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FIBRILLATION BEHAVIOUR OF MAN-MADE CELLULOSIC FIBERS UNDER MICROSCOPIC EXAMINATION

Miss Siriluk Chiarakorn

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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ปัจจุบันการเกิดขนของเส้นใยเซลลูโลสประดิษฐ์ได้เข้ามีบทบาทต่ออุตสาหกรรมเสื้อผ้าและเครื่องนุ่งห่มมากขึ้น ตลอดระยะเวลาที่ผ่านมาจึงมีการศึกษาเกี่ยวกับไฟบริลเลชันของเส้นใยเซลลูโลสประดิษฐ์ในงานวิจัยมากมาย ในงานวิจัยนี้จึงศึกษาพฤติกรรมการเกิดขนของเส้นใยเทนเซล (Tencel®) ซึ่งเป็นหนึ่งในเส้นใยเซลลูโลสประดิษฐ์ที่มีแนวโน้มการเกิดขนได้ง่ายเมื่อได้รับการขัดถูในขณะเปียกโดยอาศัยกล้องจุลทรรศน์ เพื่อหาความสัมพันธ์ระหว่างการหักเหสองแนว ความเป็นผลึกสัมพัทธ์ และความหนืดของเส้นใยกับการเกิดขนของเส้นใย เส้นใยตัวอย่างจะถูกนำมาตกแต่งสำเร็จเพื่อควบคุมระดับการเกิดขนโดยใช้สารเชื่อมโยงทางการค้าที่ภาวะแตกต่างกัน ภายหลังการตกแต่งสำเร็จเส้นใยจะถูกนำมาตรวจด้วยกล้องจุลทรรศน์เพื่อคำนวณดัชนีวัดระดับการเกิดขนและวัดสมบัติทางกายภาพ อันได้แก่ การหักเหสองแนวโดยใช้กล้องจุลทรรศน์ ความเป็นผลึกสัมพัทธ์โดยใช้เครื่องเอกซเรย์ และความหนืดโดยวิธีตามมาตรฐาน ASTM D1795-96

จากการทดลองพบว่าสมบัติทั้งสามมีความสัมพันธ์เชิงเส้นกับการเกิดขนของเส้นใย เส้นใยที่มีการจัดเรียงตัวในทิศทางเส้นใยสูงมีแนวโน้มการเกิดขนได้ง่ายเมื่อได้รับการขัดถูในขณะเปียก นอกจากนี้ยังพบว่าระดับการเกิดขนแปรผกผันกับน้ำหนักโมเลกุลและความหนืดของเส้นใย ดังนั้นการยืดดึงเส้นใยในกระบวนการผลิตซึ่งมีผลต่อการจัดเรียงตัวของโมเลกุลเซลลูโลสและความเป็นผลึกจึงสามารถควบคุมการเกิดขนของเส้นใยได้ การลดการเกิดขนของเส้นใยสามารถทำได้โดยการตกแต่งสำเร็จด้วยสารเชื่อมโยง นอกจากนี้จากความสัมพันธ์ดังกล่าวสามารถแสดงเป็นสมการเชิงเส้นเพื่อใช้ในการทำนายแนวโน้มการเกิดขนของเส้นใยได้

ภาควิชา วัสดุศาสตร์ ลายมือชื่อนิสิต

สาขาวิชา วิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ลายมือชื่ออาจารย์ที่ปรึกษา

ปีการศึกษา 2543

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Fibrillation of man-made cellulosic fibers is playing an important role on the application in apparel end uses. Investigations to explore fibrillation behaviour have been carried out intensively. In this research, fibrillation behaviour of Tencel®, a man-made cellulosic fiber, was studied by microscopic examination. Birefringence, relative crystallinity and intrinsic viscosity of the fibers were examined in order to determine how they might be correlated to the Fibrillation Index. The fiber samples were treated with commercial cross-linking agent in various conditions to control the degree of fibrillation. The fiber birefringence was observed by polarized optical microscope, intrinsic viscosity was measured by the viscosity method and crystallinity was determined by X-Ray diffraction method.

The results showed that the higher fiber structure oriented along the fiber axis, the higher tendency of fibrillation occurred. On the other hand, the fibrillation decreased when the molecular weight as well as the intrinsic viscosity increased. The application when high fibrillation is needed, increase of relative crystallinity during fiber production is proposed. However, defibrillation finishing by cross-linking agent is suggested for controlling the fibrillation at low level. In addition, simple linear relationships between each parameter to the Fibrillation Index are also presented.

Department of Materials Science Student's Signature
Field of study Applied Polymer Science and TextileTechnology Advisor's Signature
Academic Year 2000

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CHAPTER I

Introduction

Man-made cellulosic fibers have played the important part in textile industry. Due to their uniformity and high mass productions, the world's man-made cellulosic fiber comsumption are gradually increased. However, it is well known that they have the tendency to fibrillate when they are subjected to the hydromechanical stress during wet processing. The tendency of fibrillation is shown in the order of lyocell (the most easiest of fibrillate), high wet modulus rayon and viscose rayon. Fibrillation caused the disadvantages in launderability of textile end uses, but more advantages in nonwoven and also fashions.

Lyocell, one of man-made cellulosic fibers, is now widely used because of its excellent properties such as high tenacity, high wet modulus and good dimension stability comparing to other cellulosic fibers. Additionally, the production of lyocell is recognised as environmental friendly and economical process by means of closed system in which the solvent can be effectively reused more than 97 percentages. However, it is also known that lyocell has the highest tendency to fibrillate under wet abrasion, therefore, the fibrillation of lyocell is mainly concerned. Many research works have been carried out in order to find out how the fibrillation behaves and what parameters affect the fibrillation behaviour.

The fibrillation of lyocell is caused by the high molecular orientation and the lack of lateral cohesion in molecular chains. After wet spinning process, the extended molecular chains in crystalline regions are almost aligned in the direction of fiber axis and

bonded by the intermolecular forces, hydrogen bonds. However, in wet state, the hydrogen bonds linking the crystalline regions are broken apart by swelling of fibers. When the fibers are subjected to the mechanical action such as abrasion, the molecules of the outer skin are splited from the main fiber forming fibrillation along the fiber.

In order to assess the fibrillation, various methods have been proposed, but still there is no universally accepted standard. Nevertheless, the most widely use as the indicator for assessment of fibrillation is Fibrillation Index (FI). To calculate the Fibrillation Index, the length of fibers and fibrils are measured under microscope. Fibrillation Index is calculated from the sum of fibrils length divided by the fiber length. Moreover, general practice, Fibrillation Index of sample fibers is compared with Fibrillation Index of standard fibers which is ranked from 0 – 10 levels in order to classify the fibrillation in each level relatively to the standard.

Although, the Fibrillation Index is widely used because of its simple assessment, the calculation is based on only two dimensions which is not accurately representing the fiber structure. Actually, the fibrillation of fibers certainly relates to the molecular orientation in crystalline regions. Therefore, it is assumed that physical parameters relating to fiber structure such as birefringence, crystallinity and viscosity may affect the fibrillation behaviour. In addition, these physical properties should represent the characteristic of whole samples better than the length of fibers and fibrils. Thus, in order to develop the fibrillation assessment, the influence of these parameters should be studied.

The purpose of this study is to propose an alternative approach to determine the fibrillation behaviour by investigating how birefringence, intrinsic viscosity and relative crystallinity might influence the fibrillation behaviour.

CHAPTER II

Literature Review

Lyocell is generic name of organic solvent cellulosic fiber which was discovered by American Enka Corporation research in United States since 1970. The original aim of its research was to find out an alternative way to produce regenerated cellulosic fibers based on environmental friendly process. In 1989, Courtaulds Fibers Co. Ltd. launched the pilot production of lyocell staple fiber with capacity of 50 tons per year in the United Kingdom and gave brand name Tencel®. In 1992, the commercial production of lyocell fiber, then, was successfully carried out 180,000-ton annual capacity in United States. Following the Courtauld Fibers Group, the Lenzing Group began commercial production of lyocell fiber with capacity of 12,000 tons per year in July 1997. Lyocell expansion has continued significantly, the worldwide capacity of lyocell reached almost 100,000 tons per year (Tim, 1998). At present both Tencel® and Lenzing Lyocell® are well known as the high quality cellulosic fibers widely used in apparels particularly in fashion and then become the exclusive, rare and expensive fiber in this century.

2.1 The production of lyocell fiber

The lyocell commercial production was launched by American Enka in 1970. Wood pulp is dissolved in hot amine oxide to produce a clear viscous solution, which is filltered and extruded into a bath of dilute amine oxide in a gel spinning system. The fibers are washed and dried, and the solvent is recovered for further use (U.S. Patent 4 196 282).

Then, the production of lyocell was continuously developed by means of solvent spinning process.

The wood pulp is dissolved in 76 % N-Methyl-Morpholine-N–Oxide (NMMO) under shearing. There is no derivation like the xanthate process taking place. The mechanism could be explained as an interaction of the free cellulose hydrogen with the negative charged oxygen from the NMMO molecule as shown in Figure 2.1 (Schulz, 1996).

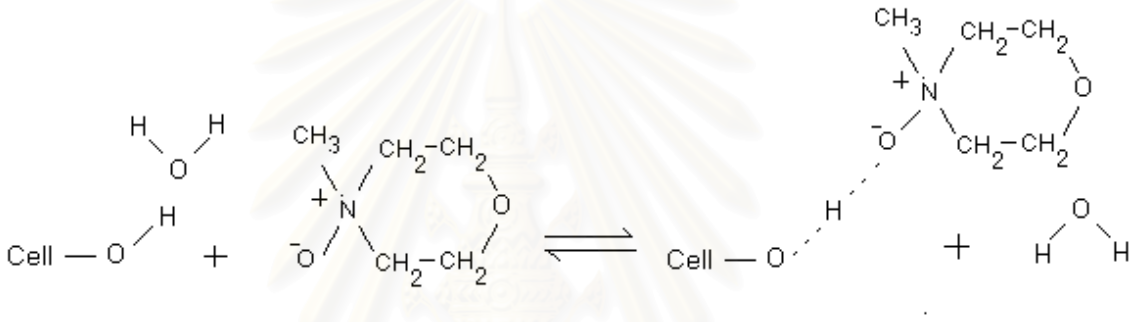

Figure 2.1 Precipitation of cellulose in concentrated NMMO solution.

Then, the viscous solution was filtered and extruded through the spinnerets into diluted aqueous NMMO bath in which fibers were formed by non-solvent quench caused by phase interchange from binodal phase to spinodal phase (Ball and Esserry, 1990). The process duration from wood pulp to fiber is about 3 hours, the temperature is 140^{o}c, pressure is given by 100 bar. After spinning process, water containing the residual solvent was concentrated and reused more than 97 percentages by evaporation the excess water within the closed loop. It was reported that this clean process caused no salt problems, no toxic residuals and COD level less than viscose process. As a consequence, the production of lyocell was well known as the environmentally and economical process for this century (see Figure 2.2).

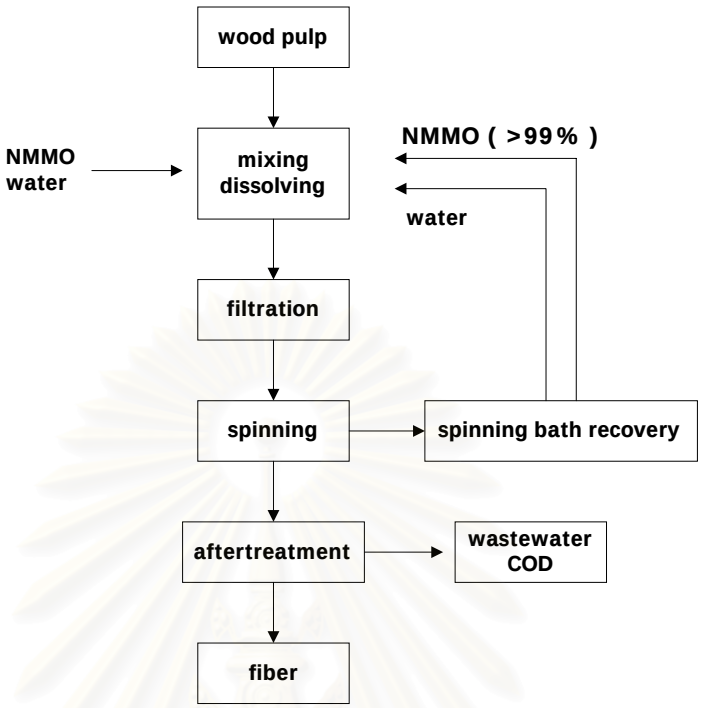

Figure 2.2 The production of lyocell fiber by NMMO process.

2.2 The properties of lyocell fiber

Due to the cellulose from NMMO process is not regenerated, the fiber has a molecular structure different from that of viscose. It also has a smooth, round cross section and longitudinal view quite different from viscose. The unique longitudinally oriented crystalline fiber structure produces a number of interesting properties. It retains an excellent properties of both synthetic fibers such as polyester and polyamide and natural fibers such as cotton.

Lenz and Schurz (1993) presented an interesting theory that was based on mainly on X-ray structural analyses. Comparison with viscose and high wet modulus rayon, lyocell has more longer and higher orientated cellulose molecules in crystalline regions. But the

lateral bondings of the crystallites are formed weaker than inside the viscose and high wet modulus rayon. This is a reason that why lyocell has the distinctive mechanical properties and has high tendency to fibrillate comparing with other man-made cellulosic fibers.

Table 2.1 Lyocell properties compared with other man-made cellulosic fibers.

Fiber properties	Cupro	viscose	modal	lyocell	cotton
Dry tenacity (cN/tex)	22	26	35	45	34
Wet tenacity (cN/tex)	14	14	20	39	41
Elongation, dry (%)	18	17	14	12	8
Loop strength	18	7	8	19	21
Wet modulus	50	50	180	270	100
Fiber count (dtex)	1.3	1-5.6	1.1-4.2	1.7	-
Price ($)	-	2	3	8	1.5

According to a technical properties (see Table 2.1), lyocell can be produced in very fine deniers like microfiber and has a good dimension stability. Moreover, its dry tenacity is twice and its wet tenacity is three times compared with the conventional cellulosic fiber. Due to its high moisture absorption, lyocell is cool to wear without static problem. Furthermore, the dye uptake of fiber is excellent; consequently, the amount of dyestuffs used in dyeing and dyestuffs residual in wastewater are less than the conventional process. The distinction of lyocell which separates it from other cellulosic fibers is the most easiest to fibrillate in wet states abrasion (Marini, 1993). This is because the cellulose – NMMO solution is a liquid crystal system causing the cellulosic liquid crystals to uniformly aligned in fiber direction. High orientation of fiber results in the lack of lateral cohesion. As a result, the high amount of fibrillation occures (Schulz, 1996). However, controlling the degree of fibrillation in optimum level brought about the improvement of handle and aesthetic properties as known as peach skin, soft denim look and sand washed effect (Otten *et al*., 1996) . On the other hand, the fibrillation caused

many problems during dyeing and finishing process. After washing, there are a lot of fibrils on the fabric surface leading to the main serious problems such as pilling effect and also decrease of color strength. It was seen that when the same amount of dye was applied to both fibers and fibrils, the fibrils appeared much lighter (Alix, 1994).

2.3 Fibrillation of lyocell fiber

Lyocell is well known as the one of cellulosic fiber having high tendency to fibrillate in wet state abrasion. The mechanism of fibrillation of lyocell has been reviewed by Akhil (1999). It has been expained that the unique crystalline structure of lyocell fibers is the main reason explaining why and how lyocell fibers normally fibrillate. In wet state, the porous regions of fibers are swollen ; as a consequence, the hydrogen bonds linking crystalline units are broken apart. When swollen structures are subjected to the mechanical action such as abrasion, the outer crystalline regions can break and peel away easily from the main fiber. These peelings are called as fibrils (see Figure 23).

Figure 2.3 Fibrillation of lyocell.

2.4 Factors affecting fibrillation

During the production of fiber, the fibrillation is dependent on both content of cellulose and content of NMMO in polymer solution. Loubinoux and Chaunis (1987) and Braverman *et al.* (1990) investigated that there was a very strong dependence of the solution viscosity on the cellulose concentration. It was shown that decrease in cellulose content leaded to the decrease in the solution viscosity. Subsequently, the tendency of fibrillation significantly reduced due to the lower elasticity and relaxation time. More dilute polymer solution allowed the stress and orientation of cellulose molecules to relax out within spin bath.

Besides, the processing conditions such as temperature and humidity were concerned. Mortimer and Peguy (1996) found that air gap length, spinneret size, line speed and draw ratio also effected on the rate of fibrillation. It was reported that longer air gap length leading to much lower fibrillation than shorter air gap length. This is because the increase in relaxation time during air gap resulting in the reduction of stress inner fiber. However, in the case of the same air gap length, the fibrillation was significantly affected by air gap conditions. Cold and dry air gap condition brought about the fibrillation significantly increased comparing to warm and humid air. It was described that warm and humid air promoted the fiber to reduce the stress within the fibers structure and allowed the adjacent cellulose molecules to slip thoroughly. This brought about the increase in intermolecular bondings.

The effect of the line speed examined by birefringence was that raising the line speed increased the tendency of the fiber to fibrillate because of the less time to relax. The residence time in air gap was lower when the line speed was higher. The results shown that the extension at break of fiber produced by high speed production was significantly reduced because the lateral and longitudinal cohesion of fiber were diminished during the process. The effect of the line speed on the fibrillation was severe in short air gap and

cold-dry air gap condition.

The draw ratio was one of main reasons affecting the high fibrillation of lyocell fiber. It was reported that the increase of fibrillation resulted from the increase of draw ratio as well as birefringence because, again, the residence time in the air gap decreased. However, the draw ratio slightly affected the fibrillation when the draw ratio was less than ten.

In addition, Peguy (1996) presented that fibrillation was strongly influenced by spin bath concentration. Fibers spun were normally coagulated in the dilute NMMO solution. Higher content of pure water gave a deeper non-solvent quench than a solution of NMMO in water resulting in the reduction of lateral cohesion among cellulose molecules. Thus, low spin bath concentration led to the increase of fibrillation. Not only did spin bath concentration but also spin bath temperature affect the fibrillation behaviour. In 1993, Eichinger *et al.* found that high fibrillation tendency was a result of a low temperature spin bath. The reason was that lower temperature caused thermal quench higher and led to more a phase separation which directly influenced the porous structure inner fiber.

Finishing parameters such as temperature and pH were indicated as the other paremeters affecting the fibrillation. In 1994, Alix described that increasing both temperature and pH of dye bath increased the degree of fibrillation. This is because more degree of swelling and also more access of water into the fibers made the outer skin of fiber break apart easily.

Nevertheless, the spinning parameters caused less effect on fibrillation than coagulated parameters. It was reported that thermal and non solvent quench during coagulation certainly perturbed the final structure of fibers more than the spinning parameters. Of course, the final structure of fiber influenced their both physical and mechaical properties.

2.5 Measurement of Fibrillation

Even though, many measurements are found out and filed in patents, there is no universally accepted standard for assessment of fibrillation. are presented in patents. Most methods are applied to commercial assessment while little are referred in laboratory. However, to measure the fibrillation, most methods are composed of two steps of examination. The first step is the inducement followed by the assessment of fibrillation.

Sonication is one of the inducement of fibrillation method to which ultrasonic are applied. Ten lyocell fibers (20 ± 0.1 mm) are placed in 10ml distilled water contained in a glass phial. An ultrasonic probe, then, is inserted in the phial surrounded with an ice bath (see Figure 2.4).

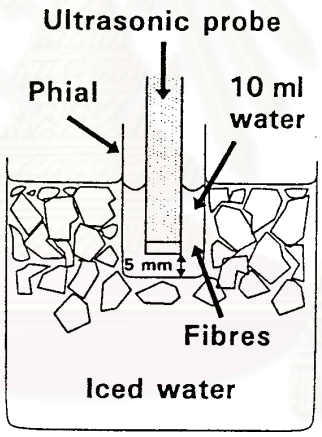

Figure 2.4 The inducement of fibrillation of lyocell fiber by sonication method.

After ultrasonic probe absolutely works for a set time, the fibers are transferred to two drops of water placed on a microscope slide. A photograph is taken under 20 times magnification of a representive area of the sample. Fibrillation Index (FI) is assessed by using the following formula :

$$FI = (n.x) / L \quad \text{.....(2.1)}$$

Where n is the number of fibrils, x is the average length of fibrils in mm and L is the length of fiber along which fibrils are counted. (U.S. Patent, 5 779 737). The measured fiber is compared with a set of standard photographs which range form 0 (no fibrillation) to 30 (the highest fibrillation).

Alternatively, fibers can be determined the degree of fibrillation by Abrasion Test. In order to calculate the abrasion value, 20 fibers are laid over a rotable shaft covered with a wet viscose fabric. Then, the fibers are fast clamped at an angle of 50 degree relative to the axis of rotation of the shaft and are loaded with a pretension weight of 70 mg at the end. The shaft is rotated at a speed of 500 rounds per minute. The breaking time of the thread is measured in order to evaluate the number of revolutions. The abrasion value, then, is calculated from the number of revolutions at break divided by the titer of fiber. However, this method probably causes an error due to small sample size.

Furthermore, the widely used method for research laboratory is Shaking Test because of its ease to carry out, more accuracy and also less complicate technique. Nevertheless, this method requires longer time comparing with the previous methods. To examine the fibrillation tendency by means of Shaking Test, 1 gram fiber is placed in a 20ml bottle contained 4ml distilled water. The 2g/l sodium carbonate is added and then the bottle is shaken on a laboratory shaking devide, type RO-10 by Gerhardt of Bonn,(DE), at speed 12 for 9 hours. Subsequently, the length of fiber and fibrils are examined under microscope. The fibrillation Index developed by Courtauld Fibers Co. Ltd. is calculated from the equation as the following :

$$FI = \Sigma l / L \quad \text{.....(2.2)}$$

L : fiber length l : fibril length

The unfibrillated fibers are evaluated as a Fibrillation Index of zero and other fibrillated fibers are graded from 0 (no fibrillation) – 10 (the highest degree of fibrillation) compared with the standard graded fibers.

2.6 Controlling of fibrillation

At present, there are several possible ways of modifying the fiber structure in order to control the degree of fibrillation. During fiber production, modifying of spinning parameters such as cellulose-NMMO solution concentration, spinneret size, air gap condition, line speed and draw ratio as shown in the earlier is possible way to carry out. Actually, it is hard to modify the production parameters which probably impact its throughput, cost and also benefit. Thus, the alternative way are continuously developed.

Defibrillation finishing is recently presented in order to control the fibrillation level after the spinning process. Many possible methods are studied and some of them are actually applied in commercial products.

2.6.1 Defibrillation by Enzymatic Treatment

Enzymatic treatment which have been normally used in cotton is now treated in several man-made cellulosic fibers such as lyocell, rayon and cellulose acetate. The satisfactory results are presented. Cellulase treatment performed best on lyocell followed by rayon but had a little effect on cellulose acetate. The enzymatic treatment was beneficial to the textile products in many ways such as softening, defuzzing, depilling, pill prevention and long lasting. The report shown that enzymatic treatment of lyocell certainly affected the reduction of fibrillation tendency and also improved the surface smoothness.

The enzymatic treatment procedures were explained by Akhil *et al.* (1999). Firstly, the fibers were induced the fibrillation by mechanical action in wet state. The hydromechanical action caused the surface of fibers to be abraded and to peel away ; consequently, the primary fibrillation occured. Cellulase enzymes , then, were treated on the fibrillated fibers which were weaker and susceptible to enzymatic hydrolysis. The primary fibrillation was significantly attacked and also removed from the surface of fibers by cellulase. When these fibers were, again, treated by other wet processing, secondary fibrillation was uniformly induced producing the improvement of handling, aesthetic and appearance.

Focher, *et al.* (1991) has reviewed that hydromechanical action alone was sufficient in removing fibrillation, but it required long processing time. Use of cellulases combined with mechanical action effectively removed the fibrillation in short time. The conventional cellulases are naturally in complexes of two main types ; exocellulase and endocellulase. Endoglucanases (EG), or endocellulases, are responsible for the random hydrolysis of cellulose chains and causes the chain ends by attacking the inner regions. Cellobiohydrolases (CBH), or exocellulases, attack the polymer chain ends and produce the oligomers, cellobiose. After the combination of two-step functions, Beta-glucosidases hydrolyze the oligomers such as cellobiose into glucose (see Figure 2.5)

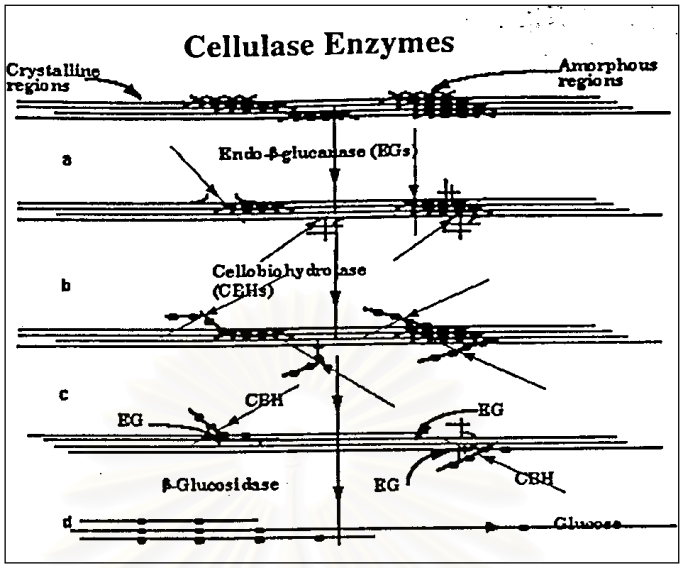

Figure 2.5 Function of cellulase component activities.

However, conventional cellulase are not desirable in textile wet processing because of the uncontrollable degradation of cellulose fibers. The engineered component cellulases developed by using modern biotechnological techniques are widely used as defibrillation finishing in industry.

2.6.2 Defibrillation by Cross-linking agent

To reduce the fibrillability during the manufacturing process, many attempts to develop the alternative defibrillation method were achieved. Hirgo *et al*. (1994) described that cross-linking reduced the fibrillation nearly to zero value; however, it lowered breaking resistance and led to a more stiff touch of fabric. In 1996, Nechwatal, Nicolai and Mieck suggested the possibility of using cross-linking reactions as a defibrillation finishing for lyocell. It was proposed that finishing cross-linking agents and special polyfunctional

reactive dyes were selected to control the degree of fibrillation. The cross-linking agent, 1,3–dimethylol–4,5–dihydroxy-imidazolidinone (DMDHI), dissolved in 30 % magesium chloride and 0.3g/l sodium fluoroborate was applied to the fibers. The cross-linking reaction was taken place by means of pad-dry-cure process at 130^{o}C for 5 minutes. The results indicated that the reduction of fibrillation of lyocell was caused by increasing concentration of DMDHI because the cross-linking agents chemically linked as covalent bond not only in amorphous but also in crystalline region like a ladder. The crystallites were the sides and the space between the sides was linked by bridging cellulose chains. The cross-linking forced the crystallites not able to slip past each other. As a result, the cellulose molecules of outer skin did not split when they were subjected to mechanical action.

Modern dyestuffs with several reactive groups, which were originally developed for higher wet fastness and better bath exhaustion, encourage research to find ways of bilaterally fixing cellulosic chains. Bilateral reaction provided the opportunity of cross-linking cellulosic molecules. This effect was of particular interest for fibers with high fibrillation. In the case where the bifuctional dyestuffs caused cross-linking reaction , the tendency of fibrillation gradually decreased, and therefore the abrasion number was expected to increase.

Nicolai, Nechwatal and Mieck (1996) concluded that reactive dyeing processes with polyfunctional dyestuffs and resin finishing reduced fibrillation of lyocell fibers. The combination of dyeing with 3% Cibacon Red C-2G and subsequent treatment with 30g/l modified DMDHI caused higher wet abrasion number than either dyeing or DMDHI treatment alone.

In a lecture given by S. Mortimer at the CELLUCON conference in 1993. It was mentioned a process for the production of a fiber having a reduced fibrillation tendency. Never dried lyocell fibers were treated with textile agent, which carried at least two reactive

groups and then were washed with an aqueous buffer. Textile agents, especially dyes having two reactive groups and colorless, were preferred. For example, vinylsulphone reactive dyes were filed in U.S. Patent 5 662 858. The application of vinylsulphone dyes achieved when in an aqueous alkaline medium, mixing with alkali carbanate and an alkali hydroxide.

In 1998, Tencel Fibers developed and filed a patent on a process utilizing a wet cross-linking system to prevent the fibrillation in the wet processing stages. This chemical system was code named AXIS. AXIS is a cross-linking agent which links the cellulose chains in order to stopping the fibrillation and eliminating the need for enzymatic treatment and resination. The reaction of cellulose with AXIS is a Michael Addition reaction. At least two, and in some cases three, of the reactive groups on the AXIS chemical react with the hydroxyl groups in cellulose chain. Not only does AXIS cause the fibrillation level to be zero but also reduce the nagative surface potential of the cellulose; therefore, fibers are easier approach by dye.

However, AXIS is dusty, with is countered by the introduction of a slurry paste, and it also has a lack of substantivity for the fiber in long liquor applications which make it expensive to apply. In order to eradicate the difficulties, the new lyocell which takes cross-linking back to the fiber production is presented. "Tencel A100®" is a lyocell fiber chemically cross-linked during production, while still in its never dried state. The process for manufacturing Tencel A100® and the application of TAHT (Triacryloylhexahydrotriazine), cross-linking agent, has been patented by Courtaulds Fibers. Start with never dried stage, cross-linking agent (TAHT) and cross-linking catalyst (TSP-trisodium phosphate) were applied to never dried Tencel tow and then fiber was cure by heating. The chemical reaction was shown in Figure 2.6

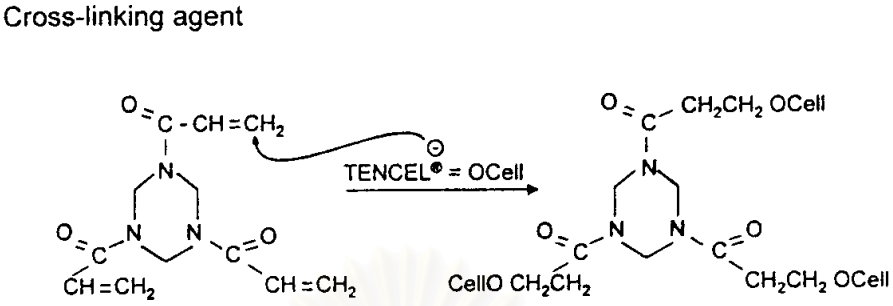

Figure 2.6 Cross-linking reaction by TAHT on Tencel® fiber.

Although Tencel A100® has lower fibrillation tendency than standard Tencel®, the report shown that it was slightly weaker than standard Tencel® being about 10% lower in both tenacity and modulus.

Actually, the mechanical properties of fibers cross-linked by pad-dry-cure process such as tenacity, elongation and loop strength decreased as the concentration of cross-linking agent increased. The reason is the degradation of cellulose chains resulted from acid hydrolysis and the immobility of crystalline regions. Like pad-dry-cure process, wet cross-linking process which was taken place in the swollen state shown the similar results. Nevertheless, comparison with the mechanical properties of fibers treated by pad-dry-cure process, the wet cure fibers were lost their strength less than dry cure fibers. This is because in wet state the cellulose molecules in crystalline regions had more mobility tendency to relax themselves during mechanical exposure.

2.7 The Microscopical Properties of Fibers

Fibers are unique unit physically alike in being very much longer than they are wide, very strong for their small cross sections and optically anisotropic. As a Consequence, the optical properties of fibers are discussed separately from crystals. Fibers do not display crystal faces, so there are fewer optical properties to be observed. Furthermore, various compositions and treatments produce variations in the optical values of a given species of fiber

To achieve the optical properties of fibers, a few fibers are cut to lengths of 1 or 2 cm and mounted in a liquid to reduce the scattering of light by the fiber in air (refractive index, n = 1.00). Water (n=1.33) is commonly used for mounting hydrophilic fibers such as cellulosic fibers and mineral oil (n=1.48) is used for hydrophobic fibers such as nylon. The fibers are examined immediately upon the mount in liquid. Cotton; for example, swells in water with corresponding changes in optical properties.

With the fibers properly mounted, the eight determinative optical properties may be observed in succession with the aid of a polarizing microscope. The fibers are first brought into focus with the analyzer out , and then are observed between crossed polars while the stage is rotated slowly. The fibers are exposed to the light which its waves vibrate into two direction : one vibration direction parallel to the fiber axis and the other vibration direction perpendicular to the fiber axis (see Figure 2.7). The eight optical properties of fiber, then, are examined as the following :

1. Brightness or greyness

Brightness results when an anisotropic fiber on the rotable stage is so oriented between crossed polars. There is a vector of each direction of vibration parallel to the direction of vibrating light rays in the analyzer (see Figure 2.7). The vector varies from nothing

(darkness) at positions of extinction to maximum brightness at a position of 45° between extinction (see Figure 2.8).

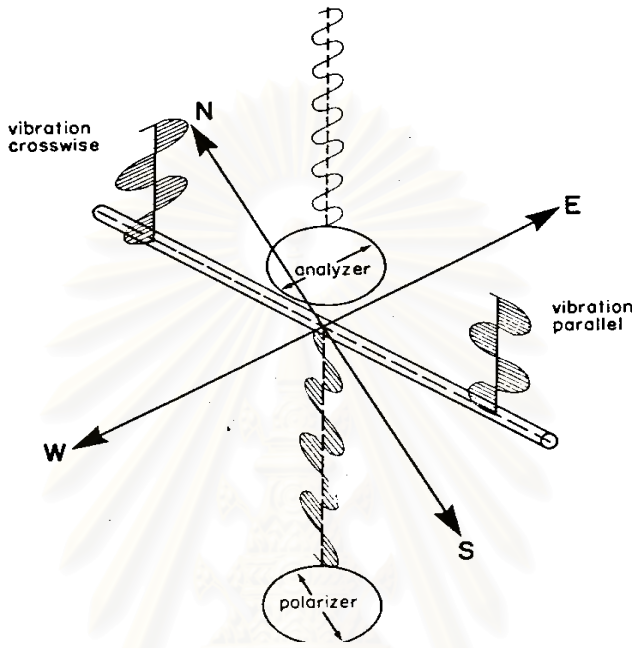

Figure 2.7 Fiber in position of brightness between crossed polars.

2. Extinction (darkness)

Complete extinction means that the whole fiber extinguishes between crossed polars every 90° of rotation. In case of the fibrillated fibers such as lyocell, when the fiber is bent, some of fibrils will be dislocated causing a local relocation of extinction. The number of dislocations indicates the number of bending. Cotton, with its spiral structure, shows no absolute extinction. Some mechanically treated man-made fibers show extinction in certain segments at a time.

3. Parallel extinction

Parallel extinction means that the axis of fiber is parallel or very closely parallel to one of the two cross lines in the eyepiece, when the fiber becomes dark during rotation of circular stage between crossed polars. Parallel extinction is shown by practically all man-made fibers, as spun, because the structural units are arranged to direction of flow through the spinneret. However, treatments such as crimping or texturizing locally alter parallel extinction if the parallel arrangment is disturbed. The extinction may be parallel or oblique to the axis of the fiber. Some fibers such as bast fibers, silk filaments and some crimped man-made fibers display segmented extinction (see Figure 2.8)

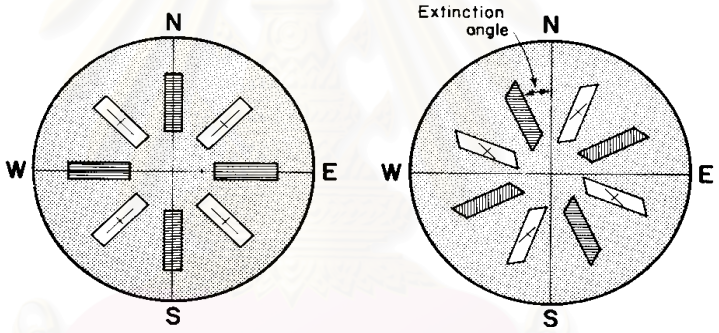

Figure 2.8 Positions between crossed polars of brightness and extinction.

4. Retardation

Retardation, the distance in nanometers that one wave train falls behind the other, is the effect of the particular fiber by polarized light. The polarizer is set so that the direction of vibration of the emerging light waves is that of north-south. The fiber is either oriented

NW/SE or SN/NE because it has maximum brightness in these two positions when the analyzer is crossed (West-East) with the polarizer (North-South).

The birefringent fiber spilts the polarized beam into two polarized rays, one vibrating lengthwise and the other crosswise of the fiber. The rays travel through the fiber at different velocities without interfering with each other because they are in different planes. Two rays from each other wave train pass through the fiber and then the analyzer in which they completely cancel each other. Thus, the color corresponding to that wavelength is lost in analyzer; on the other hand, the other rays are in phase and reinforce each other. For example, when the slower ray is in phase but about 525 nm behind the faster way, the color of light from analyzer will be red of the first order as shown in the Michel Levey scale.

Low-order grays and colors are significant because variations in thickness (denier) make so little difference in the order of retardation. Recognition of distinctive retardation colors in a mixture of two or more kinds of fibers is not only useful in forming quick qualitative desiration but also in estimating the proportions of these kinds of fibers.

5. Sign of the birefringence

Sign of the birefringence, depending on which of the two ray-bundles is the slower. Most kinds of fibers are positive because the rays vibrating lengthwise are the slower (having the higher refractive index, n). The sign is determined between crossed polars using a retardation plate. Types of negative sign at room temperature are acrylics, most cellulose triacetates and at least some sarans and vinyons. The first-order red retardation (sensitive tint) plate is good for determination gray or color of the first order.

To determine the sign of fibers showing first-order gray, a first order red plate is inserted while the fiber is in a position of maximum brightness. If the sign of birefringence is positive , the fiber will be yellow or orange. In a fiber of positive birefringence, the

slower ray vibrates parallel to the fiber axis. If the sign is negative, the fiber will be blue or magenta.

6. Quantitative birefringence

Quantitative birefringence, the numberical difference between the high and low refractive indices, is independent of path length (thickness and denier). It may be determined from the retardation per unit path length, by means of a compensator (a retardation plate). Birefringence may also be determined at the surface of the fiber by measuring the two separate refractive indices by immersion techniques.

Birefringence alone allows for a broad classification of fiber types. The weak birefringence, less than 0.01, is responsible for natural and regenerated protein, acrylics, modacrylics, acetates, saran and vinyon; whereas, the moderate to strong birefringence, 0.01-0.1, is for natural and regenerated cellulose, silk, nylons, polyolefins and vinyl. Moreover, the highest birefringent fiber which have the birefringence value above 0.1 is polyester.

Birefringence can be defined in other terms as the ratio between retardation and thickness of specimen. If the fiber is practically a cylinder as a case of man-made fibers, the thickness is the same as the diameter of fiber.

According to Michel Levey chart, weak birefringent fibers usually display first-order gray scale. In contrast to fibers with moderate and intense birefringence, the usual parallel extinction display color bands parallel to the axis.

7. Refractive index along fiber axis, $n_{||}$

The refractive index for the light from the polarizer vibrating parallel to the length of the fiber, may be measured by comparing $n_{||}$ with the refractive indices of a liquid standard.

8. Refractive index perpendicular to fiber axis, $n_{\perp}$

The refractive index for the light vibrating perpendicularly to the length of fiber, is measured in the same way as $n_{||}$ but with the fiber oriented at right angles to position used for measuring $n_{||}$.

2.8 Degree of Polymerization

The number of monomer units present in a polymer is referred to as the degree of polymerization (dp). The monomer glucose combines with another monomer of glucose to form cellobiose, which is the basic building block of the polymer cellulose. The number of glucose units reported for cotton varies widely. It depends on the variety and the method of chemical analysis used. A cotton fiber with 3000 glucose units has a dp of 3000; one with 15000 glucose units has a dp of 15000. The dp of the cellulose in rayon may range from 250 to 650. Cotton and rayon are expected to have similar properties because both are cellulosic fibers. They are expected to have some differences because they have different dp. Generally, higher-molecular-weight polymers tend to be more stable, with a higher degree of intramolecular force. The physical properties of a polymer differ radically from those of the monomers from which it is formed.

2.9 Fiber Orientation

Within a long, slender fiber are many equally long and slender polymers. Although the basic chemical compound from which a fiber is made is the major determinant of that fiber's properties, the arrangement of polymers within the fiber walls also influences the chemical and physical properties of the fiber. The polymer chains may bond together to form more rigid structures called crystallites. The chemical mechanisms responsible for producing crystalline order include covalent and ionic chemical bonding and secondary bonding such as hydrogen bonds, van der Waals' forces, and dipole-dipole interactions.

Covalent bonds, which result from shared valence electrons between atoms, form cross-links between polymer chains, ionic bonds occur when one atom of an element transfers one or more of its electrons to one or more atoms of another element. Ionic compounds are bound by the mutual attraction of the positive and negative ions of the donor and acceptor atoms. These two types of chemical bonds formed between polymers are stronger than secondary bonds.

Hydrogen bonds, which occur between the electropositive hydrogen atom and an electronegative atom such as chlorine, oxygen, or nitrogen, are the strongest of the secondary bonds. Because secondary bonding can occur at many different sites between polymer chains, there is a potential for very high associative forces to develop. These associative forces may be as a chemical attraction between two atoms. Van der Waals' forces are very weak forces that function only when molecules are close enough to be attracted by each other's transient polarization. Such forces occur when the distance between molecules is 4 to 5 angstroms and when the slightly positive and slightly negative charges on the molecules are oriented so the opposite charges could attract one another.

The arrangement of molecules within the fiber is a major determinant of fiber properties. Within the fiber are two basic forms of polymer arrangement of orientation are shown in Figure 2.9 and 2.10.

Figure 2.9 Schematic diagram of amorphous molecular orientation in a fiber.

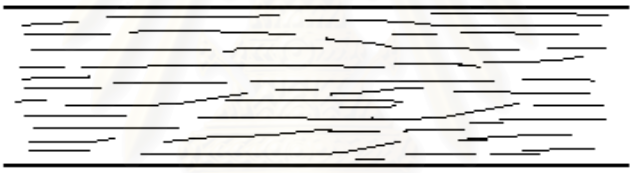

Figure 2.10 Schematic diagram of crystalline molecular structure in a fiber.

In disoriented material, the polymers are in random order (see Figure 2.9). They are at varying angles to each other and to the longitudinal fiber axis. This less-ordered portion of the fiber is referred to as the amorphous region and is said to exhibit low orientation.

When the polymers are parallel to each other and the fiber walls, they are said to be highly oriented, and the fiber is described as crystalline (see Figure 2.10). The strength of the fiber comes from the crystalline order; flexibility and extensibility come from the amorphous disorder.

It is unusual to find a fiber that is completely amorphous or completely crystalline. Glass fibers are amorphous and asbestos is crystalline, but most other fibers contain both crystalline and amorphous regions. Some fibers are highly crystalline with relatively small amorphous areas, and others are relatively amorphous with small crystalline areas. No sharp division of crystalline and amorphous areas occurs, nor are the crystalline areas embedded within amorphous areas. The shift between amorphous and crystalline areas is gradual.

The orientation of natural fibers may be changed by chemical finishing; in manufactured fibers, it is often controlled by stretching or drawing the fiber to alter the chemical and physical properties of the fiber. High orientation is associated with high fiber strength and low elongation. Low orientation tends to produce lower strength and higher elongation. Relatively crystalline fibers have better chemical resistance and are more lustrous, but they are also more brittle or less flexible. Amorphous areas within a fiber tend to improve moisture absorbency, dyeability, and pliability and to produce fibers with a soft, warm hand.

2.10 Cross-linking Behaviour of Fiber

Molecules are capable of slipping, or moving back and forth against each other, within a fiber. Molecular slippage is likely to be at a maximum in amorphous areas and at a minimum in crystalline areas. When a high degree of molecular slippage occurs, the fiber will have high elongation, but if the molecules do not return to the optimum position, the fiber may be weakened and have poor elastic recovery. In some fibers, molecules are joined to parallel molecules by chemical bonding known as cross-linking (see Figure 2.11).

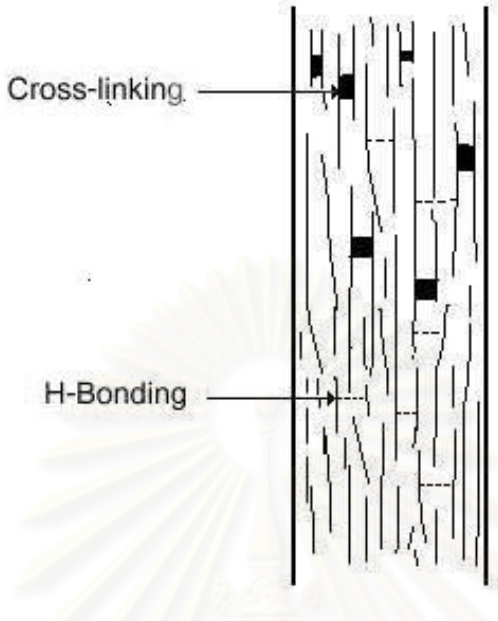

Figure 2.11 Schematic diagram of cross-linking.

In other fibers, molecules may be anchored by the associative forces of secondary bonds, which can be broken easily and reestablished at the same site or at new locations. When molecules do not contain the polar groups necessary for hydrogen bonding, weaker associative forces such as van der Waals' forces, can be established between molecular segments.

The bonding that prevents molecules from sliding over each other alters the polymer's physical properties, such as crease resistance, dimensional stability, and wrinkle resistance. The desirable effects may include better resilience and recovery from deformation, greater chemical stability, and greater resistance to biological attack. When a bulky three-dimensional molecule is formed, the polymer often is insoluble and is unlikely to melt when exposed to heat. Such side effects are undesirable for most fibers but may be desirable for industrial uses.

CHAPTER III

Experimental Procedures

3.1 Scope of research

1. Tencel® fiber was chosen to represent man-made cellulosic fibers due to its highest tendency to fibrillate under wet state abrasion.
2. The sample, Tencel® staple fiber, was finished by GP® (cross-linking agent) in various concentrations at 2 g/l, 4 g/l, 6 g/l and 8 g/l to control the degree of fibrillation.
3. Birefringence, intrinsic viscosity and crystallinity of fibrillated and defibrillated Tencel® fiber were determined as the following :
    - Birefringence was observed by Olympus Polarizing Optical Microscope.
    - Intrinsic viscosity was determined by means of ASTM D 1795-96.
    - Relative crystallinity was measured from X-ray diffractometer.
4. The fibrillation of Tencel® fiber was induced by Shaking Test in alkali aqueous solution and then assessed in terms of Fibrillation Index under microscopic examination.
5. The statistical process was used to analyse the relationship between each physical parameters and the results were proposed in mathematical equations.

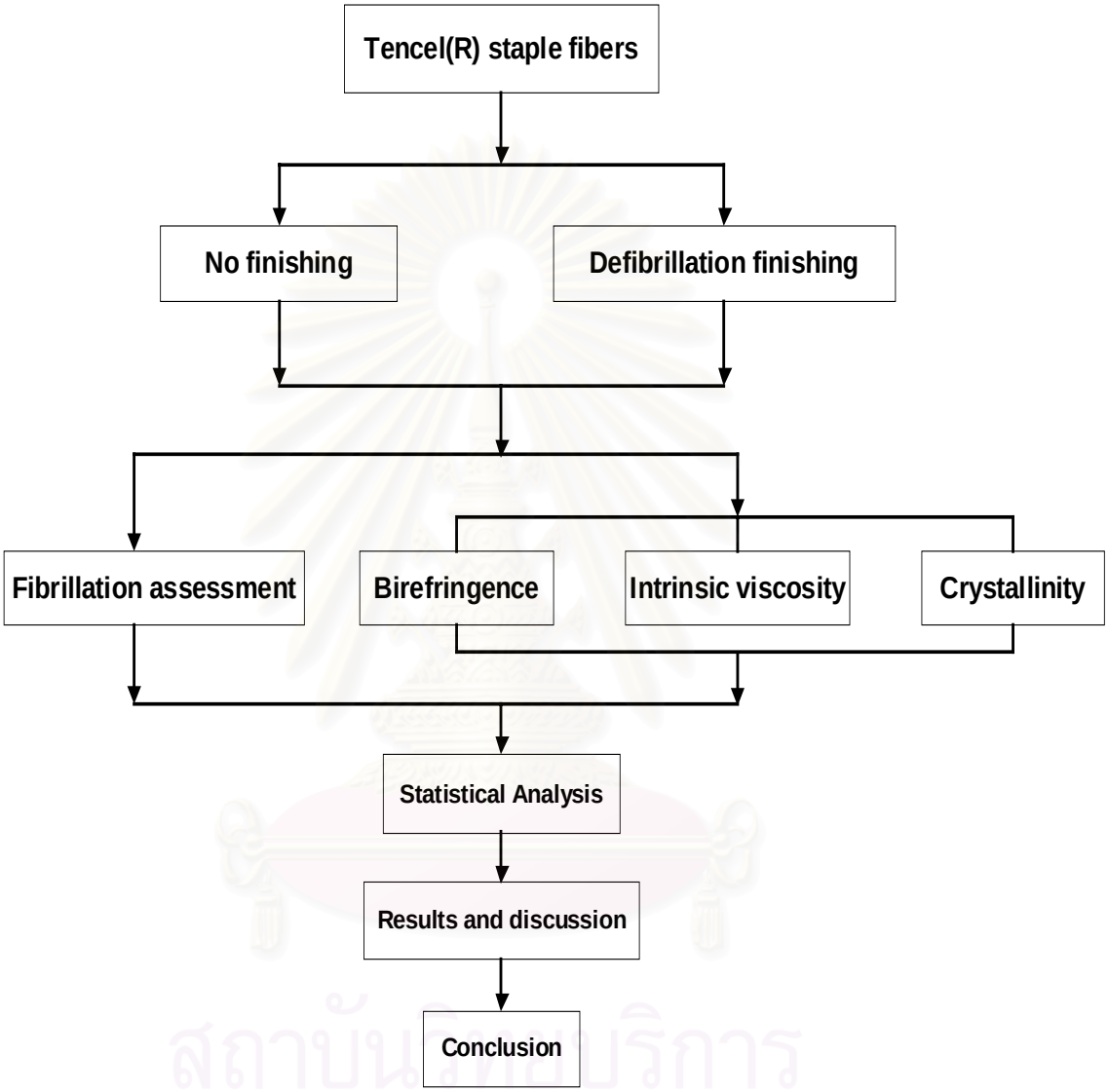

Figure 3.1 Flowchart of research scope.

3.2 Materials

Tencel® staple fibers were provided by J.P. Bosco Co.,Ltd.

Figure 3.2 Tencel® staple fiber.

3.3 Chemicals

All chemicals used in this experiment are laboratory reagent grade.

3.3.1 Defibrillation agent

GP® is an effective commercial cross-linking agent for reducing the fibrillation tendency of Tencel® fiber sold by J.P Bosco Co., Ltd. GP® is generally a white fine powder which can be dissolved in an aqueous alkali solution. Its certain properties and structure are difficult to trace because of the commercial know-how. However, from the basic characterizations, GP® is a polyfunctional colorless reactive dye containing at least two amine groups reacting with hydroxyl groups in cellulose chains to form cross-links.

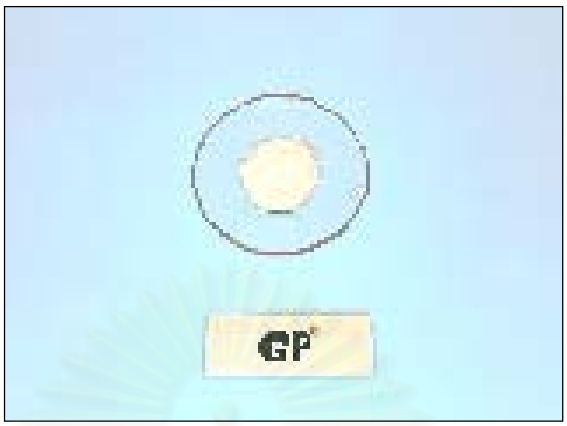

Figure 3.3 GP® (cross-linking agent).

3.3.2 Sodium Sulfate Anhydrous (Na_2SO_4)

Molecular Weight : 142.04 g/mol

Properties : white fine hygroscopic powder and water soluble

3.3.3 Sodium Carbonate Anhydrous (Na_2CO_3)

Molecular Weight : 105.99 g/mol

Properties : white hygroscopic granular or coarse powder, water soluble and weak base (pH = 8-9)

3.3.4 Cupriethylenediamine Hydroxide Solution ($Cu(NH_2CH_2CH_2NH_2)_2(OH)_2$)

Cupriethylenediamine Hydroxide Solution in copper with the molar ratio of ethylenediamine to copper of 2 ± 0.1 to 1 is used as an effective solvent for cellulose at 25° C. By means of ASTM D 1795-96, this solvent can be prepared in the laboratory as described in Test Method D 539.

Properties : deep blue solution, alkali soluble, sensitive to oxygen, light and heat.

Hazard : causes burns and harmful in contact with skin. Should wear suitable protective clothes such as gloves and eyeface protection. In case of accident of it, call for medical advice immediately.

3.4 Equipments

1. Ubbelohde viscometer, glass capillary type size 100 cm^3
2. Circulator
3. Transparent water bath (50 x 35 x 35 cm^3)
4. Accurate timer
5. Thermometer
6. Nitrogen gas
7. Mechanical shaker
8. Precision balance
9. Olympus optical polarizing microscope
10. X-ray diffractometer
11. Glasswares

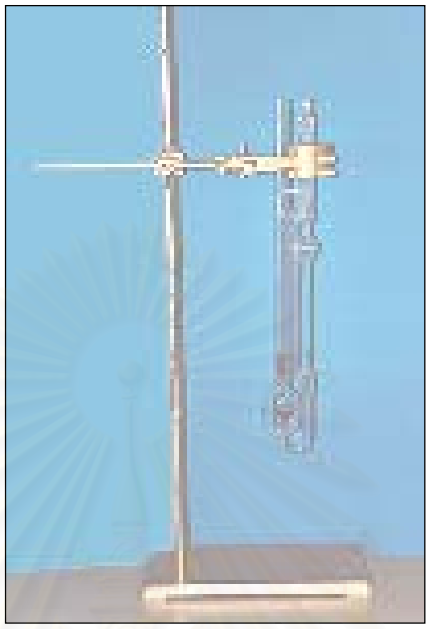

Figure 3.4 Ubbelohde viscometer

Figure 3.5 Mechanical shaker

Figure 3.6 Optical microscope

3.5 Defibrillation Finishing

In order to control the fibrillation level of fiber, GP® was treated on Tencel® fiber in various conditions.

1. Apparatus

Mechanical shaker with adjustable the speed levels from 50 – 150 revolutions per minute.

2. Materials

Tencel® staple fibers.

3. Chemical Reagents

- GP® stock solution x % by volume (x : 2%, 4%, 6% and 8%)
- Sodium sulfate stock solution 12 % by volume
- Sodium carbonate stock solution 12 % by volume

4. Sample preparation

Tencel® fibers were separated by hand to break up any lumps and dried in an oven at 80° C for 30 minutes , then, keeped in desicator.

5. Procedure of defibrillation finishing in laboratory scale

5.1 Weigh 2 grams of dry fiber and put into a flask.

5.2 Pipet 2 ml of x% GP® stock solution, 2 ml of 12% of Sodium Sulfate stock solution, 12% of Sodium Carbonate stock solution and 14 ml of distilled water into the flask.

5.3 Cover the flask with the aluminium foil and shake at medium speed level (80 revolutions per minute), 90° C for 30 minutes.

5.4 Rinse by water for 2 minutes.

5.5 Dry at 80° C for 30 minutes.

5.6 Vary the x% GP® stock solution from 2%, 4%, 6% and 8% and follow the step 5.1 to 5.5.

5.7 Defibrillated fiber, then, were divided into 4 parts for physical property examinations as follows :

- Fibrillation Assessment
- Birefringence Examination
- Intrinsic Viscosity Measurement
- Relative Crystallinity Measurement

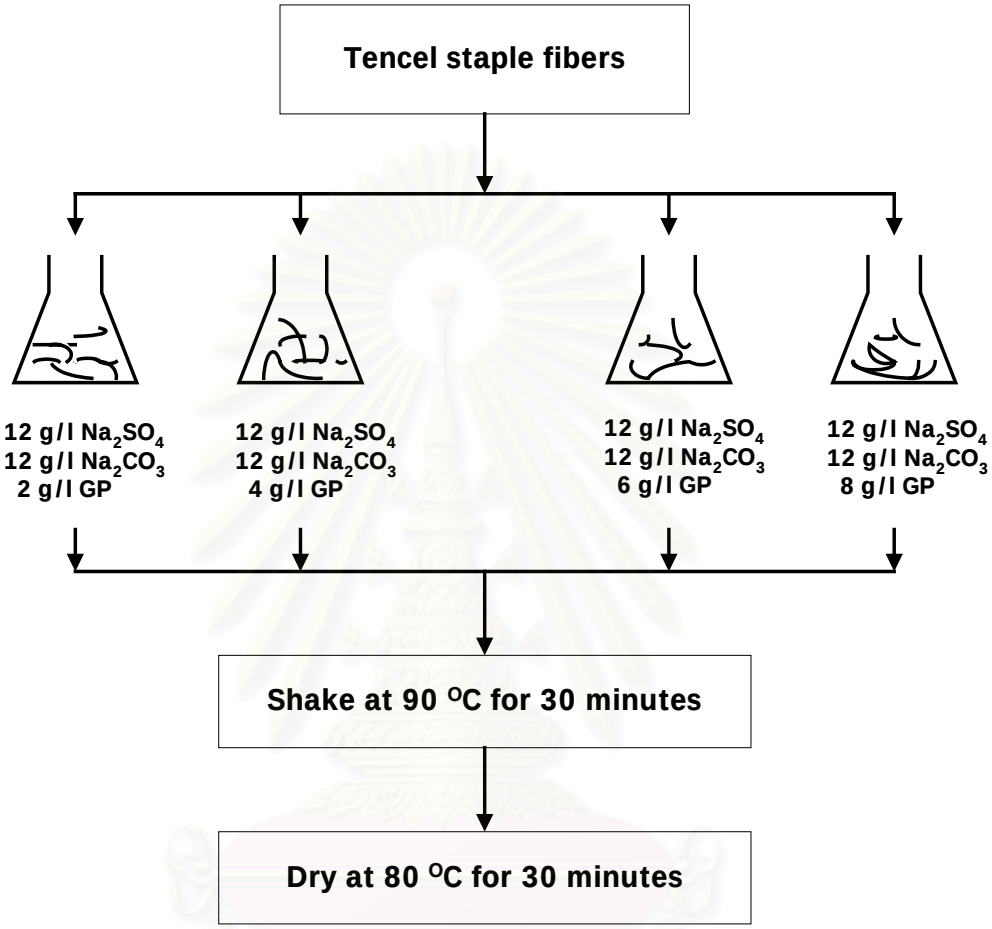

Figure 3.7 Flowchart of Defibrillation Finishing.

3.6 Fibrillation Assessment

1. Apparatus

- Gallenkamp Mechanical Shaker adjustable the speed level from 50 – 150 revolutions per minute.
- Optical microscope.

2. Test specimens

Tencel® staple fiber was defibrillated in various levels.

3. Chemical Reagent

Sodium carbonate 12 g/l

4. Test Procedure of Fibrillation Induction

4.1 Weigh 1 gram of dry defibrillated fiber and then put into a flask.

4.2 Add 50 ml of 12 g/l Sodium Carbonate in the flask.

4.3 Cover the flask with the aluminium foil and shake at high speed level (120 revolutions per minute), ambient temperature for 30 minutes.

4.4 Rinse water for 2 minutes.

4.5 Dry at 80° C for 30 minutes.

5. Test Procedure of Fibrillation Measurement

5.1 Mount the induced fibrillated fibers individually on a glass slide parallel to each other.

5.2 Examine the fibrillation of fiber under microscope in which the ruler scales are already set.

5.3 Measure the length of all fibrils and of that fiber.

5.4 Calculate the Fibrillation Index (FI) as a following equation :

$$FI = \sum l / L$$

l : length of fibrils L : length of fiber

5.5 The Fibrillation Index of the defibrillated fiber in each level are the average of measurements at least 10 fibers and consistency under 10 % of the coefficient of variation for single fibers from one sample.

3.7 Birefringence Examination

1. Apparatus

1.1 Polarizing Microscope having a rotable mechanical stage and accessories with suitable illumination.

1.2 Adjustable Retardation Compensator

1.3 Filar Micrometer eyepiece or other suitable accessory for measuring fiber diameter within ±1 μm.

2. Test Specimens

The specimens consist of at least 3 defibrillated fibers mounted separately on a slide.

3. Test Procedure

3.1 Measure the fiber diameter from micrometer eyepiece.

3.2 Position the polarizer and analyzer so that both polarization planes are perpendicular to one another and at 45° to the axis of compensator.

3.3 Align the fiber on either horizontal or vertical axis.

3.4 Rotate the stage until the image of fiber is the darkest ordinary at every 90° (position of maximum extinction).

3.5 Rotate the stage 45° further in the same direction and carefully observe the color of fiber comparing to the colors in Michel Levey Chart.

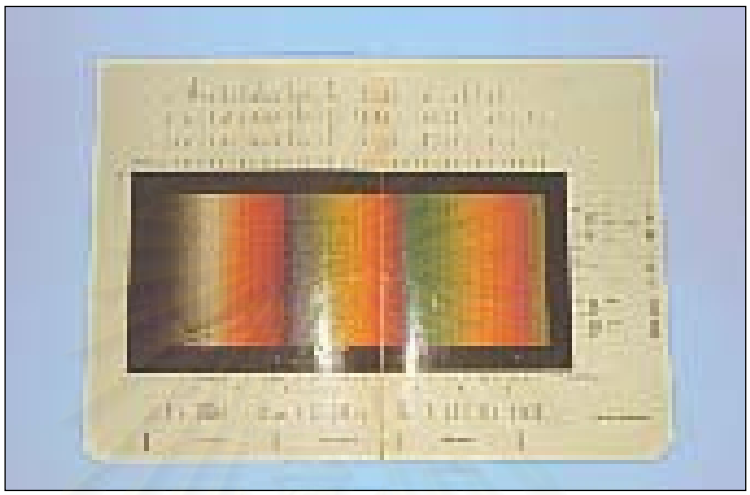

Figure 3.8 Michel Levey Chart.

3.6 Due to several color orders in the chart, it is hard to distinguish which color orders present the first color observed from the microscope. The retardation compensator is normally inserted in this position so that the color will go up in order and then if rotate the stage further 90° as the retardation compensator is inserted, now, the colors will go down in order. Therefore, the first color can be exactly estimated from both up and down color orders.

3.7 Birefringence is the average of the measurements on at least 5 fibers of each sample and consistency under 10% of the coefficient of variation.

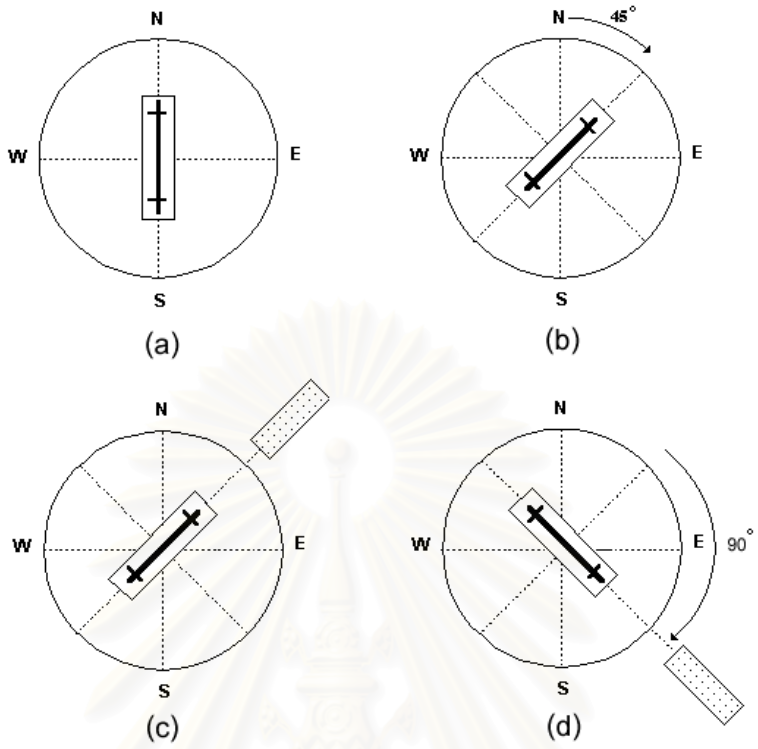

Figure 3.9 The procedure of birefringence measurement

(a) The extinction position of fiber along N/S axis (the first color observed).

(b) The brightness position of fiber after 45^0 rotation.

(c) The position of fiber while the retardation compensator is inserted (the second color observed).

(d) The position of fiber while the compensator is rotated further 90^0 (the second color observed).

3.8 Intrinsic Viscosity Measurement (ASTM D 1795-96)

1. Apparatus

1.1 Ubbelohde viscometer, glass capillary type size 100 cm^3 according to Test Method D 445.

1.2. Circulator

1.3. Transparent water bath covered with a heat insulator (50 x 35 x 35 cm^3)

1.4. Accurate stop watch

1.5. Thermometer

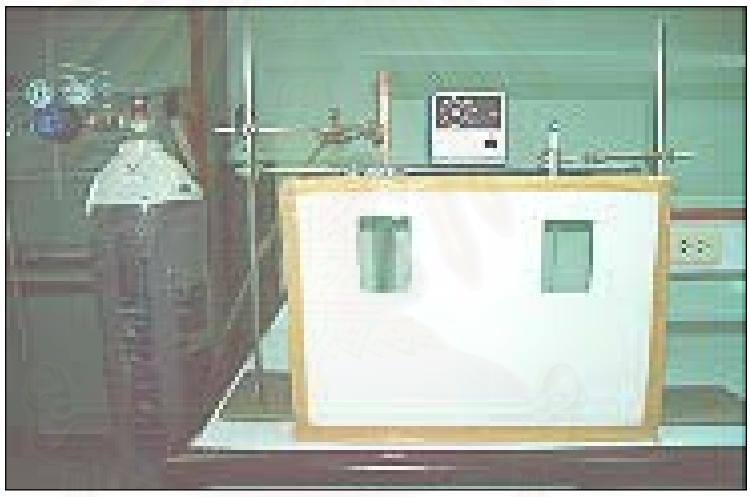

Figure 3.10 Water bath.

2. Chemical Reagent

Cupriethylenediamine Hydroxide Solution (1.00 ± 0.01 M) in copper with the molar ratio of ethylenediamine to copper of 2 ± 0.1 to 1. This solvent can be prepared in the laboratory as described in Test Method D 539.

3. Test Specimens

Defibrillated fibers should be picked apart and cut into short fibers, then, dried in the oven at 80° C for 30 minutes.

4. Preparation of solution

4.1 Weigh 0.2 grams of oven-dried defibrillated fiber and transfer to a 50 ml flask that can be tightly closed by a stopper.

4.2 Add 25.0 ml of distilled water from pipet, insert the stopper and then shake in order to disperse whole fibers.

4.3 Sweep the air from the vessel by flushing nitrogen gas.

4.4 Add 25.0 ml of 1 M Cupriethylenediamine Hydroxide Solution*, close tightly and shake vigorously by hand or mechanical shaker until the cellulose is completely dissolved.

5. Measurement of Outflow time (t_0) of solvent

5.1 Transfer 10 ml of 0.5 M Cupriethylenediamine Hydroxide Solution into the viscometer previously immersed in a water bath which control the tempereture at 25° C.

5.2 Flush nitrogen gas and close all open sites by stoppers at least 5 minutes for the tempereture of solvent reached 25° C

Open the stoppers and pump the solvent up until pass the top mark of the viscometer.

5.3 Measure the time (t_0) required for solvent flow from the top mark to the bottom mark of bulb.

---

* Alkaline solution of cellulose is sensitive to oxidation. Hence, it is necessary to avoid oxidizing agent, light, heat, acid and alkalies during the experiment.

5.4 Repeat at least twice and average the observations which the time should not differ more than 0.3%.

6. Measurement of Outflow time (t) of solution

1.1 Transfer 10 ml of the solution by pipet to a viscometer and then follow the steps as shown in the previous procedure (5.2-5.5).

1.2 Dilute the solution at least five concentrations by adding the solvent and then repeat the steps as shown in 5.2-5.5.

7. Calculation

7.1. Calculate the relative viscosity, η_{rel} as follows :

$$\eta_{rel} = t / t_0 \quad \text{.....(3.1)}$$

when t_0 : outflow time of solvent t : outflow time of solution

7.2. Calculate the intrinsic viscosity by plotting log $[(\eta_{rel} - 1) / C]$ against C.

According to the Martin Equation, the intercept of extraporated straight line through the point C = 0 gives log $[\eta]$.

The Martin Equation :

$$\log [(\eta_{rel} - 1) / C] = \log [\eta] + k [\eta] C \quad \text{.....(3.2)}$$

η : intrinsic viscosity C : concentration (g/dl)

η_{rel} : relative viscosity k : constant

3.9 Relative Crystallinity Measurement

Philips PW 3710 Diffractometer using CuK_α radiation was used to investigate the crystallinity at the condition of scanning at 40 kV and 30 mA with speed at 0.02^0 2θ / minute. The intensity of amorphous and crystalline peak at diffraction angle 2θ equal to 19.8 and 22.0 were measured relatively. The relative crystallinity was calculated from the following formula.

$$\% C = \frac{I_C}{(I_A + I_C)} \times 100 \quad \text{.....(3.3)}$$

When C : Relative Crystallinity I_A : Intensity of amorphous peak

I_C : Intensity of crystalline peak

Figure 3.11 X-ray Diffractometer.

3.10 Statistical Analysis

In this experiment, the SPSS Program version 9.0 was selected for statistical analysis. After testing, the data were analyzed by these statistical parameters.

- Descriptives such as mean (μ), standard deviation (SD) and coefficient of variation (CV)
- Pearson's correlation coefficient (r)
- Standardized Regression Coefficient (β)
- Coefficient of Determination (R^2)

Moreover, the f-Test and t-Test were also examined for the hypotheses test.

CHAPTER IV

Results and Discussion

4.1 Effect of Cross-linking Agent on Fibrillation Index

GP®, a cross-linking agent, reacted with hydroxyl groups of cellulose molecules in an aqueous alkaline medium to form covalent bonds linking between cellulose chains. The cross-linking reaction took place in the outer skin of fiber encountering the fibrillation of inner layers. Thus, the fibrillation of fiber was gradually reduced . The effects of the concentration of cross-linking agents on the Fibrillation Index, birefringence, intrinsic viscosity and relative crystallinity were presented in Table 4.1.

Table 4.1 Fibrillation Index, birefringence, intrinsic viscosity and % relative crystallinity* of Tencel® fiber treated with 0%, 2%, 4%, 6% and 8% GP®.

% GP	FI	BF	η	C (%)
0	0.45	0.0430	3.016	66.43
2	0.40	0.0432	3.284	53.20
4	0.38	0.0421	3.779	46.56
6	0.12	0.0410	7.953	23.74
8	0.30	0.0426	3.300	42.84

* FI : Fibrillation Index BF : Birefringence

η : Intrinsic viscosity C : Relative crystallinity

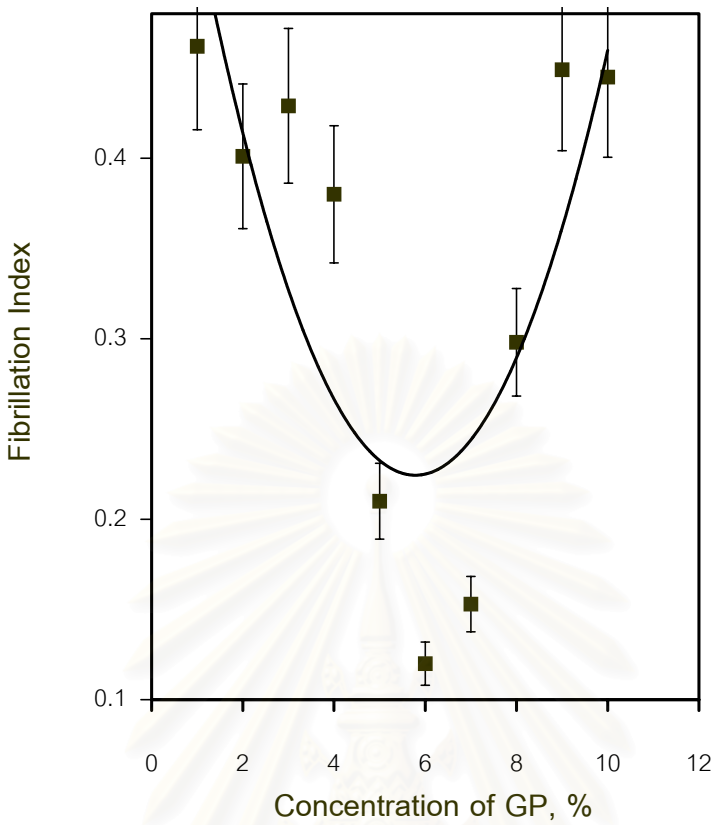

Figure 4.1 The relationship between Fibrillation Index and concentration of GP®

Figure 4.1 shows that the Fibrillation Index was not linearly proportional to the concentration of GP® as assumed at the beginning. The Fibrillation Index decreased significantly while the concentrations of GP® increased from 1% to 6%. However, defibrillation finishing more than 6% of GP® shows the opposite results, the Fibrillation Index increased sharply as a parabolar function which had a minimum level at 5.8% GP®. This is because the higher contents of GP® provided more opportunities of cellulose molecules being cross-linked so that the lateral cohesions were being risen. On the other hand, it was obviously observed in the experiment that the concentrations of GP® more than 6% resulted in the precipitation of GP® from the finishing solution before reacting with cellulose chains.

4.2 Effect of Cross-linking Agent on Relative Crystallinity

When fibers were soaked in an alkali medium, GP® was capable of penetration into the fiber structure particularly on the outer skin during defibrillation finishing. The swelling of fiber allowed the GP® molecules to react with the hydroxyl groups of celluloses in amorphous regions better than crystalline regions and led to the increase of number of pores inside the fiber structure. After treatment, the fiber structure was disturbed not only by swelling but also covalent bonds which linked vertically between cellulose chains.

The relative crystallinity was calculated from amorphous and crystalline peaks appearing at diffraction angle 2θ = 19.8 and 22.0 repectively. The results indicated that the finishing by GP® 2% up to 6% significantly effected on the reduction of relative crystallinity . Although the X-ray diffractograms in Figure 4.2 shows little differences among fibers finished in various concentrations of GP®, the relative measurement of crystallinity presented the significant changes as seen in Table 4.2.

Table 4.2 The intensity and relative crystallinity of Tencel® finished by 0%, 2%, 4%, 6% and 8% GP®

% GP	Intensity at diffraction angle 2θ (counts)			Relative crystallinity C (%)
	12.1	19.8	22.0	
0	94.82	137.17	271.44	66.43
2	85.41	127.94	145.43	53.20
4	91.67	243.52	212.17	46.56
6	90.44	386.38	120.28	23.74
8	101.95	365.11	273.64	42.84

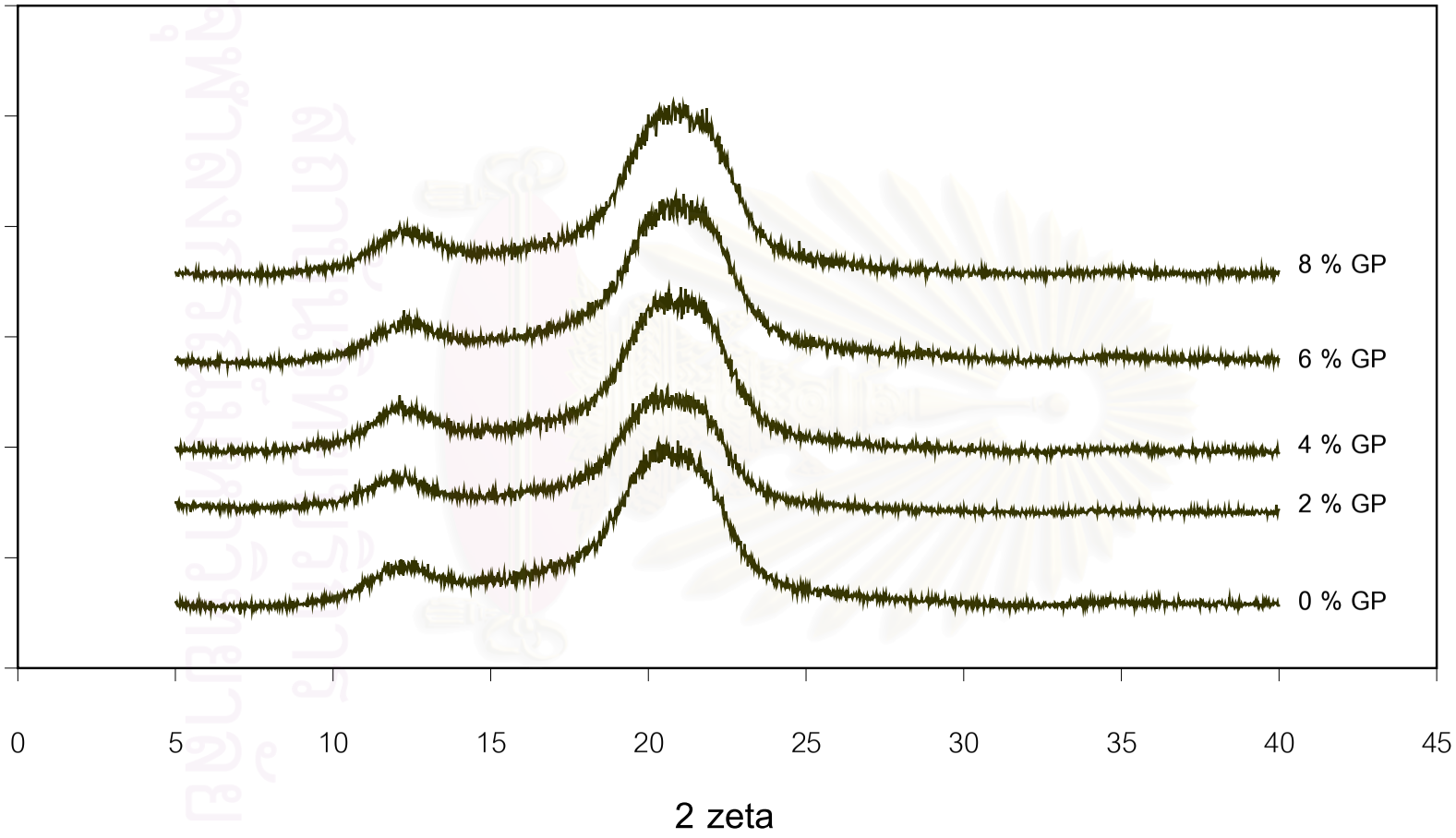

Figure 4.2 The X-ray diffractograms of Tencel finished by various concentration of GP.

4.3 Effect of Cross-linking Agent on Birefringence

Similar to the effect of cross-linking agent and crystallinity, the cross-linking impacted significantly on the orientation of fiber which directly related to the optical properties as seen in Figure 4.3.

After cross-linking, there were many covalent bonds crossing along cellulose chains which was able to retard the velocity of light in that direction. This change mainly affected the refractive index of fiber; as a consequence, the differences between both refractive index in horizontal and vertical direction was less than before finishing. Thus, it was seen that the birefringence decreased steadily while the concentration of GP® increased from 2% up to 6%. In addition, it was noticed that finishing more than 6% GP® did not effect significantly on the birefringence of fiber.

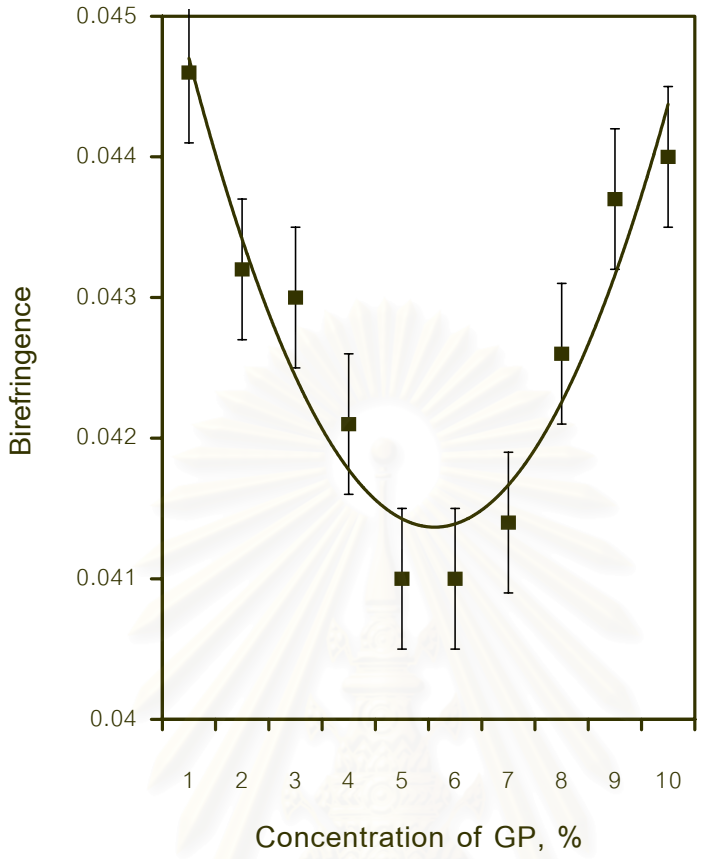

Figure 4.3 The relationship between birefringence and the concentration of GP®.

4.4 Effect of Cross-linking Agent on Intrinsic Viscosity

The relationship of intrinsic viscosity and cross-linking agent appeares in Figure 4.4. The descent of intrinsic viscosity after treatment by a GP® more than 6% was due to the precipitation of GP® as described earlier.

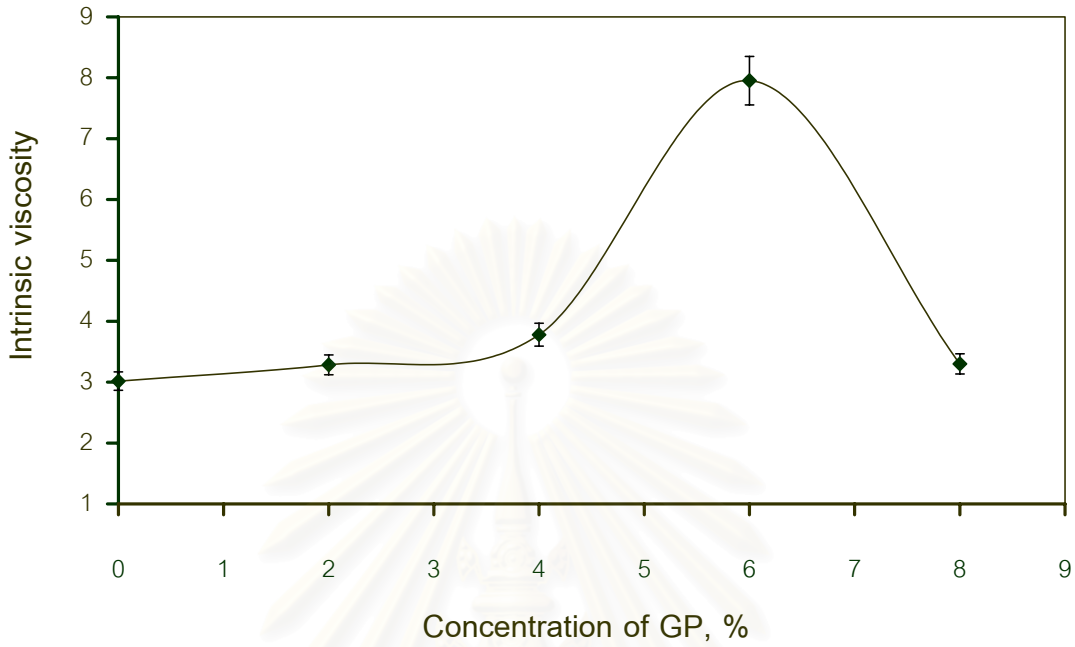

Figure 4.4 The relationship between intrinsic viscosity and the concentration of GP®.

The results indicated that the intrinsic viscosity depended on the ability of molecular chains to slip pass each other. The cellulose chains of no finished fiber was able to move easily when dissolved in the solvent. Therefore, its outflow time and also viscosity was less than finished fiber. In the case of cross-linked fiber, GP® was linked between the cellulose molecules like a ladder; subsequently, the cellulose chains were blocked and hard to slip thouroughly. When fiber was dissolved, the solvent was absorbed slowly into the inner structure and acted as a lubricant. The fiber, firstly, was swollen and then absolutely dissolved when the absorbtion limit was over than its gel point. Although the fiber was already cross-linked after finishing, it was proved that the fiber was still dissolved in the solvent due to the partial cross-linking reaction on the outer surface. Hence, the solution of celllulose finished by higher concentration of GP® required longer time to dissolve completely.

4.5 Effect of Birefringence on Fibrillation Index

Fibrillation Index varied proportionally as birefringence (see Figure 4.5). Well-oriented fibers with molecules aligned along fiber axis certainly show anisotropic properties especially on the polarized characteristics. The results indicated that high orientated fiber had more tendency to fibrillate when subjected to the mechanical action in wet state. Again, it was due to the lack of lateral cohesion between cellulose chains. This is why the tenacity measured in the perpendicular direction was also less than in the fiber direction.

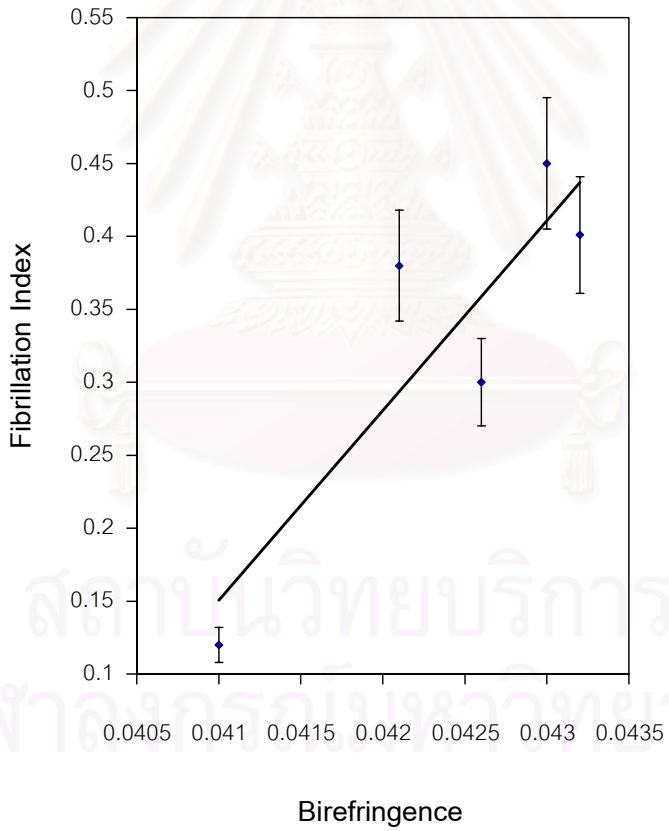

Figure 4.5 The relationship between Fibrillation Index and birefringence, r = 0.88.

From the experiment, it was noticed that when fibers were swollen in alkali solution, they were induced the negative charges on the cellulose molecules of outer skin. Each cellulose chain pushed another apart; therefore, the orientation of celluloses tended to be more disorder.

No swelling (Birefringence = 0.043)

Swelling (Birefringence = 0.041)

Figure 4.6 Photomicrographs of non swollen and swollen fiber.

It was seen from Figure 4.6 that after swelling, the birefringence of fiber was lower from 0.043 (no swelling) to 0.041 (swelling) while the fibrillation of swell fiber was greater than non swell fiber. This effect was more severe in the case of high orientated fiber which was swollen highly. Moreover, the figures also showed that the fibrillation preferred to take place in the swelling regions (low birefringence) than other regions.

Although, the birefringence was related to the Fibrillation Index, it was not suggested to be a significant parameter predicting the fibrillation behaviour. The reason was that the birefringence, evaluated directly from the comparison of observed color and color from the Michel Levy Chart, was depended on the personal justification. Particularly, the colors from swell fiber were difficult to distinguish even though the retardation plate was inserted to find the certain color. Higher swelling parts showed the descend in color order; as a consequence, its birefringence was lower than normal.

Moreover, the small sampling size might cause more error during testing because the tests results from only a few fibers were not enough to represent their whole properties. It was pointed out that the raw data collecting from a few samples always provided the high standard deviation. Consequently, the linear relationship between birefringence and Fibrillation Index was not properly used to predict the fibrillation behaviour.

4.6 Effect of Relative Crystallinity and Fibrillation Index

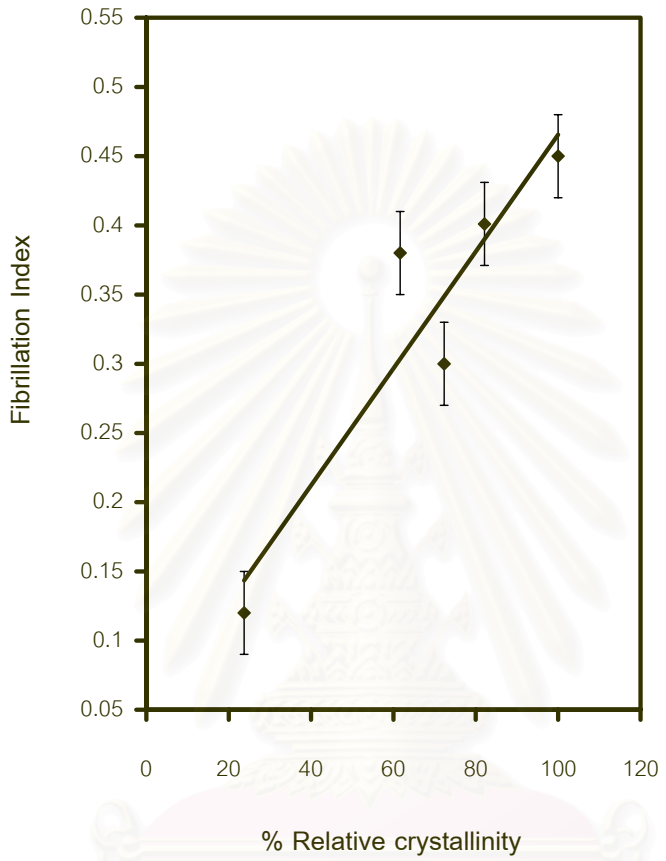

Figure 4.7 The relationship between Fibrillation Index and percentage of relative crystallinity, r= 0.93.

The linear relationship in Figure 4.7 demonstrates that Fibrillation Index is proportional to the relative crystallinity. From the previous discussions, it was said that the fibrillation behaviour of fiber was certainly affected by the molecular orientation especially in crystalline regions. For high crystalline fiber, It was severely impacted by delamination of fiber. The spinodal phase separation during fiber production provided many small pores

aligned in parallel with the molecular orientation that caused the molecular layers to split out when fiber subjected to hydromechanical forces (Mortimer, 1994).

4.7 Effect of Intrinsic Viscosity on Fibrillation Index

Mark and Houwink equation presented that the intrinsic viscosity closely related to viscosity-average molecular weight (M_V) in an exponential function as seen below :

$$\eta = K M_v^a \quad \text{.....(4.1)}$$

η : intrinsic viscosity.

M_v : viscosity-average molecular weight.

K and a : constants depend on polymer, solvent and temperature.

Due to the growing of intrinsic viscosity, it was said that viscosity-average molecular weight was also certainly affected by cross-linking. The ascent of viscosity-average molecular weight was a result of increasing lateral bridges by cross-linking. Similarly, viscosity-average molecular weight was risen by the molecular weight of GP® inside cellulose chains. Therefore, it was concluded that increasing the degree of cross-linking contributed to the growing of both viscosity-average molecular weight and intrinsic viscosity but brought about the low fibrillation tendency.

Although this linear relationship probably predicted the fibrillation particularly for fiber which had already finished by cross-linking agent, it was not assumed as the appropriate technique for non cross-linked fiber. The results from this experiment were covered only cross-linked fiber. It means that relationship between the intrinsic viscosity of

non cross-linked fiber and Fibrillation index might not follow by the result as shown in Figure 4.8.

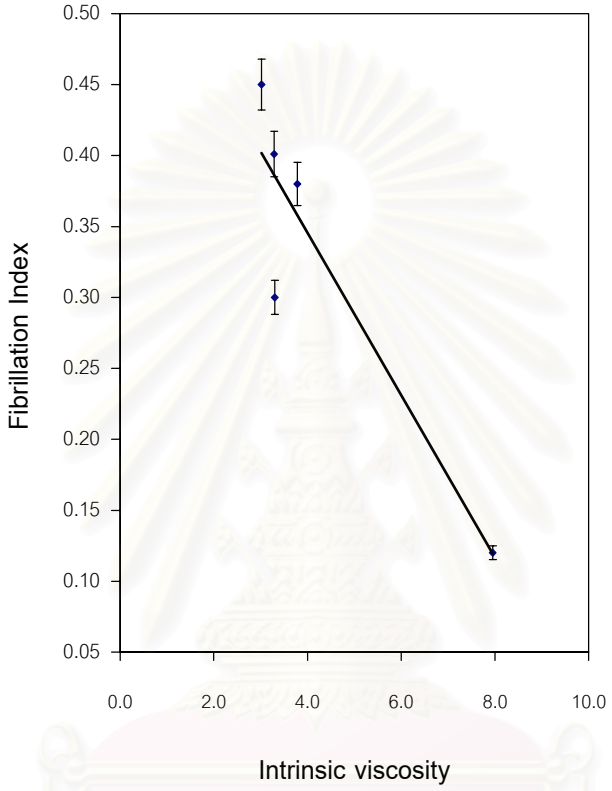

Figure 4.8 The relationship between Fibrillation Index and intrinsic viscosity, r = - 0.92.

4.8 Correlation Analysis

In order to examine how the variables are related and which one mostly influenced the fibrillation behaviour, the bivariate correlation were conducted by SPSS Program. The descriptive statistics and Pearson's Correlation Coefficient were computed from three independent variables as birefringence, intrinsic viscosity and relative crystallinity versus Fibrillation Index, the statistical results were shown in Table 4.3 and 4.4.

Table 4.3 Descriptive Statistic of Fibrillation Index, birefringence, intrinsic viscosity and relative crystallinity.

	N	Minimum	Maximum	Mean	Std. Deviation
FI	10	.12	.45	.3300	.1218
BF	10	.0410	.0432	4.24E-02	8.284E-04
[n]	10	3.0000	7.9530	4.206400	1.996828
C	10	23.74	66.43	46.5540	14.7083

Table 4.4 Pearson's Correlation Coefficients of all parameters.

		FI	BF	C	[n]
FI	Pearson Correlation	1.000	.744*	.861**	-.853*
	Sig. (2-tailed)	.	.047	.009	.027
	N	10	10	10	10
BF	Pearson Correlation	.774*	1.000	.883*	-.823*
	Sig. (2-tailed)	.047	.	.047	.025
	N	10	10	10	10
C	Pearson Correlation	.861**	.883*	1.000	-.862
	Sig. (2-tailed)	.009	.047	.	.060
	N	10	10	10	10
[n]	Pearson Correlation	-.853*	-.823*	-.862	1.000
	Sig. (2-tailed)	.027	.025	.060	.
	N	10	10	10	10

*. Correlation is significant at the 0.05 significant level (2-tailed).

**. Correlation is significant at the 0.01 significant level (2-tailed).

According to the tables, Fibrillation Index was linearly related to all parameters. However, Fibrillation Index was effected mostly by relative crystallinity ($r_{FI,C}$ = 0.86) because its correlation coefficient was closed to 1.00, followed by the intrinsic viscosity ($r_{FI,[\eta]}$ = - 0.85) which was conversely related to Fibrillation Index, and then the birefringence ($r_{FI,BF}$ = 0.74) was less significant parameter affecting the fibrillation. This is due to the less accurate by personal determination and too small sample size as discussed earlier. In consequence, in application, the relative crystallinity and intrinsic viscosity can be used as significant parameters to predict the fibrillation behaviour as well.

From the correlation coefficient between the crystallinity and Fibrillation Index, it was suggested that fibrillation of fiber was controlled by the molecular orientation. To decrease the fibrillation, the orientation of cellulose molecules as well as the crystallinity should be reduced possibly by either fiber production or finishing processes.

Furthermore, the correlation coefficient between each parameter were also examined. It was appeared that each parameter not only related to Fibrillation Index but also among themselves. The birefringence was certain related to crystallinity ($r_{C,BF}$ = 0.883). Well-orientated fiber always have more tendency to crystallize that is the reason why they usually face to the fibrillation.

4.9 Linear Regression Analysis

4.9.1 Linear regression analysis between Fibrillation Index and birefringence.

Linear regression analysis between Fibrillation Index and birefringence was shown in table 4.5 and the coefficients of regression were presented in table 4.6.

Table 4.5 Analysis of varience of linear regression between Fibrillation Index and birefringence.

ANOVA[b]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.104	1	.104	28.287	.001[a]
	Residual	2.945E-02	8	3.682E-03		
	Total	.134	9			

a. Predictors: (Constant), BF

b. Dependent Variable: FI

Table 4.6 Coefficients of linear regression between Fibrillation Index and birefringence.

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	-5.173	1.035		-4.999	.001
	BF	129.858	24.416	.883	5.319	.001

From table 4.5, the null hypothesis was denied because of the significance less than 0.10 (90% confidence level). It was concluded that Fibrillation Index linearly depended on birefringence and its relationship was mathemetically defined as equation 4.2.

$$FI = -5.173 + 129.86\,BF,\ r = 0.74 \quad \text{.....(4.2)}$$

4.9.2 Linear regression analysis between Fibrillation Index and intrinsic viscosity.

Linear regression analysis between Fibrillation Index and birefringence was shown in table 4.7 and the coefficients of regression were presented in table 4.8.

Table 4.7 Analysis of varience of linear regression between Fibrillation Index and intrinsic viscosity.

ANOVA[b]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.107	1	.107	32.052	.000[a]
	Residual	2.669E-02	8	3.336E-03		
	Total	.134	9			

a. Predictors: (Constant), [n]

b. Dependent Variable: FI

Table 4.8 Coefficients of linear regression between Fibrillation Index and intrinsic viscosity.

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	.560	.044		12.582	.000
	[n]	-5.46E-02	.010	-.895	-5.661	.000

Table 4.7 shown that the significance was less than 0.10; therefore, the Fibrillation Index was greatly affected by intrinsic viscosity as the following equation :

$$FI = 0.56 - 5.46 \times 10^{-2} \eta \,, \; r = -0.85 \quad \text{.....(4.3)}$$

4.9.3 Linear regression analysis between Fibrillation Index and relative crystallinity.

Linear regression analysis between Fibrillation Index and birefringence was shown in table 4.9 and the coefficients of regression were presented in table 4.10.

Table 4.9 Analysis of varience of linear regression between Fibrillation Index and relative crystallinity.

ANOVA[b]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.123	1	.123	97.726	.000[a]
	Residual	1.011E-02	8	1.264E-03		
	Total	.134	9			

a. Predictors: (Constant), C

b. Dependent Variable: FI

Table 4.10 Coefficients of linear regression between Fibrillation Index and relative crystallinity.

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	-4.08E-02	.039		-1.041	.328
	C	7.964E-03	.001	.961	9.886	.000

From table 4.9, the significance was less than 0.10. Thus, the linear relationship between Fibrillation Index and relative crystallinity was shown in the following equation :

$$FI = -4.08x10^{-2} + 7.964x10^{-3} C, \; r = 0.86 \quad \text{.....(4.4)}$$

4.10 Multiple Regression Analysis by Forward Method.

From previous regression analysis, the relationships between Fibrillation Index and each parameter were presented. However, the multiple regression analysis shown how all factors mathematically related to the Fibrillation Index. The analysis of varience by forward method was used to define this relationship.

Variables Entered/Removed[b]

Model	Variables Entered	Variables Removed	Method
1	C, [n], BF[a]	.	
2	.	BF	Forward (criterion: Probability of F-to-remove >= .10).

a. All requested variables entered.

b. Dependent Variable: FI

Table 4.11 Analysis of Varience of Multiple Regression by Forward Method.

ANOVA[c]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	.127	3	4.247E-02	41.167	.214[a]
	Residual	6.190E-03	6	1.032E-03		
	Total	.134	9			
2	Regression	.127	2	6.351E-02	67.591	.004[b]
	Residual	6.577E-03	7	9.396E-04		
	Total	.134	9			

a. Predictors: (Constant), C, [n], BF

b. Predictors: (Constant), C, [n]

c. Dependent Variable: FI

Table 4.12 Coefficients of Multiple Regression by Forward Method.

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	1.112	1.603		.694	.514
	BF	-23.132	37.744	-.157	-.613	.562
	[n]	-2.38E-02	.013	-.390	-1.770	.127
	C	6.404E-03	.002	.773	4.070	.007
2	(Constant)	.132	.095		1.386	.208
	[n]	-1.82E-02	.009	-.298	-1.939	.094
	C	5.894E-03	.001	.711	4.626	.002

Table 4.13 Excluded variable of Multiple Regression by Forward Method.

Model		Beta In	t	Sig.	Partial Correlation
2	BF	-.157	-.613	.562	-.243

The multiple regression presented that the significance of regression equation including all parameters was less than 0.10. From Forward Method, the birefringence was not significant enough to include in the regression equation at 90% confidence level. Consequently, the appropriate equation was demonstrated as shown in equation 4.5.

$$FI = 1.32 - 1.82 \times 10^{-2}\,\eta + 5.894 \times 10^{-3}\,C, \; r = 0.78 \quad \text{.....(4.5)}$$

CHAPTER V

Conclusions and Recommendations

From the results presented in this thesis, it was concluded that :

1. Fibrillation behaviour of lyocell fiber proportionally relates to birefringence and relative crystallinity but conversely depends on intrinsic viscosity as presented respectively in the equation 5.1 to 5.3. From linear regression analysis, the equation expresses the influence of relative crystallinity and intrinsic viscosity on the fibrillation of fiber is shown in the equation 5.4.

   1.1 The relationship between Fibrillation Index and birefringence

   $$FI = -5.17 + 129.86\ BF, \qquad r = 0.74 \qquad \text{.....(5.1)}$$

   1.2 The relationship between Fibrillation Index and relative crystallinity

   $$FI = (-4.08 \times 10^{-2}) + (7.96 \times 10^{-3})\ C, \qquad r = 0.86 \qquad \text{.....(5.2)}$$

   1.3 The relationship between Fibrillation Index and intrinsic viscosity

   $$FI = 0.56 - (5.46 \times 10^{-2})\ [\eta], \qquad r = -0.85 \qquad \text{.....(5.3)}$$

   1.4 The relationship between Fibrillation Index relative crystallinity and intrinsic viscosity

   $$FI = 1.32 - (1.82 \times 10^{-2})\ [\eta] + (5.894 \times 10^{-3})\ C, \qquad r = 0.78 \qquad \text{.....(5.4)}$$

2. The relative crystallinity and intrinsic viscosity are suggested to be significant parameters to predict the fibrillation of fiber in terms of Fibrillation Index. Therefore, the Fibrillation Index can be effectively estimated from the either equation 5.2 or 5.3.

3. In application, the fibrillation can be reduced by increasing the lateral cohesion along molecular chains. Cross-linking is suggested to effectively control the fibrillation.

4. When the high fibrillation fiber is needed, the increase of crystallinity and fiber orientation can be achieved by controlling fiber processing parameters.

Recommendations for future work

1. This experiment should be applied to other man-made cellulosic fibers which tend to fibrillate in wet abrasion such as high wet modulus rayon.
2. Further study of relationship between mechanical properties and fibrillation behaviour is recommended. This may be useful to demonstrate the alternative method to predict the fibrillation of fiber.
3. Instead of using cross-linking agent, lyocell fiber which is controlled the degree of fibrillation by its production is more appropriate to examine the relationship between the properties of fiber and its fibrillation. This is because the inner structure will not be disturbed by the chemical agent that may cause side effects.
4. It should be realized that handling with staple fiber leads to the high variation of data. The significant level of data set in the experiment depends on the objective and the application. The 90 % to 95 % confidence level is normally accepted for the general tests. However, in some cases, the 70 to 80 % confidence level can be allowed for high variation sample such as fiber.

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APPENDICES

APPENDIX A

A1 Statistical Analysis

A1.1 Correlation Analysis

In order to examine how much the variables are related to each other and which one mostly influences the fibrillation behaviour, the correlations were studied. The correlation of one independent and dependent variable was normally termed as the Bivariate Correlation while the correlation of more than 2 variables was called the Partial Correlation. Although the correlation can show how much the parameters are related, it is not able to indicate how or which directions they affect each other that is the difference between correlation and regression analysis.

The measurement of correlation is in terms of correlation coefficient (ρ). The values of correlation coefficient is between –1 to 1. If the relationship of both parameters is completely parallel linear, correlation coefficient equals to 1 but equals to –1 in converse. Thus, zero value of correlation coefficient means there is no significant relationship between them. However, in the experiment which all data is not from all population such as from testing, correlation coefficient can be evaluated as r value.

$$r = b\sqrt{\frac{Sxx}{Syy}} = \frac{Sxy}{\sqrt{Sxx.Syy}} \quad \text{.....(i)}$$

When

$$Sxx = \sum_{i=1}^{n}\left(X_i - \overline{X}\right)^2$$

$$Syy = \sum_{i=1}^{n}\left(Y_i - \overline{Y}\right)^2$$

$$Sxy = \sum_{i=1}^{n}\left(X_i - \overline{X}\right)\left(Y_i - \overline{Y}\right)$$

$$\text{R- Square} = r^2 = \frac{SSR}{SST} \quad \text{.....(ii)}$$

When SSR : Sum of Square Error

SST : Sum of Square Total

The coefficient of Determination was the square of correlation coefficient (R-Square). Similar to r value, it can present that the relationship of parameters but is valuable between 0 and 1. In the case of linear relationship, Pearson's correlation coefficient was properly used for a measure of linear association.

A1.2 Linear Regression Analysis

To clarify mathematically which relationship of those parameters are proper enough to be a regression equation for fibrillation assessment and can apply practically in the real works. The testing of hypothesis is one of researchable tool for accurate decision in the research.

In this experiment, we define the Fibrillation as the dependent variable and the birefringence, intrinsic viscosity and relative crystallinity as the independent variables. In order to set the hypotheses of regression, it is assumed that the linear relationship between independent and dependent variable were shown as the following :

$$Y_i = \beta_0 + \beta_1 X_i + \varepsilon_i \quad \text{.....(iii)}$$

When Y_i : Random observed dependent variable

X_i : Random observed independent variable

ε_i : Random Error

β_0 : Interception value

β_1 : Regression Coefficient as presented slope of linear graph

The β_1 can be classified into from cases :

1. $\beta_1 > 0$ means the parallel relationship between X and Y.
2. $\beta_1 < 0$ means the converse relationship between X and Y.
3. β_1 closed to 0 means the less relationship between X and Y.
4. $\beta_1 = 0$ means that X and Y are independent.

By statistical process, the equation 4.1 can be properly estimated by means of the Least Square Method that gives the sum of square error close to 0. The estimated equation is followed below :

$$Y_i = a + bX_i \quad \text{.....(iv)}$$

When a = Estimated interception value.

b = Estimated regression coefficient..

A1.3 Testing of Hypotheses

Firstly, the Null Hypothesis (H_0) is defined that there is no statistical significant linear relationship between Fibrillation Index and other independent parameters under 95% confidence level (significant level = 0.05). The H_1, then, presents the significant relationships between each parameter.

$$H_0 : \beta_1 = \beta_2 = \ldots = \beta_i = 0$$

$$H_1 : \beta_1 \neq \beta_2 \neq \ldots \neq \beta_i \neq 0$$

Table A1 One-Way Analysis of Varience for Linear Regression Analysis by F-Test.

	Sum of Square	df	Mean Square	F_{CAL}	Significance
Regression Residual (Error)	SSR SSE	1 n-2	MSR = SSR MSE = SSE / (n-2)	MSR / MSE	$P(F > F_{CAL})$
Total	STT	n-1			

The null hypothesis is rejected when F_{CAL} is over than F_α at degree of Freedom equaled to (1,n-1) or the significance is less than α.

A2 Raw Data

Table A2 Raw Data of birefringence (BF) and Fibrillation Index (FI) of Tencel® fiber (Lot A) finished by GP 0%, 2%, 4%, 6% and 8%.

% GP	Properties	Replication										Mean	SD	% CV
		1	2	3	4	5	6	7	8	9	10			
0 %	BF	0.042	0.044	0.040	0.042	0.049	0.038	0.044	0.039	0.044	0.048	0.043	0.0036	8.4
	FI	0.41	0.43	0.43	0.46	0.46	0.41	0.48	0.47	0.46	0.48	0.450	0.026	5.7
1 %	BF	0.050	0.040	0.040	0.042	0.048	0.042	0.046	0.050	0.044	0.044	0.045	0.0037	8.2
	FI	0.49	0.50	0.46	0.39	0.48	0.48	0.42	0.44	0.46	0.50	0.48	0.036	7.5
2 %	BF	0.044	0.045	0.043	0.039	0.045	0.044	0.043	0.039	0.045	0.038	0.043	0.0026	6.16
	FI	0.42	0.38	0.41	0.42	0.042	0.44	0.38	0.40	0.41	0.39	0.401	0.024	5.8
3 %	BF	0.037	0.044	0.042	0.038	0.043	0.044	0.045	0.043	0.044	0.045	0.043	0.0027	6.25
	FI	0.45	0.46	0.38	0.43	0.48	0.42	0.43	0.44	0.40	0.40	0.43	0.030	6.9
4 %	BF	0.052	0.041	0.039	0.042	0.043	0.041	0.044	0.041	0.044	0.044	0.043	0.0033	7.66
	FI	0.37	0.38	0.38	0.39	0.38	0.40	0.42	0.36	0.38	0.34	0.38	0.022	5.7
5 %	BF	0.038	0.039	0.044	0.045	0.044	0.040	0.039	0.042	0.043	0.038	0.041	0.0026	6.22
	FI	0.16	0.24	0.20	0.20	0.25	0.22	0.21	0.18	0.21	0.22	0.21	0.026	7.2

6 %	BF	0.044	0.036	0.043	0.039	0.045	0.044	0.042	0.043	0.039	0.042	0.039	0.0027	6.44
	FI	0.14	0.12	0.11	0.12	0.08	0.14	0.10	0.08	0.12	0.14	0.12	0.023	8.9
7 %	BF	0.039	0.040	0.039	0.043	0.042	0.044	0.042	0.039	0.044	0.042	0.042	0.0020	4.7
	FI	0.20	0.16	0.15	0.14	0.16	0.15	0.12	0.18	0.15	0.12	0.153	0.025	8.6
8 %	BF	0.044	0.045	0.039	0.044	0.038	0.040	0.045	0.042	0.038	0.045	0.042	0.0028	6.73
	FI	0.25	0.27	0.32	0.31	0.30	0.34	0.32	0.30	0.28	0.29	0.298	0.027	9.0
9 %	BF	0.045	0.037	0.045	0.044	0.043	0.045	0.043	0.040	0.042	0.046	0.043	0.0024	6.06
	FI	0.45	0.46	0.39	0.40	0.45	0.44	0.46	0.46	0.48	0.50	0.449	0.033	7.3
10 %	BF	0.041	0.045	0.038	0.043	0.042	0.044	0.045	0.044	0.038	0.046	0.043	0.0027	6.32
	FI	0.48	0.44	0.42	0.45	0.39	0.46	0.45	0.44	0.45	0.47	0.445	0.020	4.5

Table A3 Flowtime of solvent (t_0) and cellulose solution (t_n) of Tencel® fiber finished by 0% GP® in various concentrations.

NO.	t_0	t_1	t_2	t_3	t_4	t_5
1	72.12	160.76	141.29	129.46	121.02	114.69
2	72.11	159.28	141.69	129.48	121.06	115.38
3	72.08	159.38	142.17	129.29	120.92	114.63
Mean	72.11	159.81	141.38	129.41	121.00	114.90
SD	0.02	0.83	0.27	0.10	0.07	0.42
% CV	0.22	0.54	0.85	0.55	0.40	0.15
η_{rel}	1	2.2162	1.9606	1.7946	1.6780	1.5934
C*	0	0.2995	0.2500	0.2139	0.1872	0.1664
Log $[(\eta_{rel} - 1)/C)]$	-	0.6086	0.5846	0.5699	0.5589	0.5522
$[\eta]$	3.02					

* C = Concentration

Table A4 Flowtime of solvent (t_0) and cellulose solution (t_n) of Tencel® fiber finished by 2% GP® in various concentrations.

NO.	t_0	t_1	t_2	t_3	t_4	t_5
1	72.12	209.71	170.60	148.56	134.49	124.75
2	71.87	200.46	168.56	147.70	134.04	124.43
3	71.82	201.08	168.56	146.94	133.43	124.40
Mean	71.49	203.75	169.58	147.73	133.99	124.53
SD	0.16	5.17	1.44	0.81	0.53	0.19
% CV	0.22	0.54	0.85	0.55	0.40	0.15
η_{rel}	1	2.8322	2.3572	2.0535	1.8625	1.7310
C*	0	0.502	0.4183	0.3586	0.3138	0.2789
Log $[(\eta_{rel} - 1)/C)]$	-	0.5623	0.5112	0.4680	0.4391	0.4199
$[\eta]$	3.28					

* C = Concentration

Table A5 Flowtime of solvent (t_0) and cellulose solution (t_n) of Tencel® fiber finished by 4% GP® in various concentrations.

NO.	t_0	t_1	t_2	t_3	t_4	t_5
1	71.34	113.94	104.56	98.41	93.77	90.76
2	71.32	113.11	104.21	98.11	93.67	90.68
3	71.32	112.60	103.89	98.14	93.61	90.68
Mean	71.33	113.22	104.22	98.22	93.68	90.71
SD	0.01	0.68	1.46	0.17	0.08	0.05
% CV	0.02	0.60	1.40	0.17	0.09	0.05
η_{rel}	1	1.5873	1.4611	1.3770	1.3133	1.2717
C*	0	0.1020	0.085	0.0729	0.0638	0.056
Log $[(\eta_{rel} - 1)/C)]$	-	0.7603	0.7344	0.7136	0.6911	0.6805
$[\eta]$	3.78					

* C = Concentration

Table A6 Flowtime of solvent (t_0) and cellulose solution (t_n) of Tencel® fiber finished by 6% GP® in various concentrations.

NO.	t_0	t_1	t_2	t_3	t_4	t_5
1	71.34	105.43	98.14	93.42	90.00	87.33
2	71.39	104.85	98.04	93.38	89.90	87.20
3	71.36	104.42	97.78	93.15	89.74	87.40
Mean	71.36	105.53	97.99	93.32	89.88	87.31
SD	0.03	1.17	0.19	0.15	0.13	0.10
% CV	0.04	1.10	0.19	0.16	0.14	0.11
η_{rel}	1	1.4788	1.3732	1.3077	1.2595	1.2235
C*	0	0.102	0.085	0.0729	0.0638	0.0567
Log $[(\eta_{rel} - 1)/C)]$	-	0.6716	0.6425	0.6254	0.6093	0.5957
$[\eta]$	7.96					

* C = Concentration

Table A7 Flowtime of solvent (t_0) and cellulose solution (t_n) of Tencel® fiber finished by 8% GP® in various concentrations.

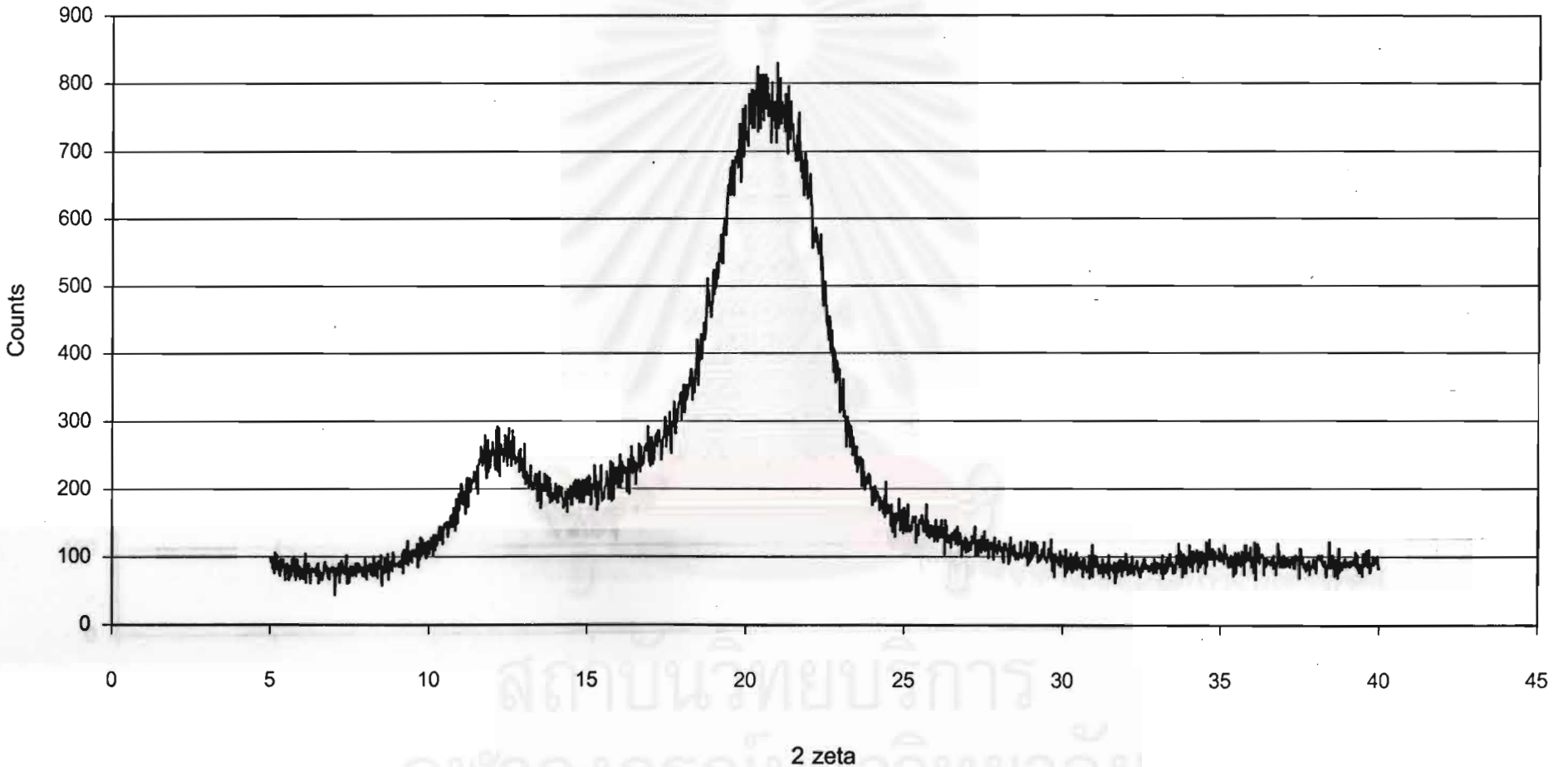
NO.	t_0	t_1	t_2	t_3	t_4	t_5
1	71.83	99.83	94.68	90.93	88.25	86.27
2	71.78	99.78	94.52	91.01	88.34	86.37
3	71.82	99.84	94.93	90.98	88.23	86.25
Mean	71.81	99.82	94.71	90.97	88.27	86.30
SD	0.03	0.03	0.21	0.04	0.06	0.06
% CV	0.042	0.030	0.22	0.044	0.068	0.070
η_{rel}	1	1.3901	1.3189	1.2668	1.2292	1.2018
C*	0	0.1005	0.0838	0.0718	0.0628	0.0558
Log $[(\eta_{rel} - 1)/C)]$	-	0.5890	0.5804	0.5701	0.5623	0.5583
$[\eta]$	3.30					

* C = Concentration

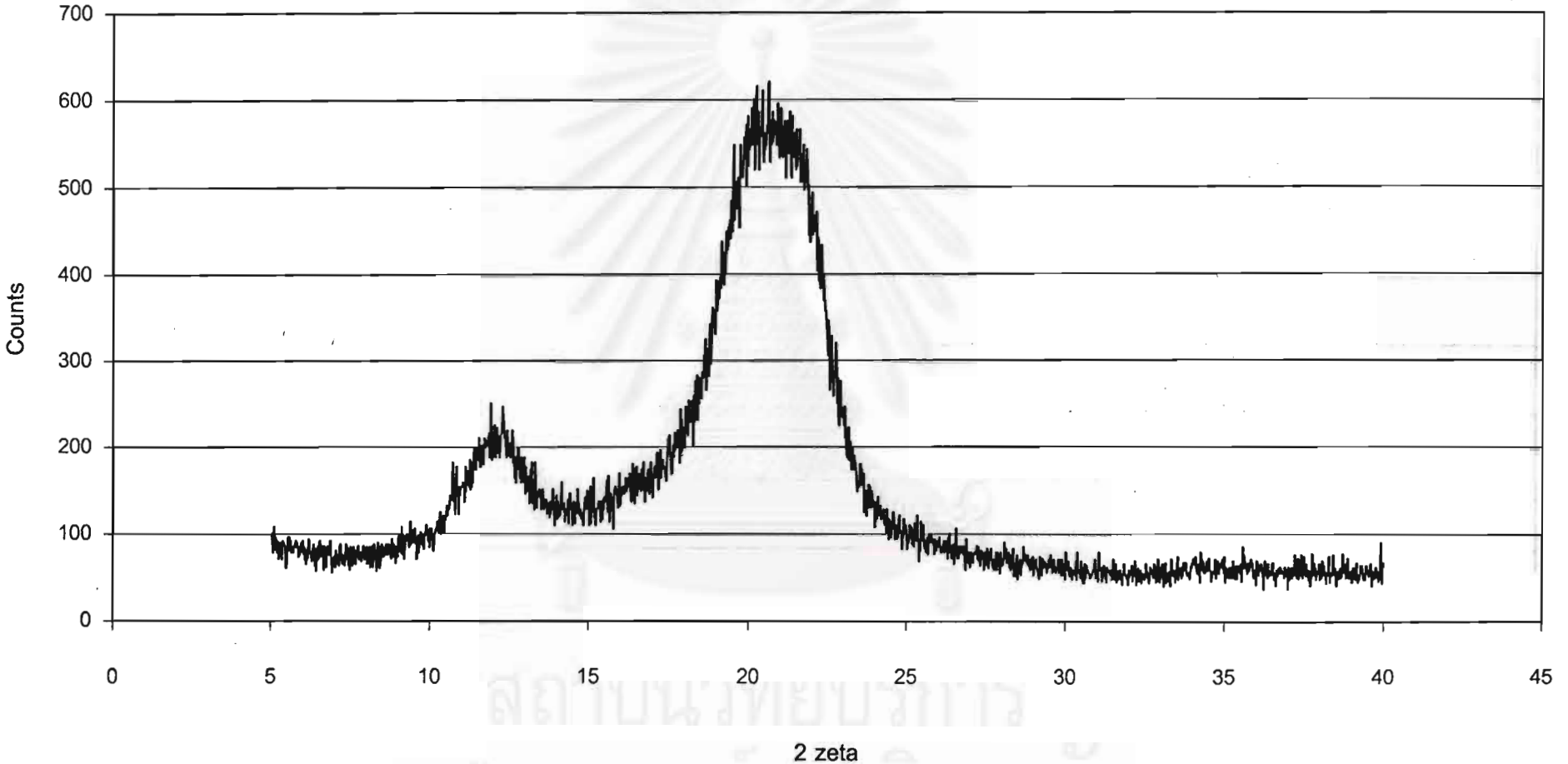
Table A8 The comparison of Fibrillation Index by calculation and observation from Tencel® lot B.

% GP	% C	$[\eta]$	FI_{observ}	FI_C	% Error	$FI_{[\eta]}$	% Error
0	62.46	2.898	0.43	0.46	6.14	0.40	6.57
2	54.85	3.373	0.44	0.40	10.04	0.38	14.58
4	51.34	3.827	0.40	0.37	8.03	0.35	12.24
6	28.11	7.582	0.25	0.18	26.82	0.15	41.59
8	53.69	3.231	0.42	0.39	7.96	0.38	8.67

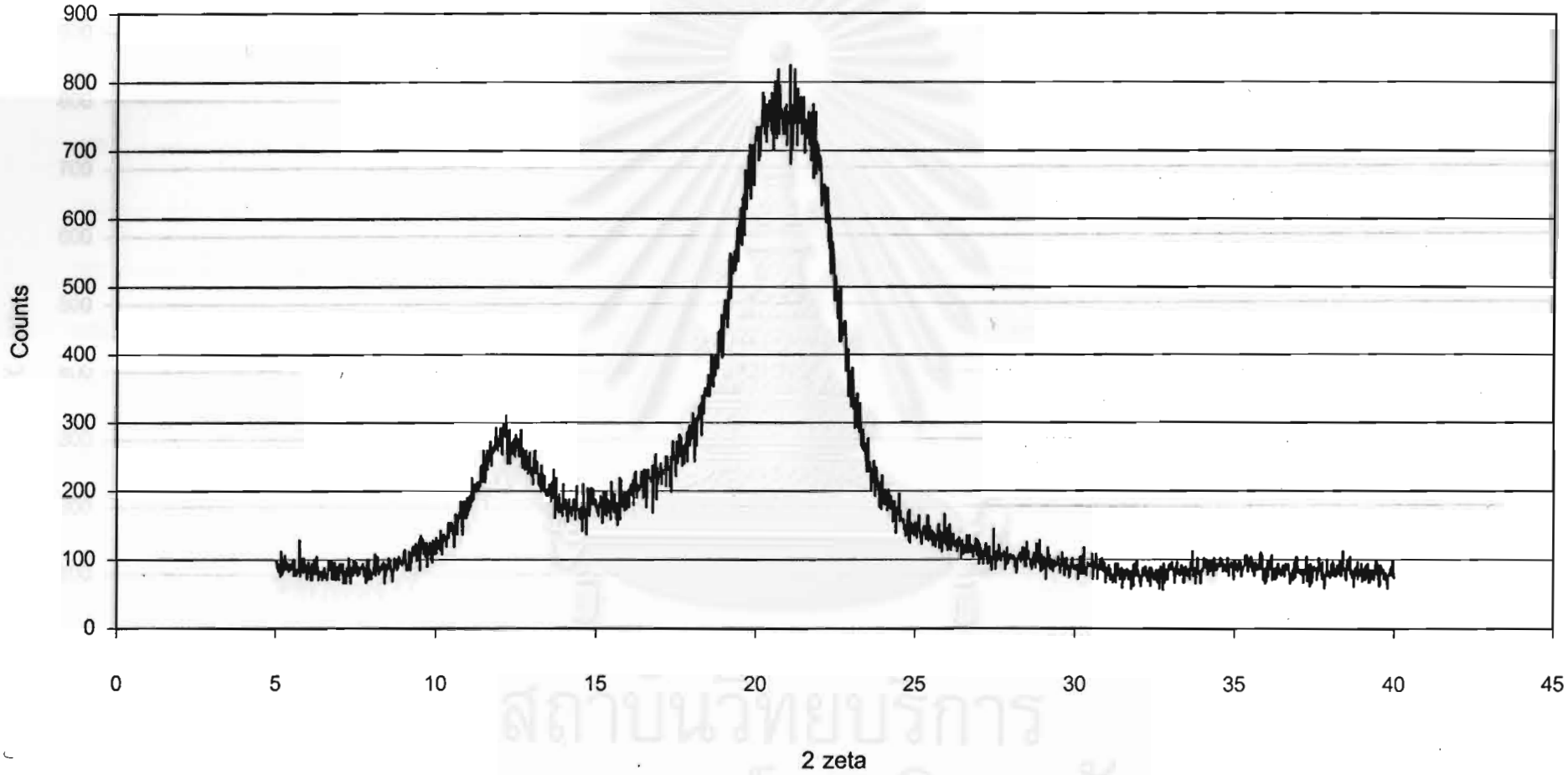
The diffractogram of Tencel treated with 0% GP



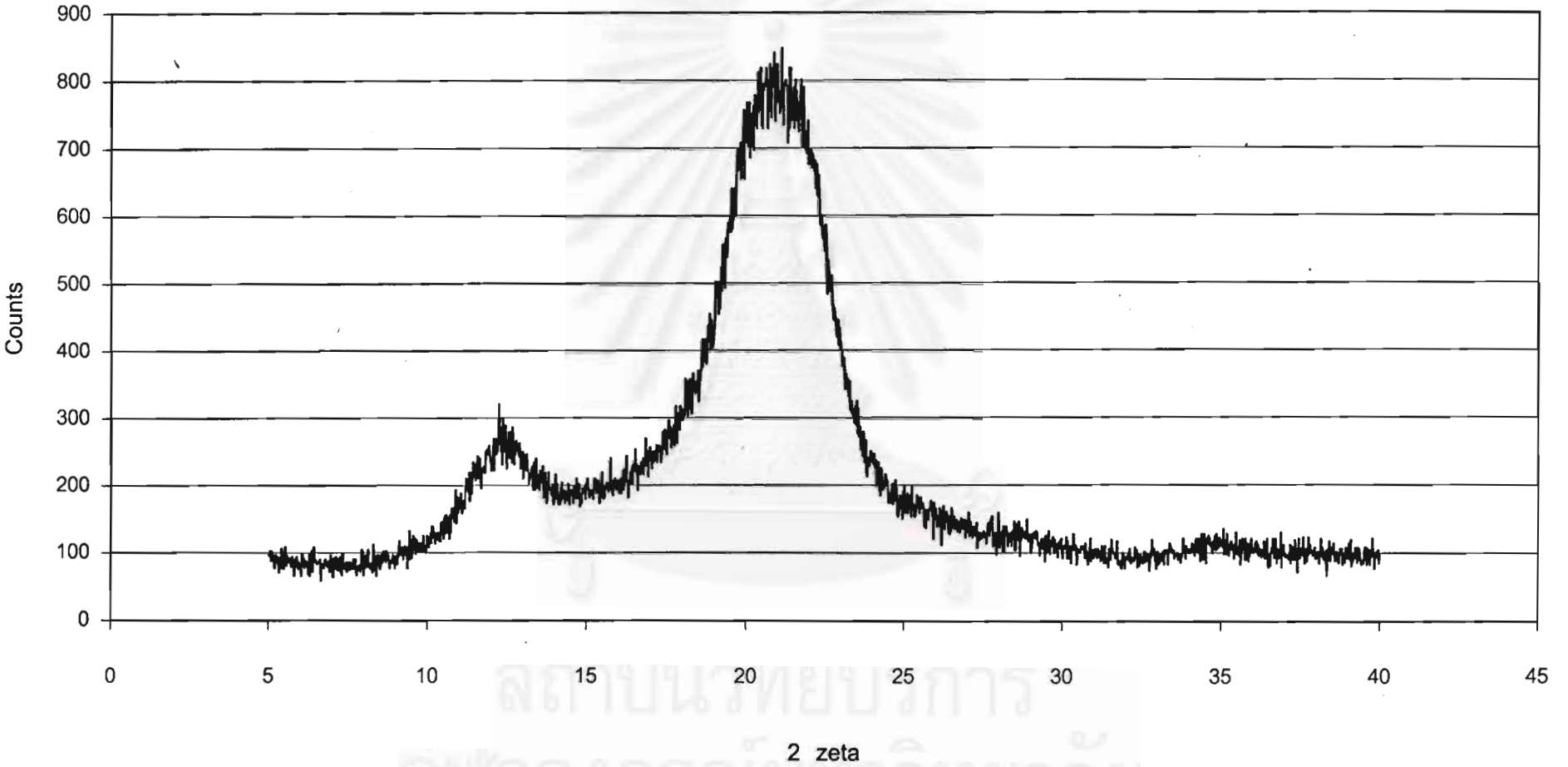
The diffractogram of Tencel treated with 2% GP



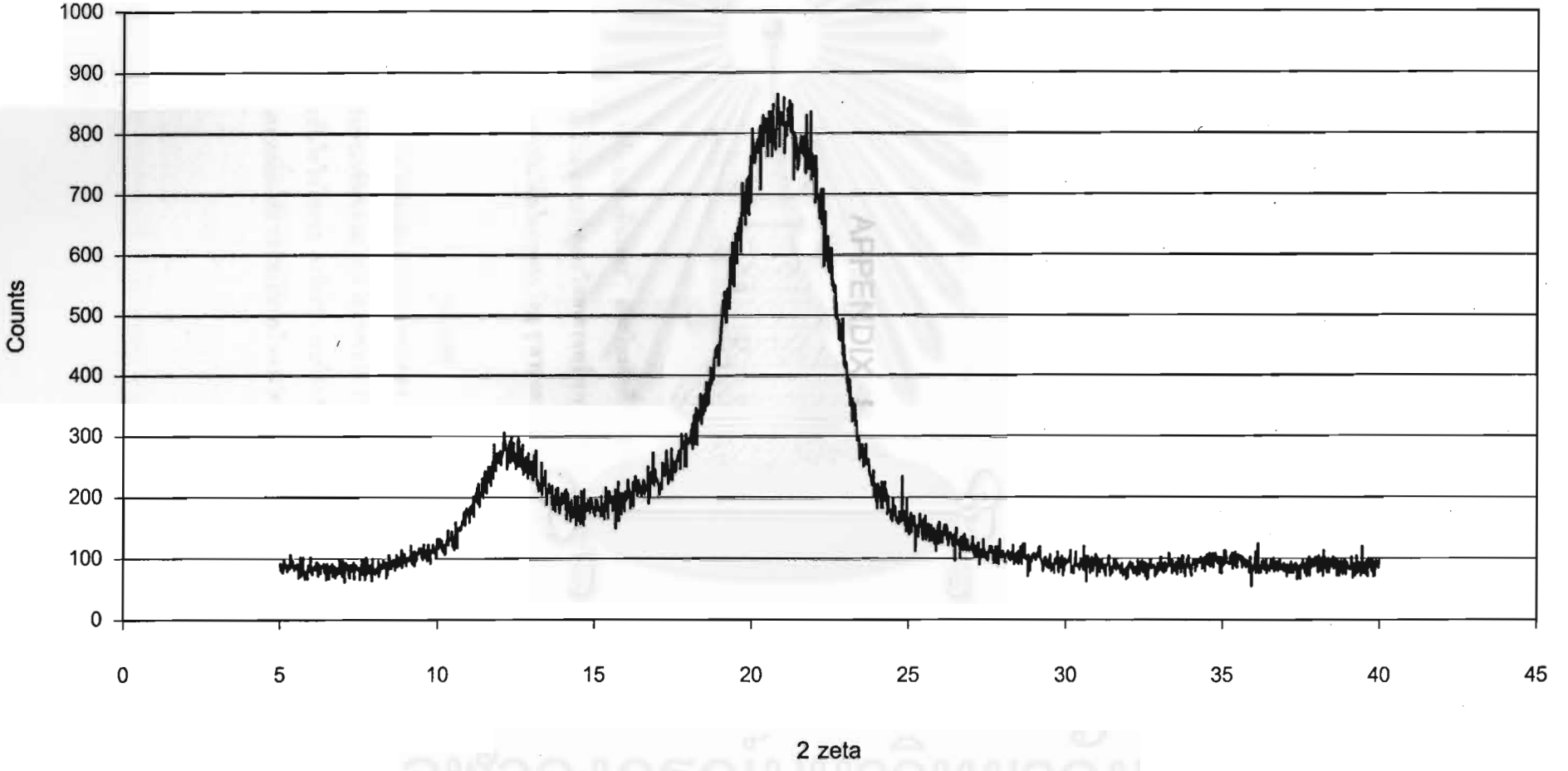
The diffractogram of Tencel treated with 4% GP



The diffractogram of Tencel treated with 6% GP



The diffractogram of Tencel treated with 8% GP



APPENDIX B

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Fibrillation Behaviour of Lyocell

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Abstract

Fibrillation of lyocell fiber is playing an important role on the application in apparel end uses. Investigations to explore fibrillation behaviour have been carried out intensively. The results were reviewed including the factors affecting this behaviour such as fiber processing parameters, finishing process and fiber structure. The standard fibrillation testing methods and fibrillation controls during finishing process were presented.

Key words : fibrillation, lyocell, fibrillation index

ไฟบริลเลชันในเส้นใยไลโอเซล

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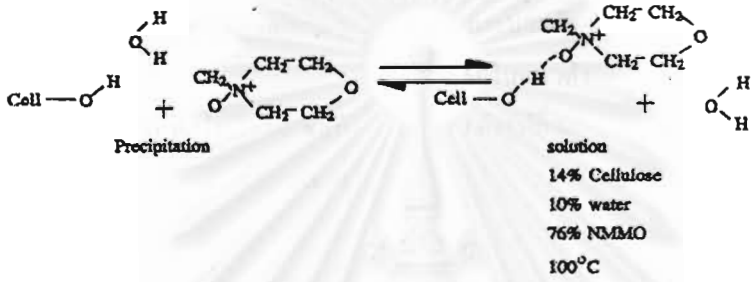
บทคัดย่อ

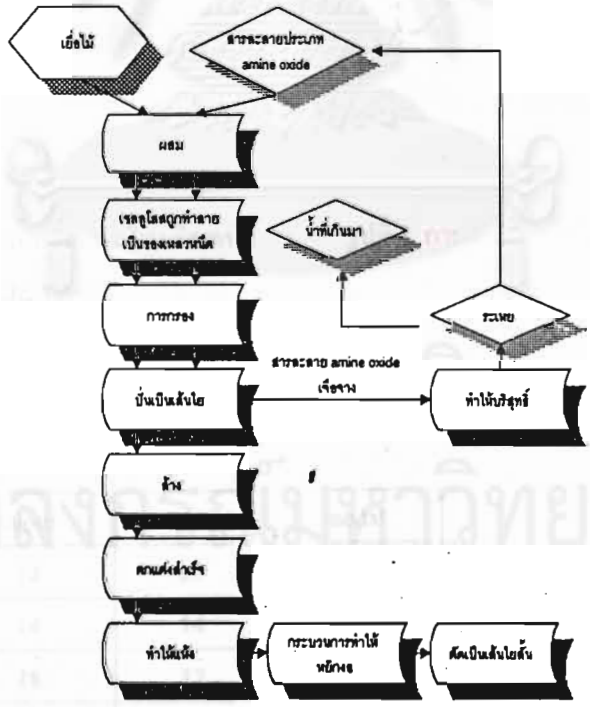
ปัจจุบันไฟบริลเลชันของเส้นใยไลโอเซลมีบทบาทสำคัญต่ออุตสาหกรรมเสื้อผ้าและเครื่องนุ่งห่มมากขึ้น ตลอดระยะเวลาที่ผ่านมาจึงมีการศึกษาเกี่ยวกับไฟบริลเลชันของเส้นใยไลโอเซลในวารสารงานวิจัยมากมาย บทความฉบับนี้จึงได้รวบรวมข้อมูลที่เกี่ยวข้องกับไฟบริลเลชันของเส้นใยไลโอเซล อาทิเช่น พฤติกรรมการเกิดไฟบริลเลชัน สาเหตุและปัจจัยที่มีผลต่อการเกิดไฟบริลเลชันในเส้นใยไลโอเซล นอกจากนี้ยังได้รวบรวมวิธีการในการวัดระดับการเกิดไฟบริลเลชันและการควบคุมไฟบริลเลชันของเส้นใยไลโอเซล

คำนำ

เส้นใยไลโอเซล (Lyocell fiber) เป็นเส้นใยเซลลูโลสประดิษฐ์ที่ได้จากกระบวนการปั่นในตัวทำละลายอินทรีย์ (organic solvent spinning) โดยการละลายเยื่อเซลลูโลสในสารละลาย N-methyl-morpholine-N-oxide (NMMO) เข้มข้น แล้วจึงอัดรีดผ่านสปินเนอเรตลงสู่สารละลาย NMMO เจือจางในอ่างตกตะกอน ภายในอ่างตะกอนสารละลายเซลลูโลสจะถูกเปลี่ยนเป็นเส้นใยดังรูปที่ 2 การแข็งตัวของเส้นใยเกิดจากการแทนที่ของ NMMO ซึ่งเป็นตัวทำละลายกับน้ำ ทำให้เกิดการเปลี่ยนแปลงของเฟสภายในเส้นใยจาก binodal phase ไปเป็น spinodal phase เป็นผลให้เซลลูโลสตกตะกอนดังรูปที่ 1



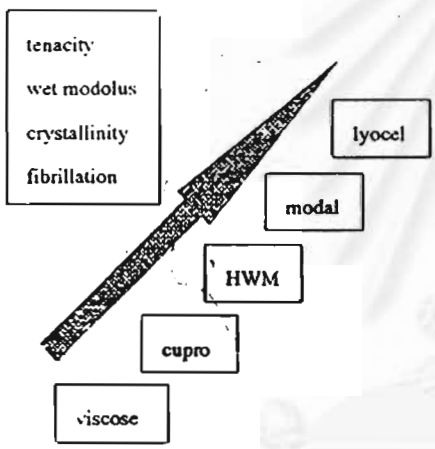
รูปที่ 1 ปฏิกิริยาการตกตะกอนของเซลลูโลส (Schulz, 1996)



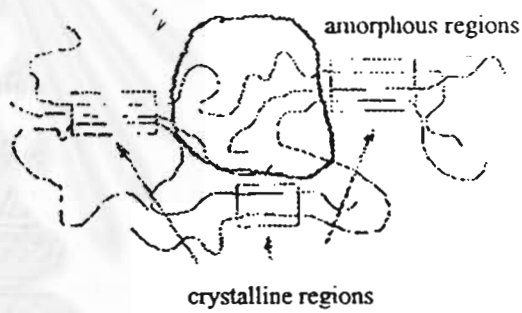
รูปที่ 2 กระบวนการผลิตเส้นใยไลโอเซล (วีระศักดิ์ อุดมกิจเดชา, 1999)

ไลโอเซลเป็นเส้นใยเซลลูโลสประดิษฐ์ที่ได้รับการปรับปรุงกระบวนการผลิตให้เป็นระบบปิดและเป็นมิตรกับสิ่งแวดล้อม โดยสามารถนำตัวทำละลาย NMMO ที่ใช้ในกระบวนการผลิตกลับมาใช้ใหม่ได้เกือบ 100% นอกจากนี้เส้นใยไลโอเซลมีความแข็งแรงทั้งในขณะเปียกและขณะแห้งสูง มีอัตราการหดตัวต่ำ มีการบวมตัวในน้ำสูงจึงดูดซึมสีย้อมและสารเคมีได้ดี และมีแนวโน้มการเกิดไฟบริล-เลชัน (fibrillation) สูงเมื่อเทียบกับเส้นใยเซลลูโลสอื่นๆ ดังตารางที่ 3

ไฟบริลเลชันเป็นสมบัติหนึ่งที่ทำให้ไลโอเซลมีความพิเศษแตกต่างจากเส้นใยชนิดอื่น เป็นผลเนื่องมาจากโมเลกุลของเซลลูโลสมีการจัดเรียงตัวอย่างเป็นระเบียบและมีความเป็นผลึกสูง ทำให้เส้นใยไลโอเซลมีความแข็งแรงมากในทิศทางเส้นใย ดังรูปที่ 4 และ 5 แต่อย่างไรก็ตามความเป็นผลึกสูงและการจัดเรียงตัวอย่างเป็นระเบียบตามความยาวของเส้นใย กลับส่งผลให้แรงยึดเหนี่ยวระหว่างโมเลกุลในแนวด้านข้าง (lateral strength) มีความแข็งแรงต่ำ เมื่อเส้นใยได้รับการขัดถูในภาวะเปียก บริเวณผิวภายนอกของเส้นใยจะเกิดการบวมตัว ทำให้พันธะไฮโดรเจนที่ยึดระหว่างส่วนที่เป็นผลึกในแนวด้านข้างแตกออก เกิดไฟบริลเลชันรอบแกนเส้นใย ดังรูปที่ 6



รูปที่ 4 ความสัมพันธ์ระหว่างความเป็นผลึกกับไฟบริลเลชันของเส้นใยไลโอเซล (Schulz, 1996)



รูปที่ 5 การจัดเรียงผลึกในเส้นใย (Schulz, 1996)

ตารางที่ 3 สมบัติของเส้นใยไลโอเซลเปรียบเทียบกับเส้นใยอื่น (Schulz, 1996)

สมบัติของเส้นใย	cupro	viscose	modal	lyocell	cotton
Dry tenacity (cN/tex)	22	26	35	45	34
Wet tenacity (cN/tex)	14	14	20	39	41
Elongation, dry (%)	18	17	14	12	8
Loop strength	18	7	8	19	21
Wet modulus	50	50	180	270	100
Fiber count (dtex)	1.3	1-5.6	1.1-4.2	1.7	-
ราคา (เหรียญสหรัฐ)	-	2	3	8	1.5

ปริมาณขนที่เพิ่มขึ้นจะเพิ่มพื้นที่ผิวในการดูดซึมสีย้อมและสารเคมีที่ใช้ในการตกแต่งสำเร็จ ซึ่งทำให้สิ้นเปลืองสารเคมีและเกิดปัญหาในระหว่างการย้อมและการตกแต่งสำเร็จ อย่างไรก็ตามหากสามารถควบคุมไฟบริล-เลชันให้อยู่ในระดับที่เหมาะสม จะช่วยเพิ่มสมบัติด้านผิวสัมผัสของผ้าให้มีความนุ่มและมีลักษณะคล้ายผิวของลูกท้อ (peach skin) ทำให้ผ้ามีลักษณะเด่นแตกต่างจากผ้าชนิดอื่น

ปัจจัยที่มีผลต่อการเกิดไฟบริลเลชันของเส้นใยไลโอเซล

1. ปัจจัยในระหว่างกระบวนการผลิต

- ความเข้มข้นของเซลลูโลส
- ความเข้มข้นของสารละลาย NMMO
- ภาวะการผลิต ได้แก่ อุณหภูมิ ความชื้น
- ความเร็วในการผลิต (line speed)
- อัตราการยืดดึง (draw ratio)

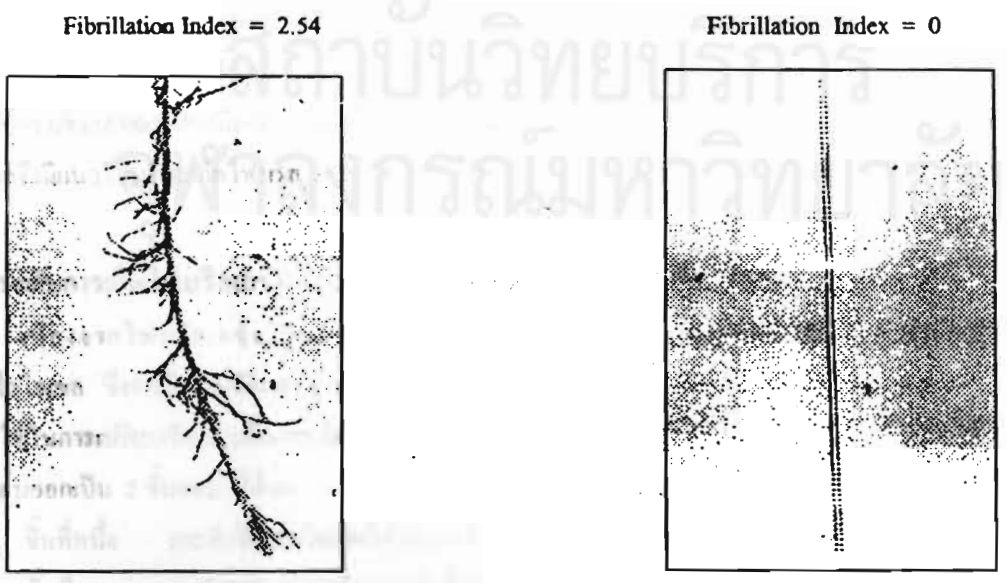
2. ปัจจัยในระหว่างกระบวนการตกแต่งสำเร็จ

- อุณหภูมิ
- เวลา
- ความเป็นกรดด่าง
- แรงกระทำเชิงกล

3. ปัจจัยทางกายภาพของเส้นใย

- การจัดเรียงตัวของโมเลกุลของเซลลูโลส (molecular orientation)
- ความเป็นผลึก (crystallinity)
- ระดับการเกิดพอลิเมอร์ (degree of polymerization)

จากการศึกษาพบว่าไฟบริลเลชันของเส้นใยเซลลูโลสประดิษฐ์ มีความสัมพันธ์กับการจัดเรียงตัวของโมเลกุลเซลลูโลสในเส้นใยโครงสร้างโมเลกุลของเซลลูโลสมีความแข็งเกร็งสูง เนื่องจากเกิดความเครียดภายในโมเลกุลที่เป็นวง (cyclic strain) ภายหลังการอัดรีดเส้นใยจะมีการจัดเรียงของโมเลกุลเซลลูโลสในทิศทางของเส้นใยสูงในบริเวณที่เป็นผลึกจะพบว่าโมเลกุลของเซลลูโลสจะเรียงตัวชิดกันมากและยึดกันด้วยพันธะไฮโดรเจน เส้นใยจึงสามารถทนต่อแรงดึงในแนวทิศทางของเส้นใยได้เป็นอย่างดี แต่ขณะเดียวกันกลับพบว่าความแข็งแรงในแนวด้านข้างของเส้นใยต่ำลง เมื่อเส้นใยได้รับแรงกระทำเชิงกลในภาวะเปียกเส้นใยจะเกิดการบวมตัว (swell) ทำให้พันธะไฮโดรเจนที่ยึดระหว่างโมเลกุลในส่วนที่เป็นผลึกแตกออก โมเลกุลของเซลลูโลสซึ่งมีความแข็งเกร็งสูงจึงพยายามคลายความเค้นที่ได้รับในกระบวนการอัดรีดลงโดยการคลายตัวออกเกิดไฟบริลเลชันขึ้น



รูปที่ 6 การเกิดไฟบริลเลชันของเส้นใยไลโอเซล (สิริลักษณ์ เจียรากร, 2000)

การจัดเรียงตัวของโมเลกุลเซลลูโลสสามารถหาได้ในเทอมของการหักเหสองแนว (birefringence) ซึ่งเป็นผลต่างระหว่างดัชนีหักเหในทิศทางของเส้นใยกับดัชนีหักเหในทิศทางตั้งฉากกับเส้นใย ดังนั้นค่าการหักเหสองแนวจึงมีความสัมพันธ์กับการเกิดไฟบริลเลชันของเส้นใย เส้นใยที่มีค่าการหักเหสองแนวมากแสดงว่าโมเลกุลของเซลลูโลสเรียงตัวในแนวทิศทางของเส้นใยมากกว่าทิศทางตั้งฉากกับเส้นใย จึงมีโอกาสเกิดไฟบริลเลชันได้มาก

นอกจากไฟบริลเลชันจะขึ้นอยู่กับการจัดเรียงตัวของโมเลกุลเซลลูโลสแล้ว ระดับการเกิดพอลิเมอร์ (degree of polymerization) เป็นอีกปัจจัยหนึ่งที่ทำให้เส้นใยเซลลูโลสประดิษฐ์แต่ละชนิดเกิดไฟบริลเลชันได้มากน้อยแตกต่างกัน เส้นใยเรยอนเป็นเส้นใยที่ผ่านกระบวนการหมักด้วยโซเดียมไฮดรอกไซด์ (alkalizing) โมเลกุลของเซลลูโลสภายหลังการหมักมีขนาดสั้นลง การจัดเรียงตัวของโมเลกุลมีความเป็นระเบียบน้อยลง เส้นใยจึงมีความเป็นผลึกต่ำขณะที่ส่วนของอสัณฐาน (amorphous) เพิ่มขึ้น เมื่อได้รับการขัดถูขณะเปียกพันธะไฮโดรเจนในส่วนที่เป็นผลึกจะแตกออก แต่พันธะระหว่างโมเลกุลในส่วนที่เป็น อสัณฐานจะช่วยยึดโมเลกุลของเซลลูโลสไว้ ทำให้เส้นใยเกิดไฟบริลเลชันน้อยลง ขณะที่เส้นใยไลโอเซลเป็นเส้นใยที่มีระดับการเกิดพอลิเมอร์สูงเนื่องจากในกระบวนการผลิตไม่ได้ผ่านกระบวนการหมัก โครงสร้างของเส้นใยจึงมีความเป็นผลึกสูงโอกาสที่พันธะไฮโดรเจนในส่วนที่เป็นผลึกจะถูกทำลายเมื่อได้รับแรงเชิงกลขณะเปียกมีมากกว่าเส้นใยเรยอน เส้นใยไลโอเซลจึงมีแนวโน้มที่จะเกิดไฟบริลเลชันได้มาก

การวัดระดับการเกิดไฟบริลเลชันของเส้นใยไลโอเซล

เนื่องจากไฟบริลเลชันเป็นสมบัติที่สำคัญของเส้นใยไลโอเซล จึงจำเป็นต้องมีมาตรฐานในการวัดปริมาณขนเพื่อใช้ในการเปรียบเทียบระดับการเกิดขน โดยแบ่งการตรวจสอบออกเป็น 2 ขั้นตอน ได้แก่

ขั้นที่หนึ่ง การทำให้เส้นใยเกิดไฟบริลเลชัน

ขั้นที่สอง การคำนวณค่าระดับการเกิดไฟบริลเลชัน

การทำให้เส้นใยเกิดไฟบริลเลชัน

วิธีทำให้เส้นใยเกิดไฟบริลเลชัน มีหลายวิธี เช่น

1. Sonication เป็นกระบวนการให้พลังงานเสียงความถี่สูงในการเร่งการเกิดขนของเส้นใย โดยการนำเส้นใยยาว 20 มิลลิเมตร จำนวน 10 เส้น จุ่มลงในหลอดแก้วภายในบรรจุน้ำกลั่นแล้วนำไปวางในอ่างน้ำแข็ง จุ่มแหล่งกำเนิดคลื่นอัลตราโซนิกลงในหลอดแก้วเป็นเวลา 15 นาที ดังรูปที่ 7 หลังจากนั้นจึงนำไปส่องดูด้วยกล้องจุลทรรศน์เพื่อคำนวณดัชนีไฟบริลเลชัน

2. Shaking Test เป็นกระบวนการทำให้เกิดไฟบริลเลชันด้วยแรงเฉือน โดยนำเส้นใยยาว 20 มิลลิเมตร จำนวน 8 เส้น ใส่ลงในขวดขนาด 20 มิลลิลิตร ภายในบรรจุน้ำกลั่น นำไปเขย่าด้วยเครื่องเขย่าความเร็วระดับ 12 เป็นเวลา 9 ชั่วโมง แล้วจึงนำไปส่องดูด้วยกล้องจุลทรรศน์เพื่อคำนวณดัชนีไฟบริลเลชัน

3. Abrasion Test เป็นกระบวนการทำให้เส้นใยเกิดการเสียดสีกับลูกรอก โดยการขึงเส้นใยบนลูกรอกให้ตึงทำมุม 50 องศา และถ่วงน้ำหนักที่ปลายข้างหนึ่งของเส้นใยด้วยลูกตุ้มหนัก 70 มิลลิกรัม เปิดเครื่องให้ลูกรอกหมุนด้วยความเร็ว 500 รอบต่อนาที นับจำนวนรอบการขัดถูจนเส้นใยขาดแล้วจึงคำนวณค่าการขัดถู (Abrasion Value)

การคำนวณค่าระดับการเกิดไฟบริลเลชัน

ดัชนีที่นิยมใช้วัดระดับการเกิดไฟบริลเลชันมีอยู่ 2 วิธี ได้แก่

1. ค่าการขัดถู (Abrasion Value) เป็นค่าที่คำนวณได้จากจำนวนรอบการขัดถูจนเส้นใยขาดต่อความละเอียดของเส้นใย ค่าการขัดถูน้อยแสดงว่าเส้นใยมีแนวโน้มเกิดไฟบริลเลชันได้มาก

Abrasion Value = จำนวนรอบ / dtex

2. ค่าดัชนีไฟบริลเลชัน (Fibriilation Index) ได้จากผลรวมความยาวขนต่อหน่วยความยาวของเส้นใย หรือในบางกรณีอาจบอกระดับการเกิดขนโดยการเปรียบเทียบค่าดัชนีไฟบริลเลชันของเส้นใยตัวอย่างกับเส้นใยมาตรฐาน ซึ่งได้ถูกกำหนดให้มีระดับการเกิดขนน้อยที่สุดจนถึงมากที่สุด

10 ระดับ ดัชนีการเกิดขนมากแสดงว่าเส้นใยมีแนวโน้มการเกิดไฟบริลเลชันมาก

Fibrillation Index = $\Sigma l / L$

L : ความยาวของเส้นใย

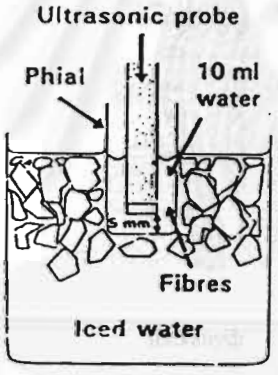
Σl : ผลรวมความยาวของขน

การควบคุมการเกิดไฟบริลเลชันของไลโอเซล

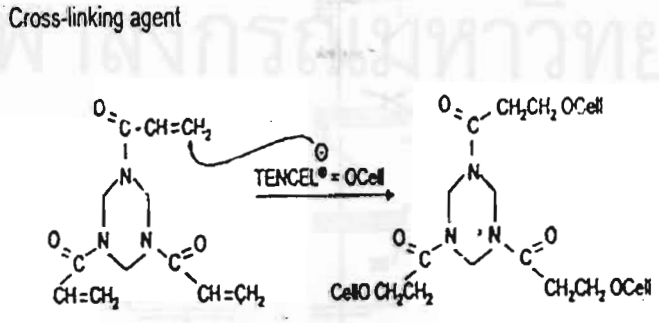
ดังที่กล่าวมาแล้วว่าไฟบริลเลชันเป็นสมบัติเด่นของไลโอเซล จึงจำเป็นต้องลดหรือควบคุมไฟบริลเลชันอยู่ในระดับที่เหมาะสม ซึ่งมีด้วยกันหลายวิธีแต่ละวิธีจึงต้องเลือกให้เหมาะสมต่อผลิตภัณฑ์และกระบวนการตกแต่งสำเร็จอื่นๆ

1. การตกแต่งสำเร็จด้วยสารเชื่อมโยง (Crosslinking Agent)

สารที่ใช้เป็นสารเชื่อมโยงมีโครงสร้างคล้ายกับสีรีแอคทีฟ แต่ไม่มีส่วนที่ทำให้เกิดสี (chromophore) และมีตำแหน่งว่องไวต่อปฏิกิริยาอย่างน้อย 2 ตำแหน่ง ส่วนวิธีการในการเคลือบสารเคมีบนเส้นใยอาจใช้วิธี Pad-Dry Cure หรือวิธีการในการย้อมแบบ Exhaustion ขึ้นอยู่กับชนิดของสารเคมีและกระบวนการผลิต ดังรูปที่ 8 และ 9 การเชื่อมโยงระหว่างโมเลกุลในแนวด้านข้างจะช่วยลดการบวมตัวของเส้นใย เมื่อได้รับแรงกระทำเชิงกลในภาวะเปียก



รูปที่ 7 วิธี Sonication เพื่อเร่งการเกิดขนของเส้นใย (Mortimer and Peguy, 1996)



รูปที่ 8 ปฏิกิริยาการเชื่อมโยงของสารเชื่อมโยงบนไลโอเซล (Eynon,1998)

2. การใช้เอนไซม์ (Enzyme Treatment)

เป็นวิธีการควบคุมให้เส้นใยให้เกิดไฟบริลเลชันในระดับที่เหมาะสมนิยมใช้กับผ้าผืน โดยแบ่งออกเป็น 3 ขั้นตอน

2.1 Primary Fibrillation เป็นขั้นตอนการเหนี่ยวนำให้เส้นใยเกิดไฟบริลเลชันโดยการให้แรงกระทำเชิงกลแก่เส้นใย

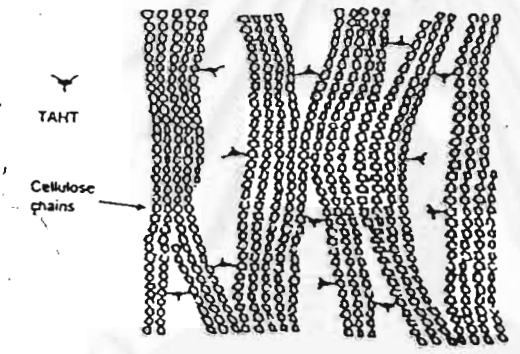
2.2 Cellulose Enzyme Treatment เป็นขั้นตอนการกำจัดขนด้วยเอนไซม์เซลลูเลส ซึ่งจะไฮโดรไลซ์โมเลกุลของเซลลูโลสในส่วนที่เป็นขนให้หลุดออกไปจากเส้นใยโดยมีขั้นตอนดังต่อไปนี้

2.2.1 Endocellulase Endoglucanase (EG) เข้าทำลายส่วนที่เป็นอสัณฐานของโมเลกุล ทำลายพันธะ 1 และ 4 ของโมเลกุลเซลลูโลส เกิดปลายโซ่โมเลกุล ณ จุดขาด

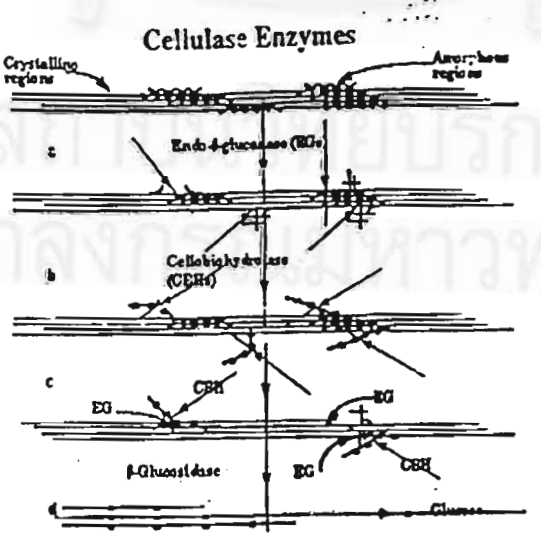
2.2.2 Exocellulase Cellobiohydrolase (CBH) เข้าทำลายบริเวณปลายโซ่โมเลกุลให้หลุดออกเป็นเซลโล-ไบโอส (cellobiose)

2.2.3 β-glucosidase เข้าไฮโดรไลซ์โอลิโกเมอร์ให้เป็นกลูโคสในที่สุด ดังรูปที่ 10

2.3 Secondary Fibrillation เป็นขั้นตอนการเหนี่ยวนำให้เส้นใยเกิดไฟบริลเลชันอีกครั้งขนที่เกิดภายหลังการใช้เอนไซม์จะมีขนาดสั้นสม่ำเสมอและมีผิวสัมผัสดีขึ้น



รูปที่ 9 การเชื่อมโยงของ Trisacryloylhexahydrotriazine บนไลโอเซล (Eynon, 1998)



รูปที่ 10 ขั้นตอนการตกแต่งสำเร็จด้วยเอนไซม์ (Kumar and Hamden, 1999)

3. การเคลือบด้วยเรซิน (Resination)

เป็นวิธีที่นิยมใช้กับผ้า โดยการเคลือบเรซินลงบนผ้าเพื่อลดการขัดสีในระหว่างกระบวนการผลิต

4. การเผาขน (Singeing)

เป็นวิธีที่นิยมใช้กับผ้าทำให้ไมโครไฟบริลที่ผิวผ้าหลุดออกไป โดยการผ่านผ้าเข้าไปในเปลวไฟอย่างรวดเร็ว

นอกจากวิธีการดังกล่าวข้างต้นแล้วปัจจุบันบริษัทผู้ผลิตหลายรายได้กำลังมุ่งเน้นไปที่การปรับปรุงกระบวนการผลิตเพื่อให้ได้เส้นใยไลโอเซลที่มีสมบัติปลอดการเกิดขน (non-fibrillation) ดังเช่น Tencel **A100** ของบริษัท Courtauld Fibers ซึ่งได้ผ่านการเชื่อมโยงด้วยสารเคมีในระหว่างกระบวนการผลิต ทำให้เส้นใยเกิดไฟบริลเลชันได้น้อยลง จึงไม่ก่อให้เกิดปัญหาเมื่อผ่านกระบวนการตกแต่งสำเร็จขั้นต่อไป

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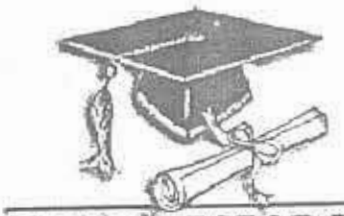

การประชุมเสนอผลงานวิชาการระดับประเทศ

First National Symposium on Graduate Research

โดยความร่วมมือของที่ประชุมคณบดีบัณฑิตวิทยาลัยของรัฐ (กคบร.)

10-11 มิถุนายน 2543 ณ มหาวิทยาลัยเชียงใหม่

PROCEEDINGS

Factors Affecting Fibrillation Behaviour of Man-Made Cellulosic Fibers

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ABSTRACT

Fibrillation behaviour of Tencel® was studied by microscopic examination. The fiber samples were treated with commercial cross-linking agent in various conditions to control the degree of fibrillation. The fiber birefringence was observed by polarized optical microscope, intrinsic viscosity was measured by the viscosity method and crystallinity was determined by X-Ray diffraction method. The results showed that the higher fiber structure oriented along the fiber axis, the higher tendency of fibrillation occurred. On the other hand, the fibrillation decreased when the molecular weight as well as the intrinsic viscosity increased . The application when high fibrillation is needed, increase of relative crystallinity during fiber production is proposed. However, defibrillation finishing by cross-linking agent is suggested for controlling the fibrillation at low level In addition, simple linear relationships between each parameter to the Fibrillation index are also presented.

Introduction

It is known that man-made cellulosic fibers have the tendency to fibrillate in wet abrasion especially Tencel® fiber. Many research works were carried out in order to find what parameters affected the fibrillation behaviour. The previous research was concentrated on the physical parameters in wet spinning process. It was reported that concentration of spinning solution, spinning temperature, air gap length, draw ratio and line speed affected the fiber structure and certainly related to the fibrillation. Moreover, the relationship between the molecular orientation of fibers and the fibrillation behaviour was also reported.

The fibrillation is caused by the high molecular orientation and the lack of lateral conesion in molecular chains. After wet spinning, the extended molecular chains in crystalline regions are bonded by the intermolecular bonding, hydrogen bonds. However, in wet state, the hydrogen bonds linking the crystalline regions are broken apart by swelling of fibers. When the fibers are subjected to the mechanical action such as abrasion, the molecules of the outer skin are splited from the main fiber as a fibril.

In order to assess the fibrillation, Fibrillation Index (FI), the most widely used as the measurement of fibrillation is calculated from the sum of fibrils length devided by fiber length. It seems that only the length of fibers and fibrils are investigated. However, the physical parameters such as birefringence, crystallinity and viscosity which probably related to the fibrillation, should be mentioned. Although the length of fibrils and fibers are required to calculate the Fibrillation Index, they do not appropriately represent whole sample sizes. On the other hand, the physical properties can exactly represent the characteristics of all samples.

The aim of this study are to investigate how birefringence, intrinsic viscosity and relative crystallinity influenced the fibrillation behaviour and also modify the Fibrillation Index by using the mathematical relationship between the Fibrillation Index and these parameters. Tencel® fiber, which is known to fibrillate under wet abrasion , was treated by the commercial cross-linking agent in various conditions to control the fibrillation levels. Then, birefringence, intrinsic viscosity and relative crystallinity were measured. The fibrillation was defined in terms of Fibrillation Index and the affects of these parameters on fibrillation of fiber were analysed.

Experimental Method

Tencel® (Lyocell fiber) and GP® (a commercial defibrillation agent) provided by J.P. Bosco Co.,Ltd. were used in this experiment. In order to control the fibrillation levels, fibers were treated in mixed solution of 12 g/l Na_2SO_4 solution, 12 g/l Na_2CO_3 solution and different GP® solution. The concentration levels was varied at 4 different levels ; 2 g/l, 4 g/l, 6 g/l and 8 g/l. The liquor ratio (weight of dry fiber to volume of mixed solution) was controlled at 1:10. Then, the mixtures were shaked under medium level at 90°c for 30 minutes. After treatment fibers were dried in the oven at 80°c for 30 minutes.

The orientation of fibers was defined in terms of birefringence which was measured by an Olympus optical microscope.

The intrinsic viscosity was measured by means of viscometry method. According to ASTM D1795-76, the intrinsic viscosity was determined from Martin equation :

$$\log [(\eta_{rel}-1) / C] = \log [\eta] + k [\eta] C$$

$[\eta]$: intrinsic viscosity C : concentration (g/dL)

η_{rel} : relative viscosity . k : constant

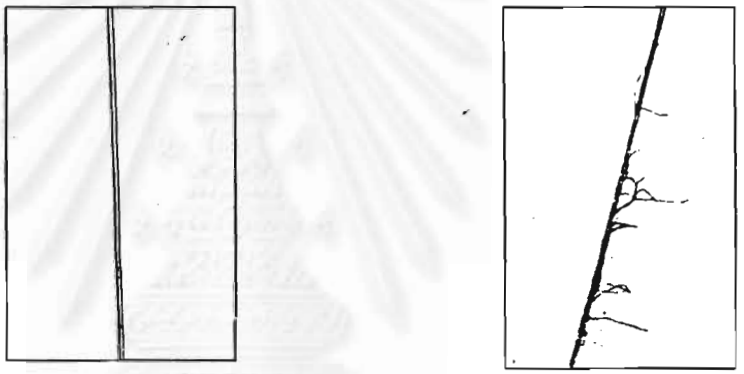
The relative crystallinity was measured from the X-Ray diffractograms, recorded by Philips PW 3710 Diffractometer.

The fibrillation of fibers was assessed by following technique : 1 gram of dry fiber was treated with 20 ml. of 12g/l Na_2CO_3 solution under high level shaking at ambient temperature for 4 hours. The fibers were, then, taken to examine through optical microscopes. The fibrillation Index (FI) was calculated by :

$$FI = \Sigma l / L$$

l : length of fibrils L : length of fiber

Two sampled fibers with different fibrillation levels are shown in figure 1



FI = 0 FI = 0.45

Figure 1 Photomicrographs of sampled fibers from optical microscope (x100) at FI = 0 and FI = 0.45

Results and Discussion

GP®, crosslinking agent, reacted with hydroxyl groups of cellulose molecules in an aqueous alkaline medium to form covalent bonds between molecular chains. The increase of lateral cohesion by crosslink caused the Fibrillation Index significantly decreased as the minimum level at 5.8% of GP® (see figure 2). However, finishing more than 6% GP® showed the opposite results. This is due to the excess of GP® treated more than 6% might aggregate and then precipitate from the turbid solution before reacting with cellulose chains.

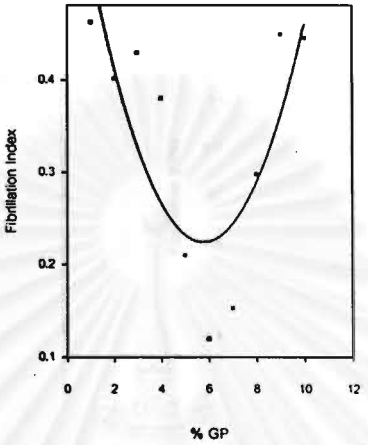


Figure 2 the relationship between Fibrillation Index and % GP

The linear relationships in figure 3(a) and 3(b) show that Fibrillation Index was proportional to both birefringence and relative crystallinity which directly related to the orientation of cellulose molecules in the fibers. High orientation along fiber axis led to the lack of lateral strength between cellulose chains and caused the molecules of outer skin to fibrillate when fibers were subjected to wet abrasion. Although the birefrigence was related to the Fibrillation Index, it was not suggested to be a significant parameter predicting the fibrillation behaviour. This is because the birefringence which directly evaluated from colors of fibers under optical microscope was depent on the personal justification.

In contrast to birefringence, the Fibrillation Index decreased significantly while the intrinsic viscosity increased due to the increase of cross linking between cellulose chains (see figure 3c). According to Staudingers (1930), the relationship between intrinsic viscosity and molecular weight was described in Mark and Houwink equation :

$$[\eta] = K M_v^a$$

$[\eta]$: intrinsic viscosity

M_v : viscosity-average molecular weight

K and a are constants which depend on polymer, solvent and temperature

The increase of the molecular weight of cellulose by cross-linking reaction brought about the intrinsic viscosity also increased. During the reaction the molecules of cross-linking agent were linked between the cellulose molecules of the outer skin like a ladder causing the lateral cohesion of fibers gradually increased. As a consequence, the

Fibrillation Index significantly decreased. This implied that the increase of molecular weight of cellulose molecules led to the decrease of fibrillation.

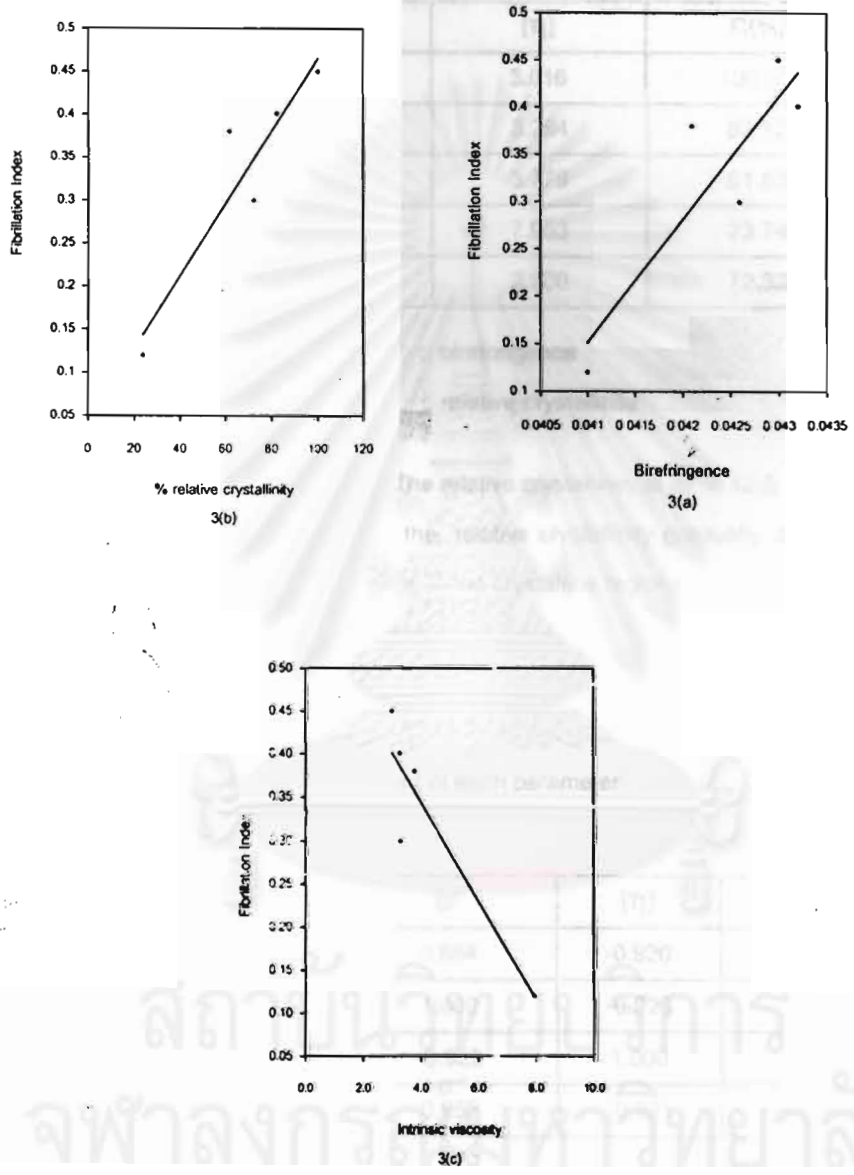


Figure 3 (a) the relationship between Fibrillation Index and birefringence, r = 0.826

(b) the relationship between Fibrillation Index and percentage of relative crystallinity , r = 0.864

(c) the relationship between Fibrillation Index and intrinsic viscosity, r = 0.846

Table 1 Fibrillation Index, birefringence, intrinsic viscosity and % relative crystallinity of Tencel® fiber treated with 0%, 2%, 4%, 6% and 8% GP®

% GP	FI	BF	[η]	C(%)
0	0.45	0.0430	3.016	100.00
2	0.40	0.0432	3.284	82.12
4	0.38	0.0421	3.779	61.63
6	0.12	0.0410	7.953	23.74
8	0.30	0.0426	3.300	72.32

FI : Fibrillation Index BF : birefringence

[η] : intrinsic viscosity C : relative crystallinity

The crystallinity of fibers were shown in table 1. The relative crystallinity at 2θ = 12.8 were measured relatively by X-ray diffractometer . It is noted that after treatment the relative crystallinity gradually decreased as a function of percentage of GP® caused by the increase of cross linking in the crystalline regions.

Table 2 The Zero Order (Pearson) Correlation Coefficient of each parameter

Pearson Correlation (r)	FI	BF	[η]	C(%)
FI	1.000	0.884	-0.920	0.929
BF	0.884	1.000	-0.923	0.952
[η]	-0.920	-0.923	1.000	-0.921
C (%)	.0929	0.952	-0.921	1.000

Table 2 shows that Fibrillation Index was related to all parameters in the order of relative crystallinity ($r_{FI,C}$ = 0.929), intrinsic viscosity ($r_{FI,[\eta]}$ = -0.920) and birefringence ($r_{FI,BF}$ = 0.884) but was significantly affected by relative crystallinity and intrinsic viscosity the more than birefringence. In application, the relative crystallinity and intrinsic viscosity can be used as significant parameters to predict the fibrillation behaviour. Furthermore, it appeared that each parameter affected not only the Fibrillation Index but also among themself.

Conclusion

1. Fibrillation behaviour of Tencel® fiber linearly related to birefringence, intrinsic viscosity and degree of crystallinity but was significantly affected by crystallinity and intrinsic viscosity. In application, defibrillation finishing by cross-linking agent is suggested to control the fibrillation of fibers. However, when the high fibrillation fiber is needed, the increase of crystallinity and fiber orientation can be achieved by controlling fiber processing parameters.
2. Instead of the conventional Fibrillation Index calculated from sum of fibrils length devided by fiber length, the Fibrillation Index can be estimated from either 2.1 and 2.2 as follows :
   - 2.1 the relationship between Fibrillation Index and intrinsic viscosity

     $FI = 0.5743 - 0.0572 [\eta]$, $r = 0.85$
   - 2.2 the relationship between Fibrillation Index and relative crystallinity

     $FI = 0.0432 + 0.0042 C$, $r = 0.86$
3. The fibrillation of Tencel® fibers can be controlled by using crosslinking agent, GP®. The suggested conditions to achieve minimum fibrillation were 5.8% GP® solution mixed with 12 g/l Na_2SO_4 solution and 12 g/l Na_2CO_3 solution at 90°c for 30 minutes.

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Biography

Miss Siriluk Chiarakorn was born in Bangkok, Thailand, on November 25, 1976. She received the first class honour in Bachelor of Science degree majoring in Polymer Science and Textile from the Department of Materials Science, Chulalongkorn University in 1998. She started as a graduate student with a major in Applied Polymer Science and Textile Technology, Chulalongkorn University in June 1998 and completed the programme in September 2000.