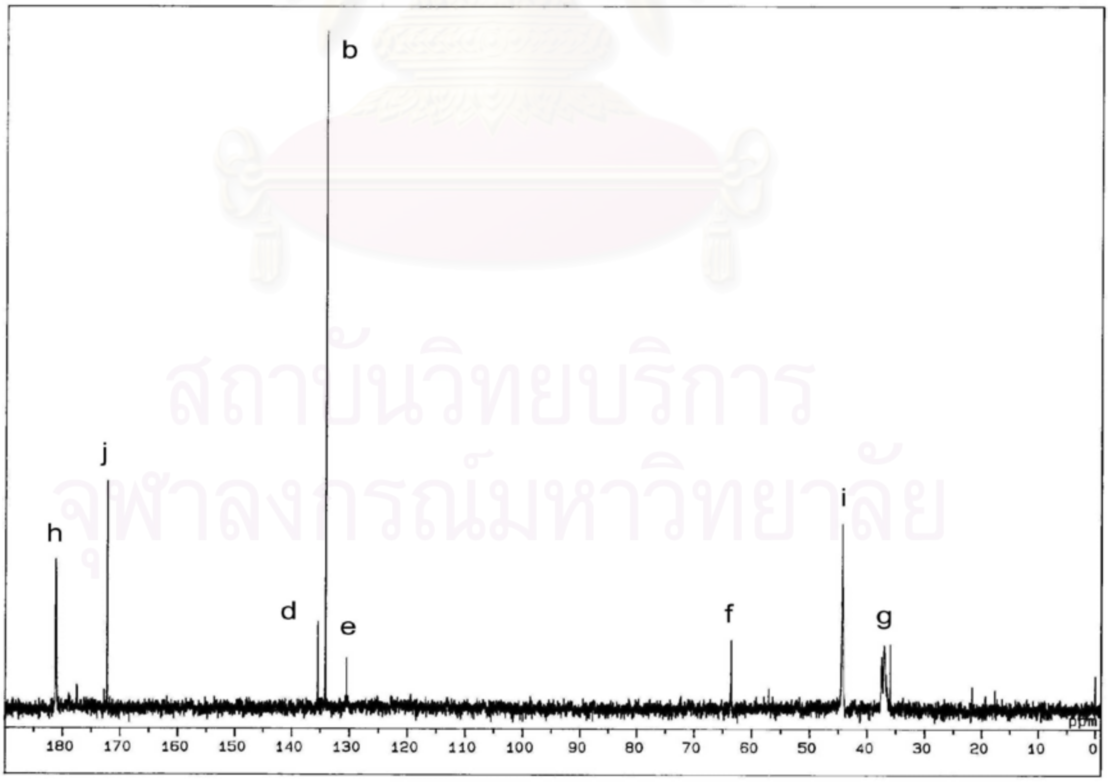


Figure 4.21 ^{13}C NMR spectrum of AA/MA with mole ratio 1to 0.2 in D_2O.

(full size spectrum can be seen in Figure A4)

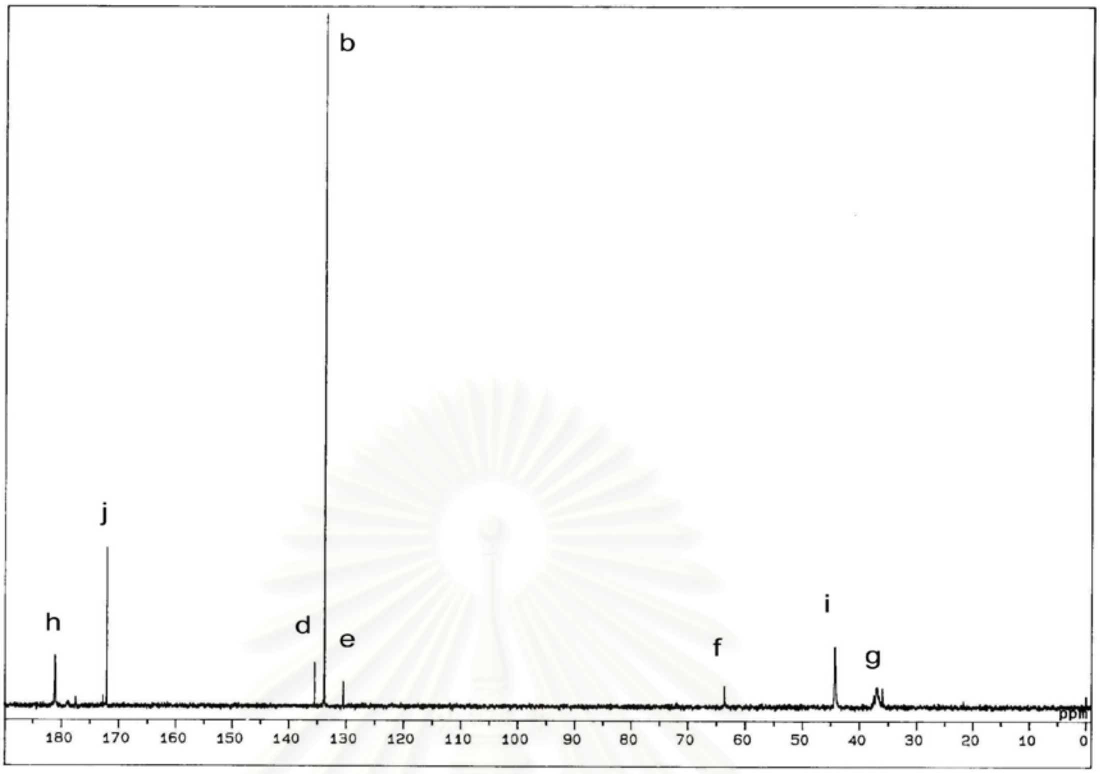


Figure 4.22 ^{13}C NMR spectrum of AA/MA with mole ratio 1to 0.5 in D_2O.

(full size spectrum can be seen in Figure A5)

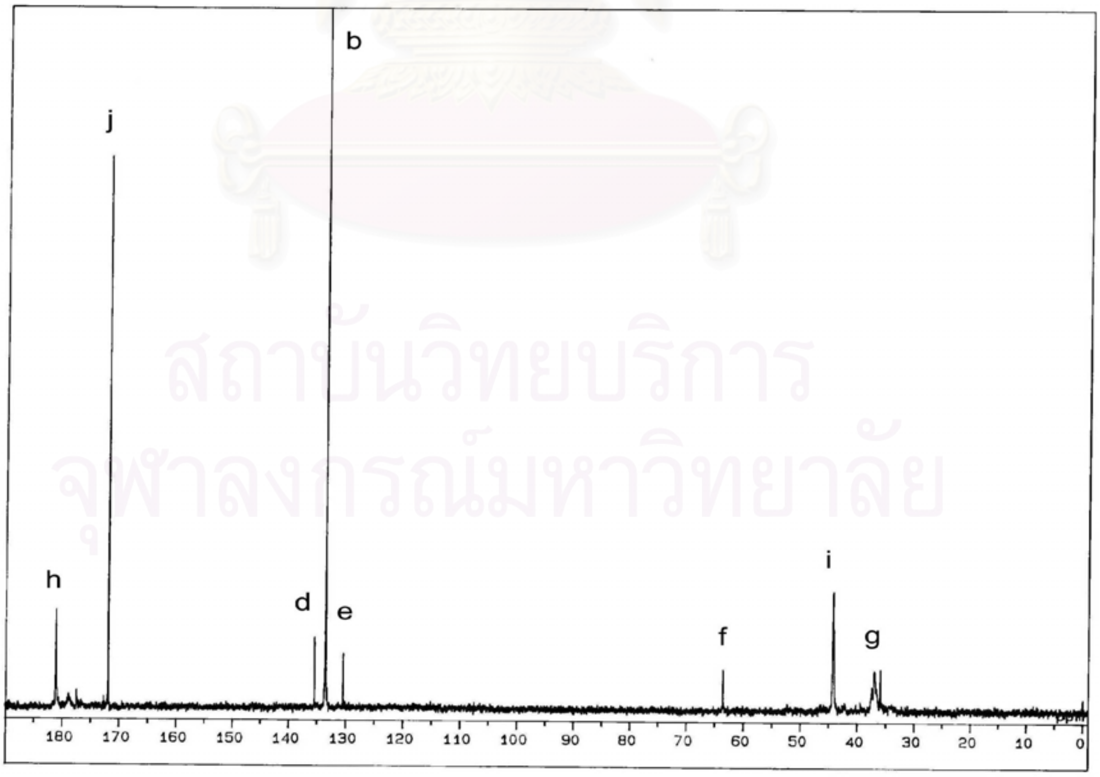


Figure 4.23 ^{13}C NMR spectrum of AA/MA with mole ratio 1to1 in D_2O.

(full size spectrum can be seen in Figure A6)

The addition of maleic acid in order to copolymerize with acrylic acid was begun with the mole ratio of AA and MA equal to 1 to 0.2. The ^{13}C NMR spectrum of this system is shown in Figure 4.21. The chemical shift assignments of polyacrylic acid were signal h (181.144 ppm), signal f (63.436 ppm), signal i (between 44.040-44.188 ppm) and signal g (between 35.864-37.344 ppm). The carbonyl carbon of polymerized maleic acid appeared as a sharp singlet at 172.179 ppm (signal j) and the methine carbon (-CHCOOH) resonated between 35.864-37.344 ppm (signal g). Nevertheless, there were residual monomers in the system too. The signal d (135.300 ppm) and signal e (130.327 ppm) were due to =CHCOOH and $=CH_2$ of unpolymerized acrylic acid, respectively. The signal b (133.962 ppm) was due to =CH of unpolymerized maleic acid.

When the amount of maleic acid in AA/MA system was increased to 1 to 0.5 (Figure 4.22) and 1 to 1 (Figure 4.23) by mole ratio, the ^{13}C NMR spectra of both systems showed the similar spectra to the system of AA/MA equal to 1 to 0.2. There were polyacrylic acid and polymerized maleic acid.

Maleic acid, likewise, does not homopolymerize due to steric effect (44) while acrylic acid can easily homopolymerize. There were showing polyacrylic acid signals in ^{13}C NMR spectrum of all AA/MA systems. Therefore, it could be concluded that there was copolymerization reaction between maleic acid and acrylic acid, and homopolymerization of acrylic acid also occurred as well.

4.11.2 Result of GPC analysis

The Gel-Permeation Chromatography (GPC) was also used to examine molecular weight of the four samples treated with AA/MA solution. The results were illustrated in the Table 4.9 below.

Table 4.9 Results of GPC analysis.

AA/MA system (mole ratio)	Mw	Mn	Polydispersity
AA/MA (1:0)	1,660,129	331,456	5.009
AA/MA (1:0.2)	1,314,081	327,181	4.016
AA/MA (1:0.5)	1,264,174	112,953	11.192
AA/MA (1:1)	714,266	78,183	9.136

Molecular weight of sample from pure AA system was highest and molecular weight of the other three samples was proportionally decreased when the amount of maleic acid increased. It could be stated that maleic acid obstructed homopolymerization reaction of acrylic acid.

CHAPTER V

Conclusions and Recommendations

Conclusions

According to the results presented in chapter IV, it could be concluded that:

1. The investigation of non-formaldehyde durable press finishing on 100% cotton fabric using unsaturated mono-and dicarboxylic acid of AA and MA was carried out through a polymerization-crosslinking treatment. The treatment with AA/MA system at 1:0.5 to 1:1 mole ratio using 12% AA and 12% catalyst under curing condition at 160°C for 3 min was found to be the most effective DP finishing for 100% cotton fabric. The results of properties of the resin finished fabric could be comparable to those of the finished fabric treated with DMDHEU. However, tensile strength of the resin finished fabrics were slightly lower.

2. Curing condition at lower-temperature and longer-time (160°C 3 min) could bring about the superior DWRA than higher-temperature and shorter-time (180°C 1 min). However, whiteness index of fabrics cured at lower-temperature and longer-time was generally lower than that of fabrics cured at higher-temperature and shorter-time.

3. It was found that the increase of dry wrinkle recovery angle (DWRA) of the finished fabric was proportional to the increase of concentration of AA and mole ratio of AA to MA. Nevertheless, the higher the concentration of crosslinking resin was used the lower the tensile strength was obtained. DWRA and tensile strength retention property were not improved at the same time. Normally, the better DWRA, the worse strength retention.

4. When the amount of the catalyst used in the finishing solution increased, the properties of treated fabric, such as DWRA and fabric strength, were better than

those of low amount of catalyst due to the completion of crosslinking reaction. Additionally, it was believed that sodium hypophosphite could reduce the yellowing on the finished fabric because it was an oxidizing agent.

5. To evaluate the efficiency of crosslinking reaction, it could be detected by using reactive dyeability, including washing and light fastness.

6. The crosslinking reaction between AA/MA copolymer and hydroxyl groups of cellulose does not complete that could be confirmed by FT-IR analysis.

7. The unreacted carboxyl group of resin could damage fabric strength and have effect on dye structure in dyed fabric or cause yellowing problem in white fabric. Therefore these finishing systems were not suggested to use on dyed fabric.

8. The mixture of some AA/MA copolymer, homopolymer of AA and impurity of AA appeared remaining in finishing solution, which could be detected by ^{13}C NMR and GPC analysis.

<u>Recommendations for future work</u>

1. More physical properties of treated fabrics, such as tear strength, durable press rating and abrasion resistance should be investigated further.

2. In order to improve diffusion or migration of monomers throughout cellulose fiber, non-conventional treatment techniques, such as wet fixation or steam fixation was recommended.

3. The use of other catalyst having low or zero phosphorus content were interesting because phosphorus-containing compounds can cause environment problem, such as the discharge of these agents into rivers tended to promote the growth of algae.

4. The polymerization-crosslinking (PC) treatment should be further developed by the alternation of unsaturated acids.

5. Combining reactive dyeing and finishing of cotton in one stage process should be conducted by using appropriate dye, which can be used in acid condition, such as vinylsulphone type of reactive dyestuff.

6. For cost reduction in finishing process, citric acid as another alternative to mix with crosslinking agent should be explored.

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APPENDICES

APPENDIX A

Wet pick-up Calculation

The percentage wet pick-up value of fabric can be determine by the following method:

1. The initial weight of each sample was measured before padding by electronic balance (±0.01 g).
2. After padding, each sample was re-weighted. Then the percentage wet pick-up can be calculated by the equation expressed below:

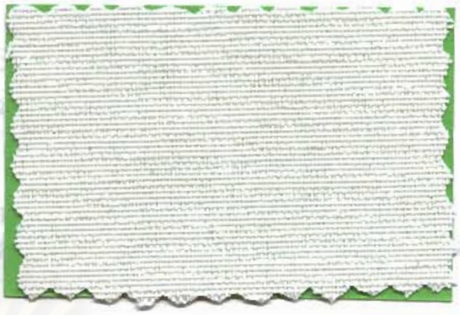
$$\%\text{wet pick-up} = \frac{\text{Weight of wet fabric} - \text{initial weight}}{\text{Initial weight}} \times 100$$

Strength Loss Calculation

The percentage strength loss of treated fabric can be calculated by according to the following equation:

$$\%\ \text{Strength Loss} = \frac{\text{Strength of unfinished fabric} - \text{strength of finished fabric}}{\text{Strength of unfinished fabric}} \times 100$$

Untreated cotton fabric



DMDHEU treated
cotton fabric

**Resin treated
cotton fabric

**Note : Cotton fabrics were treated with 12%owb AA by using mole ratio of AA/MA at 1 to 1, 2%owm $K_2S_2O_8$ and 12%owm $NaH_2PO_2.H_2O$, dried at 100°C for 3 min and cured at 160°C for 3 min.

	Cotton fabrics dyed with reactive dye	Cotton fabrics dyed with basic dye
Untreated cotton fabrics		
**Resin treated cotton fabrics before dyeing		
**Resin treated cotton fabrics after dyeing		—

**Note : Cotton fabrics were treated with 12%owb AA by using mole ratio of AA/MA at 1 to 1, 2%owm $K_2S_2O_8$ and 12%owm $NaH_2PO_2.H_2O$, dried at 100°C for 3 min and cured at 160°C for 3 min.

Raw Data of Wrinkle Recovery Measurement.

Table A1. Dry wrinkle recovery angle (DWRA) of untreated fabric.

yarn	replication						Mean	S.D.	%C.V.	(w+f)
	1	2	3	4	5	6				
w	82	80	83	83	85	80	84	2.68	3.27	166.17
f	82	82	85	83	89	83	82.17	1.94	2.37	

Table A2. Dry wrinkle recovery angle (DWRA) of fabric treated with DMDHEU.

yarn	replication						Mean	S.D.	%C.V.	(w+f)
	1	2	3	4	5	6				
w	112	118	120	118	112	112	115.33	3.72	4.55	233
f	116	118	120	116	116	120	117.67	1.97	2.40	

Table A3. Effect of AA/MA system (12%AA) and MA/AA system (12%MA) under curing condition at 180°C for 1 min on DWRA of treated fabric. (7%NaH_2PO_2)

Ratio	Yarn	replication						Mean	S.D.	%C.V.	(w+f)
		1	2	3	4	5	6				
AA/MA System											
PureAA	w	90	92	90	92	92	90	91	1.10	1.34	179.33
	f	85	90	90	88	85	92	88.33	2.88	3.51	
1:0.2	w	90	89	94	94	96	98	93.5	3.45	4.22	184.5
	f	93	89	92	90	92	90	91	1.55	1.89	
1:0.5	w	103	103	99	102	105	100	102	2.19	2.68	200.5
	f	98	99	98	98	98	100	98.5	0.84	1.02	
1:1	w	100	105	100	103	110	103	103.5	3.73	4.56	203.5
	f	98	103	100	98	103	98	100	2.45	2.99	
MA/AA system											
Pure MA	w	96	103	102	98	101	100	100	2.61	3.19	195.33
	f	92	96	96	95	97	96	95.33	1.75	2.14	
1:0.2	w	100	100	108	100	103	107	103	3.69	4.51	204.67
	f	100	102	102	100	104	102	101.67	1.51	1.84	

Table A3. (continue)

1:0.5	w	100	101	100	100	98	99	99.67	1.03	1.26	197.67
	f	96	97	99	98	100	98	98	1.41	1.73	
1:1	w	104	95	96	100	97	104	99.33	3.98	4.87	196.17
	f	96	96	95	98	99	97	96.83	1.47	1.80	

Table A4. Effect of AA/MA system (12%AA) and MA/AA system (12%MA) under curing condition at 180°C for 2 min on DWRA of treated fabric. (7%NaH_2PO_2)

Ratio	Yarn	replication						Mean	S.D.	%C.V.	(w+f)
		1	2	3	4	5	6				
AA/MA System											
PureAA	w	100	98	98	100	98	100	99	1.09	1.34	192.33
	f	95	92	91	93	95	94	93.33	1.63	1.99	
1:0.2	w	115	110	112	113	108	108	111	2.83	3.49	217
	f	106	102	105	105	108	110	106	2.76	3.37	
1:0.5	w	120	118	115	116	116	119	117.33	1.97	2.40	229.67
	f	112	112	116	110	112	112	112.33	1.97	2.40	
1:1	w	115	118	125	120	125	120	120.5	3.94	4.81	237.17
	f	115	118	116	120	115	116	116.67	1.97	2.40	
MA/AA system											
Pure MA	w	102	105	98	103	97	100	100.83	3.06	3.74	201.33
	f	104	100	100	102	97	100	100.5	2.35	2.87	
1:0.2	w	106	100	102	100	105	107	103.33	3.08	3.76	205.17
	f	101	98	98	107	100	107	101.83	4.17	5.09	
1:0.5	w	105	104	107	108	105	105	105.67	1.51	1.84	207.5
	F	103	102	100	100	103	103	101.83	1.47	1.80	
1:1	W	110	107	106	112	108	113	109.33	2.80	3.43	216
	F	107	105	107	110	106	105	106.67	1.86	2.28	

Table A5. Effect of AA/MA system (12%AA) and MA/AA system (12%MA) under curing condition at 160°C for 3 min on DWRA of treated fabric. (7%NaH_2PO_2)

Ratio	Yarn	replication						Mean	S.D.	%C.V.	(w+f)
		1	2	3	4	5	6				
AA/MA System											
PureAA	w	94	90	94	95	90	92	92.5	2.17	2.65	182.17
	f	93	88	90	89	90	88	89.67	1.86	2.28	
1:0.2	w	98	98	100	100	99	100	99.17	0.98	1.20	198.17
	f	100	100	96	100	98	100	99	1.67	2.04	
1:0.5	w	106	108	108	110	108	110	108.33	1.51	1.84	216.5
	f	110	108	108	112	105	106	108.17	2.56	3.13	
1:1	w	112	113	108	112	110	110	110.83	1.83	2.24	220
	f	106	108	110	109	112	110	109.17	2.04	2.49	
MA/AA system											
pure MA	w	103	100	98	95	96	95	97.83	3.19	3.90	194
	f	98	96	96	95	97	95	96.167	1.17	1.43	
1:0.2	w	100	97	100	103	100	102	100.33	2.07	2.52	199.33
	f	100	98	100	100	98	98	99	1.10	1.33	
1:0.5	w	105	102	103	103	102	100	102.5	1.64	2.01	203
	f	98	106	103	98	98	100	100.5	3.33	4.07	
1:1	w	103	102	106	106	110	108	105.83	2.99	3.66	209.67
	f	102	101	106	108	104	102	103.83	2.71	3.32	

Table A6. DWRA of fabric treated with AA/MA system using 8%AA and 7%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	replication						Mean	S.D.	%C.V.	(w+f)
			1	2	3	4	5	6				
180C/ 1min												
	pureAA	w	92	88	88	85	88	88	88.17	2.23	2.72	176.84
		f	87	92	90	87	88	88	88.67	1.97	2.40	
	1:0.2	w	94	90	92	90	87	93	91	2.53	3.09	184
		f	90	96	93	93	96	90	93	2.68	3.28	

Table A6. (continue)

	1:0.5	w	98	95	98	102	100	103	99.33	2.94	3.60	194.5
		f	95	94	94	95	95	98	95.17	1.47	1.80	
	1:1	w	107	103	100	102	102	100	102.33	2.58	3.16	202.16
		f	100	105	97	100	95	102	99.83	3.54	4.33	
160C/ 3min												
	pureAA	w	93	90	88	90	88	93	90.33	2.25	2.75	180.16
		f	90	88	93	88	90	90	89.83	1.83	2.24	
	1:0.2	w	90	95	95	93	93	95	93.5	1.97	2.41	189.83
		f	96	93	95	96	100	98	96.33	2.42	2.96	
	1:0.5	w	100	102	102	100	100	93	99.5	3.33	4.07	197.83
		f	94	97	98	100	103	98	98.33	3.01	3.68	
	1:1	w	105	103	104	102	107	103	104	1.79	2.19	206
		f	103	100	103	103	103	100	102	1.55	1.89	

Table A7. DWRA of fabric treated with AA/MA system using 10%AA and 7%NaH_2PO_2.

Curing Condition	AA/MA Ratio	yarn	replication						Mean	S.D.	%C.V.	(w+f)
			1	2	3	4	5	6				
180C/ 1min												
	PureAA	w	93	94	88	90	94	88	91.17	2.86	3.49	181.84
		f	89	92	89	92	92	90	90.67	1.51	1.84	
	1:0.2	w	93	95	95	93	92	96	94	1.55	1.89	187.17
		f	90	95	92	93	94	95	93.17	1.94	2.37	
	1:0.5	w	98	98	95	100	100	99	98.33	1.86	2.28	196.83
		f	95	98	98	102	100	98	98.5	2.35	2.87	
	1:1	w	102	105	102	102	100	105	102.67	1.97	2.40	203.84
		f	102	100	102	103	100	100	101.17	1.33	1.62	
160C/ 3min												
	PureAA	w	90	90	90	96	92	90	91.33	2.42	2.96	182.33
		f	90	88	90	94	92	92	91	2.10	2.56	

Table A7. (continue)

	1:0.2	w	104	98	103	103	104	100	102	2.45	2.99	199
		f	95	96	97	96	98	100	97	1.79	2.19	
	1:0.5	w	108	106	104	108	110	106	107	2.10	2.56	210.83
		f	102	104	104	106	105	102	103.83	1.60	1.96	
	1:1	w	116	110	112	110	108	110	111	2.76	3.37	218.67
		f	108	102	110	110	108	108	109.67	2.94	3.60	

Table A8. DWRA of fabric treated with AA/MA system using 8%AA and 9%NaH$_2$PO$_2$.

Curing condition	AA/MA ratio	yarn	replication						Mean	S.D.	%C.V.	(w+f)
			1	2	3	4	5	6				
180C/ 1min												
	pureAA	w	85	93	87	90	88	92	89.17	3.06	3.74	178.67
		f	90	85	90	92	92	88	89.5	2.66	3.26	
	1:0.2	w	96	94	96	93	95	90	94	2.28	2.79	185.33
		f	90	90	93	93	92	90	91.33	1.51	1.84	
	1:0.5	w	98	100	102	98	100	102	100	1.79	2.19	199
		f	98	100	96	102	98	100	99	2.10	2.56	
	1:1	w	100	106	105	100	105	103	103.17	2.64	3.23	205
		f	104	98	100	105	100	104	101.83	2.86	3.49	
160C/ 3min												
	pureAA	w	88	86	90	88	88	88	88	1.26	1.55	177.33
		f	90	88	90	93	85	90	89.33	2.66	3.25	
	1:0.2	w	95	92	97	95	95	100	99.67	2.66	3.25	190.34
		f	97	95	90	95	98	93	94.67	2.88	3.51	
	1:0.5	w	100	105	100	98	102	102	101.17	2.40	2.93	200.17
		f	100	98	102	98	98	98	99	1.67	2.04	
	1:1	w	110	110	108	108	112	110	109.67	1.51	1.84	216.67
		f	108	110	106	104	106	108	107	2.09	2.56	

Table A9. DWRA of fabric treated with AA/MA system using 10%AA and 9%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	Replication						Mean	S.D.	%C.V.	(w+f)
			1	2	3	4	5	6				
180C/ 1min												
	pureAA	w	95	90	92	92	90	90	91.5	1.97	2.41	182.33
		f	93	90	90	90	90	92	90.83	1.33	1.62	
	1:0.2	w	102	100	98	100	100	104	100.67	2.07	2.52	199.34
		f	98	96	98	100	102	98	98.67	2.07	2.52	
	1:0.5	w	103	100	100	103	102	98	101	2	2.44	201
		f	98	100	98	102	102	100	100	1.79	2.19	
	1:1	w	110	108	102	108	110	102	106.67	3.72	4.55	212
		f	110	108	102	108	102	102	105.33	3.72	4.55	
160C/ 3min												
	pureAA	w	90	88	95	95	93	88	91.5	3.27	3.99	183
		f	88	90	92	95	92	92	91.5	2.35	2.87	
	1:0.2	w	102	102	105	100	100	102	101.83	1.83	2.24	201.16
		f	100	98	98	100	102	98	99.33	1.63	1.99	
	1:0.5	w	108	106	112	108	110	110	109	2.10	2.56	216.33
		f	108	104	108	106	110	108	107.33	2.07	2.52	
	1:1	w	112	109	110	110	110	112	110.5	1.22	1.50	219.83
		f	110	108	108	108	112	110	109.33	1.63	1.99	

Table A10. DWRA of fabric treated with AA/MA system using 12%AA and 9%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	Replication						Mean	S.D.	%C.V.	(w+f)
			1	2	3	4	5	6				
180C/ 1min												
	pureAA	w	92	88	90	90	95	88	90.5	2.66	3.26	181.67
		f	93	93	88	90	93	90	91.17	2.14	2.61	
	1:0.2	w	100	100	97	96	98	102	98.83	2.23	2.72	199.66
		f	97	100	98	100	100	98	98.83	1.33	1.62	

Table A10. (continue)

	1:0.5	w	105	107	105	106	103	106	105.13	1.37	1.67	209.33
		f	107	102	100	107	105	103	104	2.83	3.46	
	1:1	w	110	108	108	110	102	104	107	3.29	4.02	215
		f	110	104	110	112	104	108	108	3.35	4.09	
160C/ 3min												
	pureAA	w	94	90	96	96	92	90	93	2.76	3.37	183.67
		f	89	88	95	90	92	90	90.67	2.50	3.06	
	1:0.2	w	102	105	100	103	100	100	101.67	2.07	2.52	202
		f	98	98	102	102	102	100	100.33	1.97	2.40	
	1:0.5	w	108	110	108	112	108	110	109.33	1.63	1.99	217.16
		f	110	107	107	108	110	105	107.83	1.94	2.37	
	1:1	w	112	116	108	112	112	110	111.67	2.66	3.25	222.84
		f	115	112	108	112	110	110	111.17	2.40	2.93	

Table A11. DWRA of fabric treated with AA/MA system using 8%AA and 12%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	Replication						Mean	S.D.	%C.V.	(w+f)
			1	2	3	4	5	6				
180C/ 1min												
	pureAA	w	93	90	87	88	88	92	89.67	2.42	2.96	178.89
		f	85	88	92	94	88	88	89.17	3.25	3.97	
	1:0.2	w	90	94	90	88	92	97	91.83	3.25	3.97	185.83
		f	90	97	93	96	93	95	94	2.53	3.09	
	1:0.5	w	104	108	108	105	104	107	106	1.90	2.32	210.67
		f	102	110	108	102	102	104	104.67	3.50	4.28	
	1:1	w	113	108	112	10	108	110	109.83	2.23	2.72	216.5
		f	110	107	107	104	108	104	106.67	2.24	2.86	
160C/ 3min												
	pureAA	w	88	85	88	90	92	90	88.83	2.40	2.93	179.16
		f	92	88	88	92	88	94	90.33	2.66	3.25	

Table A11. (continue)

	1:0.2	w	98	100	102	98	98	98	99	1.67	2.04	197.17
		f	96	102	100	95	98	98	98.17	2.56	3.13	
	1:0.5	w	105	106	110	108	105	108	107	2	2.44	210.17
		f	103	100	104	104	104	104	103.17	1.60	1.96	
	1:1	w	112	110	110	110	108	110	110	1.26	1.55	218.33
		f	106	108	108	110	110	108	108.33	1.51	1.84	

Table A12. DWRA of fabric treated with AA/MA system using 10%AA and 12%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	Replication						Mean	S.D.	%C.V.	(w+f)
			1	2	3	4	5	6				
180C/ 1min												
	pureAA	w	92	96	92	93	90	90	92.17	2.23	2.72	182.84
		f	90	92	90	90	92	90	90.67	1.03	1.26	
	1:0.2	w	98	100	98	102	100	102	100	1.79	2.19	198.17
		f	95	95	95	102	100	100	98.17	3.54	4.33	
	1:0.5	w	110	108	114	108	106	113	109.83	3.13	3.82	216.16
		f	110	106	105	105	105	107	106.33	1.97	2.40	
	1:1	w	108	113	110	113	112	113	111.5	2.07	2.53	219.83
		f	105	105	110	106	114	110	108.33	3.61	4.42	
160C/ 3min												
	pureAA	w	92	91	92	90	95	95	92.5	2.07	2.53	184.67
		f	90	92	90	93	95	93	92.17	1.94	2.37	
	1:0.2	w	100	100	102	105	98	103	101.23	2.50	3.06	202.33
		f	102	100	98	103	103	100	101	2	2.44	
	1:0.5	w	106	112	110	114	108	108	109.67	2.94	3.60	219
		f	110	108	108	108	115	107	109.33	2.94	3.60	
	1:1	w	117	121	117	115	115	110	115.93	3.60	4.40	230.66
		f	110	117	120	112	115	115	114.83	3.55	4.33	

Table A13. DWRA of fabric treated with AA/MA system using 12%AA and 12%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	replication						Mean	S.D.	%C.V.	(w+f)
			1	2	3	4	5	6				
180C/ 1min												
	pureAA	w	90	89	90	91	90	87	89.5	1.38	1.68	179.33
		f	89	87	92	92	89	90	89.83	1.94	2.37	
	1:0.2	w	98	100	10	100	103	98	99.83	1.83	2.24	199.16
		f	102	98	98	98	100	100	99.33	1.63	1.99	
	1:0.5	w	110	108	110	112	106	108	109	2.10	2.56	216.67
		f	108	106	110	106	106	110	107.67	1.97	2.40	
	1:1	w	116	120	120	114	122	112	117.33	3.93	4.81	234.66
		f	112	116	118	120	122	116	117.33	3.50	4.28	
160C/ 3min												
	pureAA	w	92	92	90	89	95	92	91.67	2.07	2.52	182.84
		f	90	89	90	94	92	92	91.17	1.83	2.24	
	1:0.2	w	105	106	102	100	102	105	103.33	2.34	2.86	204.16
		f	100	102	98	103	102	100	100.83	1.83	2.24	
	1:0.5	w	114	115	115	108	110	115	112.83	3.06	3.74	224.16
		f	115	110	115	110	108	110	111.33	2.94	3.60	
	1:1	w	118	120	120	118	117	120	18.83	1.33	1.62	237.5
		f	120	115	115	124	120	118	118.67	3.44	4.21	

Raw Data of Breaking Strength Measurement.

Table A14. Breaking Strength of untreated fabric.

yarn	Replication								Mean	S.D.	%C.V.
	1	2	3	4	5	6	7	8			
w	49.683	47.686	48.897	48.576	50.595				49.087	1.11	2.25
f	26.450	26.507	25.047	26.005	26.521	54.977	26.086	24.397	25.749	0.82	3.20

Table A15. Breaking Strength of fabric treated with DMDHEU.

Yarn	Replication								Mean	S.D.	%C.V.
	1	2	3	4	5	6	7	8			
w	32.969	32.021	30.166	32.782	32.867				32.161	1.18	3.66
f	16.733	16.329	15.361	15.369	13.412	14.078	14.915	16.233	15.30	1.15	7.49

Table A16. Effect of AA/MA system (12%AA) and MA/AA system (12%MA) under curing condition at 180°C for 1 min on breaking strength of treated fabric. (7%NaH_2PO_2)

Ratio	yarn	Replication								Mean	S.D.	%C.V.
		1	2	3	4	5	6	7	8			
AA/MA system												
PureAA	w	44.538	43.883	45.173	42.973	44.03				44.119	0.82	1.85
	f	20.174	20.276	20.380	20.579	19.930	19.294	19.592	23.655	20.485	1.35	6.58
1:0.2	w	36.091	37.114	35.427	35.109	35.731				35.894	0.77	2.15
	f	15.412	16.200	16.170	16.922	15.877	15.150	15.705	17.405	16.105	0.75	4.68
1:0.5	w	34.899	34.206	32.110	32.536	32.822				33.315	1.18	3.55
	f	14.353	13.689	13.773	13.932	15.729	14.831	13.941	13.553	14.225	0.73	5.15
1:1	w	32.544	33.781	33.613	31.980	32.678				32.919	0.76	2.31
	f	13.287	15.052	15.712	15.589	16.909	16.429	15.119	13.201	15.162	1.34	8.82
MA/AA system												
PureMA	w	22.602	24.500	22.670	22.963	22.505				23.048	0.83	3.60
	f	10.145	11.690	10.923	11.290	10.355	9.214	11.428	11.635	10.835	0.87	8.01
1:0.2	w	25.834	25.306	25.452	25.939	24.575				25.421	0.54	2.13
	f	13.228	13.382	12.167	14.209	14.178	13.307	12.972	12.285	13.216	0.75	5.70
1:0.5	w	27.614	27.907	29.467	27.841	29.352				28.436	0.90	3.15
	f	13.888	16.022	12.973	13.618	14.415	12.621	12.294	13.054	13.611	1.19	8.77
1:1	w	30.528	29.581	29.702	28.489	26.561				28.972	1.53	5.28
	f	15.877	15.844	15.249	14.753	13.622	15.350	14.684	15.346	15.091	0.73	4.87

Table A17. Effect of AA/MA system (12%AA) and MA/AA system (12%MA) under curing condition at 180°C for 2 min on breaking strength of treated fabric. (7%NaH_2PO_2)

Ratio	yarn	Replication								Mean	S.D.	%C.V.
		1	2	3	4	5	6	7	8			
AA/MA system												
PureAA	w	33.876	35.822	33.023	35.338	33.017				34.215	1.31	3.81
	f	17.949	18.704	16.074	17.671	16.371	17.852	17.678	16.988	17.411	0.87	5.02
1:0.2	w	29.414	31.690	30.675	32.177	32.049				31.201	1.16	3.72
	f	15.685	14.087	14.753	14.113	14.427	15.959	14.409	13.968	14.675	0.75	5.13
1:0.5	w	30.585	30.607	30.142	28.269	28.671				29.655	1.11	3.73
	f	13.995	14.213	13.126	12.778	12.998	13.561	13.142	12.922	13.342	0.525	3.94
1:1	w	29.687	27.669	27.403	26.612	27.446				27.763	1.15	4.13
	f	13.18	12.469	12.249	12.769	12.685	12.223	11.591	11.707	12.359	0.54	4.33
MA/AA system												
PureMA	w	25.961	23.623	23.694	23.201	24.040				24.104	1.08	4.48
	f	12.182	11.943	12.292	11.669	11.714	11.261	11.999	13.073	12.017	0.54	4.46
1:0.2	w	22.857	26.192	25.216	23.106	22.817				24.038	1.56	6.50
	f	11.297	11.966	11.369	13.216	11.718	11.613	12.013	12.358	11.944	0.62	5.20
1:0.5	w	24.348	24.455	26.491	26.175	26.670				25.628	1.13	4.42
	f	13.642	12.750	13.319	12.142	13.112	11.876	12.535	11.555	12.616	0.73	5.77
1:1	w	27.112	26.951	27.681	27.237	26.615				27.119	0.39	1.44
	f	13.184	12.616	12.453	12.445	13.953	13.274	12.108	12.457	12.811	0.61	4.74

Table A18. Effect of AA/MA system (12%AA) and MA/AA system (12%MA) under curing condition at 160°C for 3 min on breaking strength of treated fabric. (7%NaH_2PO_2)

Ratio	Yarn	Replication								Mean	S.D.	%C.V.
		1	2	3	4	5	6	7	8			
AA/MA system												
PureAA	w	36.186	37.473	36.307	34.205	33.013				35.437	1.79	5.06
	f	18.080	19.081	17.680	17.789	18.280	18.553	20.850	17.679	18.499	1.07	5.76
1:0.2	w	33.239	32.451	31.965	29.34	31.398				31.679	1.47	4.65
	f	16.399	16.797	17.482	17.231	16.902	14.885	15.712	15.816	16.403	0.88	5.34
1:0.5	w	28.987	29.83	29.531	30.804	29.444				29.719	0.68	2.28
	f	12.650	13.692	12.467	13.229	12.349	14.742	12.661	13.767	13.195	0.83	6.27
1:1	w	28.112	28.944	28.480	28.904	29.729				28.834	0.61	2.10
	f	15.165	15.019	14.004	15.434	13.832	13.936	14.644	13.777	14.476	0.67	4.62
MA/AA system												
PureMA	w	24.141	25.805	25.639	25.221	23.801				24.921	0.90	3.62
	f	14.442	12.724	15.011	14.552	12.910	12.778	12.354	13.480	13.531	1.00	7.42
1:0.2	w	26.027	25.851	25.580	26.335	23.972				25.553	0.93	3.62
	f	14.259	12.582	11.592	12.167	13.702	13.757	13.950	13.503	13.189	0.95	7.23
1:0.5	w	30.948	27.940	26.465	27.507	28.828				28.337	1.69	5.96
	f	15.053	13.838	14.297	13.969	15.011	14.242	14.269	15.349	14.504	0.56	3.84
1:1	w	32.735	29.201	30.059	27.917	31.240				30.230	1.85	6.13
	f	13.746	14.561	14.328	15.044	15.663	13.743	14.473	15.201	14.595	0.68	4.66

Table A19. Breaking strength of fabric treated with AA/MA system using 8%AA and 7%NaH_2PO_2.

Curing Condition	AA/MA ratio	Yarn	Replication								Mean	S.D.	%C.V.
			1	2	3	4	5	6	7	8			
180C/1min	PureAA	w	40.1665	44.828	41.211	43.935	43.871				42.802	2.00	4.68
		f	21.615	23.487	22.890	24.150	24.148	22.228	24.189	23.197	23.238	0.96	4.12
	1:0.2	w	35.234	35.376	34.955	35.898	35.764				35.445	0.39	1.09
		f	19.547	18.057	18.107	18.024	19.176	18.439	18.052	18.967	18.546	0.60	3.25
	1:0.5	w	33.512	32.378	31.100	32.075	31.189				32.051	0.99	3.08
		f	15.562	15.893	15.430	16.555	15.867	17.223	16.431	15.378	16.042	0.64	4.02
	1:1	w	31.158	30.384	32.005	29.479	32.901				31.185	1.34	4.29
		f	14.727	15.471	14.109	15.465	13.337	15.888	15.745	15.016	14.970	0.88	5.87
160C/3 min	PureAA	w	43.361	41.624	43.794	41.007	43.711				42.711	1.30	3.05
		f	23.662	22.508	21.089	23.435	22.691	24.043	23.301	21.955	22.836	0.98	4.27
	1:0.2	w	34.087	34.073	34.174	32.690	33.330				33.671	0.65	1.92
		f	17.913	17.138	17.306	17.491	17.049	16.972	17.652	17.525	17.381	0.32	1.86
	1:0.5	w	33.165	30.137	29.782	30.907	32.363				31.271	1.45	4.64
		f	15.686	15.241	15.353	16.274	16.558	15.818	16.05	15.050	15.754	0.53	3.34
	1:1	w	31.325	31.050	31.695	30.619	30.926				31.123	0.41	1.31
		f	14.348	14.152	14.739	14.145	15.212	13.958	14.319	14.673	14.443	0.41	2.82

Table A20. Breaking strength of fabric treated with AA/MA system using 10%AA and 7%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	Replication								Mean	S.D.	%C.V.
			1	2	3	4	5	6	7	8			
180C/1min	PureAA	w	40.770	39.728	41.526	40.638	39.453				40.423	0.84	2.07
		f	21.282	21.604	21.305	21.272	22.610	20.654	20.677	21.310	21.339	0.61	2.86
	1:0.2	w	35.217	35.531	33.260	33.257	32.055				33.264	1.26	3.79
		f	17.540	16.740	16.995	17.974	17.216	16.880	17.561	16.962	17.234	0.42	2.45
	1:0.5	w	32.208	30.783	30.723	31.728	30.814				31.251	0.68	2.17
		f	14.770	15.834	15.675	13.957	13.802	13.742	15.161	15.842	14.848	0.91	6.16
	1:1	w	30.86	30.441	29.442	28.679	27.829				29.450	1.24	4.22
		f	14.482	14.530	14.233	15.124	14.583	13.993	15.180	14.419	14.568	0.41	2.79
160C/3 min	PureAA	w	39.421	40.356	40.399	39.673	38.523				39.674	0.77	1.94
		f	22.096	24.307	20.760	20.080	22.104	21.655	23.290	23.458	22.219	1.42	6.39
	1:0.2	w	31.444	31.581	32.178	31.666	33.666				32.107	0.91	2.85
		f	16.473	15.661	15.562	15.734	15.144	15.590	16.585	17.383	16.017	0.73	4.57
	1:0.5	w	29.269	30.003	30.447	30.168	31.255				30.228	0.72	2.38
		f	14.782	13.593	13.460	14.034	14.399	14.049	14.879	14.464	14.208	0.52	3.64
	1:1	w	29.691	29.801	30.278	29.779	30.090				29.928	0.25	0.82
		f	12.848	12.764	12.830	13.178	13.751	13.702	14.271	14.294	13.455	0.64	4.73

Table A21. Breaking strength of fabric treated with AA/MA system using 8%AA and 9%NaH_2PO_2.

Curing Condition	AA/MA ratio	yarn	Replication								Mean	S.D.	%C.V.
			1	2	3	4	5	6	7	8			
180C/1min	PureAA	w	40.327	43.686	42.543	41.824	41.515				41.979	1.24	2.97
		f	24.621	24.967	22.574	22.882	23.307	23.007	24.624	23.544	23.691	0.92	3.88
	1:0.2	w	36.835	34.205	34.024	34.356	34.458				34.776	1.16	3.34
		f	18.424	19.227	19.855	18.526	18.822	20.729	18.943	19.627	19.270	0.77	4.01
	1:0.5	w	34.650	32.505	32.484	32.513	33.385				33.107	0.94	2.85
		f	16.818	16.653	16.513	16.968	16.282	16.832	17.286	17.526	16.860	0.40	2.39
	1:1	w	32.081	33.2	32.212	32.37	31.493				32.271	0.62	1.91
		f	16.386	14.882	15.693	15.691	14.976	17.383	16.588	16.111	15.964	0.84	5.24
160C/3 min	PureAA	w	43.951	42.876	41.508	43.339	41.112				42.557	1.209	2.840
		f	23.117	23.395	23.813	24.876	22.014	22.153	22.096	23.762	23.028	1.04	4.54
	1:0.2	w	33.583	36.473	35.081	35.303	33.520				34.792	1.25	3.59
		f	15.985	18.523	18.565	17.350	18.386	17.551	18.907	17.941	17.901	0.94	5.25
	1:0.5	w	31.638	32.101	34.017	32.484	31.471				32.342	1.02	3.14
		f	17.549	16.257	16.157	16.750	16.509	16.283	17.350	17.583	16.805	0.60	3.584
	1:1	w	29.993	32.86	31.097	33.026	32.131				31.821	1.27	4.00
		f	16.194	16.258	15.957	15.569	16.415	15.559	16.271	14.325	15.819	0.68	4.23

Table A22. Breaking strength of fabric treated with AA/MA system using 10%AA and 9%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	Replication								Mean	S.D.	%C.V.
			1	2	3	4	5	6	7	8			
180C/1min	PureAA	w	39.223	39.187	41.481	39.775	40.459				40.025	0.96	2.41
		f	21.644	22.953	21.294	20.814	22.663	21.595	22.495	21.302	21.845	0.76	3.50
	1:0.2	w	33.859	35.045	33.837	33.840	34.283				34.173	0.52	1.53
		f	17.344	17.321	16.892	16.826	17.256	17.667	16.535	18.659	17.313	0.65	3.76
	1:0.5	w	31.107	31.162	31.376	31.842	31.408				31.379	0.29	0.92
		f	15.201	15.355	14.471	14.792	14.206	14.474	14.713	15.517	14.841	0.47	3.16
	1:1	w	30.969	30.174	29.965	30.230	30.115				30.291	0.39	1.29
		f	12.807	14.682	14.145	14.793	14.369	14.162	14.449	13.880	14.161	0.62	4.39
160C/3 min	PureAA	w	40.654	37.871	41.202	40.643	38.173				39.709	1.56	3.93
		f	22.402	23.619	22.677	21.271	21.935	21.517	22.506	22.366	22.287	0.73	3.28
	1:0.2	w	33.730	33.020	33.391	31.973	33.522				32.927	0.70	2.12
		f	16.261	15.707	17.460	15.804	15.084	17.810	16.029	15.928	16.260	0.92	5.65
	1:0.5	w	31.631	30.194	28.834	28.614	31.924				30.240	1.53	5.07
		f	14.427	14.210	15.574	16.015	15.149	15.636	15.111	16.264	15.298	0.72	4.71
	1:1	w	31.923	29.043	30.969	30.644	29.802				30.476	1.10	3.62
		f	13.864	13.863	14.387	13.800	12.223	13.690	13.307	14.046	13.648	0.65	4.77

Table A23. Breaking strength of fabric treated with AA/MA system using 12%AA and 9%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	Replication								Mean	S.D.	%C.V.
			1	2	3	4	5	6	7	8			
180C/1min	PureAA	w	44.173	36.786	39.152	39.684	40.241				40.004	2.675	6.69
		f	22.427	21.831	21.008	21.764	21.532	22.334	22.811	23.724	22.179	0.84	3.79
	1:0.2	w	34.347	34.847	33.361	32.963	32.983				33.700	0.85	2.53
		f	17.804	18.352	18.314	17.459	17.102	17.032	17.038	16.366	17.433	0.69	3.95
	1:0.5	w	30.232	31.212	31.745	29.861	30.400				30.690	0.77	2.51
		f	15.859	16.517	15.423	15.023	15.317	15.279	15.515	14.804	15.467	0.53	3.42
	1:1	w	31.897	31.370	28.608	31.389	30.313				30.715	1.31	4.27
		f	15.879	15.652	15.021	14.349	15.060	14.736	15.958	14.253	15.114	0.662	4.38
160C/3 min	PureAA	w	38.861	38.522	39.460	38.563	40.641				39.209	0.88	2.25
		f	19.121	21.991	21.860	19.985	21.289	21.462	21.463	19.234	20.801	1.17	5.63
	1:0.2	w	32.388	34.071	33.028	34.288	31.217				32.998	1.26	3.82
		f	16.021	16.291	15.934	15.624	16.341	15.596	16.840	16.239	16.111	0.41	2.54
	1:0.5	w	29.327	29.971	29.075	29.619	30.668				29.732	0.62	2.09
		f	13.952	14.579	13.489	14.222	15.298	14.738	14.053	15.263	14.449	0.64	4.42
	1:1	w	31.293	29.825	29.64	30.197	29.851				30.161	0.66	2.20
		f	13.989	14.738	13.967	14.322	14.148	14.708	14.285	14.940	14.387	0.37	2.55

Table A24. Breaking strength of fabric treated with AA/MA system using 8%AA and 12%NaH_2PO_2.

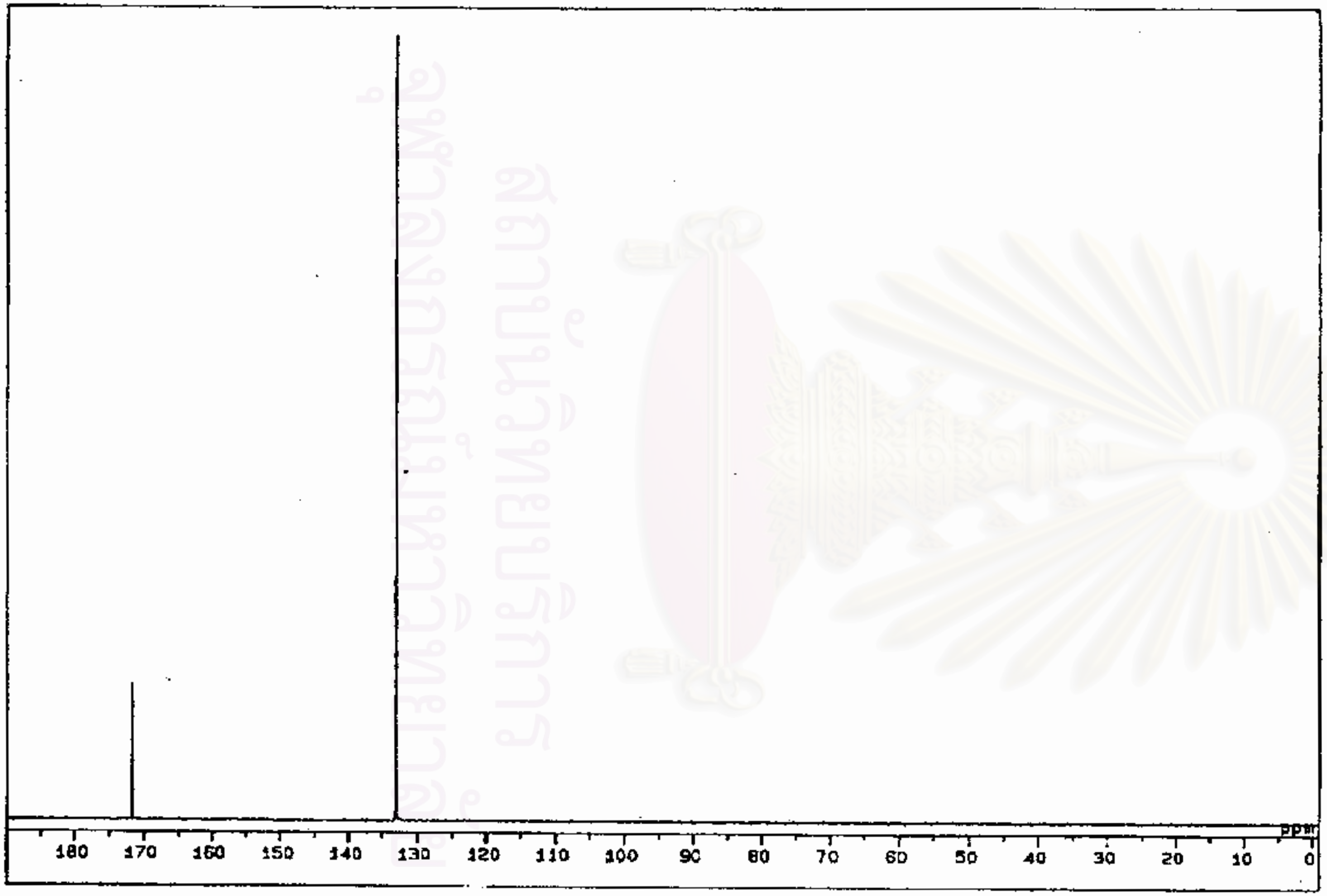
Curing condition	AA/MA ratio	yarn	Replication								Mean	S.D.	%C.V.
			1	2	3	4	5	6	7	8			
180C/1min	PureAA	w	44.538	43.883	45.173	42.973	44.030				44.119	0.82	1.85
		f	24.767	22.643	23.603	25.385	23.058	23.430	24.787	24.185	23.982	0.95	3.98
	1:0.2	w	36.091	37.114	35.427	35.109	35.731				35.894	0.77	2.15
		f	19.600	19.779	20.539	19.364	19.526	19.435	20.877	20.015	19.892	0.55	2.77
	1:0.5	w	34.899	34.206	32.110	32.536	32.822				33.315	1.18	3.55
		f	17.137	17.967	17.446	17.031	17.753	17.911	17.724	18.671	17.705	0.52	2.94
	1:1	w	32.544	33.781	33.613	31.980	32.678				32.919	0.76	2.31
		f	16.050	17.416	16.066	16.601	16.093	16.472	17.330	17.320	16.669	0.60	3.61
160C/3 min	PureAA	w	41.361	42.032	43.284	41.685	42.982				42.269	0.83	1.97
		f	23.524	23.707	24.124	24.490	24.215	23.541	23.544	24.823	23.996	0.49	2.06
	1:0.2	w	36.515	34.253	34.087	36.395	35.603				35.371	1.15	3.26
		f	17.860	17.905	18.864	19.791	18.713	17.626	18.318	17.987	18.383	0.71	3.88
	1:0.5	w	34.573	33.030	35.166	33.196	33.064				33.8058	1.00	2.94
		f	18.400	18.223	17.971	18.345	16.696	17.815	16.657	17.354	17.683	0.71	3.99
	1:1	w	33.915	31.965	32.393	33.114	33.192				32.916	0.76	2.30
		f	16.257	16.662	15.982	15.874	16.314	16.043	16.947	15.760	16.230	0.41	2.50

Table A25. Breaking strength of fabric treated with AA/MA system using 10%AA and 12%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	Replication								Mean	S.D.	%C.V.
			1	2	3	4	5	6	7	8			
180C/1min	PureAA	w	43.278	40.079	40.394	40.037	39.735				40.705	1.46	3.58
		f	23.159	22.776	22.809	22.245	22.167	22.010	22.914	22.474	22.569	0.41	1.80
	1:0.2	w	35.408	33.262	34.887	33.767	35.894				34.644	1.11	3.19
		f	17.482	15.848	16.474	17.174	16.873	17.776	18.842	18.692	17.395	1.03	5.95
	1:0.5	w	30.729	30.850	31.447	31.126	31.457				31.122	0.33	1.07
		f	16.306	15.278	16.132	15.351	15.702	15.305	15.496	15.253	15.603	0.41	2.63
	1:1	w	29.887	30.307	33.353	31.538	31.081				31.233	1.35	4.32
		f	13.581	13.938	14.063	13.354	14.430	14.082	13.390	14.626	13.933	0.47	3.34
160C/3 min	PureAA	w	40.618	40.078	39.557	39.202	39.076				39.706	0.64	1.61
		f	22.682	21.919	22.612	21.923	21.712	22.810	22.535	23.300	22.437	0.54	2.41
	1:0.2	w	34.144	35.135	34.785	34.288	33.803				34.431	0.53	1.54
		f	17.202	17.204	18.095	16.894	17.937	16.215	18.609	17.451	17.451	0.75	4.31
	1:0.5	w	31.539	31.295	31.808	32.431	32.473				31.909	0.53	1.65
		f	16.277	16.938	14.673	15.797	14.703	14.369	14.228	15.380	15.296	0.98	6.38
	1:1	w	31.902	31.951	29.768	29.532	31.658				30.962	1.21	3.89
		f	14.148	13.969	13.051	13.724	13.519	14.375	13.747	13.572	13.763	0.41	2.97

Table A26. Breaking strength of fabric treated with AA/MA system using 12%AA and 12%NaH_2PO_2.

Curing condition	AA/MA ratio	yarn	Replication								Mean	S.D.	%C.V.
			1	2	3	4	5	6	7	8			
180C/1min	PureAA	w	42.853	41.618	40.594	38.841	40.564				40.894	1.48	3.62
		f	22.541	22.702	21.146	21.453	21.425	21.509	22.896	22.595	22.033	0.71	3.22
	1:0.2	w	32.605	33.551	35.187	32.641	33.882				33.573	1.06	3.16
		f	17.362	19.681	17.480	17.319	16.775	16.860	17.333	17.843	17.582	0.91	5.19
	1:0.5	w	33.516	32.481	30.444	30.504	31.075				31.604	1.35	4.26
		f	15.961	14.890	15.786	15.719	16.163	15.604	15.632	15.577	15.667	0.37	2.37
	1:1	w	32.184	32.442	31.011	30.170	29.703				31.102	1.20	3.87
		f	14.085	14.696	14.089	14.370	14.062	15.636	15.815	15.927	14.835	0.82	5.55
160C/3 min	PureAA	w	38.849	40.831	38.731	38.008	39.820				39.249	1.10	2.79
		f	21.918	21.995	21.843	21.853	21.845	21.908	22.211	22.298	21.984	0.18	0.80
	1:0.2	w	32.833	32.985	34.468	33.498	32.187				33.194	0.85	2.57
		f	16.817	16.594	15.977	17.521	17.203	17.622	16.686	18.024	17.056	0.66	3.88
	1:0.5	w	29.29	29.381	29.512	30.504	27.755				29.288	0.99	3.37
		f	13.996	14.714	15.456	14.213	14.346	16.196	15.515	15.323	14.970	0.77	5.14
	1:1	w	30.653	31.409	30.752	30.305	29.491				30.522	0.70	2.30
		f	14.705	14.683	13.161	14.360	14.770	14.157	14.520	14.655	14.501	0.59	4.05



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14-NOV-2000 15:10:53.54

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 * CHULALONGKORN UNIVERSITY *
 *        JNM-A500          *
 ***************************

SFILE : [.NMO]MA-BCM
COMNT : MA-13C

EXMOD : SINGL
IRMOD : BCM
POINT :     16384
FREQU : 33898.31 Hz
SCANS :       170
DUMMY :         4
ACQTM :       0.4833 sec
PD    :       2.0000 sec
RGAIN :        23
PW1   :      4.90 usec
OBNUC : 13C
OBFRQ :    125.65 MHz
OBSET : 127958.00 Hz

IRNUC : 1H
IRFRQ :    500.00 MHz
IRSET : 162410.00 Hz
IRATN :       120
IRRPW :      55.0 usec
IRBP1 :        30
IRBP2 :         6
IRRNS :         0

ADBIT :        16
CTEMP :      28.9 c
CSPED :        14 Hz
SLVNT : D2O
RESOL :      2.07 Hz
BF    :      2.07 Hz
REFVL :      0.00 ppm
XE    : 24018.89 Hz
XS    :  1061.05 Hz

OPERATOR :
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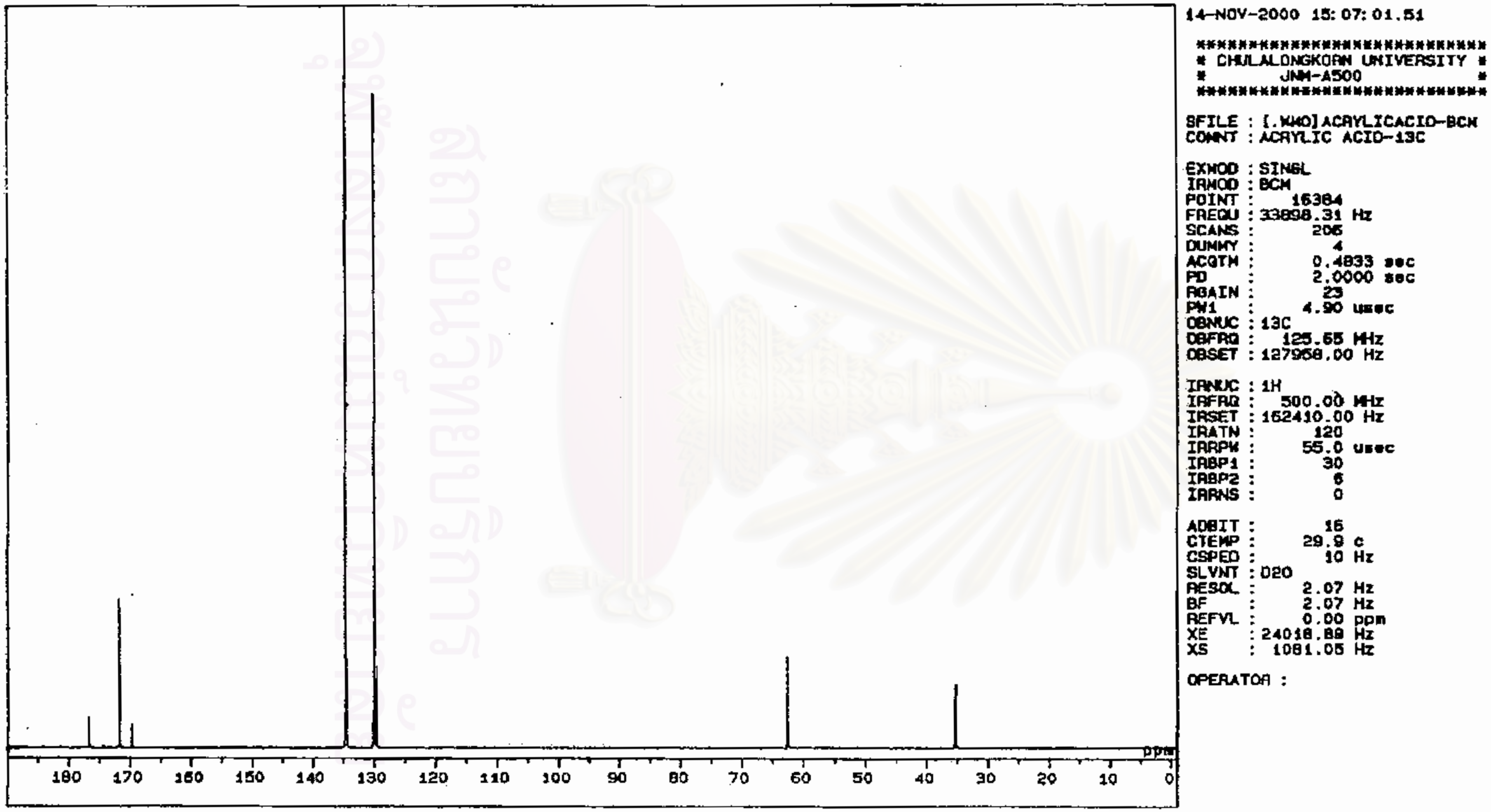
Figure A1. ^{13}C NMR spectrum of maleic acid in D_2O.



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14-NOV-2000 15:07:01.51

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SFILE : [.WWO]ACRYLICACID-BCM
COMNT : ACRYLIC ACID-13C

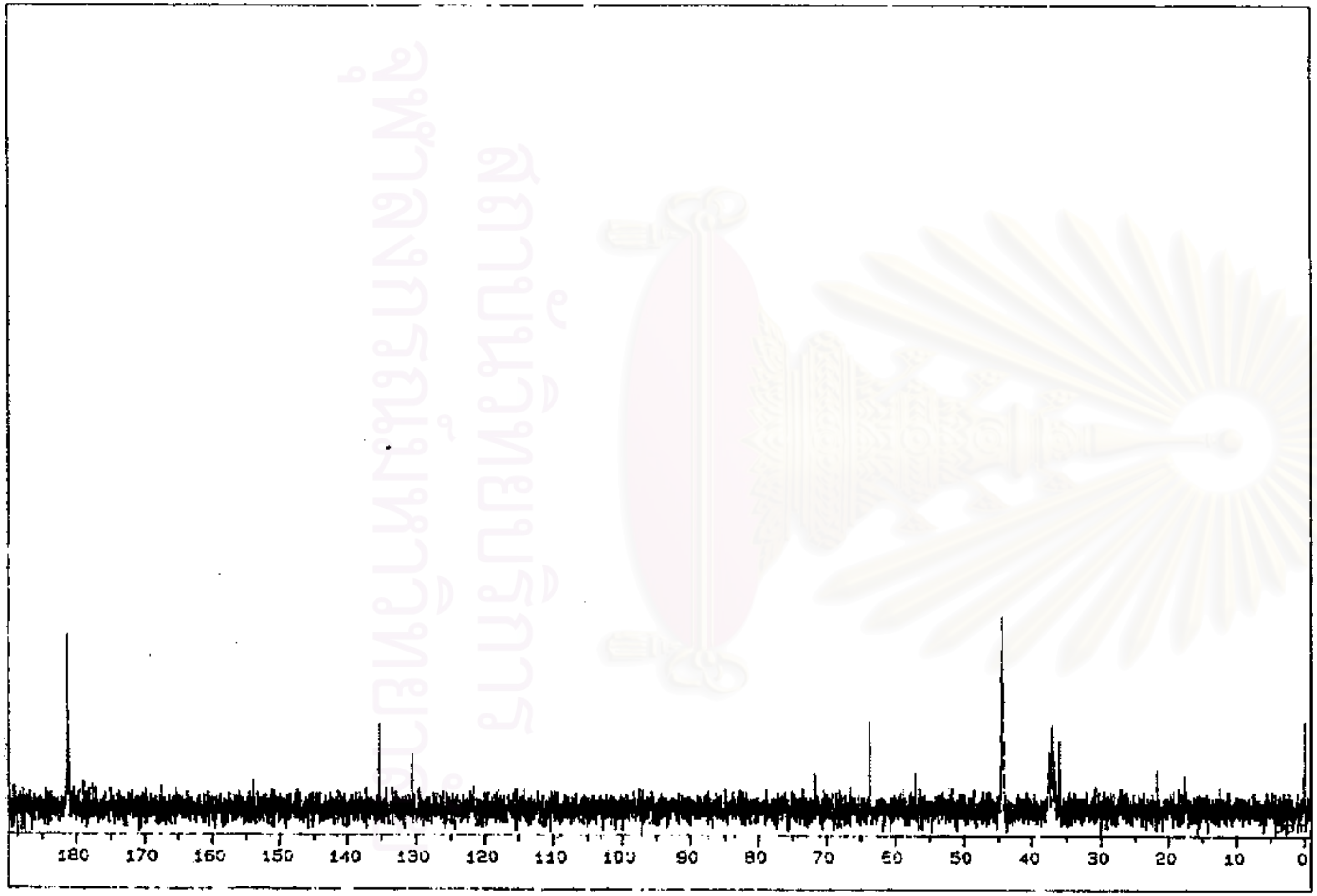
EXMOD : SINGL
IRMOD : BCM
POINT :    16384
FREQU : 33898.31 Hz
SCANS :      206
DUMMY :        4
ACQTM :      0.4833 sec
PD    :      2.0000 sec
RGAIN :       23
PW1   :     4.90 usec
OBNUC : 13C
OBFRQ :   125.65 MHz
OBSET : 127958.00 Hz

IRNUC : 1H
IRFRQ :   500.00 MHz
IRSET : 162410.00 Hz
IRATN :      120
IRRPW :     55.0 usec
IRBP1 :       30
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     29.9 c
CSPED :       10 Hz
SLVNT : D2O
RESOL :     2.07 Hz
BF    :     2.07 Hz
REFVL :     0.00 ppm
XE    : 24018.89 Hz
XS    :  1081.05 Hz

OPERATOR :
```

Figure A2. ^{13}C NMR spectrum of acrylic acid in D_2O.



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14-NOV-2000 14: 42: 37.32

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SFILE : [.WMO]USA1-11-BCM
COMNT : USA1-11-13C

EXMOD : SINGL
IRMOD : BCM
POINT :    16384
FREQU : 33898.31 Hz
SCANS :      723
DUMMY :        4
ACQTM :      0.4833 sec
PD    :      2.0000 sec
RGAIN :       23
PW1   :     4.90 usec
OBNUC : 13C
OBFRQ :   125.65 MHz
OBSET : 127958.00 Hz

IRNUC : 1H
IRFRQ :   500.00 MHz
IRSET : 162410.00 Hz
IRATN :      120
IRRPW :     55.0 usec
IRBP1 :       30
IRBP2 :        6
IRRNS :        0

ADBIT :       15
CTEMP :     49.9 c
CSPED :       12 Hz
SLVNT : D2O
RESOL :     2.07 Hz
BF    :     2.07 Hz
REFVL :     0.00 ppm
XE    : 24018.89 Hz
XS    :  1068.63 Hz

OPERATOR :
```
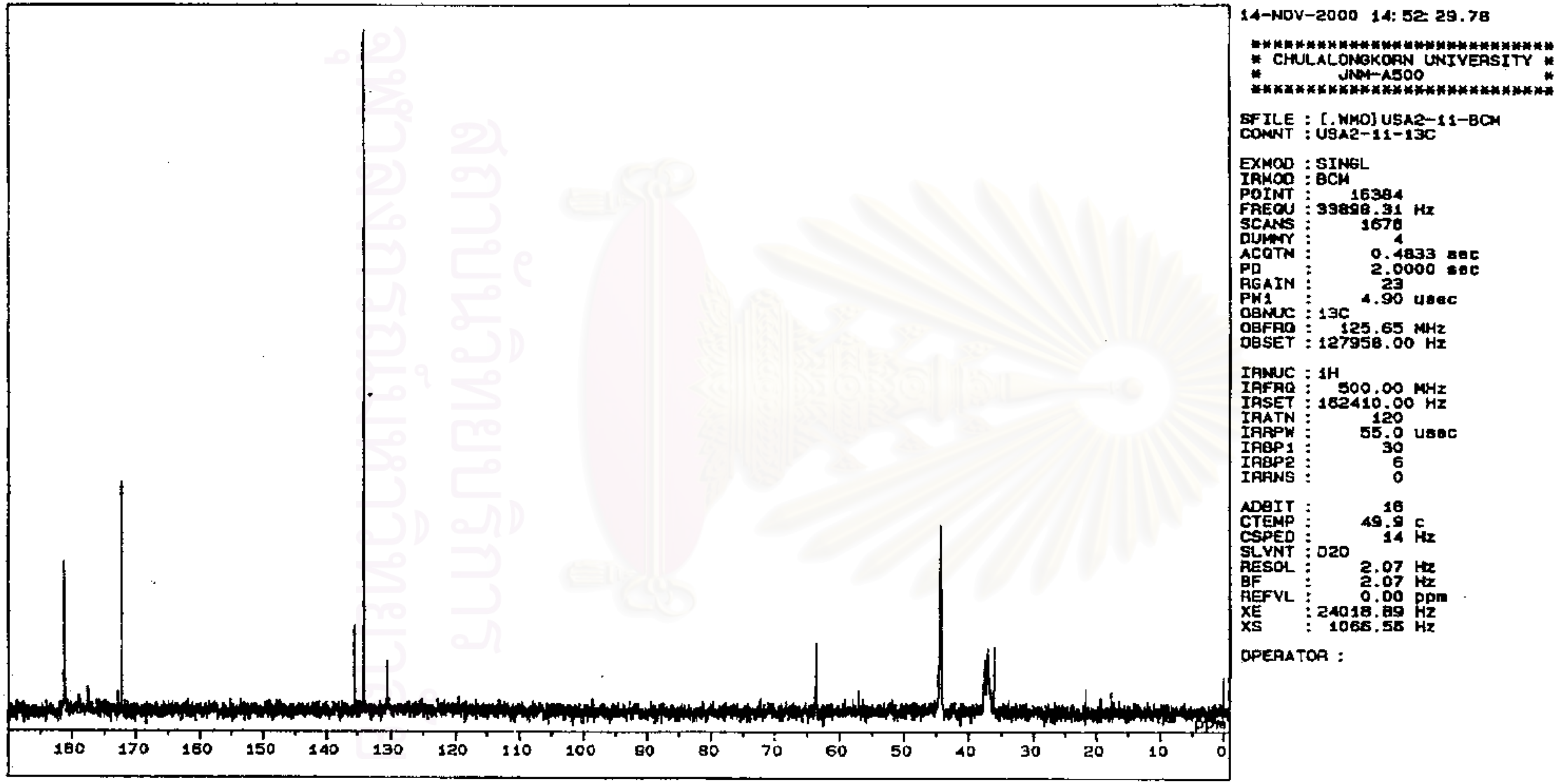

Figure A3. ^{13}C NMR spectrum of pure AA in D_2O.



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14-NOV-2000 14:52:29.78

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SFILE : [.NMO]USA2-11-BCM
COMNT : USA2-11-13C

EXMOD : SINGL
IRMOD : BCM
POINT :    16384
FREQU : 33898.31 Hz
SCANS :     1676
DUMMY :        4
ACQTN :      0.4833 sec
PD    :      2.0000 sec
RGAIN :       23
PW1   :      4.90 usec
OBNUC : 13C
OBFRQ :   125.65 MHz
OBSET : 127958.00 Hz

IRNUC : 1H
IRFRQ :   500.00 MHz
IRSET : 162410.00 Hz
IRATN :      120
IRRPW :     55.0 usec
IRBP1 :       30
IRBP2 :        6
IRRNS :        0

ADBIT :       16
CTEMP :     49.9 c
CSPED :       14 Hz
SLVNT : D20
RESOL :     2.07 Hz
BF    :     2.07 Hz
REFVL :     0.00 ppm
XE    : 24018.89 Hz
XS    :  1066.56 Hz

OPERATOR :
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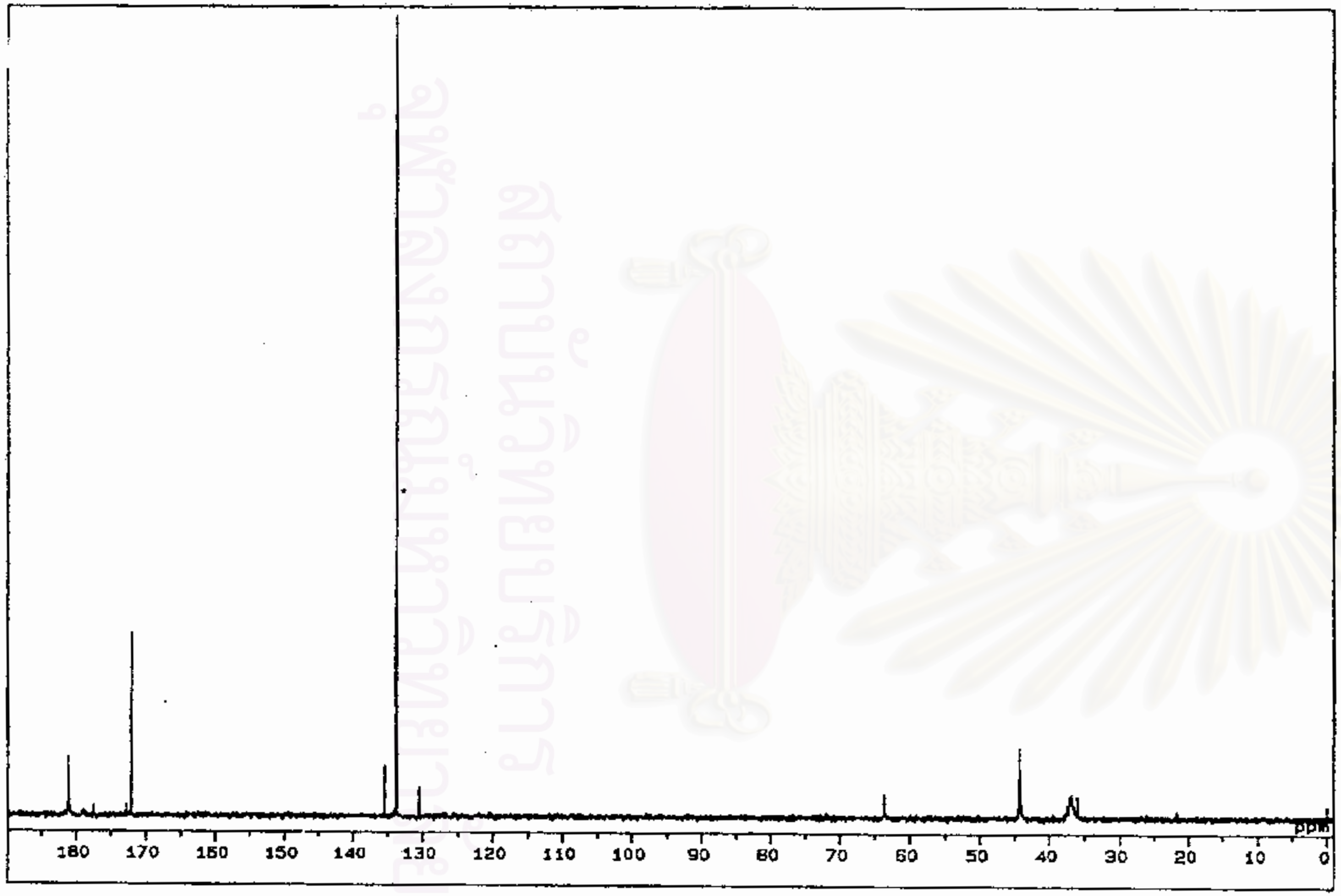
Figure A4. ^{13}C NMR spectrum of AA/MA with mole ratio 1:0.2 in D_2O.



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14-NOV-2000 14:54:38.28

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SFILE : [.WMO]USA3-11-BCM
COMNT : USA3-11-13C

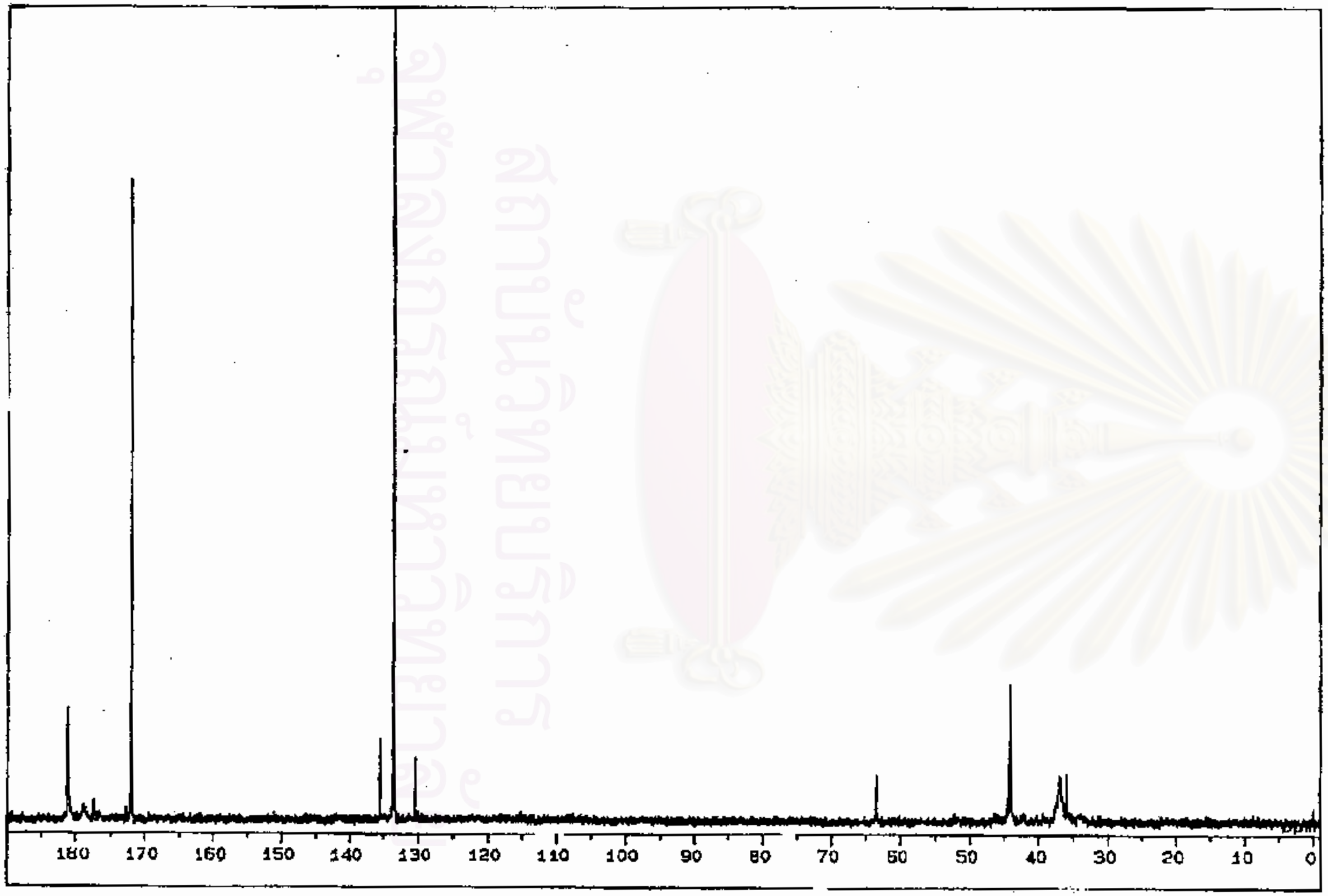
EXMOD : SINGL
IRMOD : BCM
POINT :      16384
FREQU : 33898.31 Hz
SCANS :       1698
DUMMY :          4
ACQTN :     0.4833 sec
PD    :     2.0000 sec
RGAIN :         23
PW1   :       4.90 usec
OBNUC : 13C
OBFRQ :    125.65 MHz
OBSET : 127958.00 Hz

IRNUC : 1H
IRFRQ :    500.00 MHz
IRSET : 162410.00 Hz
IRATN :        120
IRRPW :       55.0 usec
IRBP1 :         30
IRBP2 :          6
IRRNS :          0

ADBIT :         16
CTEMP :       49.9 c
CSPED :         13 Hz
SLVNT : D2O
RESOL :       2.07 Hz
BF    :       2.07 Hz
REFVL :       0.00 ppm
XE    : 24018.89 Hz
XS    :  1070.70 Hz

OPERATOR :
```

Figure A5. ^{13}C NMR spectrum of AA/MA with mole ratio 1:0.5 in D_2O.



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14-NOV-2000 14:58:52.20

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 * CHULALONGKORN UNIVERSITY *
 *         JNM-A500         *
 ***************************

SFILE : [.WHO]USA4-11-BCM
COMNT : USA4-11-13C

EXMOD : SINGL
IRMOD : BCM
POINT :      16384
FREQU : 33898.31 Hz
SCANS :       1753
DUMMY :          4
ACQTM :       0.4833 sec
PD    :       2.0000 sec
RGAIN :         23
PW1   :       4.90 usec
OBNUC : 13C
OBFRQ :    125.65 MHz
OBSET : 127858.00 Hz

IRNUC : 1H
IRFRQ :    500.00 MHz
IRSET : 162410.00 Hz
IRATN :        120
IRRPW :       65.0 usec
IRBP1 :         30
IRBP2 :          5
IRRNS :          0

ADBIT :         16
CTEMP :       49.9 c
CSPED :         11 Hz
SLVNT : D2O
RESOL :       2.07 Hz
BF    :       2.07 Hz
REFVL :       0.00 ppm
XE    : 24018.89 Hz
XS    :  1076.91 Hz

OPERATOR :
```

Figure A6. ^{13}C NMR spectrum of AA/MA with mole ratio 1:1 in D_2O.

APPENDIX B

การตกแต่งกันยับผ้าฝ้าย
ด้วยกรดพอลิคาร์บอกซิลิก

รศ.ดร.วีระศักดิ์ อุดมกิจเดชา : สถาบันวิจัยโลหะและวัสดุ จุฬาลงกรณ์มหาวิทยาลัย
อุษา ฐานะสุนทรฤกษ์ : ภาควิชาวัสดุศาสตร์ คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

Durable press finishing agents in textile wet processing have been reviewed. It was found that most of the chemicals used were contained with formaldehyde which have been classified as toxic chemical. Therefore, many investigations have been concentrated on development of formaldehyde free chemical to be a better alternative. Polycarboxylic acid has shown a very promising potential in industry usage. This paper presented a conclusive study of the polycarboxylic acids serving this specific purpose and also pointing out the advantages of those chemicals.

สารเคมีที่นิยมใช้ตกแต่งกันยับมีหลายชนิด ส่วนใหญ่พบว่ามีฟอร์มัลดีไฮด์เป็นส่วนประกอบอยู่ด้วย แต่เนื่องจากฟอร์มัลดีไฮด์จัดเป็นสารพิษ ดังนั้นสารตกแต่งกันยับที่ปราศจากฟอร์มัลดีไฮด์จึงเป็นทางเลือกใหม่ที่ได้รับความสนใจมากขึ้น โดยเฉพาะอย่างยิ่งกรดพอลิคาร์บอกซิลิกที่สามารถใช้งานได้ดีในเชิงอุตสาหกรรม การศึกษาทดลองนำกรดพอลิคาร์บอกซิลิกมาใช้เป็นสารตกแต่งกันยับผ้าฝ้ายได้ถูกรวบรวมอยู่ในบทความนี้ รวมทั้งแสดงให้เห็นข้อดีของสารเคมีประเภทนี้

คำนำ

การตกแต่งสำเร็จผ้ามีหลายชนิดด้วยกัน ตามวัตถุประสงค์การใช้งานและขึ้นกับสมบัติพื้นฐานของผ้า การตกแต่งให้ผ้าเรียบหรือกันยับเป็นการตกแต่งสำเร็จผ้าที่นิยมทำกันมากในปัจจุบัน โดยจะทำกับผ้าที่ยับง่าย พวกผ้าใยเซลลูโลส เช่น ผ้าเรยอน และผ้าฝ้าย ซึ่งนอกจากจะทำให้ผ้ายับยาก และรีดง่ายขึ้นแล้วยังช่วยทำให้ผ้าคงรูปไม่หดตัว ดูแลรักษาง่าย ชื่อที่ใช้เรียกการตกแต่งชนิดนี้มีมากมาย เช่น durable press, permanent press, easy care และ wash-and-wear รวมทั้ง wrinkle free ซึ่งเป็นชื่อที่รู้จักกันแพร่หลายในทางการค้า

สารเคมีที่ใช้ในการตกแต่งกันยับ ในยุคแรกๆ นิยมใช้ฟอร์มัลดีไฮด์ หรือสารที่มีฟอร์มัลดีไฮด์เป็นส่วนประกอบ แต่เนื่องจากพบว่าผ้าที่ผ่านการตกแต่งแล้วอาจปลดปล่อยฟอร์มัลดีไฮด์ออกมาได้ ดังนั้นจึงมีการตรวจสอบความเป็นพิษของสารขึ้นทั้งโดยผู้ผลิต ผู้บริโภคและหน่วยงานที่เกี่ยวข้อง พบว่าฟอร์มัลดีไฮด์เป็นสารเคมีที่เป็นพิษ มีผลทำให้ระคายเคืองตาอย่างรุนแรง รวมทั้งทำให้เยื่อบุของเหลวและผิวหนังระคายเคือง ถึงแม้ว่าจะไม่ปรากฏว่าฟอร์มัลดีไฮด์เป็นสารก่อมะเร็ง แต่เมตาโบไลต์บางอย่างของมันรวมทั้ง N-methylol ซึ่งได้จากปฏิกิริยาระหว่างฟอร์มัลดีไฮด์กับกรดอะมิโนและโปรตีนซึ่งอยู่ในสิ่งมีชีวิตอาจก่อให้เกิดมะเร็งได้ในหนูทดลอง ดังนั้นจึงมีการคิดค้นสารเคมีตัวใหม่ซึ่งปราศจากฟอร์มัลดีไฮด์มาใช้ทดแทน ได้แก่ สารกลุ่มซิลิโคน (silicones) ไกลออกซอล (glyoxal) และกรดพอลิคาร์บอกซิลิก (polycarboxylic acid) โดยเฉพาะอย่างยิ่งกรดพอลิคาร์บอกซิลิกเป็นสารที่ปลอดฟอร์มัลดีไฮด์ที่ได้รับความสนใจมากที่สุดในปัจจุบัน

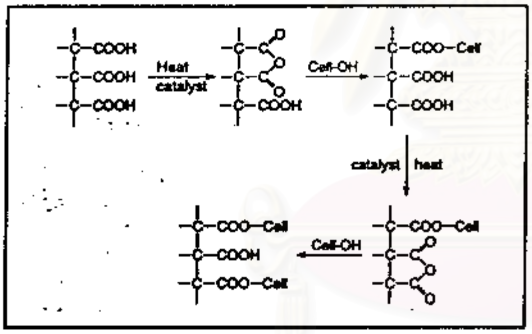
1. การใช้กรดพอลิคาร์บอกซิลิกตกแต่งกันยับผ้าฝ้าย

กรดพอลิคาร์บอกซิลิกที่ใช้มีทั้งที่มีโครงสร้างแบบเชิงเส้นและแบบวงแหวน แบบเชิงเส้นก็มีทั้งชนิดอิ่มตัวและชนิดไม่อิ่มตัวที่สามารถเกิดปฏิกิริยาพอลิเมอไรเซชันได้ ขนาดโมเลกุลที่ใช้ส่วนใหญ่เริ่มตั้งแต่ 3 คาร์บอนอะตอมขึ้นไป ดังตัวอย่างที่ปรากฏในตารางที่ 1 กรดพอลิคาร์บอกซิลิกเหล่านี้สามารถเกิดการเชื่อมโยงกับเซลลูโลสด้วยพันธะเอสเทอร์ (ester linkages) โดยที่กรดต้องมีหมู่คาร์บอกซิล (-COOH) อยู่ที่คาร์บอนอะตอมที่ติดกันในสายโซ่โมเลกุลหรือวงแหวน ทำการอบผนึกที่อุณหภูมิประมาณ 160-215 องศาเซลเซียส และมีด่างอ่อนเป็นตัวเร่งปฏิกิริยา เกิด

ตารางที่ 1 กรดพอลิคาร์บอกซิลิกที่ใช้เป็นสารตกแต่งกันยับ

ชนิดของกรด	องค์ประกอบทางเคมี
Tricarboxylic acids	- propanetricarboxylic (PTCA) - citric acid
Tetracarboxylic acids	- butanetetracarboxylic acid (BTCA) - cyclopentanetetracarboxylic acid
Hexacarboxylic acids	- cyclohexanehexacarboxylic acid
Polymeric carboxylic acids	- polyacrylic acid - polymaleic acid
Copolymeric carboxylic acids	- maleic acid/itaconic acid copolymer

ไซคลิกแอนไฮไดร์ (cyclic anhydride) ก่อน แล้วจึงเกิดปฏิกิริยาเอสเทอริฟิเคชั่น (esterification) กับเซลลูโลสได้ กลไกการเกิดปฏิกิริยานี้เรียกว่า "cyclic anhydride mechanism" ดังสมการเคมีรูปที่ 1



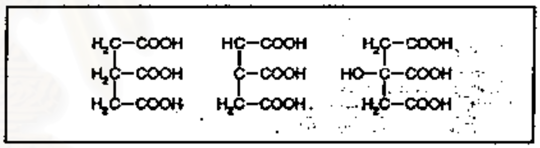
รูปที่ 1 cyclic anhydride mechanism

โครงสร้างของกรดเป็นแบบเชิงเส้นชนิดอิ่มตัวมีหมู่คาร์บอกซิลอย่างน้อย 3 หมู่ในแต่ละโมเลกุลจึงจะเกิดการเชื่อมโยงได้ เมื่อได้รับความร้อนหมู่คาร์บอกซิลที่อยู่ใกล้กัน 2 หมู่จะเกิดปฏิกิริยาเปลี่ยนรูปเป็นไซคลิกแอนไฮไดร์ ทำให้โมเลกุลของน้ำหลุดออก 1 โมเลกุล และไซคลิกแอนไฮไดร์ทำปฏิกิริยากับหมู่ไฮดรอกซิลของเซลลูโลสเพียง 1 หมู่เกิดเป็นพันธะเอสเทอร์ และได้หมู่คาร์บอกซิลกลับคืน 1 หมู่เพื่อทำปฏิกิริยากับหมู่คาร์บอกซิลที่เหลือต่อไป เกิดเป็นการเชื่อมโยงระหว่างสายโซ่โมเลกุล กรดพอลิคาร์บอกซิลิกที่ว่องไวต่อการเกิดปฏิกิริยามากที่สุดคือ กรดที่สามารถเกิดเป็นวงแหวนแอนไฮไดร์ที่มีสมาชิก 5 หรือ 6 ตัวได้

การตกแต่งกันยับผ้าจะได้ผลดีขึ้นกับหลายปัจจัยด้วยกัน ได้แก่ สารเคมี ตัวเร่งปฏิกิริยาอุณหภูมิและเวลา รวมทั้งวิธีที่ใช้ด้วย วิธีนี้นิยมใช้กันทั่วไป คือ วิธีจุ่มน้ำยา-อบแห้ง-อบผนึก (pad-dry-cure) โดยนำผ้ามาจุ่มลงในอ่างที่มีสารตกแต่งกันยับ ตัวเร่งปฏิกิริยาและสารเติมแต่งอื่นๆ แล้วนำไปอบให้ผ้าแห้งก่อนนำไปอบผนึกอีกครั้งเพื่อให้สารติดแน่นกับผ้า

2. ผลการศึกษาการตกแต่งกันยับผ้าฝ้าย

จากการศึกษาทดลองนำกรดคาร์บอกซิลิกที่มีหมู่คาร์บอกซิลิก 3 หมู่ต่อโมเลกุล ได้แก่ กรดซิตริก (citric acid; CA) กรดอะโคนิติก (aconitic acid; AA) และกรดโพรเพนไตรคาร์บอกซิลิก (propanetricarboxylic acid; PCA) หรือกรดไตรคาร์บอลลิลิก (tricarballylic acid) มาตกแต่งผ้า ดังรูปที่ 2



รูปที่ 2 สูตรโครงสร้างของ tricarballylic acid, aconitic acid และ citric acid

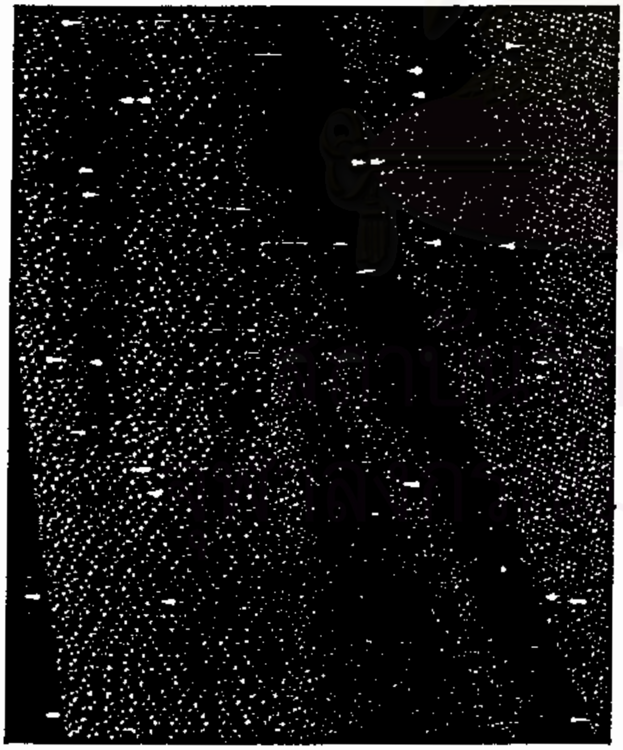
พบว่ากรดอะโคนิติก และกรดไตรคาร์บอลลิลิกทำให้ผ้ามีระดับความคงทนต่อการยับ (durable press rating; DP rating) และมีมุมการคืนตัวหลังการยับ (wrinkle recovery angle; WRA) ดีที่สุด แต่กรดทั้ง 3 ชนิดทำให้ความแข็งแรงที่จุดขาดและความขาวของผ้าลดลง โดยเฉพาะกรดอะโคนิติกและกรดซิตริก ดังตารางที่ 2 พบว่าเกิดจากการมีพันธะคู่ของกรดอะโคนิติก และกรดซิตริกอีกทั้งสามารถสลายตัวหรือเกิดการขจัดน้ำกลายเป็นกรดซิตริกได้ที่อุณหภูมิสูง ดังนั้นจึงเลิกใช้กรดอะโคนิติกในการตกแต่งผ้า แต่กรดซิตริกยังคงได้รับความสนใจอยู่เนื่องจากราคาถูก หาได้ง่ายและไม่เป็นพิษ ประกอบกับทำให้ผ้ามีสมบัติดีพอใช้ ถึงแม้จะทำให้ผ้าเหลืองแต่ก็ได้มีการพยายามนำสารเติมแต่งมาช่วยปรับปรุงความขาวของผ้า ได้แก่ สารพวก tertiary alkanolamine เช่น triethanolamine (TEA) triisopropanolamine (TPA) และ N-methyldiethanolamine (MDA) ซึ่งสารทั้ง 3 ตัวช่วยให้ความขาวของผ้าดีขึ้นได้ รวมทั้งยังช่วยเพิ่มความแข็งแรงและความคงทนต่อการขัดถูด้วย

ตารางที่ 2 สมบัติของผ้าที่ผ่านการตกแต่งกันยับด้วยกรดไตรคาร์บอกซิลิก

Acid	Durable Press Rating	Conditioned wrinkle recovery angle, W+f,(deg)	Breaking strength, w(lb)	CIE Whiteness Index
Aconitic	3.7	257	27	<0
Citric	3.2	230	29	34
Tricarballylic	3.7	251	27	53
Untreated	1.0	189	51	83

Acids were equivalent to 6.3% tricarballylic; catalyst was 4.2% $NaH_2PO_2.H_2O$

จากการทดลองใช้กรดที่มีหมู่คาร์บอกซิลิก 4 หมู่ เช่น BTCA เป็นสารตกแต่งกันยับผ้าพบว่า เป็นสารที่มีประสิทธิภาพสูงทำให้ผ้ามี DP rating, WRA Breaking strength, Tearing strength และความทนทานต่อการซักดี ไม่ทำให้ผ้าเหลืองและไม่มีกลิ่น ปัจจุบันเป็นสารตกแต่งกันยับที่มีประสิทธิภาพดีที่สุด แต่ข้อเสียคือ ราคาแพง และต้องใช้ตัวเร่งปฏิกิริยาที่มีราคาแพง นอกจากนี้ยังหาซื้อไม่ค่อยสะดวกนัก

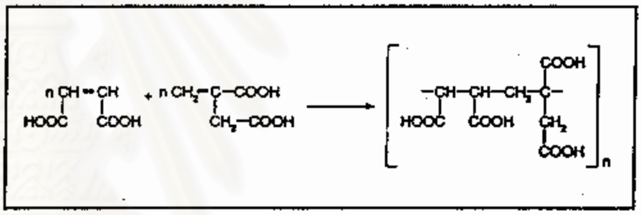


ตัวเร่งปฏิกริยาก็เป็นตัวแปรที่สำคัญอีกตัวหนึ่งในการตกแต่งกันยับผ้า และจากการทดลองต่างๆ ที่ผ่านมาสรุปได้ว่าโซเดียมไฮโปฟอสไฟต์เป็นตัวเร่งปฏิกริยาที่มีประสิทธิภาพดีที่สุด แต่มีข้อเสียที่ราคาแพงและทำให้เฉดสีของผ้าที่ย้อมด้วยสีซัลเฟอร์และสีรีแอคทีฟเปลี่ยนไป รวมทั้งยังสามารถสลายตัวที่อุณหภูมิสูงเกิดเป็นฟอสไฟน์ซึ่งเป็นสารพิษและเป็นก๊าซที่ติดไฟได้

กรดคาร์บอกซิลิกไม่อิ่มตัวที่สามารถเกิดปฏิริยาพอลิเมอไรเซชั่นได้เป็นกรดพอลิคาร์บอกซิลิกสายยาวก็เป็นอีกทางเลือกหนึ่งที่น่าสนใจ ซึ่งกรดคาร์บอกซิลิกไม่อิ่มตัวที่จะนำมาเป็นสารตกแต่งกันยับนั้นต้องมีหมู่ไฮดรอกซิลอย่างน้อย 2 หมู่บนอะตอมคาร์บอนที่อยู่ติดกันในแต่ละโมเลกุลจึงจะสามารถเกิดการเชื่อมโยงกับเซลลูโลสได้ และตำแหน่งของหมู่คาร์บอกซิลที่เหมาะสมกับการเกิดปฏิกิริยาได้ต้องเป็น cis conformation เช่น กรดมาลิอิก (maleic acid) เป็นกรดที่สามารถเกิดเป็นวงแหวนแอนไฮไดร์ได้ทันทีได้รับความร้อน เนื่องจากหมู่คาร์บอกซิล 2 หมู่นั้นมีการจัดเรียงตัวแบบ cis และกรดมาลิอิกก็สามารถเกิดพันธะเอสเทอร์กับผ้าฝ้ายได้ทันทีที่มีอุณหภูมิสูง และมีตัวเร่งปฏิกิริยาที่เป็นด่าง ส่วนกรดฟูมาริก (fumaric) ซึ่งเป็น trans Isomer ของกรดมาลิอิกไม่สามารถเกิดเป็นวงแหวนแอนไฮไดร์ได้และไม่สามารถเกิดปฏิกิริยากับเซลลูโลสได้

กรดพอลิคาร์บอกซิลิกที่ใช้เป็นสารตกแต่งกันยับที่ดีมักมีขนาดโมเลกุลไม่ใหญ่นัก สามารถเข้าไปยึดจับกับเซลลูโลสแบบโครงสร้าง 3 มิติได้ทั่วถึงดังที่กล่าวมาแล้ว ผ้าที่ผ่านการตกแต่งแล้วจะมีสมบัติการคืนตัวดีและทนต่อการซักด้วยเครื่อง แต่ข้อเสียที่เห็นได้ชัดคือผ้ามีความแข็งแรงและความทนทานต่อการขัดถูน้อยลง ดังนั้นการตกแต่งกันยับผ้าวิธีใหม่จึงถูกพัฒนาขึ้นโดยการทำให้เกิดการเชื่อมโยงพร้อมกับการพอลิเมอไรซ์ขึ้น (polymerization-crosslinking treatment: PC) เรซินจะต้องมีหมู่ฟังก์ชั่นที่สามารถเกิดการเชื่อมโยงกับเส้นใยได้ และต้องมีหมู่ฟังก์ชั่นที่สามารถพอลิเมอไรซ์ได้ ได้แก่ กรดคาร์บอกซิลิกไม่อิ่มตัวที่มีหมู่คาร์บอกซิล 1 หรือ 2 หมู่ก็ได้ (unsaturated mono-or-dicarboxylic acid) เนื่องจากมีความไม่อิ่มตัวหรือพันธะคู่จึงสามารถพอลิเมอไรซ์แบบแรดิเคิลได้ (radical polymerization) และการที่มีหมู่คาร์บอกซิลอยู่ด้านข้างจึงสามารถเกิดการเชื่อมโยงกับเซลลูโลสได้ด้วย เรซินจะแทรกซึมเข้าไปภายในเส้นใยที่พองตัวขณะเปียกแล้วเกิดการเชื่อมโยงกับเส้นใยพร้อมๆกับเกิดพอลิเมอไรซ์ได้เป็นพอลิเมอร์สายยาวที่มีความยืดหยุ่น ช่วยให้ความแข็งแรงของผ้าไม่ลดลงมากนัก

กรดมาลิอิก (maleic acid) และกรดอิทาโคนิก (itaconic acid) เป็นกรดไม่อิ่มตัวที่มีหมู่คาร์บอกซิล 2 หมู่ต่อโมเลกุลซึ่งไม่สามารถเกิดเป็นโฮโมพอลิเมอร์ได้ ถูกนำมาพอลิเมอไรซ์ร่วมกันได้เป็นโคพอลิเมอร์ (copolymer) ในผ้าฝ้ายโดยใช้โปแทสเซียมเปอร์ซัลเฟตเป็นตัวเร่งปฏิกริยาพอลิเมอไรเซชัน และใช้โซเดียมไฮโปฟอตไฟต์เป็นตัวเร่งปฏิกิริยาเอสเทอริฟิเคชันกับเซลลูโลส พบว่าผ้าที่ได้มี DP rating และมี WRA ดีขึ้น โดยที่อัตราส่วนโมลของมอนอเมอร์ทั้งสองเป็น 1:1 และอัตราส่วนระหว่างมอนอเมอร์กับโซเดียมไฮโปฟอสไฟต์เป็น 1:1 หรือ 1:1.33 ผ้าจะมีสมบัติดีที่สุดดังตารางที่ 3 และจากตารางที่ 4 พบว่าเมื่อความเข้มข้นของมอนอเมอร์ในอ่างชุบเพิ่มขึ้น DP rating และ WRA จะสูงขึ้นจนสามารถเทียบกับ DMDHEU ได้ ขณะที่ Tearing strength retention และ Stoll flex abrasion retention ดีกว่า และเมื่อใช้อุณหภูมิอบผนึกที่ 160-190 องศาเซลเซียส ผ้าที่ได้จะสามารถคงสมบัติเชิงกายภาพและมีดัชนีความขาวดีกว่าผ้าที่ผ่านการตกแต่งด้วย DMDHEU โดยเฉพาะ Tearing strength retention นั้นสูงกว่าอย่างเห็นได้ชัด และในทุกภาวะการทดลองพบว่า Stoll flex abrasion retention ของผ้าที่ผ่านการตกแต่งแล้วสูงกว่าผ้าที่ยังไม่ผ่านการตกแต่ง แต่ Breaking strength ก็ยังต่ำอยู่ ซึ่งอาจเกิดจากพอลิเมอร์นั้นยังคงอยู่ที่ผิวเส้นใยหรือซึมเข้าไปในเส้นใยเพียงเล็กน้อย ซึ่งสามารถพิสูจน์ได้ด้วยการย้อมสีเบสิก



รูปที่ 3 โคพอลิเมอร์ของกรดมาลีอิกและกรดอิทาโคนิก

Book Corner

ชื่อหนังสือ : TTIS Textile Buyer's Guide 2000
เจ้าของ : บริษัท ทีทีไอเอส จำกัด
ราคา : 600 บาท/เล่ม

เป็นการรวบรวมรายชื่อบริษัทอุตสาหกรรมสิ่งทอในประเทศไทย โดยแยกเป็นผู้ผลิต ผู้ค้า และบริษัทที่ให้บริการที่เกี่ยวข้องกับอุตสาหกรรมสิ่งทอ

หมายเหตุ : สมาชิกสมาคมอุตสาหกรรมฟอกย้อมพิมพ์และตกแต่งสิ่งทอไทยได้รับส่วนลด 15% โดยสามารถติดต่อซื้อได้ที่ *สมาคมฯ โทรศัพท์/โทรสาร 229-3431-2*

ตารางที่ 3 ผลของอัตราส่วนโมลของมอนอเมอร์ทั้งสองและอัตราส่วนโมลของมอนอเมอร์กับตัวเร่งปฏิกิริยาต่อสมบัติของผ้า[a]

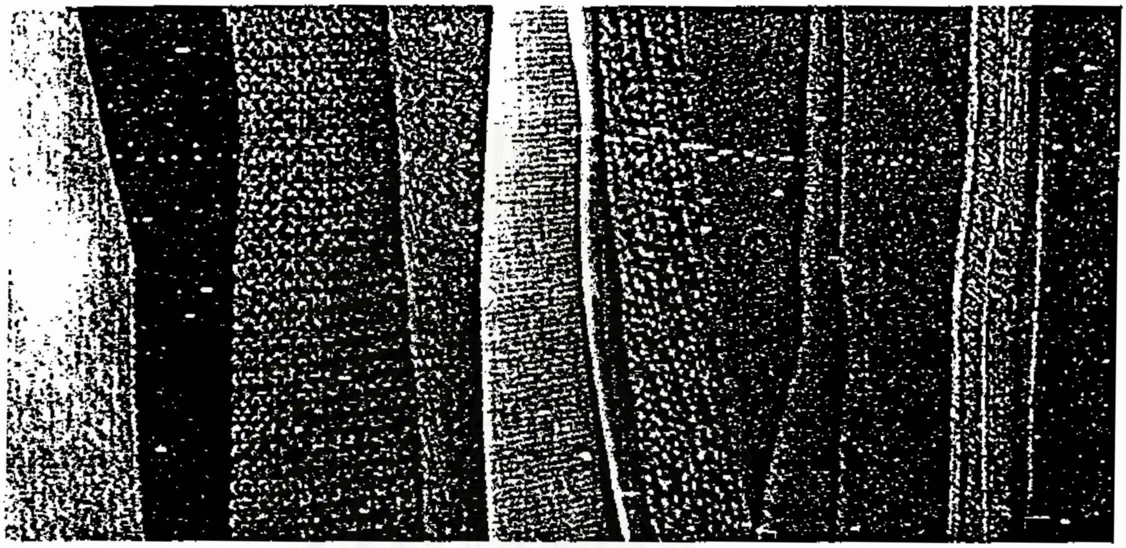
Monomer, Mole ratio	Acid-cat Mole ratio[b]	Add-on[c], %	DP Rating	WRA Degree (w+f)	TS, %[d] W	F	BS[e], %	SFA[f], %	BL[g], cm
Untreated	-	-	1.5	171	100	100	100	100	3.7
DMDHEU-treated[h]	-	4.0	4.5	278	55	59	45	18	3.0
MA	1:1	9.1	3.5	219	67	73	56	99	2.9
MA/IA (2:1)	1:1	9.6	4.0	254	78	82	56	196	2.5
MA/IA (1:1)	3:1	7.4	4.0	233	82	91	64	323	2.7
	2:1	7.7	3.5	242	93	86	73	269	3.0
	1:1	11.6	4.4	268	76	90	49	214	2.7
	1:1.33	10.8	4.4	256	79	90	57	226	2.7
MA/IA (1:2)	1:1	10.8	4.0	258	68	87	67	131	2.7

[a]Treating bath : 12% monomers, 1.5% owm $K_2S_2O_8$, NaH_2PO_2, 1% softener, and 0.1% Triton X-100. Dry : 100°C/10 minutes. Cure: 180°C/2 minutes. Wash and tumble dry. [b]Molar ratio between monomer and $NaH_2PO_2.H_2O$. [c] Add-on (%) = ((weight after treatment and washing-initial weight)/initial weight)x100. [d]Tearing strength retention (wrap and fill). [e]Breaking strength retention. [f]Stoll flex abration. [g]BL : Bending length. [h]Treatment bath : 12% DMDHEU, 1.5% $Zn(NO_3)_2.6H_2O$, 1% softener, and 0.1% Triton X-100. Dry : 100°C/5 minutes. Cure : 165°C/3 minutes, wash and tumble dry.

ตารางที่ 4 ผลของความเข้มข้นของมอนอเมอร์ต่อสมบัติของผ้า[a] *(อัตราส่วนโมลของมอนอเมอร์ทั้งสองเป็น 1:1)*

Monomer conc. % owb (curing °C/min)	Add-on %	DP Rating	WRA Degree (w+f)	TS, % W	F	BS, %	SFA, %	BL, cm	WL[b]	Cuene Insol. %	% Acetyl	-COOH Content (mequi/100g sample)	ΔE Basic Blue9
6.2 %	5.2	3.7	242	85	98	62	221	2.7	46.7	6.4	0.1744	31.3	74.6
8.9 %	8.4	4.0	271	83	97	59	148	2.5	47.0	22.4	0.1946	55.8	74.7
12 % (160/3.5)	11.4	4.2	272	62	89	58	143	2.5	44.7	-	0.4545	35.8	75.0
12 %(170/2)	11.3	4.0	273	70	88	60	158	2.5	49.7	-	0.3010	45.1	74.9
12 %(180/2)	11.6	4.4	268	76	90	49	214	2.7	49.0	53.3	0.6416	76.1	74.5
12 %(190/2)	11.3	4.4	283	51	78	58	133	2.4	30.3	-	0.3946	40.6	74.8
15.6 %	3.5	4.5	290	46	82	54	81	2.5	45.5	58.0	0.9120	69.3	75.3
DMDHEU-treated									48.3	94.5	-	-	42.2
Untreated									56.3	2.7	-	5.7	54.8

[a]Treatment bath : monomers, 1.5% owm $K_2S_2O_8$, 8.8% $NaH_2PO_2.H_2O$, 1% softener, and 0.1% Triton X-100. Dry : 100 °C/10 minutes. Cure : 180 °C/2 minutes, unless otherwise specified. The abbreviations are same as before. [b]Before washing



4. สรุป

จากผลการทดลองเหล่านี้แสดงให้เห็นว่าการตกแต่งกันยับแบบ polymerization-crosslinking treatment นี้สามารถใช้ได้ผลดี ทำให้สมบัติโดยรวมของผ้าดีขึ้น ในขณะที่มีราคาถูกและไม่ปลดปล่อยฟอร์มัลดีไฮด์ อย่างไรก็ตามความแข็งแรงของผ้านั้นยังไม่ดีนัก สมมติฐานขั้นต้นอาจเนื่องมาจากการใช้วิธี pad-dry-cure ในการตกแต่งผ้าทำให้การแทรกซึมของพอลิเมอร์เข้าไปในเส้นใยไม่ดีพอ ซึ่งถ้าเปลี่ยนไปใช้วิธิการผนึกเปียก (wet fixation) หรือการอบผนึกด้วยไอน้ำ (steam fixation) อาจช่วยทำให้ดีขึ้นได้ หรืออาจเนื่องมาจากการเชื่อมโยงระหว่างพอลิเมอร์กับเส้นใยหนาแน่นมากเกินไป ซึ่งสามารถปรับปรุงให้ดีขึ้นได้โดยเลือกใช้มอนอเมอร์หรือสารเติมแต่งที่เหมาะสม

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