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นางสาวดวงกมล วิบูลย์รัตน์ศรี

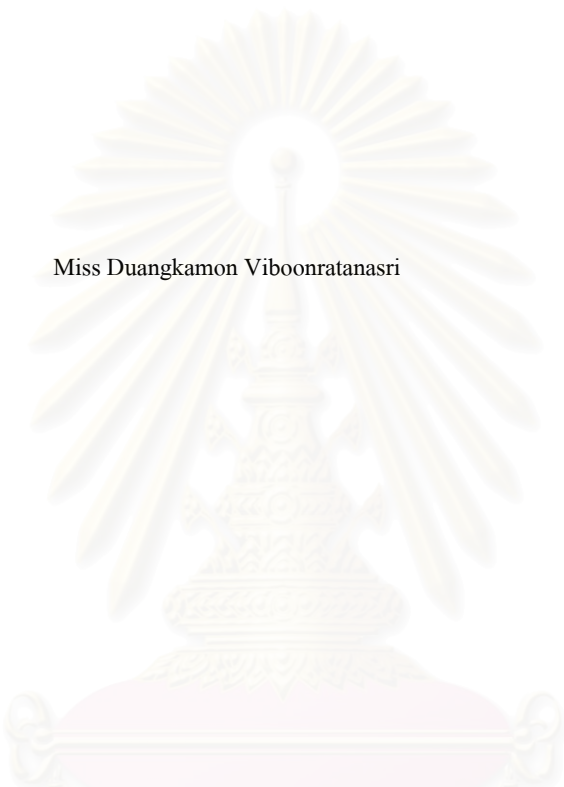
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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

HYDROPHILIC FINISHING OF POLYESTER FABRIC WITH MODIFIED CHITOSAN



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ไคโตซานดัดแปรเตรียมได้จากปฏิกิริยาระหว่างไคโตซาน (น้ำหนักโมเลกุล 10^6 และ 10^5) กับ ฟทาสิกแอนไฮไดรด์ ซึ่งใช้อัตราส่วนโดยโมลระหว่างไคโตซาน: ฟทาสิกแอนไฮไดรด์ = 1:12 และ 1:18 ฟทาสิกแอนไฮไดรด์ที่เตรียมได้ถูกนำมาพิสูจน์หาโครงสร้างด้วยเทคนิคฟูเรียร์ทรานสฟอร์มอินฟราเรดสเปกโทรสโกปี (FT-IR) และเทคนิคโปรตอนนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี (^1H NMR) จากผลการวิเคราะห์ยืนยันว่าไคโตซานทำปฏิกิริยากับฟทาสิกแอนไฮไดรด์ได้ โดยพบพีกของหมู่คาร์บอนิลเอไมด์ที่ตำแหน่ง 1640 cm^{-1} และพีกหมู่อมิโนลดลงเมื่อใช้ปริมาณฟทาสิกแอนไฮไดรด์เพิ่มขึ้น และจากผลของ NMR ปรากฏพีกที่ตำแหน่ง 7-8 ppm ซึ่งเป็นพีกของวงอะโรมาติก ทำให้คาดการณ์ได้ว่าไคโตซานดัดแปรมีส่วนที่ไม่ชอบน้ำ และชอบน้ำ โดยส่วนที่ไม่ชอบน้ำ (หมู่ฟทาสิกแอนไฮไดรด์) มีความคล้ายคลึงกับพอลิเอสเตอร์ จึงคาดว่าจะได้ไคโตซานดัดแปรเหมาะสมสำหรับเคลือบบนผิวผ้าพอลิเอสเตอร์ โดยต่อมาจะนำฟทาสิกแอนไฮไดรด์มาตกแต่งผ้าพอลิเอสเตอร์ด้วยเครื่องจุ่มอัด ที่ตั้งแรงอัดไว้ที่ 80 เปอร์เซ็นต์ (% wet pick up) และทำการอบแห้งโดยอาศัยเครื่อง mini stenter ที่อุณหภูมิ 180-200 องศาเซลเซียส เป็นเวลา 3 นาที

ผ้าพอลิเอสเตอร์ที่ผ่านการตกแต่งถูกนำมาทดสอบหาความสามารถในการดูดซับความชื้น ความสามารถในการเปียก และคุณลักษณะผิวของเส้นใยหลังการเคลือบ และหลังการซักด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) จากผลการทดลองพบว่า ฟทาสิกแอนไฮไดรด์ไคโตซานสามารถยึดติดได้ดีกว่าไคโตซานที่ยังไม่ได้ดัดแปร จึงเป็นการยืนยันว่าส่วนฟทาสิกแอนไฮไดรด์ของฟทาสิกแอนไฮไดรด์ไคโตซานมีบทบาทในการช่วยยึดติดของฟทาสิกแอนไฮไดรด์ไคโตซานบนผิวผ้าพอลิเอสเตอร์ นอกจากนี้จากการทดสอบความสามารถในการเปียกยังพบว่า ผ้าพอลิเอสเตอร์ที่ผ่านการตกแต่งด้วยไคโตซานดัดแปรสามารถเปียกน้ำได้ดีกว่าผ้าพอลิเอสเตอร์ที่ยังไม่ได้ผ่านการตกแต่ง และผ้าพอลิเอสเตอร์ที่ผ่านการตกแต่งด้วยไคโตซานที่ยังไม่ได้ดัดแปร จากผลการทดลองพบว่า การใช้ฟทาสิกแอนไฮไดรด์ไคโตซาน ซึ่งเตรียมจากการใช้ไคโตซานที่มีน้ำหนักโมเลกุล 10^6 ด้วยอัตราส่วนของไคโตซาน:ฟทาสิกแอนไฮไดรด์ = 1:18 ความเข้มข้น 9 กรัม/ลิตร และใช้อุณหภูมิในการอบแห้งที่ 190 องศาเซลเซียส เป็นเวลา 3 นาที เป็นภาวะที่เหมาะสมในการตกแต่งผ้าพอลิเอสเตอร์ให้มีสมบัติชอบน้ำ

ภาควิชาวัสดุศาสตร์ลายมือชื่อนิติดี.....
 สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอลายมือชื่ออาจารย์ที่ปรึกษา.....
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KEY WORD: PHTHALOYL CHITOSAN/ POLYESTER FABRIC/ WETTABILITY

DUANGKAMON VIBOONRATANASRI: HYDROPHILIC FINISHING OF POLYESTER FABRIC WITH MODIFIED CHITOSAN. THESIS ADVISOR: ASSOC. PROF. KAWEE SRIKUKIT, Ph.D, THESIS COADVISOR: MISS PRENEE RATTANAWALEEDIROJN, 66 pp. ISBN 974-53-1670-9.

The modified chitosan was prepared by the reaction of chitosan (molecular weight = 10^5 and 10^6) with phthalic anhydride using the chitosan : phthalic anhydride mole ratio of 1 : 12 and 1 : 18. Characterizations of the produced phthaloyl chitosan by FTIR and ^1H NMR confirmed the successful reaction as evidenced by the presence of carbonyl amide band (1640 cm^{-1}), the decrease in NH_2 band due to its conversion, and the NMR signal of the aromatic ring at 7-8 ppm, respectively. As a result of introduction of the phthaloyl moiety, the modified chitosan was expected to become both hydrophobically and hydrophilically. Furthermore, this group is resemble to the poly(ethylene terephthalate) (PET) aromatic segment, making the modified chitosan suitable for surface coating of PET fabric. After that, the obtained phthaloyl chitosan was applied onto PET fabric using a pad mangle to obtain 80% of wet pick up and was thermofixed in a mini stenter at the temperature between $180\text{-}200^\circ\text{C}$ for 3 minutes.

The finished polyester fabrics were subjected to an evaluation of moisture regain, wettability, as well as surface examination using scanning electron microscopy (SEM). From SEM evidence, the phthaloyl chitosan could exhibit better adhesion performance when compared to the unmodified chitosan finished polyester. This confirmed that the phthaloyl moiety of the modified chitosan played the determined role in controlling the adhesion ability of the phthaloyl chitosan. Wettability test showed that wetness of treated fabric with modified chitosan improved significantly when compared to untreated polyester fabric and treated polyester fabric with unmodified chitosan. It was found that using phthaloyl chitosan (prepared with the mole ratio of chitosan ($M_w=10^6$):phthalic anhydride 1:18) with the concentration of 9 g/l and curing temperature at 190°C for 3 minutes was the optimum condition for hydrophilic finishing of polyester fabric in this experiment.

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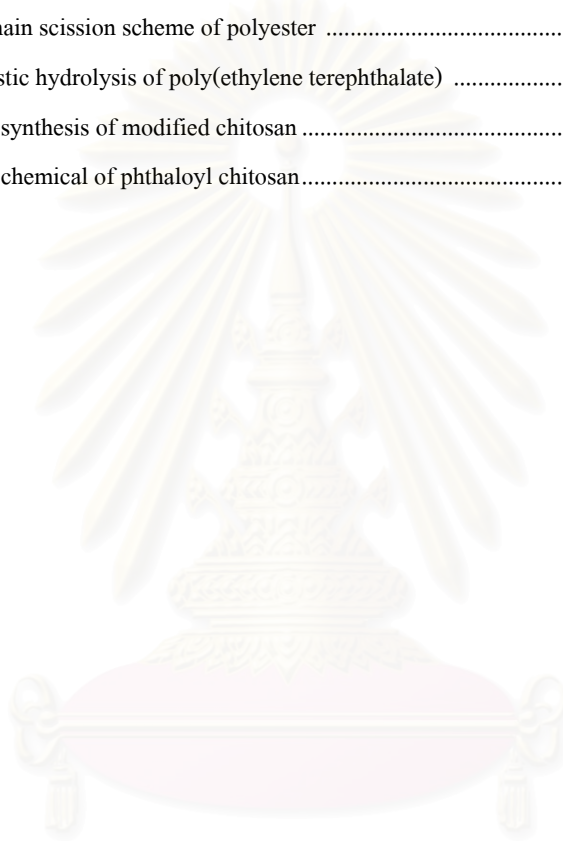
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CHAPTER I

Introduction

Thermoplastic synthetic fibers, typically polyester are widely used mainly for clothing and industrial applications since they are excellent in mechanical properties, chemical resistance, heat resistance, etc. However, due to the hydrophobicity of polyester in nature, the properties associated with hydrophilic characteristic such as antistatic property, sweat-absorbing properties and soil-releasing property which are suitable for producing clothes are restricted [1].

Polyester fabrics used in direct contact with or near the skin as innerwear, intermediate wear, sports wear, are inferior to natural fibers in the feeling of comfort since perspiration from the skin makes the wearer feel stuffy and sticky. Moreover, polyesters are more electrostatic than other fibers in heat-sensitive group [2]. Static is characteristic of fibers that have low moisture absorbency. Static is very annoying since it causes clothes to cling to each other. The disadvantages of static causes lint fiber attract to the surface of fabric so that it is difficult to keep dark-colored fabrics looking neat.

To eliminate these disadvantages, many methods have been improved in commerce. For example, blends of cotton, rayon, wool or linen with polyester textured filament yarn [3]. These are limited when dyeing process. Moreover, the controls of static build-up on polyester fabrics are done by increasing ammonium compounds, commercially available as fabric softeners to help controlling static [4], but most finishes are not durable.

Research and development activities for improving the surface of polyester such as the production of multicomponent fibers or sheath/core fibers [5-7], sea/land fibers [8-10] have attracted much attention. The cross-section of these fibers indicates two layers. The out layer (sheath) is hydrophilic-hydrophobic copolymer which is more hydrophilic in order to absorb moisture and dissipate static charge, where as, the inner layer (core) has only hydrophobic properties. The production of this kind of fibers requires sophisticated technology. The other disadvantages of these fabrics are the problem of dyeing due to the difference in hydrophilic-hydrophobic copolymer and the problem of reduction in color fastness.

In addition, the method of grafting hydrophilic copolymer or hydrophobic copolymer onto the surface of polyester, for example, the grafting of acrylic acid, poly(acrylic acid) or ethyl acrylate onto polyester using benzoyl peroxide initiator [11]. An improved efficiency of grafting

copolymerization may be achieved by pretreatment of polyester prior to grafting. Study of glow discharge plasma [12] or swelling assist treatment [13] of polyester shows the better wettability and dissipability of static charge. However, the disadvantages of graft copolymerization by some techniques are that it consumes treatment time and is not appropriate for applying to polyester fabrics in the view of commercial interests.

Alternative approach in improving hydrophilicity of polyester is by hydrolysis of polyester using alkali such as sodium hydroxide [14], or enzyme such as lipase [15]. Coating polyester surface by antistatic layer such as silver halide also improves [16].

Recently research has reported an attempt to use natural materials such as chitosan for improving antistatic of polyester. Since the chitosan has free amine groups, it was possible to crosslink them with the hydroxyl groups functionalized polyester using a catalyst and some diacids to produce an antistatic finish. After the polyester was crosslinked, electrostatic voltage was found to decrease than untreated polyester, which is greater than the possible hydrophilic contribution of chitosan.

Thus, the purpose of this thesis is to improve wettability of polyester fabrics by coating modified chitosan onto the surface of polyester fabrics in order to achieve the permanent hydrophilicity. The modifier used in this study is phthaloyl chitosan, which contains hydrophobic and hydrophilic parts. The presence of the phthaloyl group is attributed to the hydrophobic characteristic. Therefore, it is expected that this moiety would physically attach to polyester surface, hence allowing the durable adhesion of chitosan on the fiber surface.

The scope of this research will be focused on the synthesis and characterization of the modified chitosan, the effect of application factors affecting the adhesion capability of the modifier on the polyester surface, and finally the evaluation of surface properties of modified polyester such as moisture regain, wettability and adhesion ability of the modified chitosan.

CHAPTER II

Literature Review

2.1 History of polyester fibers

The groundwork for the development of polyester fibers was laid by Dr. W. H. Carothers in his experiments with giant molecular structure. Dr. Carothers had published research information on polyester, and after studying his works, British research chemists decided to examine the possibilities of polyesters. During the period from 1939 to 1941, investigations were conducted in the laboratories of the Calico Printers Association, Ltd., by J. R. Whinfield, J. T. Dickson, W. K. Birtwhistle, and C. G. Ritchie. The work resulted in the development of a polyester fiber known in Britain as Terylene. In 1946, E. I. Du Pont de Nemours & Co., purchased the exclusive rights to produce this polyester fiber in the United States. Having conducted intensive development work, by 1951, Du Pont was commercially producing the fiber, which is called Dacron.

Subsequently, other companies became interested in polyester fiber. In 1958, Eastman Chemical Products, Inc., announced its own version of polyester, which is called Kodel. The following year, the Celanese Corp. of America obtained licenses to use certain patents owned by Du Pont and entered the market with a polyester called Fortrel, which is now sold by the Celanese affiliate, Celanese Fibers Marketing Co.

In 1966, American Enka Co. announced its Enka polyester fiber and Chemstrand Co., now Monsanto Textiles Co., introduced its Blue "C" polyester fiber, but subsequently discontinued this and other filament fibers in favor of certain staple polyester fibers such as Spectran. In 1967, the American Viscose Division of FMC Corp. (now Avtex Fibers Inc.) introduced its Fiber 200 polyester with the trademark Avilin, and Hoechst Fibers, Inc., (now Hoechst Fibers Industries) an outgrowth of an alliance between Hercules, Inc., and Farberwerke Hoechst AG, presented its Trevira polyester fibers. Since then, additional companies entered the polyester competition. The polyester fibers may be primarily divided into two varieties: PET poly (ethylene telephthalate) and PCDT poly (-1, 4-cyclohexylene-dimethylene telephthalate) [17]. The comparison of PET and PCDT fiber may be written in Table 2.1 [4].

Table 2.1 Comparison of PET and PCDT fibers [4]

Fiber	PET	PCDT
Formula	$\left[\text{CO}-\text{C}_6\text{H}_4-\text{COO}-(\text{CH}_2)_2\text{O} \right]_n$	$\left[-\text{OCH}_2-\text{C}_6\text{H}_{10}-\text{CH}_2\text{OCO}-\text{C}_6\text{H}_4-\text{CO}- \right]_r$
Commercial names	Avilin, Dacron, Fortrel, Kodel IV, Trevira	Kodel II
Processing	Filaments are hot drawn	Drawn at higher temperature
Type of fiber produce	Filament or staple Textured yarns	Staple and low pilling
Physical properties	Stronger, resistant to abrasion Higher density (1.38) Lower melting point (480° F)	More elastic Greater bulking properties Greater resiliency Lower density (1.22) Higher melting point (540° F)

2.2 Polyester manufacture

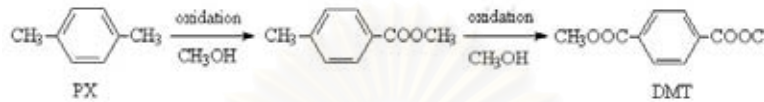
Polyethylene terephthalate is made by the condensation of terephthalic acid (TA) or a derivative such as dimethyl ester (DMT) with ethylene glycol. The polymer is melted and extruded (spun) through a spinneret, forming filaments and stretching the filaments to several times their original length, forming an oriented semicrystalline structure and imparting the desired physical properties. For copolyesters or other polyesters such as polybutylene terephthalate (PBT), the process is similar to the standard PET process with only minor modification.

2.2.1 Raw materials and synthesis procedure

(a) Terephthalic acid (TA)

Terephthalic acid is made from para-xylene, which must be free from the ortho and meta isomers. The para-xylene comes from the C8 fraction of the naphtha that is distilled from the petroleum. At one time it could not be separated from the ortho and meta isomers by distillation, because the boiling points of all three are very close together; it was in practice separated by crystallisation: p-xylene freezes at 13° C., m-xylene at -48° C. And o-xylene at -25° C. Nitric acid oxidation of the p-xylene is used by Du Pont; at a temperature

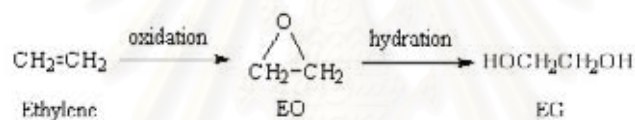
of 220°C. under the pressure of 30 atm. to maintain liquid conditions with the yield of 80-90 % of terephthalic acid. An alternative which is probably used in the U.K. is to oxidize the p-xylene with air at 200°C using cobalt toluate as a catalyst. The first product is toluic acid which is esterified to methyl toluate further oxidized to give monomethyl terephthalate. Monomethyl terephthalate or the terephthalic acid from the nitric acid process is converted into dimethyl terephthalate. The DMT process is shown in Scheme 2.1 [18].



Scheme 2.1 The DMT Process [18]

(b) Ethylene glycol

Ethylene is obtained from petroleum cracking, which is catalytically oxidized with air to ethylene oxide, which is hydrated to ethylene glycol in Scheme 2.2 [18].

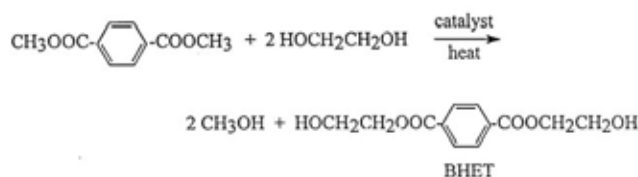


Scheme 2.2 The process of acid hydrolysis for producing ethylene glycol (EG) [18]

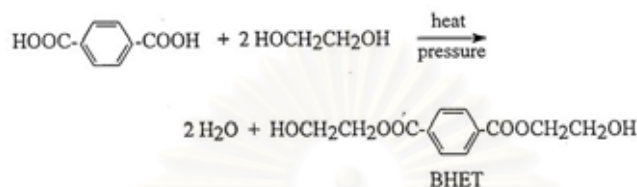
(c) Polymerization

The polyester is produced commercially in two steps: monomer formation by ester interchange of DMT with glycol or esterification of TA with glycol, followed by polycondensation by removing excess glycol to promote chain extension (Schemes 2.3, 2.4 and 2.5) [19]

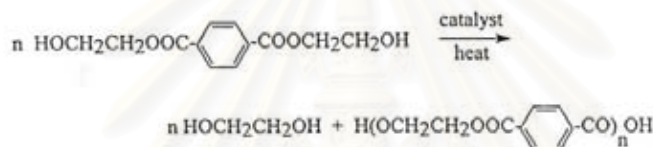
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Scheme 2.3 Ester interchange [19]



Scheme 2.4 Esterification [19]



Scheme 2.5 Polymerization of polyester [19]

The monomer is formed by the catalyzed ester interchange reaction between molten DMT and glycol at 200 °C and atmospheric pressure. A mixture of mostly bis-β-hydroxyethyl terephthalate (BHET), very low molecular weight polymer, and by product methanol is obtained; the methanol is distilled off and recovered. Catalysts include divalent salts of manganese, cobalt, magnesium, zinc, or calcium. In the direct esterification of TA, the carboxyl groups of TA catalyse the reaction and no added catalyst is required. Higher temperature and pressure increase the reaction rate. The monomer, which is the same from both methods except for some small end-group differences, is polymerized, usually in the presence of an antimony catalyst; other catalysts, such as compound of titanium and germanium, are used to a limited extent. Additives such as TiO₂ can be added at the different steps of the process. To promote chain extension, the excess glycol is removed from the highly viscous melt at ca 280 Pa (1.5 mm Hg). Heating is continued at this temperature until the desired degree of condensation is obtained. The molecular weight is

usually controlled by determination of melt viscosity, frequently using the power input to the agitator as an indicator. Side reactions also occur; the esterification of ethylene glycol gives 3-oxapentamethylene glycol (diethylene glycol), which becomes incorporated into the polymer chain and lowers the softening point of the polymer. By product formation of cyclic oligomers such as trimers and tetramers of TA and glycol also occur in minor amounts, depending on reaction conditions.

More recently, pure terephthalic acid (PTA) has replaced DMT as the raw material because of advantages in processing, handling, and polymer quality, as well as reduced production costs. Capital costs and energy consumption are lower, and there is less excess glycol. Reaction efficiencies are better. The storage life of PTA is practically indefinite, and storage and inventory costs are lower (15% less on a weight basis). No catalyst or methanol is needed. However, the choice is also influenced by availability of the raw materials and the size of the operation; small-scale plants tend to favor DMT.

The starting products are polymerized at high temperatures and then filtered to remove any impurities. The molten polymer may be spun directly, or it may be extruded, cooled, and cut into small pellets or chips, which can be stored for later extrusion.

During the extrusion step, the molten polymer (or remelted chips) is metered through a spinneret. The filaments solidify in cooling air and are taken up on large bobbins, or pirns. The filaments must be drawn to orient the polymer and develop the fiber properties of the filament. The fiber may be completely drawn after extrusion, or it may be partially drawn to form a partially oriented yarn (POY). Filaments intended for staple fibers or untextured at later processing step may be produced as POY. Careful control of the drawing process is required to produce the tenacity and elongation required by the customer. The processes in polyester manufacture are shown in Figure 2.1 [19] and Figure 2.2 [20]

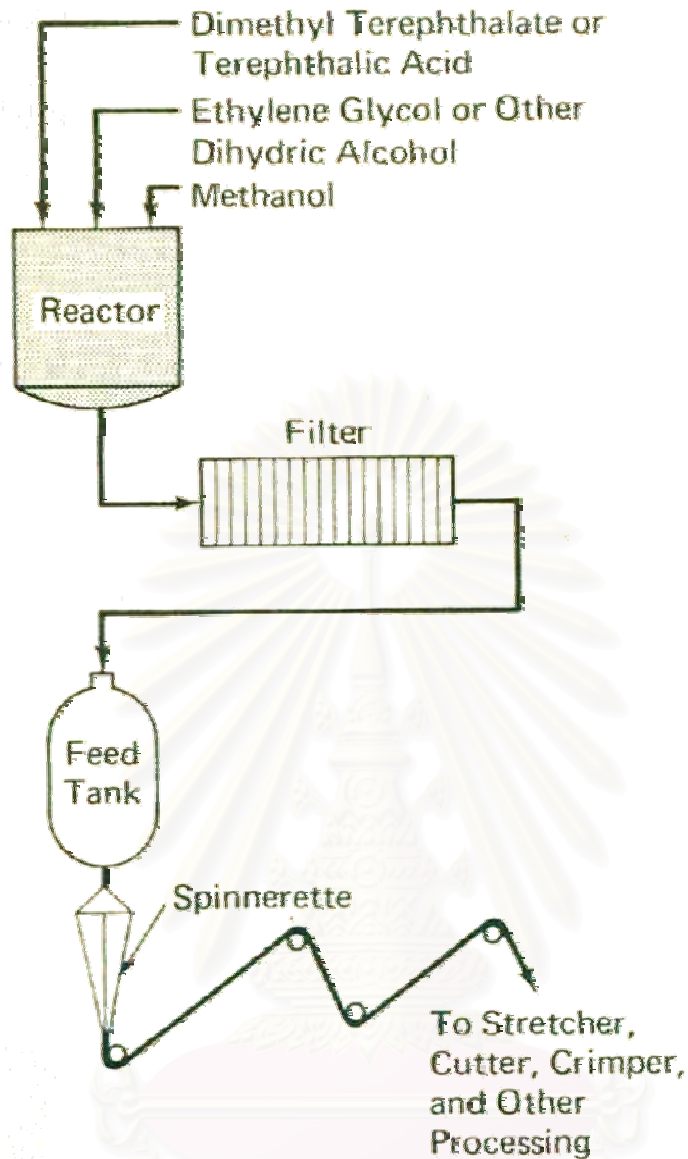


Figure 2.1 Flow diagram for the process used to manufacture polyester [19]

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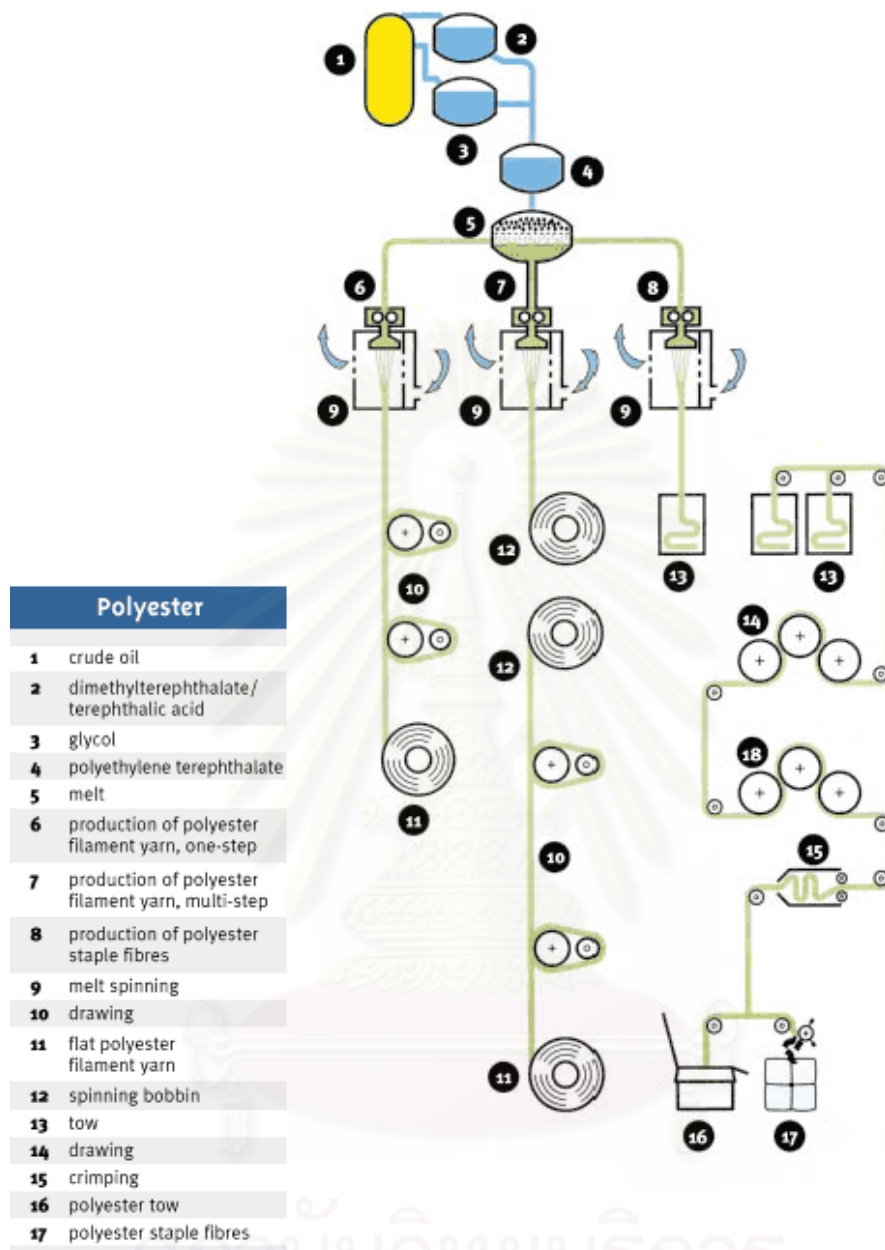


Figure 2.2 Polyester fiber manufacturing processes [20]

2.3 Properties: Mechanical physical and chemical properties

2.3.1 Tensile properties

The strength of the fiber ranges from 2.5 to 9.5 grams per denier (g/d). The tenacity of polycarbonate is approximately 4.5 g/d. Fibers with tenacities of 2.5 to 3.5 g/d are used almost exclusively for apparel. Yarns made from microdenier fibers have lower tensile strength than comparable denier yarns made from conventional polyesters. The fibers with tenacity over 7 g/d are used in industrial fabrics. Polyester fibers do not lose strength when it wet [3].

Elongation varies with the type of fiber and ranges from about 10 to 60 percent; polycarbonate fiber elongation is 20 to 45 percent. In general, fibers with high tenacity have low elongation, and low-strength fibers have higher elongation. Elastic recovery of polyesters is very good. Most of the high tenacity polyesters exhibit 100 percent recovery. Some Kodel fibers have lower (75 to 95 percent) recovery [3].

One of the most unpleasant deficiencies which had not been predicted when first using synthetic fibers for textile purpose by which presented manufacturers of synthetic fibers and textile experts with problems and which is still not completely resolved, is 'pill' formation. 'Pilling' denotes formation of pills or small fiber balls, also called neps or slubs, which form on textiles due to the migration of fiber ends from the textile and which are particularly annoying with apparel textiles. They impair the appearance of garments so markedly that the wearer, for aesthetic reasons, ultimately dispenses with them, although there is plenty of wear still left in them. Fabrics made from polyamide blends exhibit more pronounced pill formation than other blended yarns [21].

2.3.2 Density

The density of most polyesters is 1.38 g/cm^3 . The 200-series Kodel fibers have lower density (1.23 g/cm^3). The density of PEB polyesters is about 1.34 g/cm^3 , and that of the polycarbonates is 1.23 g/cm^3 . Fiber has been heavily delustered with TiO_2 may have a density of about 1.4. The low mass of polyester means that fabrics made from it will be light. Because heavier fabrics tend to give a better drape, some attempts have been made to increase the weight of polyester. Kuraray of Japan has added a ceramic component to one of its fibers to produce a specific gravity of about 1.5 [3].

2.3.3 Moisture

Polyester fibers have very low moisture regain of 0.4 percent at standard conditions. Even at 95 to 100 percent relative humidity, the moisture content is only 0.6 to 0.8 percent. The low moisture pick up of the fibers makes them quick-drying and at times difficult to process. Low moisture levels are also associated with a high buildup of static electricity. As with nylon, care must be taken with polyester fibers in environments when static buildup will present the problems [3].

2.3.4 Thermal properties

Polyester fibers melt at temperatures from 238 to 290 °C (460 to 554 °F). As the fiber melts, it forms gray or tawny-colored bead that is hard and noncrushable.

When it is burnt, the fiber produces dark smoke and acrid odor and (like nylon) exhibits a melt-drip characteristic. The burning polymer falls away from the unignited material and self-extinguishes.

The T_g of polyester is 80 °C. The fiber is easily molded with heat, a property that has made it the ideal fiber for producing textured yarns. Care must be taken in heat-setting polyester yarns and fabrics. Materials that are not properly heat-set will shrink in laundering and lose creases that were thought to have been permanently set in place.

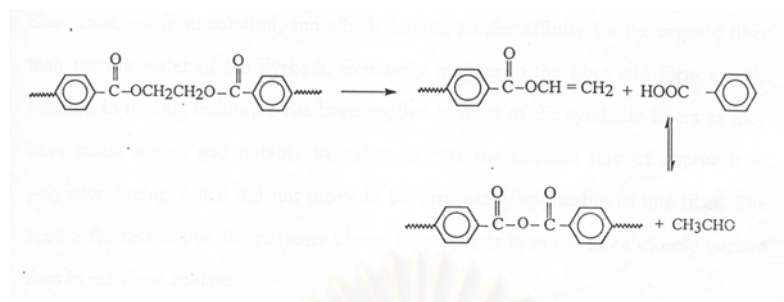
Polyesters retain 70 to 80 percent of their strength following prolonged exposure to 150 °C (250 to 300 °F); at lower temperatures there is minimal or no loss of strength. At temperatures above 150 °C, strength loss occurs rapidly. Some polymer types may be more heat-resistant than other.

The safe ironing temperatures of polyester are listed as 120 to 150 °C (250 to 300 °F). Lightweight fabrics should be ironed at the lower temperature [3].

The thermal degradation of polyester and model compounds proceeds by a molecular mechanism with random chain scission at ester link, although a radical mechanism has also been proposed.

The degradation product can undergo further changes, but at ordinary processing temperatures, a certain proportion of carboxyl end groups is introduced into the polymer structure. Color formation upon degradation has been attributed to the formation of

polyenaldehyde and from a further breakdown of poly(vinyl ester). A chain scission scheme is shown below (Scheme 2.6) [19].



Scheme 2.6 A chain scission scheme of polyester [19]

2.3.5 Chemical properties

Polyesters have very good resistance to weak acids and alkalies, even at high temperatures. Strong alkalies weaken the fiber at room temperature and quickly degrade it at elevated temperatures. The resistance to strong acids at room temperature is good. Prolonged exposure to boiling hydrochloric acid or 96 percent sulfuric acid disintegrates the fiber. The Kodel 200 fibers are more resistant to acids and alkalies than the others. Hot m-cresol is used to dissolve the fiber in fiber identification tests, and certain mixtures of phenol with trichlorophenol or tetrachloroethane also dissolve it.

2.4 Difficulties of polyester in processing and use of polyester textiles [21]

Despite the many and generally acclaimed desirable properties of polyester fibers, many requirements of the finishers and consumers have not as yet been satisfied; the accomplishment of these will determine the research and development program in all stages from raw material to end-product for many years to come.

2.4.1 Electrostatic charges

The characteristic of polyester is hydrophobicity, it does not absorb water or moisture well. As a result, friction can cause static electricity to occur. (Electric resistivity of natural fiber is 10^9 to $10^{10}\Omega\cdot\text{cm}$) This static electricity causes electric shock, fiber contamination during textile finishing, malfunction of electric devices such as

computers, explosions caused by its ignition of materials, close adhesion between clothes and human skin, and other mishaps.

2.4.2 Moisture content absorption

The low moisture sorption of polyester fiber poses both advantage and disadvantage. The advantage of low moisture sorption is the very rapid drying of garments after laundering. However, the strong hydrophobic character of polyester fibers frequently is a disadvantage. The low moisture sorption or absorbtivity of polyester textiles, however, gives rise to a further disadvantage which must be taken into account in the manufacture of garments: polyester fabrics impair or inhibit perspiration, since they do not absorb this and thus cannot conduct it towards the exterior where it can evaporate. This phenomenon is especially pronounced with pure, i.e. 100 percent, tight polyester fabrics. This disadvantage must and can be surmounted by the textile manufactures namely by producing garments which are worn near to the body (underwear) in a very loose woven or knitted construction or, in the case of outer garments, by not using pure polyester yarn but polyester blended with other yarn; (i.e. cotton rayon) this will satisfy the physiological requirements of normal body perspiration.

2.4.3 Dyeing difficulties

The main difficulties consisted, on the one hand, in discovering suitable dyestuffs and, on the other, in finding a satisfactory process with which to apply the dyestuffs to polyester fibers so as to ensure the necessary durability, light and wash fastness.

Even though many coloring difficulties which existed a few years ago have been surmounted and it is nowadays possible to produce dyeing or printing on polyester or polyester-blend fabrics in the various stages of manufacture which satisfies fastness requirements, a polyester fiber must still be regarded as one of the fibers which it is difficult to dye. The necessity to the manufacturer of polyester textiles for material and installation; they are thus, e.g., higher than those incurred by textile finishers of natural fibers. However, one consideration must be taken into account: dyeing processes for

natural fibers have been developed in the course of centuries, whilst experience with dyeing of polyester fiber has accumulated only within the last 5 to 10 years. In view of the brief duration of this development, the achievements are very considerable because nowadays it is possible to carry out adequate dyeing of polyester-wool or polyester-cotton blends in a one-bath process. In the course of the vigorous development of our modern science and technology, new possibilities will be found to reduce the still relatively high expenditure involved in the dyeing of polyester textiles.

2.5 Previous research works on an attempt to improve the wettability of polyester fibers

It is known that, because of their excellent physical properties, polyester fibers are recently utilized for a wide variety of purposes not only for manufacturing inner-wears and outer-wears but also for making household goods such as bed sheets and carpets. However, polyesters are disadvantageous in that they are hydrophobic and, when used in the form of apparel, they present only a limited sweat absorbing property and hence give a stuffy easily, and are readily charged with electricity so that they attract dust. To eliminate these disadvantage, surface wettability of polyester leads to changes in surface performance particularly water absorbency and antistatic dissipation. Several methods including multicomponent fiber production, hydrolysis of polyester fibers, graft polymerization and hydrophilic etc. have been studied.

2.5.1 Multicomponent fibers

Japanese Patent Laid-Open No. 51-136924 [22] proposed a sheath-core type conjugated staple fiber with a hydrophilic polyester as the core component and a non-hydrophilic polyester as the sheath component. The hydrophilic polyester used was a polyalkylene glycol copolymer or a polyalkylene glycol copolymer mixed with sulphonic acid or acid phosphonic ester derivatives and it was intended to increase enhancing water absorbability for both ends of the staple fiber. However, the present inventors found that even though the staple fiber was improved in water absorbability, it was not improved in moisture absorbability.

Japanese Patent Laid-Open No. 51-11116 [23] proposed an antistatic conjugated fiber of sheath-core type with a specific polyester ester as the core component. However,

the intended effect was to make the fiber antistatic, and since a polyester obtained by copolymerizing a polyalkylene glycol alone was used as the core component, the tensile properties (strength-elongation characteristic) of the fiber are adversely affected. Furthermore, due to losing structure the sheath/core polyester is easily dyed lower the fastness properties is impaired.

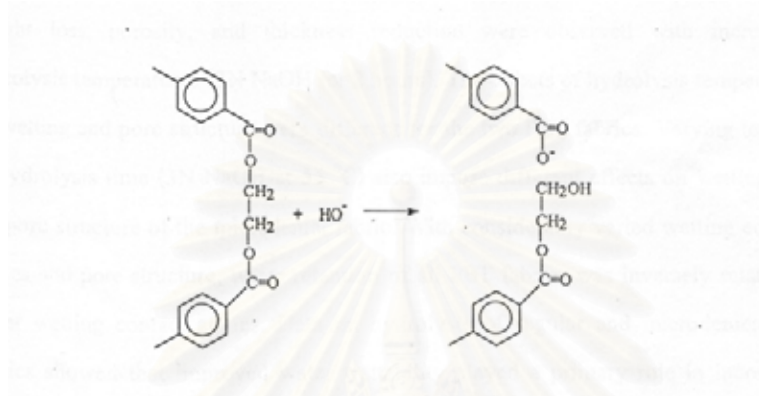
The research and development by Blackwell [5] who introduced a process for producing multicomponent fibers provides a dispersion of a particulate additive or chemical compound such as antistatic agent in a nonaqueous liquid carrier, forms a blend of a first thermoplastic polymer such as polyester fibers and the dispersion by injection the dispersion into an extruder which is part of a fiber extrusion apparatus and which extruder is extruding the first thermoplastic polymer. Then forming a blend of the additive in the first thermoplastic polymer. They provides a second thermoplastic polymer to the fiber extrusion apparatus, in a preselected, mutually separate relative arrangement, directs the arrangement of blend and the second thermoplastic polymer to two spinneret which is a part of a fiber the extrusion apparatus while maintaining the preselected, mutually separated relative arrangement. Extrudes the directed arrangement of the blend and the second molten polymer through the spinneret to form multicomponent fiber, and additives the multicomponent fibers.

Tanoke et al. [7] introduced the conductive composite filament and process for producing the same. A highly oriented, undrawn, conductive, composite filament was provided. This filament was white or colorless and had antistatic properties durable over a long period when clothing utilizing the fiber were actually put on and washed. The filament was a sheath-core composite filament comprising a sheath of a fiber-forming thermoplastic polymer (polyester) and a core of a composition comprising a conductive material which comprised a conductive metal oxide.

2.5.2 Hydrolysis treatment of polyester fibers

Norman R. H. et al. [22] proposed the surface hydrolysis described as a method to increase the hydrophilicity of polyester fabric. Through the action of a caustic solution

at elevated temperatures, portions of the polyester molecules are cleaved to produce terminal hydroxyl and carboxylate groups, as depicted in Scheme 2.7 [22]. The reaction can be accelerated by the addition of quaternary ammonium salts to the bath. Even if further hydrolysis were to occur in laundering, the new groups generated would be identical with those initially present, so no net charge would result. As was mentioned earlier, hydrolyzed polyester provides better adhesion for a variety of topical finishes.



Scheme 2.7 Caustic hydrolysis of poly(ethylene terephthalate) [22]

Hsieh Y. L., Cram L. A. [14] studied the enzymatic hydrolysis to improve wetting and absorbency of polyester fabric. The ability of six hydrolyzing enzymes to improve the hydrophilicity of several polyester fabrics was studied. Five of the six lipases improved the water wetting and absorbent properties of regular polyester fabrics more than alkaline hydrolysis under optimal conditions (3 N NaOH at 55 °C for 2 hours). Compared to aqueous hydrolysis, the enzyme reactions were highly effective under more moderate conditions, which were relatively low concentration (0.01 g/l), shorter reaction time (10 minutes), at ambient temperature (25 °C), and no buffer. Improved water wettability is accompanied by full strength and mass from alkaline hydrolysis. The wetting and absorbent properties of sulfonates polyester and microdenier polyester fabrics were also improved by lipases.

Hsieh Y. L., Miller A., Thompson J. et al. [15] proposed the basic hydrolysis by studying the wetting, pore structure, and liquid retention of hydrolyzed polyester fabric.

This study investigated the contributions of surface wetting and pore structure to liquid retention of fibrous materials using regular and microdenier poly(ethylene terephthalate) (PET) fabrics with aqueous sodium hydroxide. Increasing levels of weight loss, porosity, and thickness reduction were observed with increasing hydrolysis temperatures (3 N NaOH for 2 hours). The effects of hydrolysis temperature on wetting and pore structure were different for the two poly(ethylene terephthalate) fabrics. Varying lengths of hydrolysis time (3 N NaOH at 55 °C) also impose different effect on wetting and the pore structure of the microdenier fabric. With considerably varied wetting contact angles and pore structure, water retention of all poly(ethylene terephthalate) fabrics was inversely related to water wetting contact angles. Data on hydrolysis of regular and microdenier poly(ethylene terephthalate) fabrics showed that improved water wettability played a primary role in increasing water retention of these hydrophobic fabrics. Pore size distribution and pore connectivities can be limiting factors in liquid retention of hydrolyzed PET fabrics with modified wetting properties and porosity.

2.5.3 Grafting method

Grafting technique is the technique that introduces different polymer onto any polymeric substrate to achieve additional properties.

Sacak M., and Oflaz F. [24] studied benzoyl-peroxide-initiated graft-copolymerization of poly (ethylene terephthalate) fibers with acrylic acid. The grafting of acrylic acid onto poly(ethylene terephthalate) fibers subjected to no-swelling treatment using benzoyl peroxide was investigated. The temperature was found to increase the graft yield. The graft yield increased up to benzoyl peroxide concentration of 4.0×10^{-3} M and slightly decreases at higher initiator concentrations. The effect of solvents such as dimethylformamide, dimethylsulfoxide, pyridine and some alcohols upon the grafting were examined by carrying out the graft copolymerization at various water/solvent ratios. Pyridine was found to inhibit the grafting totally. The properties of the grafted fibers such as density, diameter, dyeability and moisture regain were also investigated. It was concluded due to the observations made in these properties that the grafting took place mainly in the subsurface regions of the fibers and a diffusion barrier occurred after the

grafting value of 8-9 percent. The overall activation energy for grafting was calculated to be 9.9 kcal/mol.

Buchenska J. [25] proposed the modification of polyester fibers by grafting with poly(acrylic acid). The grafting of acrylic of poly(ethylene terephthalate) using benzoyl peroxide was investigated. The influence of the main parameter of grafting, the effect of additives on the degree of grafting and the amount of homopolymer formed during the process were determined. Furthermore, the values of apparent activation energy was calculated. Also the influence of the degree of grafting on the moisture sorption and swelling of modified fibers were determined. By an additional treatment of the grafted fibers with antibiotics, it was possible to provide the fibers with antibacterial properties.

Meral Karakisla, Mehmet Sacak [26] studied the grafting of ethyl acrylate onto monofilament polyester fibers using benzoyl peroxide. Ethyl acrylate was grafted onto monofilament poly(ethylene terephthalate) fibers using benzoyl peroxide as a chemical initiator. Breaking tenacity and densities of grafted fibers decreased while breaking elongation increased with the graft yield. Scanning electron micrographs showed that the fiber geometry and its diameter were not affected by grafting.

Mehmet Sacak and Meltem Celik [27] studied the grafting of acrylamide onto poly(ethylene terephthalate) fibers using hydrogen peroxide as the redox initiator was investigated. Benzoyl alcohol was found to be the favorite medium for this grafting. Maximum graft yield (7.6 percent) was reached at 95 °C; the graft yield decreased at higher temperatures and finally was inhibited at 120 °C. The effect of monomer and initiator concentrations on grafting was also studied.

Narumon Kanchanapinpong [28] studied the treatment of the hydrophilic / hydrophobic copolymer; the poly(hydroxyethylmethacrylate-co-benzoyl ethyl methacrylate), poly(HEMA-co-BEMA) onto poly(ethylene terephthalate) fabrics. Poly(HEMA-co-BEMA) with hydrophilic:hydrophobic ratio of 32.5:7.5 to 70:30 and their concentration of 25 and 50 percent (o.w.f.) exhibited optimum water wetness.

Moreover, this copolymer could improve the color fastness to heat as result of hydrophilicity modified PET surface.

2.5.4 Coating antistatic agent

Van Paesschen et al. [29] studied the adhesion of hydrophilic layers on polyester filament. The adhesion of hydrophilic layers on a dimensionally stable polyester film support was improved by applying after longitudinal stretching of the polyester film a single adhesive layer thereon. The thus covered polyester film was stretched in transverse direction and heat-setted at 180 °-220 °C. The adhesive layer comprised 30 to 80 percent by weight of a chlorine-containing copolymer, 5 to 30 percent by weight of a gelatin, 5 to 40 percent by weight of a plasticizer for the gelatin and 0 to 30 percent by weight of a metal-complexing antistatic agent. The polyester film may be a film of poly (ethylene terephthalate) and the hydrophilic layer applied to single adhesive layer may be a light-sensitive gelatin silver halide emulsion layer.

Van Paesschen et al. [30] proposed the process of applying antistatic coating compositions to polyester film. In this study, a process was provided for adhering an antistatic layer to a dimensionally stable polyester film support, e.g. a film of poly(ethylene terephthalate). An unstretched or only monoaxially stretched polyester film is applied an antistatic layer from an aqueous coating composition. After drying of the antistatic layer, it was stretched biaxially or in a direction perpendicular to the first stretching operation, together with the polyester film support and thereafter the polyester film was heat-setted. The aqueous coating composition comprises 30 to 80 percent by weight of an electron conductive product, 10 to 40 percent by weight of a stretch-improving agent and 10 to 40 percent by weight of an inert filler material. The polyester film support may be provided on its opposite side with a subbing layer and one or more light-sensitive gelatin silver halide emulsion layer.

Caldwell et al. [31] proposed a textile hydrophilic treatment process which functioned by applying a polymeric coating. The polymeric coating adhered to the fiber by cross-linking a high molecular coating which provided a structured composition with

an insoluble exterior that had the desired hydrophilic properties under conditions of wearing and laundering. The process described in this patent provided a hydrophilic insoluble coating having antistatic and antisoiling properties by coating the fabric with a soluble or solutions containing a polyhydric alcohol and additions polymers of α , β -ethylenically-unsaturated acids. Under the proper conditions, the polyhydric alcohol reacted with the aliphatic polyacid to partially cross-link the polymer to provide and external coating of the fiber. The patentee stated that ester linkages were formed to provide a partially cross-link, flexible polymeric material which functioned very much as an ion exchange resin. The polymeric polybasic acid was cross-link to the extent that it is no longer soluble but some of the acedic ions were available to furnish ions for conducting static charges. The esterification was necessary to provide an insoluble coating with durability to standard laundering conditions. The patentee stated that the hand of the fabric was affected by the amount of the polymeric additive applied so a minimum amount consistent with effective surface characteristic was desirable.

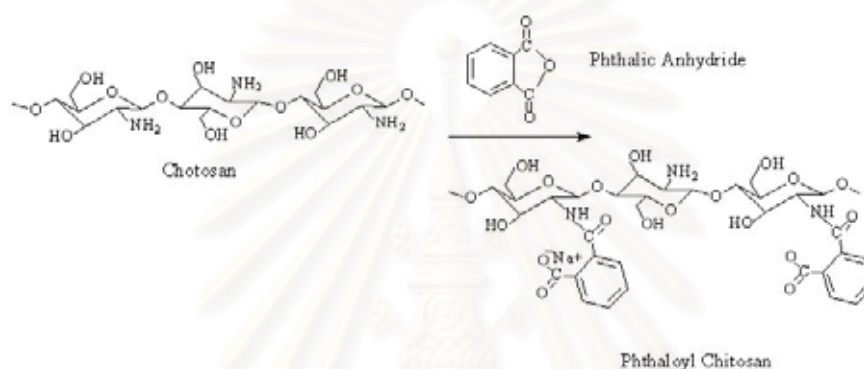
Seong-il Eom [16] proposed using chitosan as an antistatic finish for polyester fabric because polyester fabrics are electrostatic and much research has been conducted to develop antistatic treatments for them. Since polyester has hydroxyl functional groups, it was possible to crosslink them with the amine groups of chitosan using a catalyst and some diacids to produce an antistatic finish. After the polyester was crosslinked, electrostatic voltage was found to decrease below $1/10^{\text{th}}$ of that of untreated polyester, which is greater than the possible hydrophobic contribution of chitosan. Tensile strength of the cured fabric was increased by chitosan crosslinking. But in the case of high weight loss by alkaline treatment, this increase was not sufficient to compensate for the loss of the tensile strength by alkaline hydrolysis.

2.6 Concept of modification of the chitosan to use as finishing agent for polyester fabric

In this experiment, the idea on how to improve surface properties of polyester fabric by coating application of the phthaloyl chitosan having hydrophilic and hydrophobic moieties was explored. The main purpose of this work is to develop simple practicable of polyester surface modification.

Chitosan [(1→4)-2-amino-2-deoxy- β -D-glucan], a new material that appeared in the 1980s, has various and excellent characteristics that can be used for a multitude of purposes: agricultural, nutritional, and pharmaceutical, among other. Using chitosan for various applications in textile field has also been researched, such as improving dyeability, using as an antibacterial finish or developing new, sensible materials. Chitosan shows polyelectrolyte characteristic in solution and high moisture regain even in low relative humidity. [16]

Phthaloyl chitosan was prepared by the reaction of chitosan with phthalic anhydride. Since the phthaloyl group was bulky and hydrophobic; the thus modified chitosan exhibited both hydrophilicity and hydrophobicity.



Scheme 2.8 The synthesis of modified chitosan

The hydrophobic part of modified chitosan is similar to polyester structure. Therefore, it could penetrate into polyester. As a result, it was expected that the modified chitosan could exhibit the durability on the polyester surface. In this experiment, the application of modified chitosan will be carried out using a padding machine. It was anticipated that during treatment at temperatures higher than T_g of polyester, the polymer chains open-up and allow hydrophobic part of the modified chitosan to penetrate fiber surface. The hydrophilic part which differs from the polyester in terms of hydrophobicity still attaches firmly onto the fiber surface. By anchoring the hydrophobic part inside the fiber. It is believed that the modified chitosan can be adhered firmly onto the fiber surface, resulting in imparting the permanent hydrophilic property to the polyester fiber surface; as show in scheme 2.8. The penetration of hydrophobic part into polyester surface could occur during high temperature treatment (thermofixation). It is believed that the hydrophobic part could be absorbed by polyester due to hydrophobic attraction, hence leaving

hydrophilic part onto fiber surface. As a result, surface properties of treated polyester would be notably enhanced. After treatment the surface modification polyester fabric was subjected to evaluation of moisture regain, wettability, surface analysis, washing fastness and antibacterial property.



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CHAPTER III

Experimental

3.1 Materials and Chemicals

- Woven, grey polyester fabric was purchased from Teijin Polyester Company
- Two types of commercial flake grade chitosan with molecular weight (M_w) of 10^6 (approx. 85% degree of deacetylation)and 10^5 (approx. 95% degree of deacetylation) were bought from Biolife co., Ltd. and Seafresh co., Ltd., respectively.
- All chemicals used throughout this work were reagent grade. The details of chemical properties are shown in table below;

Table 3.1 chemicals and their properties used in this experiment.

Chemical	Property	Formula	Source
Acetone	Organ solvent	CH_3COCH_3	Carlo erba
Acetic acid	Organic acid	CH_3COOH	Lab-scan
Sodium Hydroxide Pellet	Alkali	NaOH	Carlo erba
Phthalic anhydride	-	$\text{C}_7\text{H}_4\text{O}_3$	Ajex finechem
Ammonium hydroxide solution	-	NH_4OH	APS finechem
Standard soap (without optical brightening agent)	Detergent	undisclosed	SDC enterprises
Dyes - Indosol Rubinole SF-RGN sgr ,	Direct dyes	undisclosed	Clariant

3.2 Equipment

1. Digital hot plate/ Stirrer, PMC 720 series (Dataplate)
2. Laundering machine, Gyrowash (James H. Heal)
3. Padder machine, Pad-mangle (Labtech Newave Lab Equipments co.,Ltd.)
4. Mini stenter, H.T steamers (Rapid co., Ltd.)
5. Mechanical stirrer, RW 20 (IKA-Labortechnik)
6. Electrical analytical balance, AG 204 (Mettler Toledo)
7. Infrared moisture determination balance, And AD-4715 (A&D co., Ltd.)

8. Fourier-Transform Infrared spectrometer (FT-IR), 1760x (Perkin Elmer)
9. Nuclear Magnetic Resonance spectrometer (NMR), DPX-300 (Bruker Avance)
10. Scanning Electron Microscopy (SEM), JSM-5410 LV (JEOL)
11. Glasswares
 - Beakers
 - Pipettes
 - Volumetric flasks
 - Stirring rods
 - Cylinders
 - Erlenmeyer flasks
 - Dropper

3.3 Preparation of Phthaloyl Chitosan

First, 3 wt% chitosan in 1%(v/v) acetic acid aqueous solution was prepared, while phthalic anhydride was dissolved in warm acetone and stirred for a period of times in order to concentrate the solution. The ratio of chitosan to phthalic anhydride was 1:12 and 1:18 by mole, respectively. Then chitosan solution was slowly poured in concentrated phthalic anhydride solution under vigorous stirring using a magnetic stirrer. After a hour, the pH value of the mixture was quickly adjusted to pH 11 using sodium hydroxide. Chitosan became gel due to its insolubility in the basic condition. Under the continues stirring for 2 hours at room temperature the chitosan underwent the reaction with phathalic anhydride, resulting in the phthaloyl chitosan. The produced phthaloyl chitosan contained the free carboxyl group was in turn soluble in basic condition. After the complete reaction (complete soluble) was observed, the modified chitosan was precipitated in acid condition ($\text{pH} < 3$) by adding acetic acid. The product was filtrated and washed to remove untreated phthalic acid. The obtained phthaoyl chitosan was dissolved again in aqueous ammonium hydroxide solution containing 1 wt% wetting agent and kept as a stock solution for further application onto polyester fabric.

3.4 FT-IR analysis

Infrared spectroscopy is the most widely used technique for identification of organic compounds. Principally, infrared spectroscopy is based on the interaction of infrared radiation with molecular dipole moment in the sample. When a sample compound is placed in the IR beam, it absorbs particular frequencies.

For the Fourier Transform Infrared Spectrometer (Figure 3.1), infrared light from suitable source passes through a scanning Michelson interferometer and Fourier Transformation gives a plot of intensity versus frequency. The interferometer splits a radiation beam into two paths and recombines them so that the intensity variation of the exit beam can be measured by a detector as a function of path difference. The computer controls optical components, collects and stores data, performs computations on data, records the data and displays spectra.

In this experiment, identification of modified chitosan by FT-IR technique was carried out using the transmission technique to obtain IR spectra. The method of sample preparation used in this experiment was performed by dissolving the sample in ammonium hydroxide solution (solvent). Solid films of sample could be achieved by casting modified chitosan solution onto KBr plates and then allowing solvent (ammonium hydroxide solution) to evaporate, if necessary, hair drier was used to quicken evaporation of solvent. The infrared spectra of modified chitosan films were recorded by Perkin Elmer 1760X FT-IR spectrometer. The following parameters were employed; scan range $4,000\text{--}400\text{ cm}^{-1}$. All the spectra were transferred to the computer for further analysis and plotting by Perkin Elmer software.

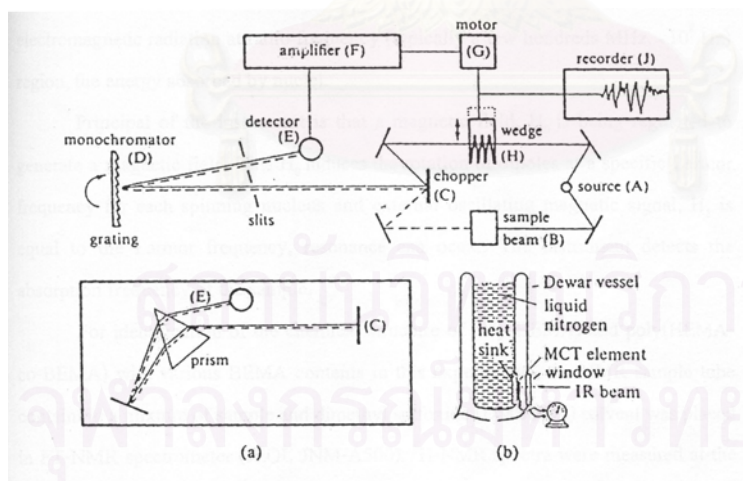


Figure 3.1 Schematic diagram of Fourier Transform Infrared Spectroscopy

3.5 NMR Analysis

Nuclear Magnetic Resonance Spectroscopy (NMR) (Figure 3.2) and is the form of spectroscopy concerning with radio-frequency induced transition between magnetic energy level of atomic nuclei. NMR is an important method for material characterization and for the study of polymer structure-property relationships. NMR signals can be assigned to specific atoms along the polymer backbone and side chains.

The properties of the NMR signals depend on the magnetic environment of the NMR active nuclei, and the local field that they experience.

NMR equipment comprising a magnet, radio frequency oscillator, sample holder and a detector that is capable of producing an electrical signal suitable for display on a recorder or an oscilloscope, or which is suitable for input to a computer.

NMR spectra are absorption spectra which are the results of sample absorbing electromagnetic radiation frequency (typically a few hundreds MHz. $\sim 10^8$ Hz) region, the energy absorbed by nuclei.

Principle of the instrument is that a magnetic field, H_0 is being regulated to generate a magnetic field. This H_0 induces the rotation of dipoles at a specific Larmor frequency for each spinning nucleus and external oscillating magnetic signal, H_1 is equal to the Larmor frequency, resonance can occur. The instrument detects the absorption frequency of the sample.

For identification of the chemical structure of modified chitosan with various phthalic anhydride contents in this experiment. The method of sample preparation used in this experiment was performed by dissolving the sample in ammonium hydroxide solution (solvent). Solid films of sample could be achieved by casting modified chitosan solution onto plates and then allowing solvent (ammonium hydroxide solution) to evaporate, if necessary, oven dried was used to quicken evaporation of solvent. The NMR sample tube containing a mixture of sample film and (D_2O) solvent was placed in NMR spectrometer (DPX-300). 1H -NMR spectra were measured at the radio frequency of ~ 300 MHz.

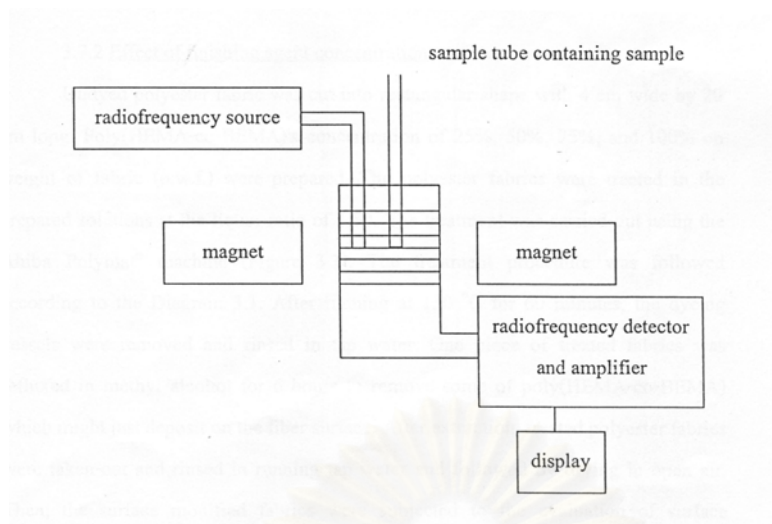


Figure 3.2 Schematic diagram of Nuclear Magnetic Resonance Spectroscopy

3.6 Application of phthaloyl chitosan onto polyester fabric

The phthaloyl chitosan stock solution was diluted to 3, 6 and 9 g/l. The polyester fabric was then treated with the prepared solution using a pad mangle set a pressure nip at 80 percent wet pick up. Then treated polyester fabrics were dried at 100 °C for 5 minutes and cured at 180, 190 and 200 °C for 3 minutes using mini stenter machine. The treated fabrics were washed and dried in open air. Following that, the surface modified fabrics were subjected to the evaluations of surface performance including moisture regain, wettability, surface analysis and antibacterial property.

3.7 Evaluation of properties of treated polyester fabrics

3.7.1 Determination of moisture regain

Moisture regain is the percent weight of moisture based on the dry weight by Infrared moisture determination balance (AND AD-4715). The regain of the material is considered to be the amount of moisture at the 24 hours [32]. (Standard condition: temperature 27 ± 2 °C and relative humidity $65 \pm 2\%$)

$$\text{Percent of moisture regain} = \frac{\text{Original weight} - \text{Dry weight}}{\text{Dry weight}} \times 100$$



Figure 3.3 Infrared moisture determination balance (AND AD-4715)

3.8 Evaluation of wettability of treated polyester fabrics [33]

Wettability was evaluated by moisture wicking test. Cut the polyester fabric samples(untreated, chitosan treated and phthaloyl chitosan treated PET) to size 2.5 x 17.5 cm. Clip the polyester fabric having top and bottom margin 0.6 cm. with a 2-3 g. clip. After that fill 400 ml to 600 ml of 1% dye solution into the 1000 ml beaker. Immerse the edge of the polyester fabric in the beaker of standard color 0.6 cm. in the surface of standard color for 3 minutes and measure the distance of color.

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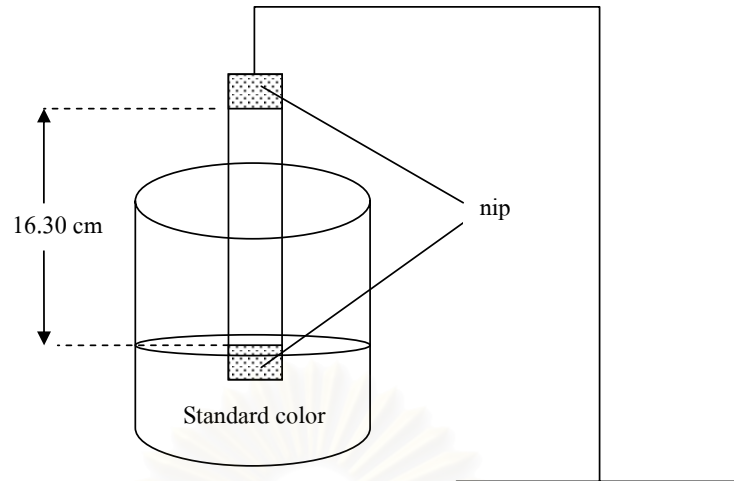


Figure 3.4 Moisture wicking test [33]

3.9 Surface analysis of modified polyester fabric by Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) (Figure 3.5) forms an image by scanning probing across the specimen, the probe is focused electron beam. The probe interacts with a thin surface layer of the specimen, a few micrometers thick at most. The detected signal used to form the TV-type image in the number of low energy secondary electrons emitted from the sample surface [37].

In this experiment, The surface of treated modified polyesters and verify laundering of them were identified by JSM-5410 scanning microscope instrument.

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Figure 3.5 scanning microscope instrument

3.10 Evaluation of laundering of treated polyester fabric [34]

Prepared 0.37% detergent of total volume in 200 ml. of total liquor. Detergent solution and 10 stainless steel balls were added in 500 ml. stainless steel lever lock canister, and preheated at $40 \pm 3^\circ \text{C}$ for at least 2 minutes in laundering machine. After put specimen, size is 50x100 mm. (2.0x4.0 in.), in each canister and ran the laundering machine at 40°C (105°F) and 40 ± 2 rpm. For 45 minutes. Then, kept each test specimen in a separate beaker. Rinsed three times with distilled water at $40 \pm 3^\circ \text{C}$ ($105 \pm 5^\circ \text{F}$) for 1 minute with occasionally stirred or hand squeezed and dried them in the oven ($71^\circ \text{C}/160^\circ \text{F}$). After that analyzed them by SEM.



Figure 3.6 Gyrowash machine

3.11 Antibacterial finishes on textile materials [35]

Apply 1 ± 0.1 ml of *Staphylococcus aureus* inoculum onto fabrics, which are 4.8 ± 0.1 cm in diameter. Use the amount of fabric that will absorb the 1.0 ± 0.1 ml of inoculum. Transfer the swatches to the jar. As soon as possible after inoculation ("0" contact time), add 100 ± 1 ml of neutralizing solution to each of the jars containing the inoculated untreated control swatches and inoculated treated test swatches. Shake the jars vigorously for one minute. Make serial dilutions with water and plate (in duplicate) on nutrient agar. Dilution of 10^{-1} , 10^{-2} , 10^{-3} and 10^{-4} are usually suitable.

Incubate these jars (the inoculated untreated control swatches and inoculated treated test swatches) at $37 \pm 2^{\circ}\text{C}$ for 24 hours (24 hours contact time). Shake the jar vigorously for one minute. Make serial dilutions and plate (in duplicate) on nutrient agar. Dilution of 10^{-1} , 10^{-2} , 10^{-3} and 10^{-4} are usually suitable for treated test fabrics. Incubate all plates (both of "0" and 24 hours contact time) for 24 hours at $37 \pm 2^{\circ}\text{C}$.

Report bacterial counts as the number of bacteria per sample (swatches in jar) not as the number of bacterial per ml of neutralizing solution. Calculate percent reduction of bacteria by the specimen treatments by the following formula.

$$R = \frac{100(B-A)}{B}$$

Where

R = % reduction

A = the number of bacteria recovered from the inoculated treated test specimen swatches in the jar incubated over the desired contact period

B = the number of bacteria recovered from the inoculated treated test specimen swatches in the jar immediately after inoculation (at "0" contact time)

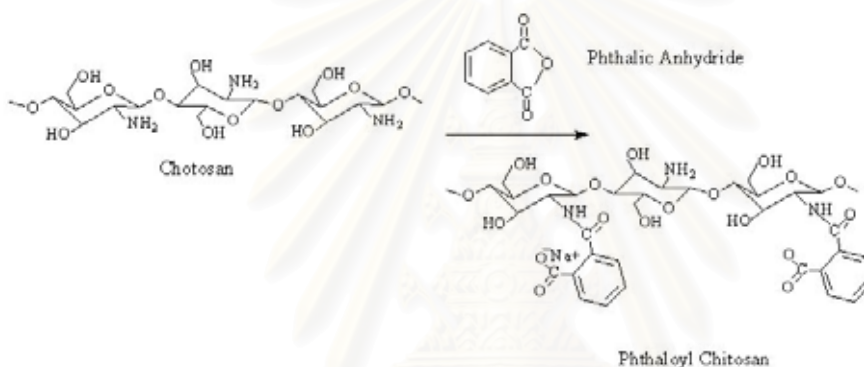
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CHAPTER IV

Results and Discussions

4.1 Synthesis of modified chitosan

The aim of this project was to utilize chitosan as finishing agent for improving wettability of polyester fabric. Chitosan is hydrophilic natural polymer, which has poor adhesion to hydrophobic surface such as polyester. Hence, in this experiment, the hydrophobic group was introduced to the chitosan backbone by the reaction of chitosan free amino group with phthalic anhydride, resulting in the hydrophobically modified chitosan. It would be expected that the modified chitosan could exhibit the better adhesion to polyester surface. The modification of chitosan with phthalic anhydride is represented in the scheme 4.1.



Scheme 4.1 The chemical of phthaloyl chitosan

In a typical modification procedure, chitosan was first dissolved in 1% by volume of acetic acid solution. In the mean time, phthalic anhydride was separately dissolved in acetone. Then, the chitosan solution was slowly added to the phthalic anhydride solution under vigorous stirring. It was observed that colloidal particles of phthalic anhydride were formed and well dispersed in chitosan solution. After the extended stirring to remove acetone, pH value of the mixture was quickly raised to pH 11 by the addition of concentrated NaOH solution. In alkaline condition, the chitosan free amine group existed, then immediately reacting with the phthalic anhydride. As a result, the hydrophobic phthaloyl group was introduced into chitosan backbone via the amide linkage. As can be seen, the phthaloyl chitosan contained the free carboxylic group which could be converted to the carboxylate by pH adjustment. In the carboxylate form, it was

observed that the phthaloyl chitosan was soluble in neutral or alkaline aqueous solution. This phenomenon was totally opposite to the virgin chitosan only which must be dissolved in acidic condition.

From the experiment results, the complete solubility of the phthaloyl chitosan in neutral or alkaline condition was found when using chitosan free amine group to phthalic anhydride mole ratio of at least 1:12. It was assumed that, at this ratio or above, the modified chitosan contained high enough phthaloyl carboxylate groups which enabled chitosan to soluble in alkaline medium. For the subsequent studying the effect of varying the hydrophobic phthaloyl groups on hydrophilic finishing of polyester fabric, the modification of chitosan with the mole ratios of chitosan amine group to phthalic anhydride of 1:12 and 1:18, respectively was carried out. Two types of chitosan, low molecular weight (100,000) and high molecular weight (1,000,000) were selected to investigate the effect of molecular weight of chitosan on the adhesion capability of the modified chitosan on polyester surface.

4.2 FT-IR characterization of the phthaloyl chitosan

FT-IR analysis was carried out in order to confirm the chemical structure of modified chitosan. The infrared spectra of chitosan and the phthaloyl chitosan are showed in figure 4.1. Figure 4.1 sample (I), (II), (III) and (IV) represent the spectrum of phthaloyl chitosan with chitosan ($M_w = 10^6$):phthalic anhydride mole ratio of 1:12, the spectrum of phthaloyl chitosan with chitosan ($M_w = 10^6$):phthalic anhydride mole ratio of 1:18, the spectrum of phthaloyl chitosan with chitosan ($M_w = 10^5$):phthalic anhydride mole ratio of 1:12 and the spectrum of phthaloyl chitosan with chitosan ($M_w = 10^5$):phthalic anhydride mole ratio of 1:18, respectively.

From the spectrum of virgin chitosan, the major characteristic absorption bands are found at 1598 cm^{-1} and 3400 cm^{-1} which are assigned to the -NH_2 bending and (N-H stretching), respectively. Other absorption bands at 1156 cm^{-1} due to asymmetric stretching of the C-O-C bridge) and 1096 cm^{-1} as well as 1031 cm^{-1} due to the skeletal vibration involving the C-O stretching) are characteristics of typical saccharine structure. When considering the spectra of phthaloyl chitosan, new peaks appear at 1710 cm^{-1} and 1640 cm^{-1} which are indicative of chemical bonds arising from the reaction of chitosan. Mostly, these bands are corresponding to the distinctive characteristics of carbonyl group (-C=O) and carbonyl amide bond (-CO-NH). This finding can be assured that the appearance of these new bands arise from the reaction

between chitosan and phthalic anhydride. Further evidence confirming the successful reaction is the change in the peak intensity of NH_2 stretching at 3400 cm^{-1} . As can be seen, the notable decrease in the intensity of this band of the phthaloyl chitosan is obviously observed. Also, the decreasing band intensity is found to be dependent to the chitosan to phthalic anhydride mole ratio; the higher the ratio the more the decrease in the peak intensity of NH_2 stretching. It could be concluded that this fact was strongly related to the conversion of the free NH_2 group to carbonyl amide group as a result of the reaction between chitosan and phthalic anhydride. Following table (Table 4.1) summarizes the infrared absorption peaks found in virgin chitosan and the phthaloyl chitosan.

Table 4.1 The absorption bands of chitosan and phthaloyl chitosan

Peak	Chitosan (cm^{-1})	Phthaloyl chitosan (cm^{-1})
N-H (stretching)	3400	3300
O-H (polymer)	-	3200
carbonyl amide bond (-CO-NH)	-	1640
- NH_2 bending	1598	-
Aromatic ring	-	1560
Bridge oxygen stretching	1156	1156
C-O stretching	1096 and 1030	1096 and 1030

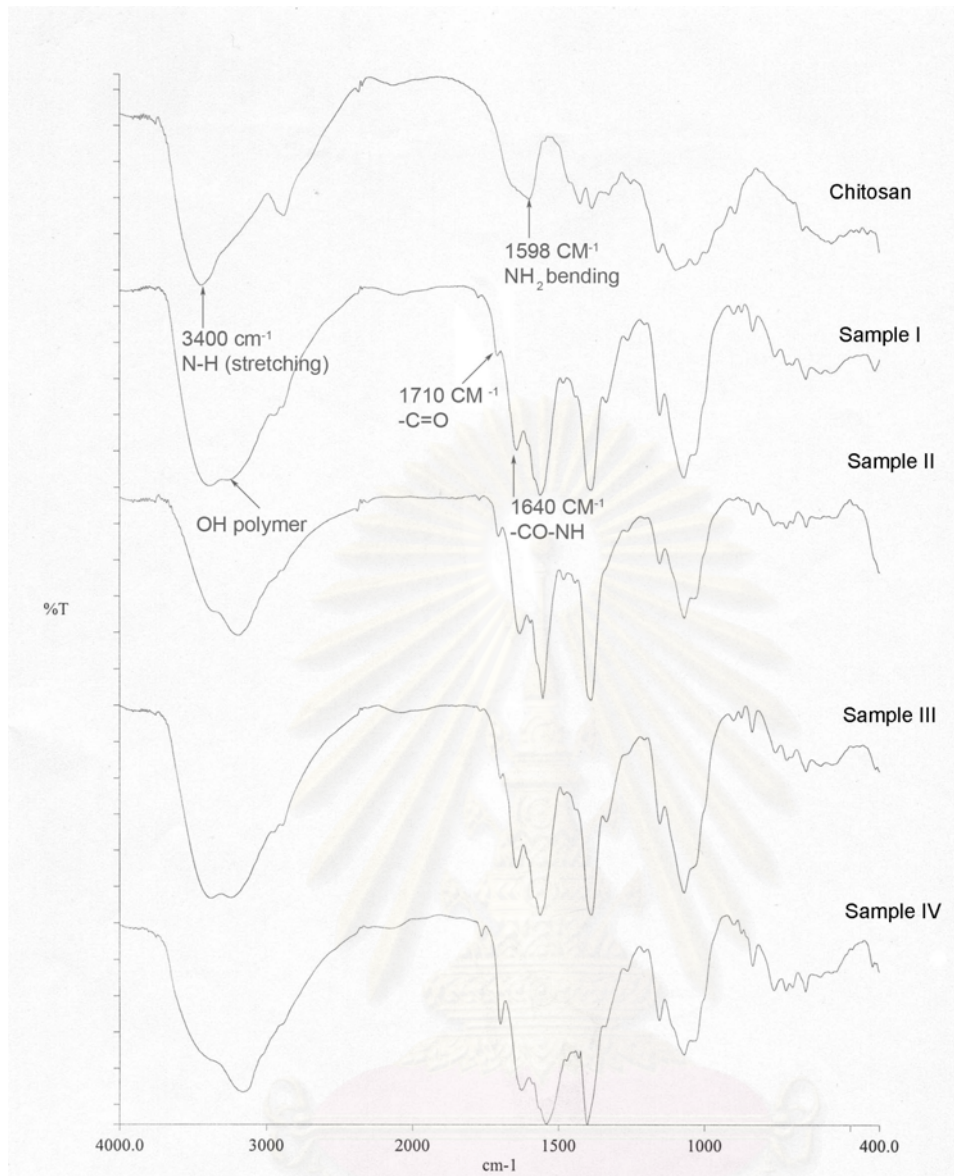


Figure 4.1 The FT-IR spectra of chitosan and phthaloyl chitosan with varying molecular weight of chitosan (M_w) and the mole ratio of chitosan to phthalic anhydride (Sample I, II, III and IV).

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4.3 $^1\text{H-NMR}$ study of modified chitosan

In this experiment, proton NMR analysis was included in order to provide the supportive evidence of the reaction between chitosan and phthalic anhydride. NMR signals of the aromatic protons of the phthaloyl group can be used as the strong evidence further confirming the successful reaction. The $^1\text{H-NMR}$ spectra of the original chitosan and the modified chitosan are given in Figure 4.3 and 4.4, respectively. As can be seen, the NMR spectrum of the virgin chitosan shows the absent signals of aromatic protons reflecting the nature of chitosan which lacks of aromatic ring. On the other hand, the spectrum of the phthaloyl chitosan strongly exhibits the presence of the aromatic ring which typically gives the NMR signals at 7-8 ppm (Figure 4.4). This finding provides the confirmation that chitosan was chemically reacted with phthalic anhydride, producing the desirable phthaloyl chitosan as expected. The details of the $^1\text{H-NMR}$ assignments of chitosan as the phthaloyl chitosan were as follows [36]: chitosan: $^1\text{H-NMR}$ ($\text{D}_2\text{O}/\text{F}_3\text{CCOOD}$) $\delta = 4.76$ (H1), $\delta = 3.09$ (H2), $\delta = 3.43\text{-}3.81$ (H3, H4, H5, H6), $\delta = 1.96$ (NOCOCH_3), phthaloyl chitosan: $\delta = 7.30\text{-}7.90$ (aromatic ring), respectively.

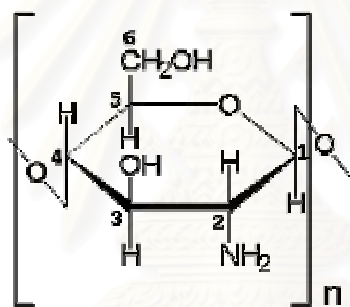


Figure 4.2 The Structure of chitosan

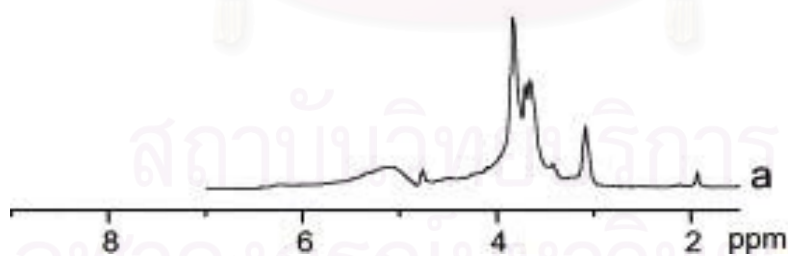


Figure 4.3 $^1\text{H-NMR}$ spectrum of chitosan in ($\text{D}_2\text{O}/\text{F}_3\text{CCOOD}$) solvent [36]

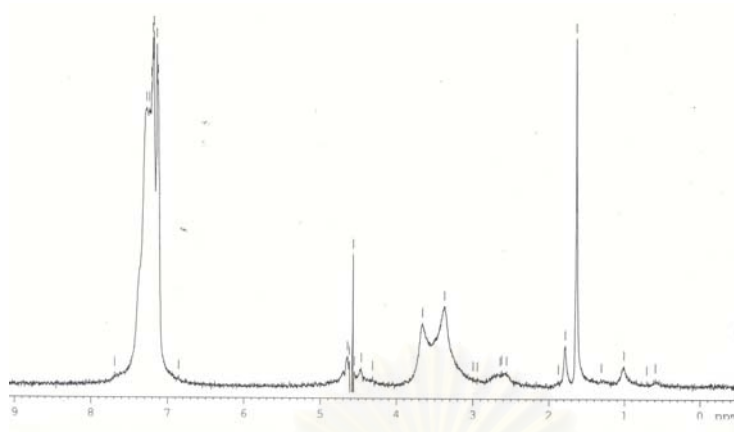


Figure 4.4 $^1\text{H-NMR}$ spectrum of modified chitosan in D_2O solvent

4.4 The application of the phthaloyl chitosan to polyester fabric

As a result of chemical modification of chitosan, the produced phthaloyl chitosan possessed both hydrophobic segment and hydrophilic segment. The balance between hydrophobicity and hydrophilicity was controlled by varying the chitosan:phthalic anhydride mole ratio. The aim of this study was to prepare the phthaloyl chitosan for coating polyester fabric in order to impart the durable hydrophilic property. Basically, chitosan is naturally hydrophilic polymer. However, its disadvantage is due to poor ability of adhering onto hydrophobic substrate including polyester. This was the reason why we attempted to increase the hydrophobic property of chitosan by introducing the phthaloyl group, resulting in the modified chitosan that exhibited the good adhesion onto polyester. Therefore, the application of the phthaloyl chitosan onto polyester fabric was carried out using pad-dry-cure method. Typically, polyester fabric was padded with the solution of phthaloyl chitosan followed by drying and thermofixed at the temperature ranging from $180\text{-}200^\circ\text{C}$ for 3 minutes in the laboratory mini stenter. It was believed that those high treatment temperatures would promote the good adhesion of the phthaloyl chitosan by strong physical attachment due to the anchoring of the phthaloyl segment into polyester surface.

In this section, the hydrophilic properties of phthaloyl chitosan treated PET fabric were evaluated including the percent moisture regain, wettability, laundering and antibacterial testing, respectively.

4.5 Moisture regain of modified polyester fabric.

The percent moisture regain of PET samples was determined by infrared moisture balance. The fabric samples (untreated PET, chitosan treated PET and phthaloyl chitosan treated PET) were measured after conditioning for 24 hours. The percent moisture regain was calculated using equation described in section 3.7.1. The results are shown in table 4.2 and figure 4.5.

The percent moisture regain of untreated PET is found only 0.39% which is the lowest value. The reason for the low moisture absorption was due to the hydrophobic characteristic of PET. In the case of chitosan treated PET, the percent moisture regain is found in the range of 0.47-0.62%. The results also illustrate that the percent moisture regain tends to increase with an increase in the concentration of chitosan applied. For the PET treated with phthaloyl chitosan, the percent moisture regain is found in the range of 0.48-0.91%. As can be seen, the phthaloyl chitosan treated PET exhibited increasing tendency towards moisture absorption when compared to both chitosan treated PET and untreated PET. The results further show that the percent moisture regain is somewhat dependent on the fixation temperature and the phthaloyl chitosan concentration. An increase in treatment temperature (from 180 °C – 200 °C) and the applied concentration (3 g/l – 9 g/l) led to an improvement in the moisture absorption ability of phthaloyl chitosan treated PET. In this experiment, chitosan with the molecular weights of 10⁵ and 10⁶ was modified with phthalic anhydride at the chitosan:phthalic anhydride mole ratio of 1:12 and 1:18, respectively. From figure 4.5, the phthaloyl chitosan obtained from the high molecular weight chitosan ($M_w = 10^6$) and the chitosan to phthalic anhydride mole ratio of 1:18 exhibits the optimum result of the percent moisture regain. As expected, the high molecular weight chitosan was capable of adhering onto PET surface than the lower M_w chitosan. In addition, the modified chitosan having the higher ratio of the phthaloyl group is likely to possess an increase in the percent moisture regain. The reason for this phenomenon was that the introduction of the phthaloyl group into chitosan resulted in the modified chitosan which contained hydrophobic group resembling to the repeating unit of PET. As a result, one could believe that the phthaloyl group of the modified chitosan would preferably attach to PET surface by hydrophobic interaction.

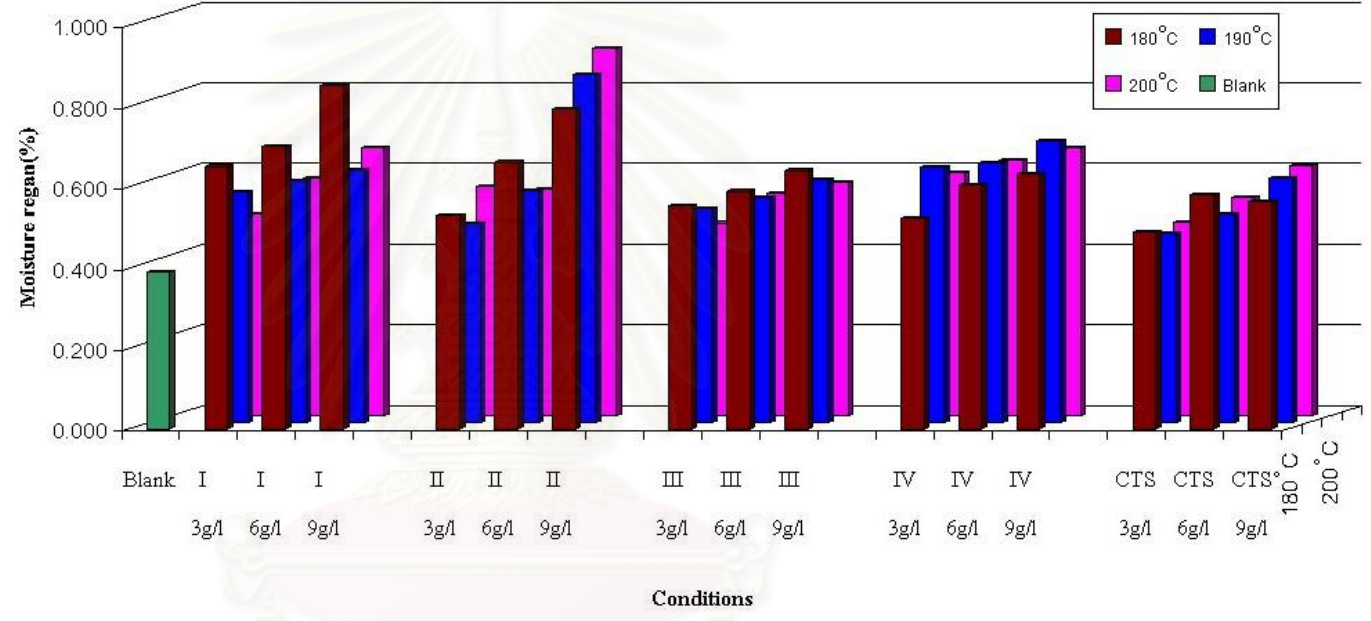
Table 4.2 Percent moisture regain of untreated polyester, treated polyester with modified chitosan and chitosan

Condition	Concentration of agent (g/l)	Cured temperature (°C)	Percent moisture regain (%)
Blank	-	-	0.390
Sample I (CTS:PA=1:12; $M_w = 10^6$)	3	180	0.651
		190	0.570
		200	0.501
	6	180	0.701
		190	0.599
		200	0.591
	9	180	0.853
		190	0.627
		200	0.666
Sample II (CTS:PA=1:18; $M_w = 10^6$)	3	180	0.528
		190	0.493
		200	0.561
	6	180	0.661
		190	0.575
		200	0.570
	9	180	0.792
		190	0.864
		200	0.912

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Condition	Concentration of agent (g/l)	Cured temperature (°C)	Percent moisture regain (%)
Sample III (CTS:PA =1:12; $M_w = 10^5$)	3	180	0.553
		190	0.531
		200	0.478
	6	180	0.589
		190	0.557
		200	0.551
	9	180	0.641
		190	0.603
		200	0.578
Sample IV (CTS:PA=1:18; $M_w = 10^5$)	3	180	0.522
		190	0.633
		200	0.605
	6	180	0.606
		190	0.644
		200	0.634
	9	180	0.632
		190	0.699
		200	0.664
Chitosan	3	180	0.489
		190	0.468
		200	0.481
	6	180	0.580
		190	0.516
		200	0.543
	9	180	0.563
		190	0.606
		200	0.621

Figure 4.5 Effect of temperature, fixation time and amount of treating agents (chitosan and phthaloyl chitosan) on the percentage moisture regain of treated polyester fabric



4.6 Wetness test

The polyester fabrics were treated with chitosan, modified chitosan as described in section 3.8. The wetness test was evaluated by moisture wicking test. The measured distance of dye solution are reported in figure 4.6, 4.7 and table 4.3

The results show that the distance of dye solution obtained from the untreated polyester fabric and phthaloyl chitosan treated PET fabrics was 2.35 cm and between 3.9-7 cm, respectively. As can be seen, the dye solution traveled a lot faster on the phthaloyl chitosan treated PET, implying that the treated PET exhibited a significant improvement in wettability when compared with untreated PET. The effect of temperature, fixation time and the amount of phthaloyl chitosan on the wettability was found in similar manner to the percent moisture regain determination

Therefore, the ratio of chitosan:phthalic anhydride, molecular weight of chitosan and thermofixed temperature were effective to properties of polyester fabric such as wettability, moisture regain and adhesion.



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Table 4.3 Distance of standard color (Wettability) of untreated polyester, treated polyester with modified chitosan and chitosan

Condition	Concentration of agent (g/l)	Cured temperature (°C)	Distance of standard color (cm)
Blank	-	-	2.35
Sample I (CTS:PA=1:12; $M_w = 10^6$)	3	180	4.65
		190	5.05
		200	4.45
	6	180	5.50
		190	6.40
		200	6.05
	9	180	6.15
		190	5.75
		200	6.25
Sample II (CTS:PA=1:18; $M_w = 10^6$)	3	180	5.95
		190	5.35
		200	4.75
	6	180	6.60
		190	5.95
		200	4.75
	9	180	7.00
		190	5.75
		200	5.25

Condition	Concentration of agent (g/l)	Cured temperature (°C)	Distance of standard color (cm)
Sample III (CTS:PA=1:12; $M_w = 10^5$)	3	180	4.10
		190	3.90
		200	4.30
	6	180	4.50
		190	4.8
		200	4.75
	9	180	4.55
		190	4.95
		200	5.00
Sample IV (CTS:PA=1:18; $M_w = 10^5$)	3	180	5.40
		190	4.30
		200	4.40
	6	180	5.40
		190	4.60
		200	4.50
	9	180	6.60
		190	5.15
		200	6.25
Chitosan	3	180	3.45
		190	3.55
		200	2.90
	6	180	2.75
		190	4.50
		200	3.00
	9	180	2.85
		190	2.50
		200	2.40

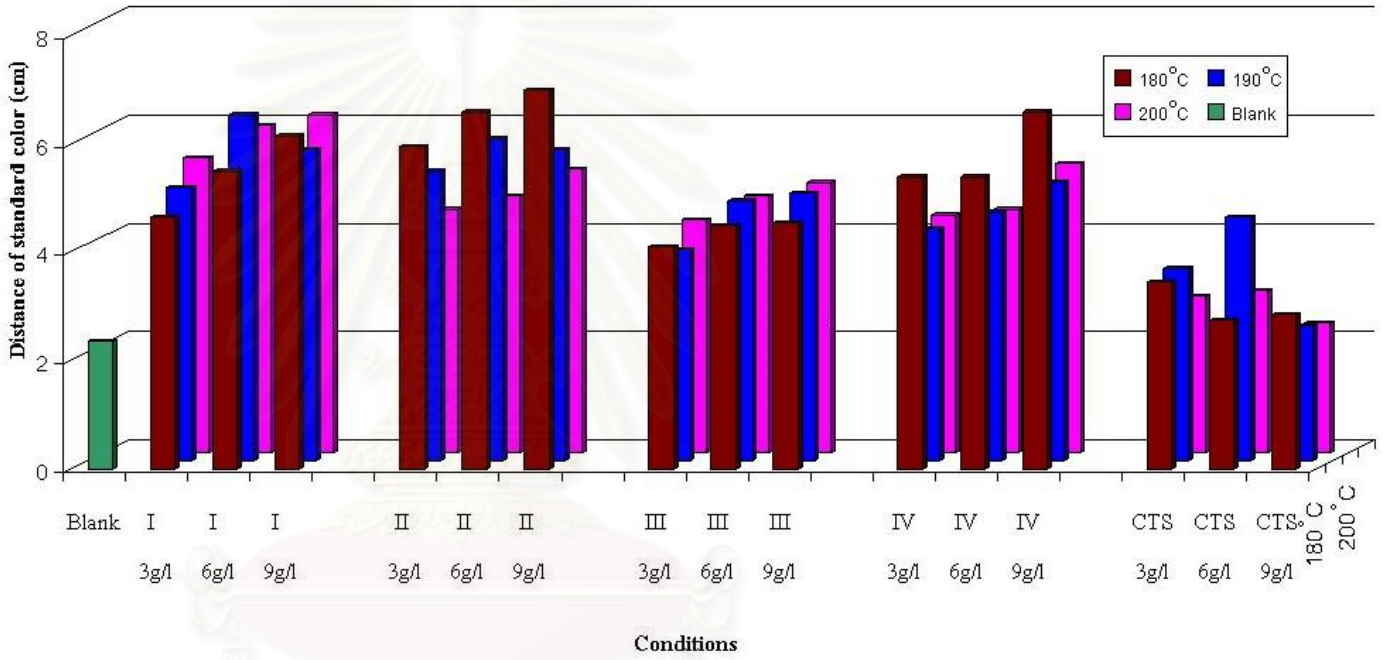


Figure 4.6 Effect of temperature, fixation time and amount of treating agents (chitosan and phthaloyl chitosan) on the distance of standard color of treated polyester fabric



Figure 4.7 Wetness of untreated polyester fabric and treated polyester with phthaloyl chitosan (chitosan ($M_w=10^6$):PA =1:18; concentration 9 g/l)

4.7 Scanning Electron Microscopy of polyester fabric modified with phthaloyl chitosan

After polyester fabric was treated with phthaloyl chitosan and virgin chitosan. Scanning Electron Microscopic (SEM) analysis was performed in order to investigate the modifying agent after surface modification and compared with uncoated and treated with chitosan by JSM-5410 LV scanning electron microscope. The results are shown in figure 4.8

Scanning electron micrograph results reveal that attachment of modified chitosan onto the polyester surface was not even and found every area on modified fabrics, probably due to large molecular weight of them. So that the modification of phthaloyl chitosan agent can adhesive on polyester surface. On the other hand, Figure 4.8 (CHITOSAN), the chitosan disadhere on polyester surface; the structure of chitosan is not the same as polyester structure.

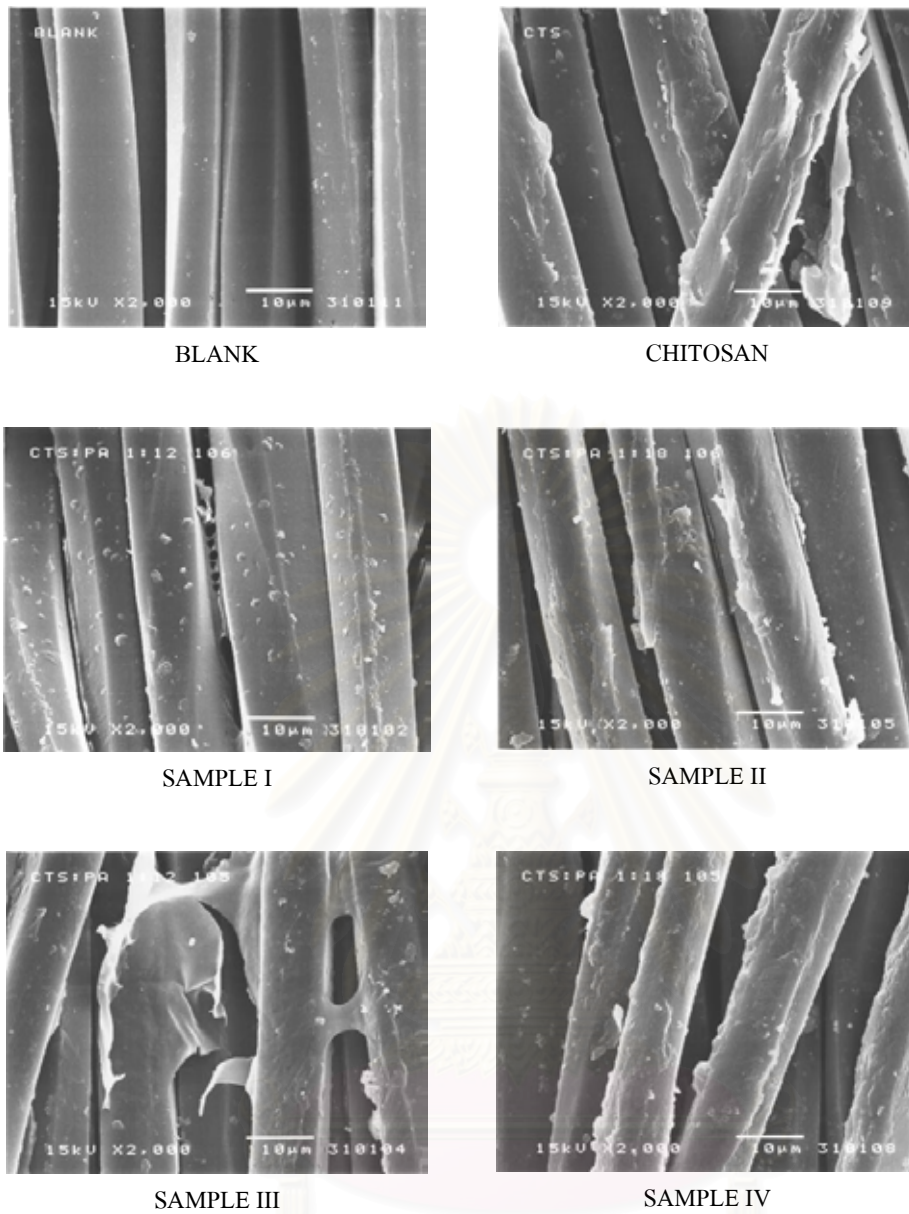


Figure 4.8 Scanning Electron Micrograph of untreated fabrics and treated fabric with chitosan and modified chitosan (SAMPLE I, II, III and IV)

4.8 Laundering of treated polyester fabric

Fastness evaluation of treated PET was carried out using laundering testing (AATCC test method 61-2001). After that, the evidence of the presence of coatings was confirmed by SEM. The results are shown in figure 4.9

After washing test, SEM result of chitosan treated PET reveals that chitosan was largely removed as evidenced by a little presence of chitosan observed on the PET surface. Also from the micrograph, it can be commonly seen that chitosan was clearly separated from the PET surface, indicating the rather poor adhesion of chitosan on hydrophobic PET surface. In the case of phthaloyl chitosan treated PET, SEM micrograph shows that most of PET surface is covered by the coating film. Also, it is evident that the coating film adheres firmly on the PET surface, suggesting that the phthaloyl chitosan offered a better adhesion on the PET surface which exhibited some resistance to washing test. It could be concluded that chitosan, which is hydrophilic and poorly attached to PET, could be hydrophobically modified by phthalic anhydride, leading to the modified chitosan suitable for durable polyester coating.



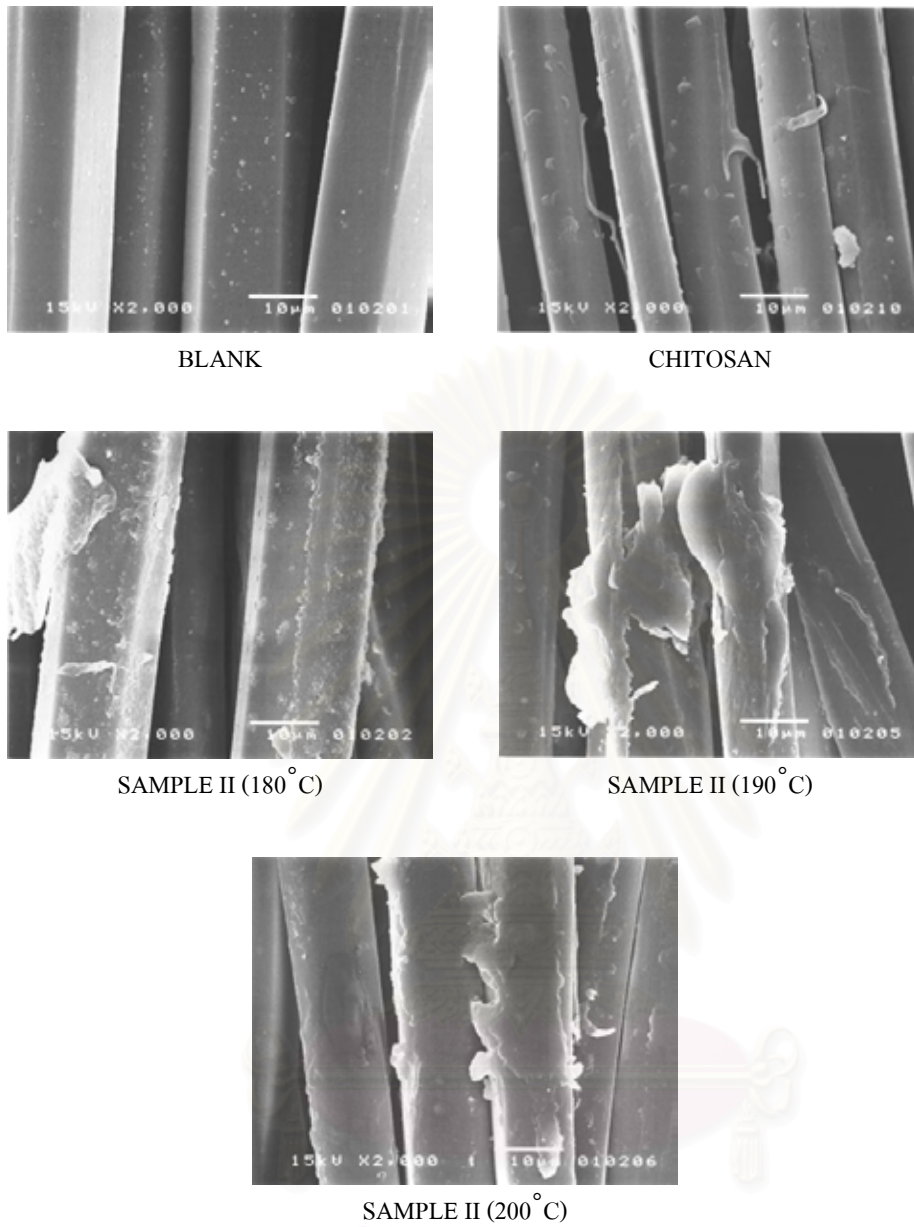


Figure 4.9 Scanning Electron Micrograph of untreated fabrics and treated fabric with chitosan and modified chitosan (After laundering test)

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4.9 Antibacterial finishes on textile materials

Antibacterial tests of the modified polyester fabric, finished with the concentration of phthaloyl chitosan (using the mole ratio of 1:18 chitosan ($M_w=10^6$):phthalic anhydride) of 9 g/l, were performed against the Gram-positive bacterium *Staphylococcus aureus*. The original chitosan treated polyester fabrics plate cultured under the same condition was used as a control.

Figure 4.10 shows the number of bacterial colonies grown on the plates of different fabric samples. In all case, there is no difference in the bacterial colonies grown on plate after inoculation (at "0" contact time) and after 24 hours contact time. It should be noted that by this test method the fabric was contact with bacterial cells for 24 hours in the solution, not in air. This means the modified fabric cannot prevent the bacterial growth in the surrounding solution due to the absence of contact between fabric and tested bacteria. Other experimental possible explanation is that the concentration of chitosan is not high enough for bacterial inhibition and amine groups of chitosan which are responsible for antimicrobial activity were partly substituted by phthaloyl groups from phthaloylation reaction. On the other hand, this may imply the strong adhesion between phthaloyl chitosan and the surface of polyester fiber since the amount of finishing agent released in the solution was too small to inhibit the bacterial growth in the surrounding solution.

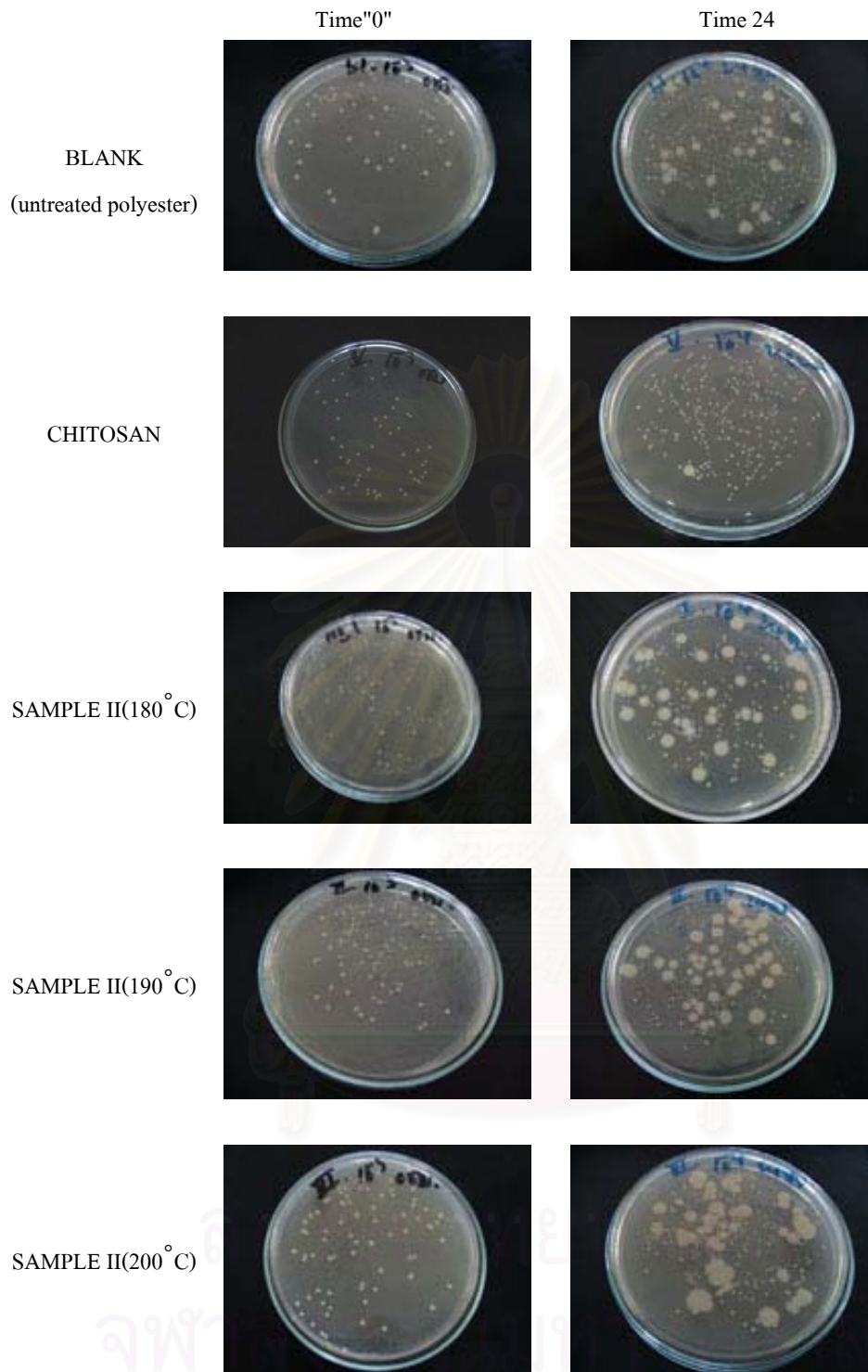


Figure 4.10 antibacterial testing of untreated and treated polyester fabrics with chitosan and phthaloyl chitosan (thermofixed temperature at 180,190 and 200 °C)

CHAPTER V

CONCLUSION

5.1 Conclusion

The modified chitosan for surface coating of polyester fabric was prepared by the reaction of chitosan (molecular weight = 100,000 and 1,000,000) with phthaloyl anhydride using the chitosan:phthalic anhydride mole ratio of 1:12 and 1:18, respectively. Characterization of the modified chitosan was undertaken by FTIR and proton NMR analysis. The results confirmed that chitosan with the varying hydrophobicity and hydrophilicity ratio could be obtained by varying the reactants ratio as above.

The modified chitosan obtained was applied to PET fabric in order to achieve the durable hydrophilicity of PET fabric. The finished polyester fabrics were subjected to an evaluation of moisture regain, wettability, as well as surface examination using Scanning Electron Microscopy (SEM). From SEM evidence, the phthaloyl chitosan could exhibit better adhesion performance when compared to the unmodified chitosan treated polyester. This confirmed that the phthaloyl moiety of the modified chitosan played the determined role in controlling the adhesion ability of the phthaloyl chitosan. Wettability of treated fabrics was found that wetness of treated fabric with modified chitosan improved significantly when compared to untreated polyester fabric and treated polyester fabric with unmodified chitosan. The modified chitosan which exhibited optimum adhesion performance on PET was obtained from the modification conditions as follows: mole ratio of the chitosan to phthalic anhydride of 1:18 and chitosan molecular weight of 10^6 . The applied concentration of 9 g/l and fixation temperature of 190°C for 3 minutes gave the best results in terms of surface properties.

Additionally, treated polyester with phthaloyl chitosan was tested the antimicrobial activity for 24 hours. However, the results showed that the phthaloyl chitosan treated PET did not exhibit the antimicrobial property.

5.2 Recommendations for future work

1. Application parameters such as time, concentration should be in further investigated.
2. Other experiments should be carried such as antistatic property, color fastness, tensile properties and drapability.

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APPENDICES



สถาบันวิทยบริการ
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APPENDIX A

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Appendix A

Percent moisture regain of untreated and treated polyester fabrics

Table A1. Data of original weight and dry weight (temperature 105 °C) of untreated polyester fabric

Conditions	Time	Original weight (g)				Dry weight (g)			
		1	2	3	average	1	2	3	average
Blank (untreated polyester)		5.151	5.151	5.150	5.151	5.130	5.131	5.131	5.131

Table A2. Data of original weight and dry weight (temperature 105 °C) of treated polyester fabric with phthaloyl chitosan and chitosan (thermofixed at temperature 180 °C)

Conditions	Time	Original weight (g)				Dry weight (g)			
		1	2	3	average	1	2	3	average
Sample I (CTS:PA = 1:12; $M_w=10^6$)	3 g/l	2.474	2.473	2.474	2.474	2.457	2.457	2.458	2.458
	6 g/l	2.549	2.549	2.549	2.549	2.530	2.531	2.533	2.531
	9 g/l	2.602	2.600	2.603	2.602	2.580	2.579	2.580	2.580
Sample II (CTS:PA = 1:18; $M_w=10^6$)	3 g/l	2.537	2.537	2.536	2.537	2.523	2.523	2.524	2.523
	6 g/l	2.487	2.487	2.487	2.487	2.471	2.471	2.470	2.471
	9 g/l	2.503	2.503	2.503	2.503	2.484	2.483	2.483	2.483
Sample III (CTS:PA = 1:12; $M_w=10^5$)	3 g/l	2.486	2.485	2.485	2.485	2.471	2.472	2.472	2.472
	6 g/l	2.517	2.517	2.517	2.517	2.501	2.502	2.503	2.502
	9 g/l	2.514	2.514	2.514	2.514	2.497	2.498	2.498	2.498
Sample IV (CTS:PA = 1:18; $M_w=10^5$)	3 g/l	2.568	2.567	2.568	2.568	2.554	2.554	2.555	2.554
	6 g/l	2.548	2.547	2.548	2.548	2.533	2.532	2.532	2.532
	9 g/l	2.600	2.599	2.599	2.599	2.583	2.583	2.583	2.583
Chitosan	3 g/l	4.567	4.565	4.565	4.566	4.588	4.588	4.588	4.588
	6 g/l	4.314	4.314	4.314	4.314	4.339	4.339	4.339	4.339
	9 g/l	4.382	4.382	4.382	4.382	4.406	4.407	4.407	4.407

Table A3. Data of original weight and dry weight (temperature 105 °C) of treated polyester fabric with phthaloyl chitosan and chitosan (thermofixed at temperature 190 °C)

Time		Original weight (g)				Dry weight (g)			
		1	2	3	average	1	2	3	average
Sample I (CTS:PA = 1:12; $M_w=10^6$)	3 g/l	2.645	2.645	2.645	2.645	2.630	2.630	2.630	2.630
	6 g/l	2.632	2.632	2.632	2.632	2.616	2.616	2.617	2.616
	9 g/l	2.516	2.516	2.515	2.516	2.499	2.500	2.501	2.500
Sample II (CTS:PA = 1:18; $M_w=10^6$)	3 g/l	2.512	2.512	2.514	2.513	2.501	2.500	2.500	2.500
	6 g/l	2.565	2.565	2.567	2.566	2.550	2.552	2.551	2.551
	9 g/l	2.569	2.567	2.568	2.568	2.546	2.546	2.546	2.546
Sample III (CTS:PA = 1:12; $M_w=10^5$)	3 g/l	2.527	2.526	2.526	2.526	2.513	2.513	2.513	2.513
	6 g/l	2.588	2.586	2.586	2.587	2.572	2.572	2.573	2.572
	9 g/l	2.448	2.448	2.447	2.448	2.433	2.433	2.433	2.433
Sample IV (CTS:PA = 1:18; $M_w=10^5$)	3 g/l	2.542	2.542	2.541	2.542	2.526	2.526	2.525	2.526
	6 g/l	2.604	2.604	2.604	2.604	2.587	2.587	2.588	2.587
	9 g/l	2.497	2.497	2.498	2.497	2.480	2.480	2.480	2.480
Chitosan	3 g/l	4.062	4.061	4.061	4.061	4.080	4.081	4.080	4.080
	6 g/l	4.262	4.263	4.264	4.263	4.285	4.285	4.285	4.285
	9 g/l	4.071	4.070	4.070	4.070	4.095	4.095	4.095	4.095

Table A4. Data of original weight and dry weight (temperature 105 °C) of treated polyester fabric with phthaloyl chitosan and chitosan (thermofixed at temperature 200 °C)

Time		Original weight (g)				Dry weight (g)			
		1	2	3	average	1	2	3	average
Sample I (CTS:PA = 1:12; $M_w=10^6$)	3 g/l	2.608	2.608	2.608	2.608	2.595	2.594	2.596	2.595
	6 g/l	2.212	2.212	2.212	2.212	2.197	2.199	2.201	2.199
	9 g/l	2.647	2.647	2.647	2.647	2.629	2.630	2.629	2.630
Sample II (CTS:PA = 1:18; $M_w=10^6$)	3 g/l	2.571	2.571	2.572	2.571	2.556	2.557	2.557	2.557
	6 g/l	2.442	2.442	2.443	2.442	2.428	2.428	2.429	2.429
	9 g/l	2.636	2.636	2.637	2.636	2.609	2.612	2.613	2.613
Sample III (CTS:PA = 1:12; $M_w=10^5$)	3 g/l	2.524	2.524	2.524	2.524	2.511	2.512	2.512	2.512
	6 g/l	2.524	2.524	2.525	2.524	2.510	2.510	2.511	2.511
	9 g/l	2.495	2.494	2.494	2.494	2.480	2.480	2.480	2.480
Sample IV (CTS:PA = 1:18; $M_w=10^5$)	3 g/l	2.607	2.607	2.606	2.607	2.591	2.591	2.591	2.591
	6 g/l	2.592	2.591	2.591	2.591	2.576	2.575	2.575	2.575
	9 g/l	2.579	2.579	2.579	2.579	2.563	2.562	2.562	2.562
Chitosan	3 g/l	4.505	4.505	4.504	4.505	4.526	4.527	4.526	4.526
	6 g/l	4.112	4.111	4.110	4.111	4.133	4.133	4.134	4.133
	9 g/l	4.190	4.190	4.190	4.190	4.216	4.216	4.216	4.216



APPENDIX B

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DS       : 4
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FIDRES   : 0.363918 Hz
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RG       : 256
DQ       : 61.500 usec
DE       : 4.50 usec
TE       : 300.2 K
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D12      : 0.0000000 sec
D13      : 0.0000000 sec
D19      : 0.0000000 sec
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NUC1     : 1H
NUC2     : 13C
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P13      : 0.0000000 sec
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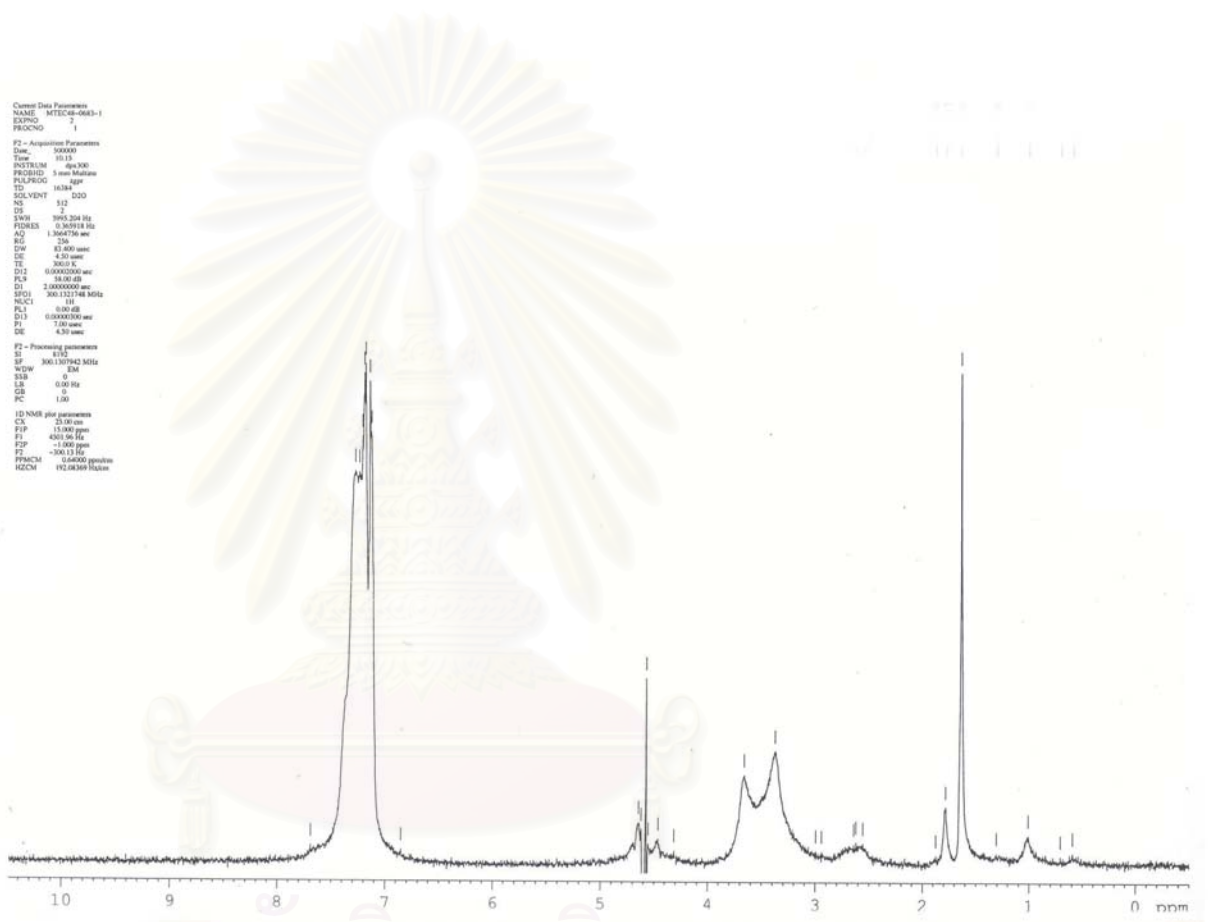


Figure A1 ¹H-NMR spectrum of modified chitosan(SAMPLE I) in D₂O solvent

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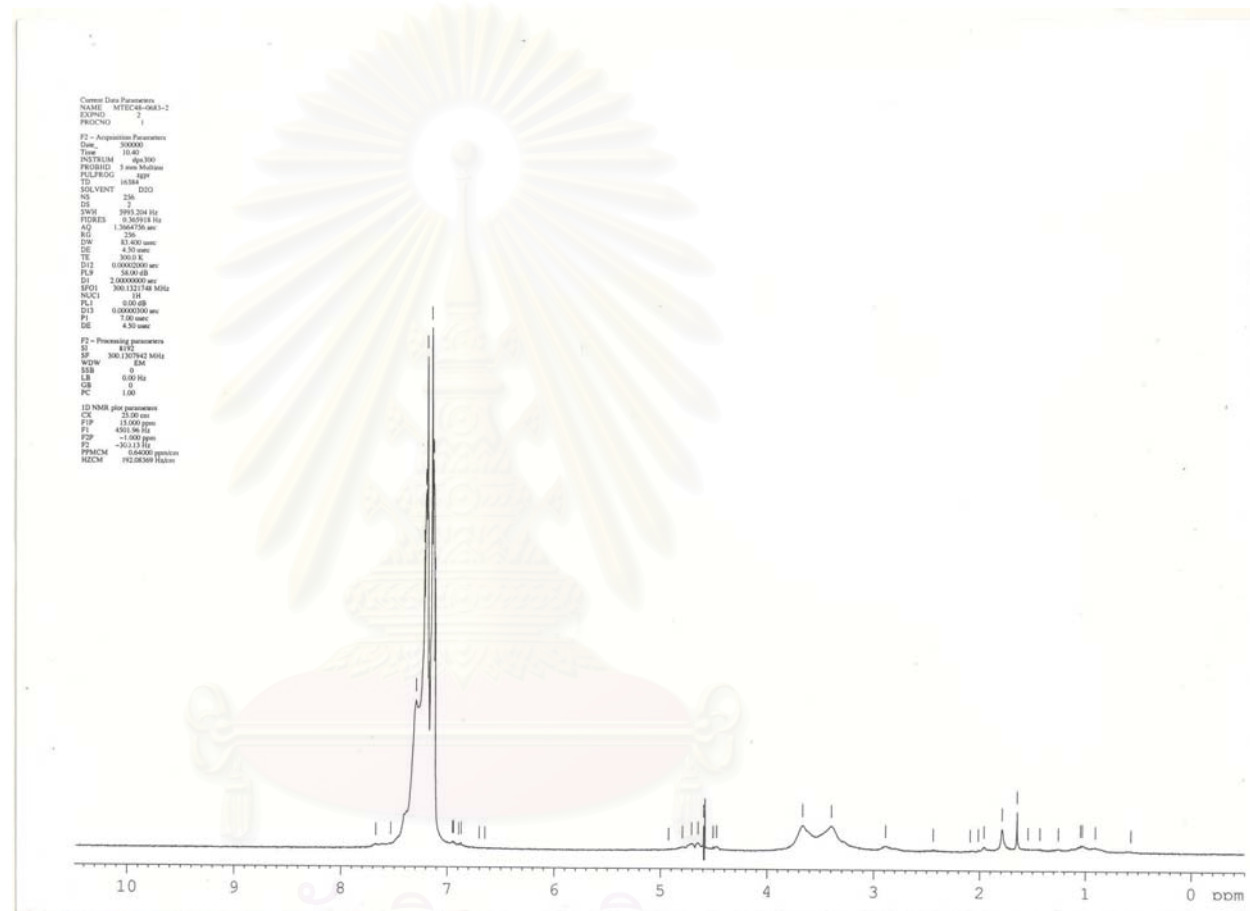


Figure A2 ¹H-NMR spectrum of modified chitosan(SAMPLE II) in D₂O solvent

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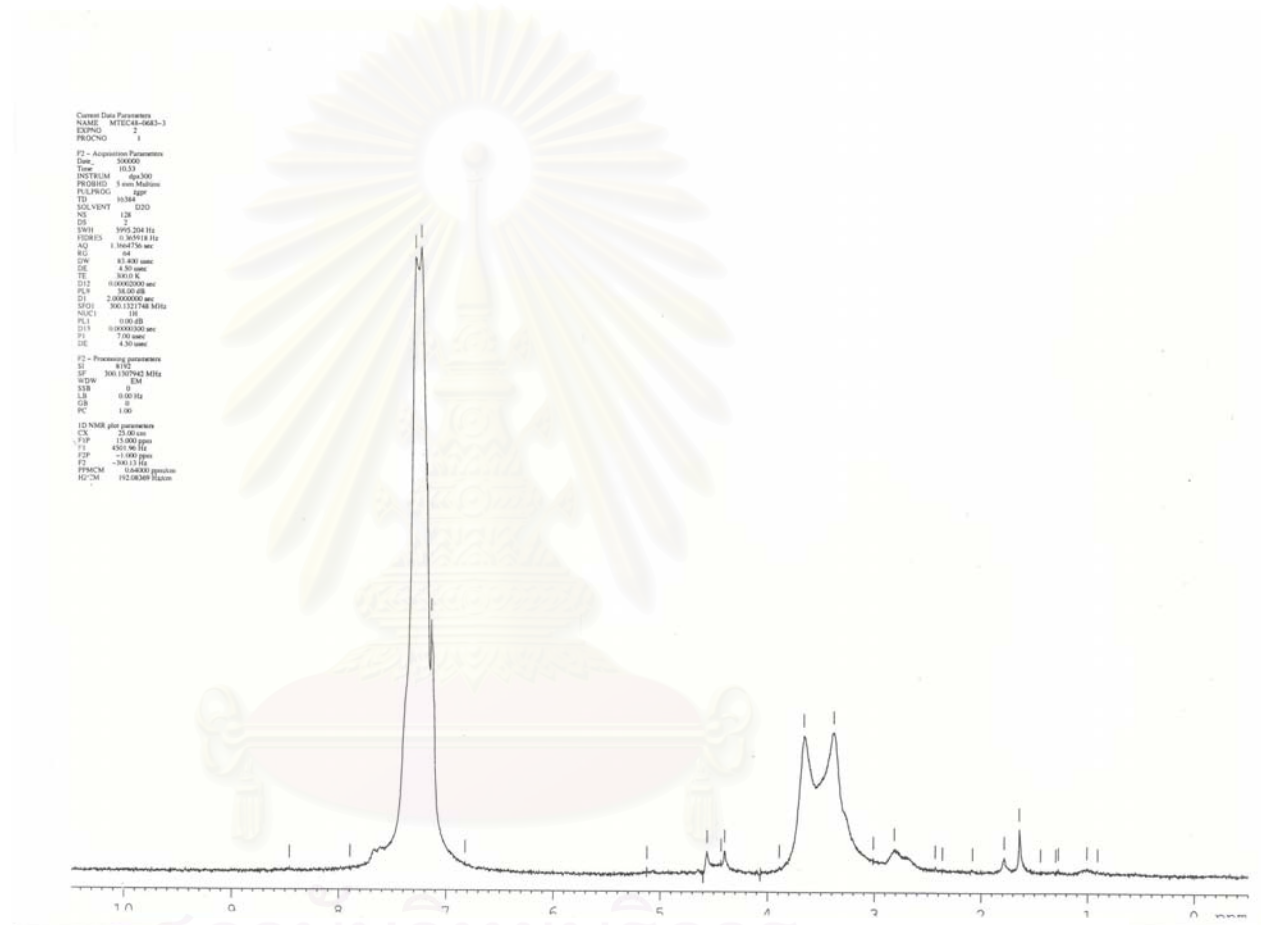


Figure A3 $^1\text{H-NMR}$ spectrum of modified chitosan(SAMPLE III) in D_2O solvent

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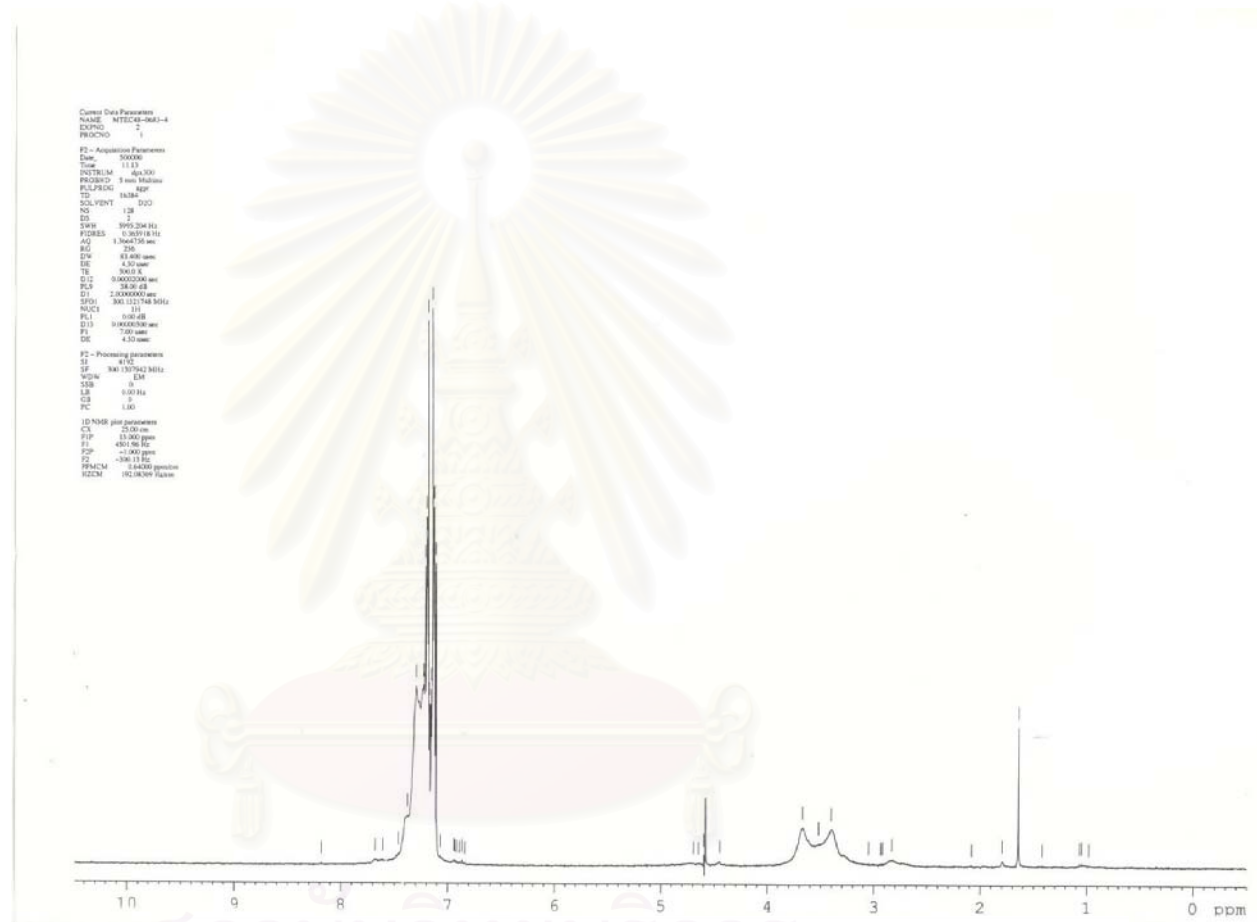


Figure A4 $^1\text{H-NMR}$ spectrum of modified chitosan(SAMPLE IV) in D_2O solvent

สภามหาวิทยาลัย
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BIOGRAPHY

Miss Duangkamon Viboonratanasri was born in Ayuthaya, Thailand, on April 26, 1982. She received a Bachelor of Science degree with a major in Material from Chulalongkorn University in 2003. She started as a graduate student in the Department of Materials Science with a major in Applied Polymer Science and Textile Technology, Chulalongkorn University in June 2003, and completed the program in May 2005.



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