Production of functional textile filaments from chemically modified cellulose fibers

by

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Abstract

Cellulose is the most abundant natural polymer on earth originated from renewable plant biomass. Among all plant sources, cotton fibers contain the highest amount of pure cellulose, which is used directly in textile fibers for yarn and fabric production. Cellulose fibers (more commonly referred to as pulp fibers) are extracted through various pulping processes to remove the lignin and hemicellulose, which increases the overall alpha-cellulose contents. However, cellulose fibers have a lower aspect ratio and do not fulfill the technical requirements for textile and yarn production. However, the aspect ratio can be increased by dissolving the cellulose fibers in an appropriate solution to regenerate them for getting continuous filaments. Currently, cellulose regeneration processes require toxic chemical processes that are not environmentally friendly and required extensive pre-treatment. In this study, we developed a green method to produce textile filaments from existing kraft pulp (cellulose) fibers. The cellulose fibers were chemically modified to produce a low-substituted carboxymethylcellulose (CMC) and dialdehyde cellulose (DAC). The CMC and DAC gels were then extruded through a wet-spinning process to obtain cross-linked textile filaments. These filaments have a low content of carboxylic groups (~1.4 mmol/g cellulose) and aldehyde groups (~1.5 mmol/g cellulose) and underwent a significant reduction of water absorption with high mechanical strength. In this work, the degree of hydrophilicity of the produced filaments was optimized by controlling the functional groups (carboxyl and aldehyde). We also focus on other conditions that affect the hydrophilicity of the filaments to achieve similar absorption properties of cotton fabric (i.e., water uptake - 1.5 g/g yarn).

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Acronyms

CMC	Carboxymethyl cellulose
DAC	Di-aldehyde Cellulose
CMF	Carboxymethyl Fiber (Cellulose)
MCA	Sodium monochloroacetate
NMMO	N-methylmorpholine-N-oxide/water mixure
IL	Ionic Liquid
EMIAc	1-ethyl-3-methyl-imidazolium acetate
BSWK	Bleach Soft wood Kraft Pulp
AGU	Anhydroglcose unit
XRD	X-ray diffraction
SEM	Scanning electron microscopy
CS$_2$	Carbon disulfide
MCC	Microcrystalline cellulose
DP	Degree of polymerisation
DS	Degree of substitute
DEAE	diethylaminoethyl
SO$_2$	Sulfur dioxide
MPa	Megapascal
PHK	Pre-hydrolysis kraft
AS	Acid sulfide
SSL	Spent sulfite liquor
MWD	Molecular weight distribution
CNF	Cellulose nanofiber
PFD	Process Flow Diagram
BSWK	Bleached softwood kraft pulp
IPA	Isopropyl alcohol
ZnSO$_4$,	Zinc sulphate
Na$_2$SO$_4$	Sodium sulphate

H₂SO₄	Sulphuric acid
FTIR	Fourier Transform Infrared Spectroscopy
CI	Crystallinity index

Chapter 1

Background and Introduction

Global climate change, marked by habitat and resource depletion, increased incidents of toxins being released into the atmosphere, and rising temperatures, currently poses the greatest risk to our health and well-being. Vast forestry reserves can address these challenges, with expertise in green chemistry to provide carbon-neutral textiles and other cellulosic materials with next-generation function through a forward-thinking, environmentally conscious and economically viable manufacturing pipeline. This technology will dramatically expand the portfolio of wood-derived textiles to the pulp and paper sector, which is presently suffering economic constraints, bringing much-needed product expansion, manufacturing innovation and job growth to that hard-hit industry. Global volumes of textile production currently exceed 100 million metric tons per year, of which 63% is produced from petroleum (mainly polyester) [1]. This manufacturing stream is linked to a non-renewable carbon deposit and is marked by high-energy processing technologies that produce high-risk effluents. The remaining 37 and 31% were derived from cotton, which are characterized by high water and pesticide use, and only 1% is obtained from the wool. Non-cotton, cellulose-derived fibers currently account for about 5 million tons (5%) per year in a fast-growing market.

Many of these fibers are made by "rayon" or "viscose" processes, in which cellulose is modified with carbon disulfide into cellulose xanthate [2]. Although carbon disulfide (CS_2) is a necessary component of this process, it has a recommended daily exposure limit of 10 ppm. Post-production fiber modification, including fiber coloration and the introduction of antimicrobials, present an additional chemically intensive step, which is largely conducted in developing nations where relaxed environmental regulations do not prevent effluent discharge into the local water supply of these areas. These characteristics of textile production create a need for technological innovation

that can transform a renewable carbon source into next-generation textiles under manufacturing conditions that are environmentally sensitive and economically viable.

In this study, textile filaments were produced from the modified BWSK pulp (cellulose) fibers using an environmental-friendly process. A significant advantage of this new process is the fact that the filaments are manufactured directly from modified pulp fibers without the production of cellulose xanthate, eliminating the use of carbon disulfide (rayon process). The resulting filaments can be modified under environmental-friendly conditions by taking advantage of the newly introduced carboxyl groups to incorporate the added function. The current study addresses a series of fundamental scientific challenges that prevent this technology from advancing to market, including the high cost and inefficient production of carboxymethyl cellulose (CMC) fibers, whereby we introduced a small amount of negatively-charged carboxyl groups (-COOH) onto the cellulose fibers. In addition, we developed another type of modified cellulose (dialdehyde cellulose "DAC"), which offers numerous advantages for the preparation of textiles filaments. Both CMC and DAC contain unique chemical handles that play an important role in the formation of the filaments, as well as in their physical and chemical properties.

Objectives:

The main aims of the project are:

- Production of textile filaments from chemically modified cellulose
- Optimize the chemically modified cellulose properties (functional groups) and extrusion of textile filaments through a laboratory spinneret.
- Explore the conditions that affect the physical and chemical properties (cross-linking, water absorption, tensile etc.) of textile filaments and their characterization.

Chapter 2

All fibers are not textile fiber. Textile fibers have some properties that help it to convert into yarn. Series of physical processes are done to turn the textile fiber into the string like weaving, knitting, braiding, felting, and twisting as well as producing fabric. The necessary properties for threads to be spun into yarn include a minimum length of 5 millimeters, flexibility, cohesiveness, and enough mechanical strength [3]. Other essential properties have elasticity, fineness, uniformity, durability, and luster.

2.1. Fiber properties related to textile technology

The quality of the textile fibers and yarns are characterized according to their various standard properties for the end usages. The major fiber properties are discussed below along with their importance.

2.1.1. Fiber length.

Fiber length is one of the significant concerns while producing different textiles fibers. Processing textile yarn from fibers, the length is the most critical property as it translates off the fiber strength to yarn strength. Most of the natural fibers have a restricted length and are usually mentioned as staple fibers. The typical length of cotton fibers is 30 mm whereas for wool, it is around 80 mm. Man-made fibers can be produced continuously with unlimited length and later they are cut into small pieces to have staple fibers. Fiber length affects yarn strength because longer fibers provide a more significant range of contact points between individual fibers where friction forces develop and hold fibers along. That's why fibers that are shorter than 12 mm are not suitable for spinning[4].

The degree of hairiness increases with the increase of fiber length and most of the yarns are made from staple fibers. Excessive hairiness due to short length fibers makes the yarn tough to use in knitting, weaving and sewing because fibers may be cut off and get accumulated in thread guides causing yarn breakage. For most purposes, longer fibers are preferable. However, short fibers have the advantage of cloth characteristics, where it is desirable to produce a soft, hairy and warm-handling surface [5]. Here a large number of projecting fiber ends are desired, and although the number of ends can be strongly influenced by the method of spinning employed, under any given set of conditions, it must vary inversely as the mean fiber length. The fabric prickliness can be determined by calculating the Buckling load of textile fibers. The following equation states that Young's modulus, diameter, and fiber length are the key factors of determining fabric prickliness [6].

Buckling load, $P_E = \pi^2 \left(\frac{EI}{4l^2}\right)$,

Where,

E = Young's modulus of the fiber,

I = Moment of inertia;

l = Length of the fiber.

2.1.2. Fiber diameter.

The aspect ratio of fiber is the ratio between the fiber length and fiber width (fiber diameter) plays an important role in the effect of mechanical properties of hybrid composites. A higher aspect ratio gives more effective stress transfer to the matrix[7]. Textile fibers need to have at least aspect ratio of 1000 or more [5, 8]. e.g. wool: 3000; cotton: 1500 [9]. For the production of textile materials, fiber should have minimum of 15 mm in length and 10-50 μm in width[6].

Fiber diameter defines the minimum thickness of the staple fiber yarn that may be achieved in spinning. At the same time using finer fiber for the manufacture of yarn of the same thickness is advantageous because of the multiplied variety of fibers that contribute to the yarn strength. Fiber

diameter features a significant impact on comfort in attire production be-cause using thicker fibers might cause a prickly sensation connected with skin [10]; this generally happens if low-quality thick wool fibers are used. Finer fibers, on the opposite hand, are prone to the formation of entangled balls of fibers on the fabric surface known as pilling. The study revealed that the mechanical properties of any fabric influence the discomforts in wear and the fabric prickliness is directly related to the diameter, thickness, and surface roughness of the fibers[11].

The flexibility of a circular beam of fiber is a function of the reciprocal of the diameter hence reducing the diameter of fiber increases its flexibility [12]. Fineness is one of the significant properties of fiber quality that refers the cross-sectional thickness. The fine fibers are mostly responsible for obtaining fine yarns. As the straight thickness of yarn diminishes, the quantity of filaments additionally diminishes by the diameter of the yarn. The expansion in fiber surface because of a decrease in fiber breadth adds to an attachment of filaments to obtain a similar quality with less twist than coarser filaments. These attributes combine to the hand feel of the items created from them.

2.1.3. **Fiber tensile strength**,

Fiber's mechanical property consists of fiber strength, elongation, elasticity, abrasion resistance, modulus of elasticity. Fiber strength refers to the fiber resistance to exterior damage, which mostly determines the durability of the textile goods. Tensile elongation and elastic restoration are primary mechanical properties that define strength, durability, functionality to stretch and conform to elaborate shapes and functionality to return to original structure and dimensions in all products made from the fibers. These properties are vital for successful fiber processing in terms of applying some external forces.
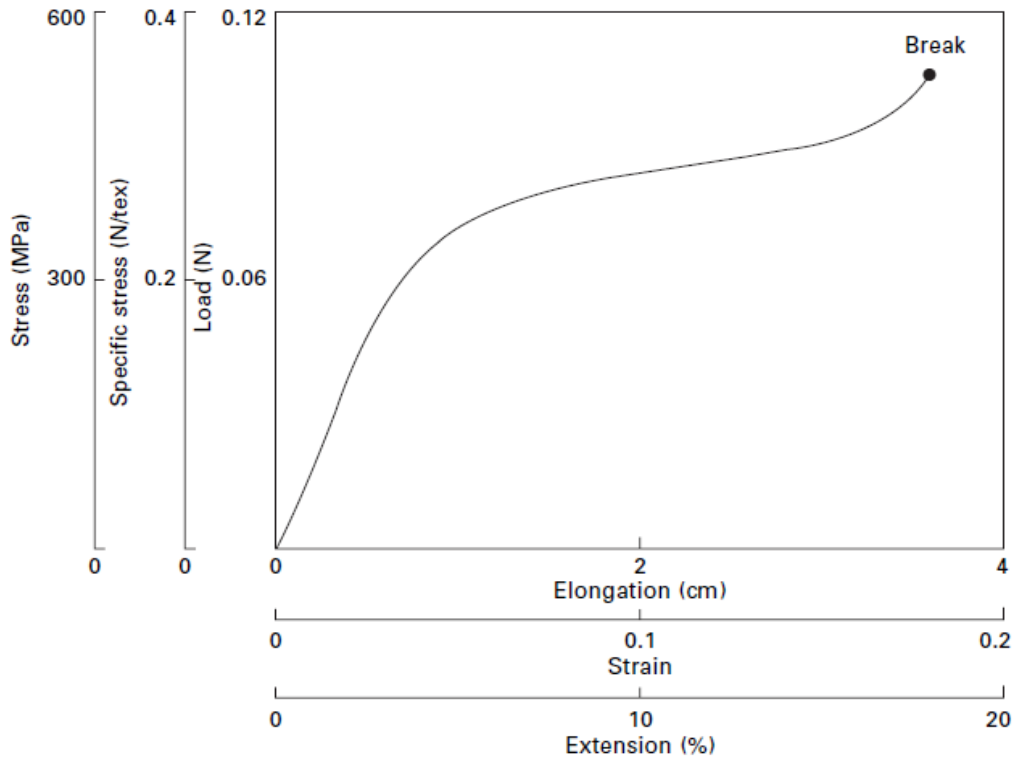
Figure 2.1: Load–elongation curve, source [5]

The behavior of an individual fiber under a gradually increasing applied force is completely expressed by the load–elongation curve with its end-point breakage. In most physical and engineering applications, the load is replaced by stress, defined as stress = load /area of cross-section. The SI unit of stress is newton per square meter (N/m2), which is also called a pascal (Pa or MPa).

In textile technology, however, we are more often interested in materials in terms of their weight, rather than in terms of their bulk. In addition, the area of cross-section of textile yarns and fabrics is not well defined, since it is confused by the space between fibers. The primary definition of fineness is the linear density. It is more convenient to use linear density (mass-based quantity) instead of non-defined area which give consistent information from the molecular to the macroscopic level.

Mass = Volume × Density
$$m = A_o \times l \times \rho$$

$$\frac{\text{Mass}}{\text{Length}} = \frac{m}{l} = A_o \times \rho$$

$$A_o = \frac{\text{Mass per unit length}}{\text{Density}} = \frac{m}{l\rho}$$

$$\sigma_e = \frac{F}{A_o} = \frac{F}{m/l} \times \rho$$

$$\sigma_e = \sigma_s \times \rho$$

Solid cylinder

Engineering stress =
$$\sigma_e = \frac{\text{Load}_{\text{at break}}}{\text{Cross-sectional area}} = \frac{F}{A_o} \; cN/cm^2$$

Fiber

Specific stress =
$$\sigma_s = \frac{\text{Load}_{\text{at break}}}{\text{Mass / length}} = \frac{F}{tex} \; cN/tex$$
tex = Mass (g)×10^3/length (m)
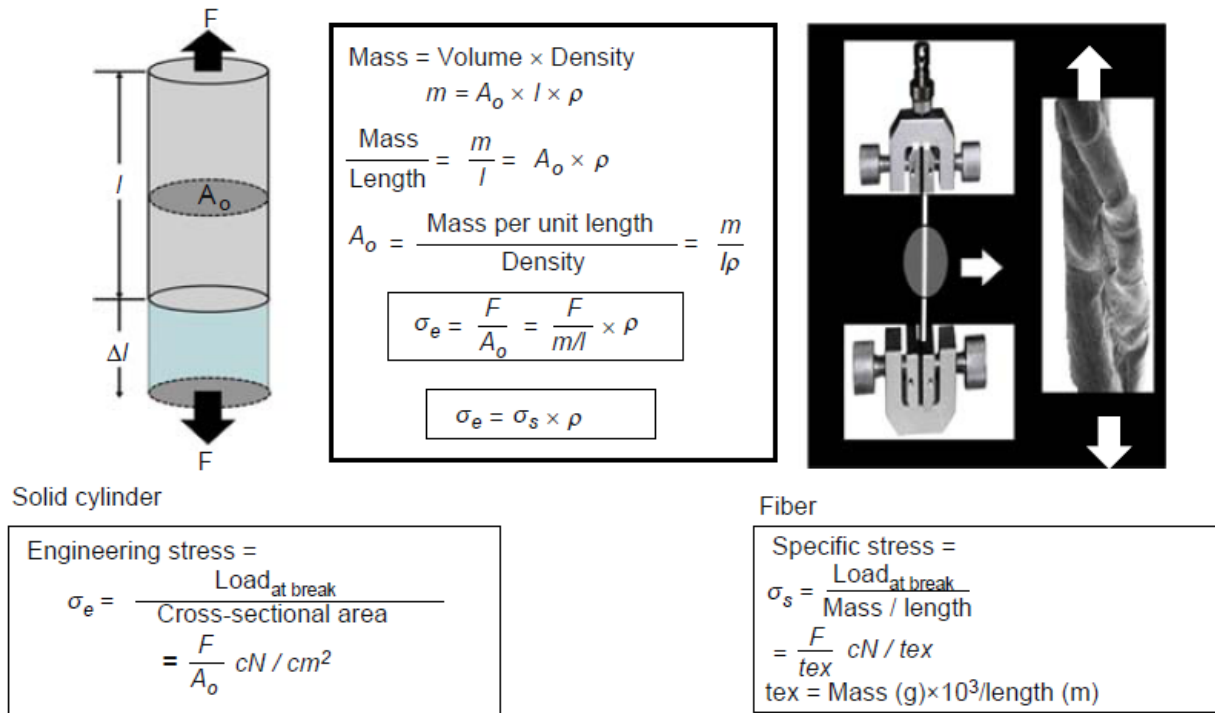
Figure 2.2 : The difference between specific stress and engineering stress[12].

The normalized force is termed the specific stress and is defined as specific stress = load/linear density, the consistent SI unit for specific stress would be N m/kg. When manufactured fibers were introduced in the first half of the 20th century, the unit chosen was gram force per denier, usually written as g/den, and this unit is still widely used. In order to get a unit of similar size to g/den, cN/dtex is often found.

2.1.4. Crimp

Crimp is defined as the waviness of a fiber that has technological importance in several contexts. Crimp can be referred to bends, twists or curls along the fiber length. It is measured by the number of crimps or waves per unit length as well as by the percentage increase in extent of the fiber on
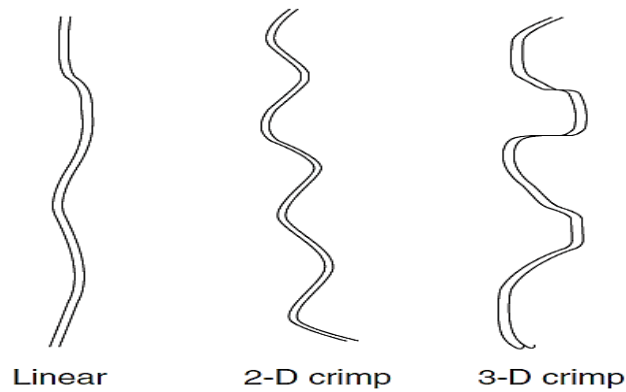
Figure 2.3: Fiber crimp. Source[6].

removal of the crimp. Fig. 2.3 represents the natural linear fibers and some other 2D and 3D crimp fibers. Linear fibers have less elongation rate than the crimped fibers. Crimp is a natural property of many natural fibers such as cotton and wool. Crimp helps in developing fiber cohesion in sliver, roving and yarn; an excessive crimp may cause difficulties in disentangling the raw fiber mass. Man-made fibers are initially produced as straight filaments but after that crimp can be developed by a specific treatment in order to improve fiber handle.
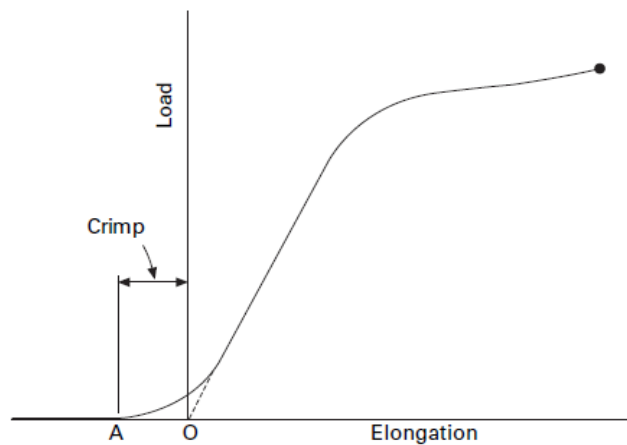
Figure 2.4: Load–elongation curve of a crimped fiber [5]

The crimp is normally pulled out by a suitable small tension in measuring linear density, and it can be removed by a pre-tension at the beginning of the tensile strength measurement. The crimp is given by AO (Figure 2.4) and may be expressed as a percentage of the initial length [13].

2.1.5. **Friction coefficient**

Friction is the force resisting the relative motion of solid surfaces, fluid layers, and material elements sliding against each other. Friction force is affected by fiber count, normal force applied, roughness of the fiber surface and area of contact, fiber crimp, and a cross sectional shape [14] ,[15] . To ensure good fiber cohesion, the friction coefficient is important; this prevents fiber slippage about each other, thereby strengthening the yarn. On the opposite hand, a high friction coefficient makes the yarn challenging to process due to the friction forces that might also develop between the moving yarn and yarn guides. Normally textile fiber coefficient of friction is maintained μ_s= 0.2– to .3 [15];
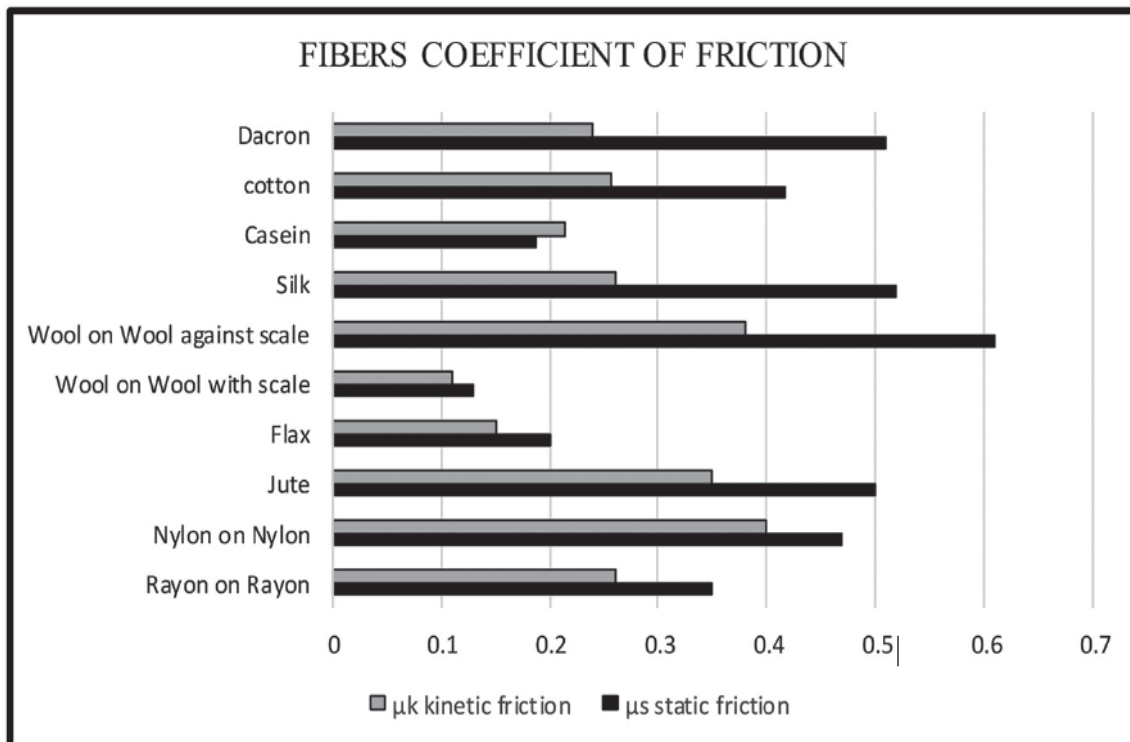
Figure 2.5: Fiber coefficient of static and kinetic friction. Source[16]

The classical laws of friction of Amontons are not valid for inter-fiber friction. The coefficient of friction is not a constant but decreases in general with increasing load[17].

2.1.6. Accumulation of electrostatic charge

Whenever two dissimilar materials and at least one is an insulation property are tubbed together electric charge formation and accumulation of electric charge occurs. The intensity of the electrostatic charge has a marked influence on collection efficiency and is a function of fiber surface roughness and the inherent property of the polymer. Other factor equal, the rougher the surface, the higher the generated charge. Rough fibers like wool tend to develop higher charges than smooth surface such as made from continuous filament fiber, rayon [18].

Accumulation of electrostatic charge may be a negative property for any fibers because it ends up in a repulsive force between fibers and therefore reduces fiber's cohesion. The electrostatic charge also makes fibers tough to process by causing fibers to stay to the operating parts of spinning machinery.

2.1.7. Moisture regain characterizes

Moisture regain is a fiber's characteristic that is maintained by its chemistry, relative humidity and temperature of the surrounding environment. moisture regain helps in dissipating electrostatic charges that are usually trouble with man-made fibers. In the context of moisture, the cotton fiber is categorized as a "hygroscopic fiber," or a fiber that can absorb water from a moist atmosphere, and conversely, lose water in a dry atmosphere.

Cellulosic structure of cotton fiber has over 95% cellulose[19, 20]. It was also mentioned that cotton fiber contains about 60% to 80% crystalline regions[12] that significantly influence water uptake properties of the fibers. However, higher crystallinity increases the strength on the other hand the elongation increases with decreasing crystallinity. Moreover, lower crystallinity enhances the higher amorphous region which allows higher water uptake as well as introduces more active chemical sites for reaction. The crystalline cellulose in wood fibers generally in the ranges of 55

to 70% [21]. Several studies reported that only 4% moisture regain can increase the fiber tenacity by more than 6 cN/tex. This is because of the formation of H-bonding between the fibers which increase the fiber strength. Few other studies also revealed that increasing surrounding humidity from 3% to 5% can increase the fiber tenacity at least 1 cN/tex. In this context, tensile properties of the natural fibers increases after immersing in water – hence the specific strength and the specific modulus of most natural fibers dropped dramatically (50%) upon immersion in water[22].

2.1.8. **Impurities content**

Impurities content in the raw fiber materials to a large extent affects stability of all spinning processes. Typical dimensions of impurities present in natural fibers such as cotton and wool are comparable to and often exceed the diameter of average yarn. The remaining impurities after the spinning processes in the fibers can significantly reduce the quality and cause of severe breakage of the yarns. As indicated below picture figure 2.6, the performance characteristics of any end products are a function of combination intermediate products (Yarn/Fabric) as well as initial raw materials
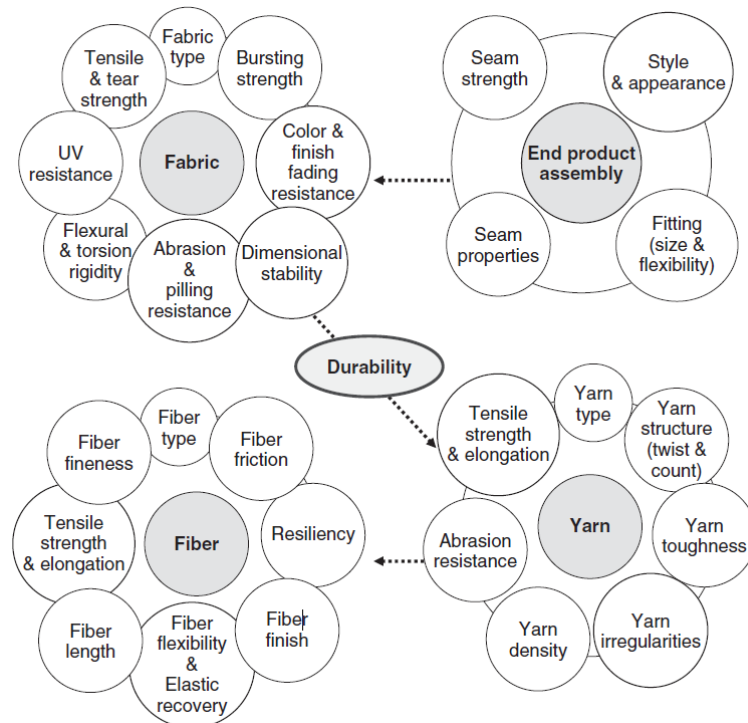
Figure 2.6: key factors contributing to the durability of fibrous products, source[15]

(Fiber). Accordingly, the design of a fibrous product must begin with the aid of setting up the different elements making the product meeting and the attributes that are applicable to the favored overall performance characteristic. So, in order to design a fibrous product, one should consider raw materials (fiber) to get end-user desired specific products.

The quality of different textile yarns, fabrics and as well as other related end products mostly depends on the sources of fibers. It is challenging to separate fiber's properties, which are essential for spinning from those that affect the final product's performance characteristics. For example, Table 2.1 shows the comparison the properties of cotton, viscose, and polyester fibers. The analysis of this table shows that these three fibers are complementary in their properties; this explains why cotton/polyester blends are often used in the textile industry.

Table 2.1: Properties of natural (cotton), synthetic (polyester) and regenerated (viscous) fiber [23]

Natural Fiber	Synthetic Fiber	Regenerated Fiber
Fibers come from natural source	Fibers are manmade, long chain of plastic molecule.	Fibers are made from natural materials
Comes plant and animal	Produced from petroleum-based chemicals	Chemically treated of natural fibers
Biodegradable	Less biodegradable	Biodegradable
Renewable sources	Nonrenewable source	Renewable sources
Cotton, wool, silk	Polyester, Nylon	Viscus rayon
Porosity high and comfortable	No porosity, solid	Porosity is similar to Natural Fiber
Regenerated fibers tend to have similar properties to natural fibers		

2.2. Types of textile fiber

Fibers are the fundamental parts of the building blocks of making textile yarns and fabric. Fibers that can be spun into yarn or processed into textiles such as a woven fabric, knit fabric, non-woven and so on through a suitable interlacing technique are known as a textile fiber. Generally, textile fibers can be divided into two main types: Natural fiber and Artificial fiber or manmade fiber Based on the supply, we can classify the textile fiber into natural and artificial fiber.
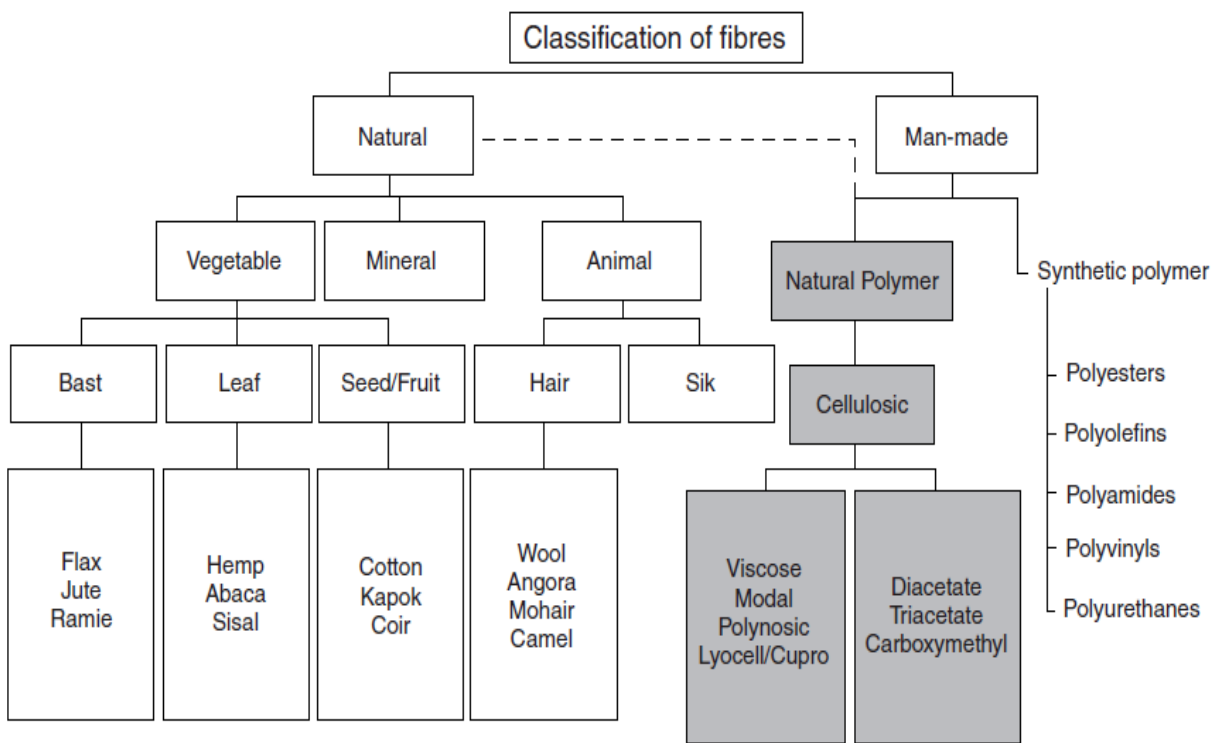
Figure 2.7 : Classification of fibers [2]

2.2.1. Natural fibers

Natural fibers has become increasingly important in recent years due to the growing awareness to protect ecological and environmental resources, including shrinking forest resources [24, 25].

Natural fiber comes from a natural supply and its primary sources from plants and animals. Natural fiber, any hair-like raw material that can be immediately extracted from an animal, plant, or mineral origin and processed into nonwoven fabrics like felt or paper or, once spinning into

yarns, into woven cloth. A natural fiber may additionally further outline as an agglomeration of cells within which the diameter is negligible as compared with the length. Although nature abounds in fibrous materials, particularly cellulosic sorts like cotton, wood, grains, and straw, only a little variety may be used for textile products or other industrial
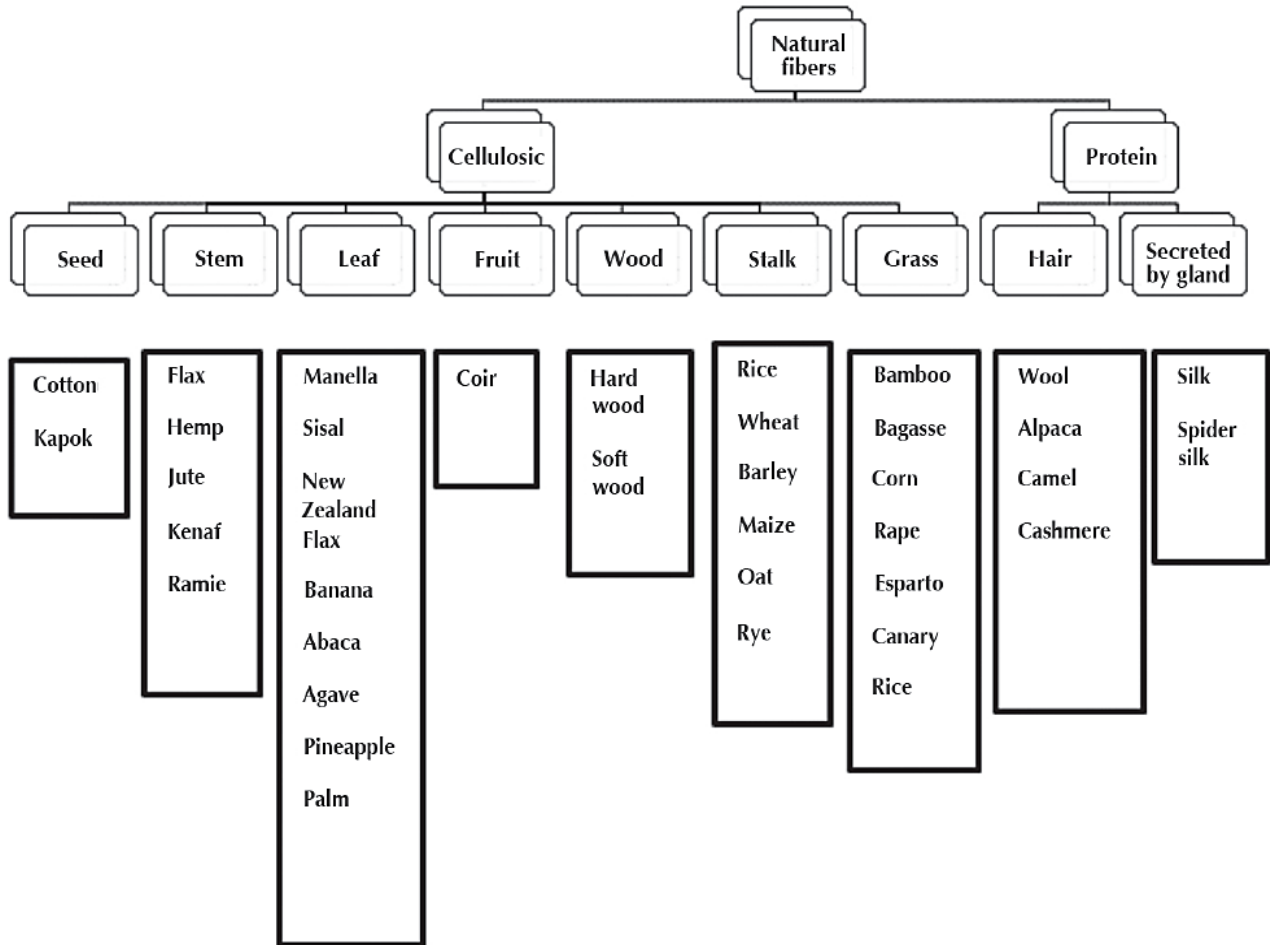
Figure 2.8: Natural fiber classification[16]

purposes. Natural fiber may be divided into two types, such as protein fiber and cellulosic fiber. Six naturally occurring fibrous silicates are called asbestos; asbestos is the only mineral fiber[26].

2.2.1.1 Protein fibers

Protein fibers are another form of high-molecular-weight natural polymer in which the amino acid monomers are linked with another by peptide bonds. Protein fibers are the most convenient dyeable fibers because of having various reactive functional groups like -COOH, NH$_2$ etc. This fiber can

be used in dying process with a high range of dye under neutral, slightly basic or acid conditions. Protonated occurs and form NH or Amino group from the protein fibers under acid condition. In this form, they can highly attract dyes containing acid anions including acid and mordant dyes [27]. For this high range of dying capability protein fibers have great demand in textile industry. Protein fibers are mainly an animal origin, and wool and silk fibers that are commonly used in the textile industry

Wool fiber: Wool is the most widely used and found natural protein-based staple fiber that grows and is collected mainly from sheep. This fiber is one of the renewable and sustainable resource. The chemical composition and structure of wool is composed of α-keratin [28] that is formed by polypeptide chains composed of amino acids[29].
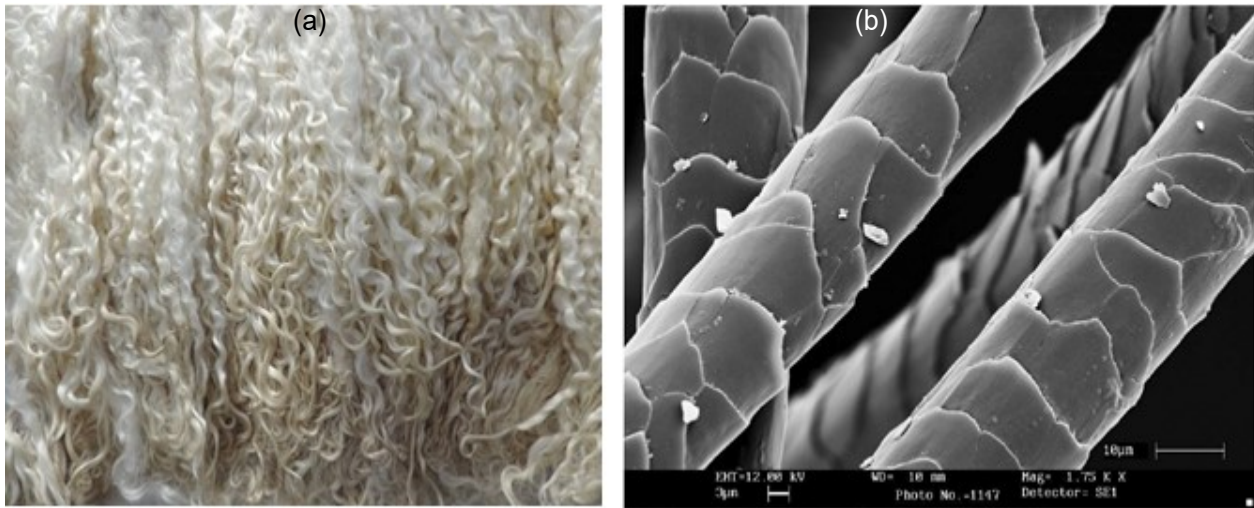
Figure 2.9: Wool fiber (a) (Source: www.craftsy.com) and Longitudinal view of wool fiber (b)

Chemically, the peptide chains are formed by the amino acids and linked together by covalent bond between carboxylic group and the amine groups which leads to the formation of amide bonds (-CONH-). Physically, wool fiber consists of two layers such as outer layer which is called cuticle and the inner part which is called cortex. Moreover, in some wool fibers, there may have a central cavity that is called medulla. The outer cuticle layer is made by some overlapping flat scales (Fig. 2.9 b); dimensionally their thickness is between 0.2 and 0.4 μm, 30–50 μm in width and 16 μm in length [30, 31].

Wool fiber are mostly popular for good insulation characteristic which is because of having low thermal conductivity of 54 mW/m/°K [5]. Due to the complex chemical structure, it is difficult to mimic the exact wool fiber. Synthetic wool fiber does not persists with natural wool fiber in moisture uptake and thermal conductivity rather than only mechanical properties [32-34].

Silk fiber: Silk is a fine, strong, long filament produced by the larva of certain insects, especially the silkworm, when constructing their cocoons. It is another protein fiber composed of fibroin. Early in 2640 BC, the ancient Chinese learned how to reel the silk and make it into fabric silk [6]. The domesticated moth *Bombyx mori* which are also known as mulberry silkworm produces silk filaments. The filaments consist of fibroins and these fibroins are attached by a protein gum called

Figure 2.10: Silk fiber-Silk cocoon (a)(source: www.materialdistrict.com), cross sectional view (b)

sericin. Chemically fibroin is highly crystalline and uniform that are made of different amino acids. The amino acids i.e. glycine, alanine, serine, and tyrosine are about 85% of the total residues of fibroin[35, 36].

The chemical compositions are, in general, silk fibroin of 75–83%, sericin of 17–25%, waxes of about 1.5%, and others of about 1.0% by weight [37]. The sericin gum is hydrophilic protein that is removed and separated simply by boiling water. Later, the degummed cocoons are unwinder to collect the raw silk fibers (Fig. 2.10 a). A single silk filament can be up to 2000 m in length [38].

The polypeptide chains of fibroins are connected by hydrogen bonds between the CO and NH groups. Figure 2.10b represents the cross- sectional view of the silk fibers where it is observed that the filaments are more likely elliptical and triangular. The average diameter of silk filaments are 10 to 15 μm and the linear density ranges from 0.19 and 0.44 tex[37]. Due to high strength (tenacity 38 cN/tex) and breaking elongation (27.2%) silk is considered as the sophisticated and expensive fiber material[39].

2.2.1.2 Cellulosic fibers

Many natural cellulosic fibers can be obtained from different parts of plants such as seeds (cotton), leaves (manila, sisal), the husk of coconuts (coir), and stems where examples include flax, hemp, jute and ramie which are often referred to as bast fiber crops. These natural fibers comprise the essential plants of natural fibers that can be used to manufacture composite materials[25] as well as textile yarn. The viability of using one or another type of fibers limited its applications in the composite industry.

The global production of textile fibers increases linearly over the last decides to reach 85.6 million tons, 60.3 million tons is chemical fiber [40-42]. As illustrated in Figure 2.11, the natural fiber production is almost constant for the last ten years. The total world production 2013 of natural fibers [42] is estimated at 33 million tons, including 26 million tons of cotton lint, 3.3 million tons of jute, 1.2 million tons of clean wool, and 900,000 tons of coir (fibers made from coconut husks).
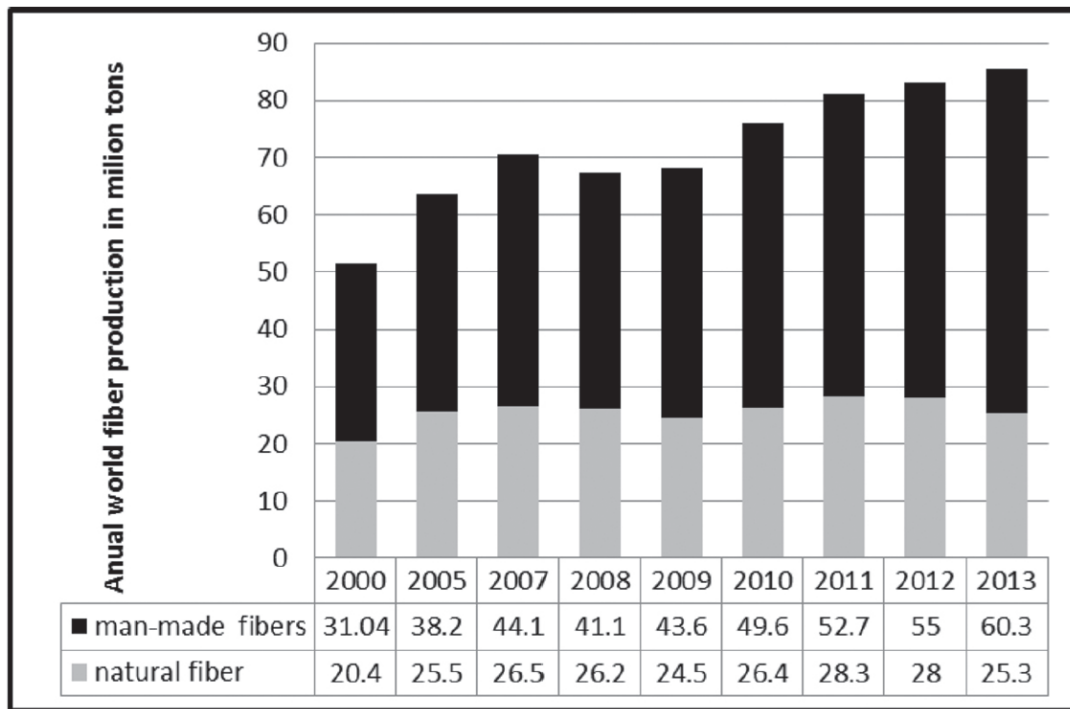
Figure 2.11: Total annual production of natural fiber [16]

Production of all other natural fibers, including abaca, flax, hemp, kapok, ramie, sisal, silk, and other fibers summed to approximately 1.6 million tons. Cotton represents the highest annual production of the natural fibers, produced worldwide throughout 50 countries, which shows the change of the production of natural and chemical (man-made) fibers in the period of 2000–2013, indicating the tendency in reduction of the production of natural fibers on the contrary to the increase of the demand for manmade fibers. The global production of fibers increased by 3.4% in 2014 to reach 96 million tons [43]. Among the natural fibers, cotton is the most dominating fiber in the textile sector, and this fiber is replacing and meeting future demand by the manmade fibers. Next section will describe on the properties of cotton and wood fibers.

Cotton fiber:

Cotton fiber is one of the most widely used natural textile fibers originated from plants and accounts for about one-third of the total world production of textile fibers. Cotton fibers grow on the surface of the seed of cotton plants (Fig. 2.12 a). Cotton fiber contains 90–95% cellulose [19]

, an organic compound with the general formula $(C_6H_{10}O_5)_n$. Cotton fibers also contain waxes, pectin, organic acids, and inorganic substances which produce ash when the fiber is burnt.

Figure 2.12: Cotton seed (a) and longitudinal view of cotton fibers (b) [5, 44]

The factors that are affecting the cotton properties are mostly the plant species, the soil, climate weather as well as the farming processes. The characteristic of fiber length which is used in the industry is called the staple length. Typical staple length of Asian cottons is 9.5-25 mm, for American 19-35 mm, for Egyptian-type cottons known as South American extra-long staple cotton, 38-63 mm. The longest cottons, however, account for only some 5% of all cotton produced; most fibers used in the industry are from 20 to 32 mm long [4]. The fineness of cotton fiber can be defined (i) by its linear density, which is typically between 0.13 and 0.21 tex, (ii) by Micronaire reading measured by airflow instruments with typical range between 2.0 and 6.5 and (iii) despite the fiber's non-circular cross-section (Figure 2.12b), by its diameter (width) which is estimated to be between 12 and 20 μm [45] . Individual cotton fibers can show tensile strength of up to 5 cN and breaking elongation up to 10% but the usual characteristic of strength is tenacity; this is the ratio of the tensile strength to the linear density. The values for the tensile strength of single fibers range from about 1.275 cN/dtex to approximately 3.13 cN/dtex [46].

Wood fibers:

Textile composites based on cellulose fibers from wood and plants constitute a relatively new and promising class of composite and textile materials [47-50]. They are environmentally friendly, and they offer good technical performance. A vast number of scientific literatures on cellulose fibers for textile applications has been compiled during the last decade but divided into two separate fields depending on the origin of the fibers, that is, from wood or annual plants. This section will cover wood fibers.

The wood can be classified into two groups according to trees: softwood and hardwood. Gymnospermae is commonly known as needle wood or softwood; angiosperm is called broadleaf wood or hardwood. Hardwood and softwood are only a common way of separating them, while hardwood is harder than softwood, but there are still exceptions to the rule; as one type of hardwood, poplar is softer than some softwood. softwood fiber is long, thin, and pure, contains fewer impurities; hardwood fiber is short and thick, contains more impurities. Wood fibers are made of 35% softwood and 65% hardwood in this world.

For wood fibers, the cellulose chain has an average length of 5 μm corresponding to a degree of polymerization (i.e., glucose units) of 10,000 [51]. The cellulose content of unprocessed fibers is 40–50% w/w for wood fibers, and in the range of 60–70% w/w for plant fibers. Wood fibers show lower cellulose crystallinity than plant fibers, with typical values in the ranges of 55–70 and 90–95% w/w, respectively. Softwood fibers generally have a length of 1.5–5.0 mm, a diameter comprising between 15 and 80 µm and an aspect ratio of around 100. The aspect ratio of individual bast (plant) fiber cells is in the region of 1000–1200 [52].

As earlier discussed, in order to use any fiber in the textile sector, the minimum fiber's aspect ratio is required ≥ 1000. However, in the case of wood fiber's aspect ratio is around 100. So, we cannot use this fiber in the textile sector directly. Instead, we must go through the wood pulping process to get the wood pulp and later some chemical modification processes to get wood fiber textile filament. Details will be discussed later in man-made regeneration fiber's section later.

Figure 2.13: Wood and wood fiber, Source
(https://materialdistrict.com/material/wood-fiber-textiles)

2.2.2 Manmade fibers

Man-made fiber whose chemical composition, structure and properties are significantly modified during the manufacturing process. It was started by scientist Robert Hooke in 1664 [53] with a suggestion to make "Artificial Silk" by following the way of silkworms secreting the natural silk fibers and ended in 1891 by discovering viscose process [54] with the help of a lot of famous scientists. Man-made fibers constitute what modern times have become a large and important class of fibers widely used in the manufacture of textiles [19]. Fibers are composed of polymers that may (like cellulose) or may not (like polyamide) occur naturally. These fiber's chemical and physical properties may differ but the production process follows three general stages [55]. These three stages are solid fiber to liquid phase (gel) formation, fiber spinning through the spinneret followed by solidification, and, finally, post-treatment (mechanical, thermal, or chemical). Man-made fibers also can be divided into two types depending on their source that are modified/regenerated. So man-made long-chain polymer of a plastic molecule produced from petroleum products is called synthetic fibers. On the other hand, regenerated fibers are modified/regenerated from natural resources, and these man-made long-chain fibers are called natural polymer or regenerated fibers. Others regenerated fibers list are shown in the next page in table 2.2.

Table 2.2 : Different types of Man-made fiber [26]

Man-made fibers (produced as continuous filaments)	Regenerated cellulosic		Rayon (viscose and Cuprammonium) Acetate Lyocell Triacetate
	Synthetics	General use synthetics	Polyester Acrylic Nylon (polyamide) Olefin Rubber Spandex PLA (polylactide or polylactic acid
		Specialist synthetics	Aramid Modacrylic Saran
	Inorganics		Carbon Glass Metallic
	Regenerated protein		Azlon

Synthetic fibers:

Polyesters, polyvinyl, polyamides are the source of petroleum products of man-made fibers. Polyester fiber is an example from the large group of 'truly' man-made fibers since they are produced from synthesized polymers which do not exist in nature. This fiber can be found in several areas of application ranging from classical textiles to technical and special textile structures[56]. "Polyester fiber is currently defined as a manufactured fiber in which the fiber forming substance is any long-chain synthetic polymer composed of minimum 85%, by weight, of an ester of a substituted aromatic carboxylic acid, including but not restricted to terephthalate units, naphtholate units, and para substituted hydroxybenzoate units" [57, 58].There are many different polyester types, but a condensation reaction produces all of them, and they all contain ester functional group COO. The tensile properties of polyester fibers vary depending on
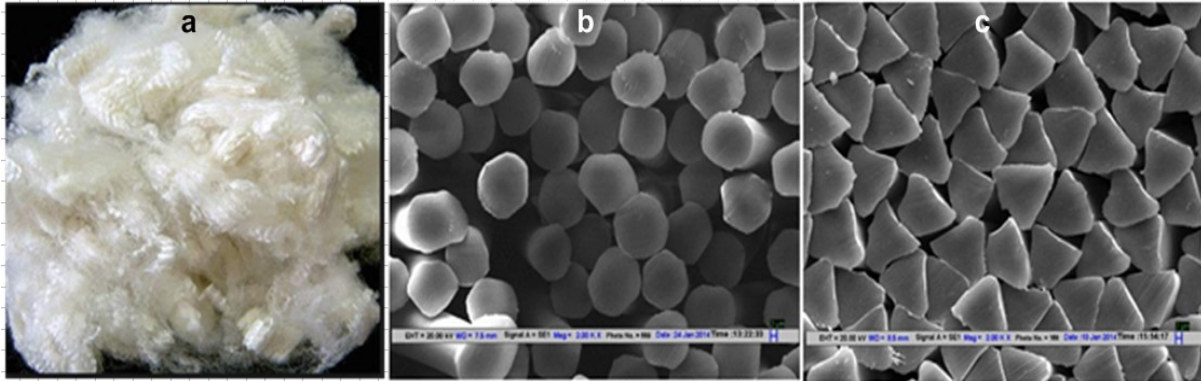
Figure2.14.Polyester fiber (a),SEM of polyester fiber cross section (b)Circular (c)Triangular. [59]

the parameters of the manufacturing process. Like other man-made fibers, polyester can be produced with a variety of characteristics: high tenacity and low extensibility (85 cN/tex and 7%, respectively) or with low tenacity and high extensibility (26 cN/tex and 40%, respectively) [60].

The flow of air through inter-yarn spaces is an essential means of providing comfort in hot, humid conditions. Yarn and fabric structural parameters affect the air permeability properties of textiles by influencing the shape and area of channels, through which the airflow occurs [61]. Plated fabrics knitted with the triangular polyester fiber and combed cotton yarn was observed to be more permeable to the passage of air, as shown in Figure 2.13c Triangular fibers are distinct from circular fibers in having edges, which may restrict the tight packing of fibers in the yarn structure with the consequence that the fabric structure becomes more void space and fabric porosity increases.

Man-made Regenerated fiber:

 Viscous rayon, lyocell and cupro etc. fibers are the example of natural manmade polymer as they are made from cellulose. Rayon is semisynthetic fiber that is made from naturally occurring wood cellulose. Therefore, rayon is not defined as synthetic base polymer but as natural base polymer.

Moreover, the physical and chemical properties of rayon are more likely those of natural fibers made of cellulose, such as cotton or linen, rather than from other fully synthetic fibers such as nylon or polyester. Depending on the spinning processes the hand feel, and texture of the rayon products can be compared to the other natural fibers like wool, silk etc. That's why, rayon is called "Artificial Silk".

Regenerated staple fibers are produced in a verity of linear densities ranging from 0.17 to 0.88 tex and lengths from 38 to 120 mm [4] to suit the characteristics of other commonly used textile fibers such as cotton. Mostly, two types of textiles fabrics are produced widely, such as general
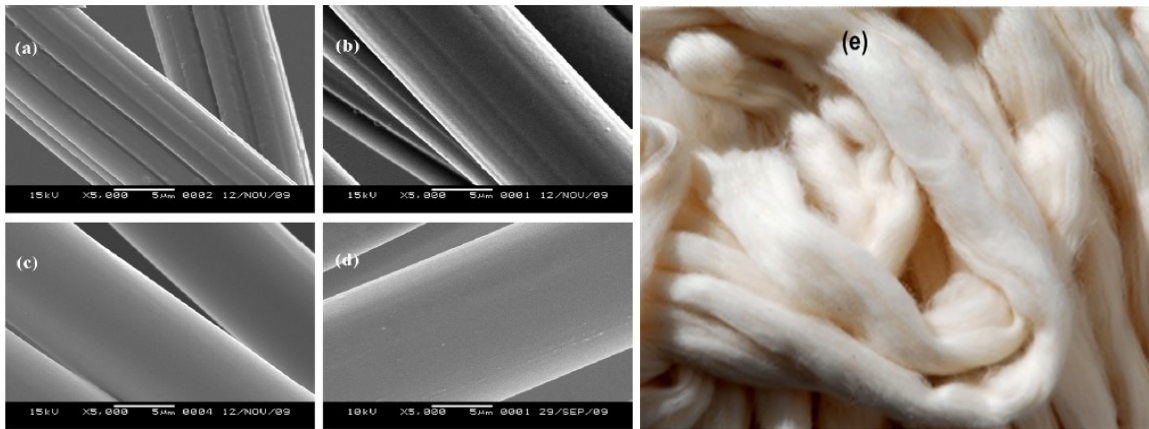
Figure 2.15: SEM of the regenerated cellulose fibers (a) Viscose fiber, (b) Newdal fiber, (c) Lyocell fiber, (d) IL-cell fiber and (e) regenerated fibers [62]

apparel and technical textiles. Apparel fabrics should have low tenacity (around 18 cN/tex) and high extensibility(around 27%) to obtain softness on the other hand technical fabrics are more rigid and strong which have average tenacity of 41 cN/tex and extensibility of 12%[5]. Surface conditions and physical properties much depend on the regeneration process used in fact, from figure 2.15 fiber surface from the Lyocell process is smooth and uniform.

Though the wood fiber and cotton fiber have main chemical composition is cellulose, but cotton fiber can be used directly to yarn production because of the high aspect ratio on the other hand, having lower aspect ratio wood pulps are not suitable for spinning. Cotton fiber and wood pulp have average aspect ratio of 1250 and 100 respectively [52, 63, 64]. Moreover, cotton fibers that

are shorter than 12 mm are not considered suitable for spinning and therefore have no commercial value for the textile industry because of the low aspect ratio. Feather keratin fibers (hairs, wools) have an average diameter of 5 μm[65], while silkworm silk fibers have 10–15 μm [37] and their aspect ratio is very high given in Table 2.3.

Table 2.3: Fiber's aspect ratio different fibers.

Fiber type	Mean length, mm	Diameter/ mean width, μm	Fiber aspect ratio	Ref.
Hard wood	1-2	10-50	28-56	[66]
Soft wood	1.5-5	15-80	60-100	[52]
Cotton	10-60	20	900-1650	[16, 67]
Wool	150	30	5000	[47, 68]
Silk (silkworm)	$>10^4$	12	high	[12]
Viscous rayon	Continues	4-60	high	[12]
Flax	33	19	1737	[47, 68]
Hemp	25	25	1000	[47, 68]
Jute	2	20	100	[47, 68]
Kenaf	5	21	238	[47, 68]
Ramie	10-15	20-75	2000-6000	[69]
Sisal	3	20	150	[47, 68]
Bamboo	2.7	14	193	[47, 68]

Fiber aspect ratio is influenced by how fibers are extracted and processed. Moreover, mechanical properties of fiber composites are strongly influenced by both the aspect ratio and fiber orientation. However, significant adhesion of fiber/matrix interface is required for high performance that enhance and transfer the stress to the fiber to carry extra tension[7].

Cellulose is a crystalline structural polysaccharide. It accumulates as the most abundant biopolymer present, primarily in wood biomass. The architecture of the unique hierarchical structures of cellulose is linear glucan chains ➡ crystalline cellulose microfibrils 3–10 nm wide consisting of 30–40 cellulose chains ➡ bundles of microfibrils ➡ cell walls ➡ fibers ➡ plant tissue ➡ trees or other plants[70] . The terms nanofibrils, nanofibers and elementary fibrils are usually employed as synonyms.

Cellulose fibers consist of microfibrils where the individual cellulose molecules are laterally connected by hydrogen bonding among the hydroxyl groups[71]. Crystalline celluloses are linked to amorphous regions to form the microfibrils as represented in the figure 2.15. Depending on different cellulose sources, each microfibril is few millimeters in length and 2-10 mm in diameter [72, 73].. Nano crystal cellulose (NCC) has a very low aspect ratio (10–100) while Microfibril cellulose (MFC) have a high aspect ratio (>1000) [74-76] and also showed in table 2.4. Different enzymatic hydrolysis are performed to obtain microfibrillated cellulose[77]. Microcrystalline cellulose (MCC), is prepared by removing the amorphous regions from cellulose microfibrils, usually by acid hydrolysis.

Figure 2.16: Schematic structure of an elementary plant fiber [79]

Table2.4: Dimension of different nano cellulose [78]

Cellulose structure	Diameter (nm)	Length (nm)	Length/ diameter
Microfibril cellulose	2-10	>10000	>1000
Microfibrillated cellulose	10-40	>1000	100-150
Cellulose whisker	2-20	100-600	10-100
Microcrystalline cellulose	>1000	>1000	>1-10

In short, cellulose is the main chemical ingredient in both wood fiber and cotton fiber, but due to the low aspect ratio of wood fiber, it cannot be used as a textile fiber. If it is possible to increase wood cellulose fiber's aspect ratio, then wood fiber can be used as a textile fiber. The microfibril cellulose has a high aspect ratio than MCC or cellulose whisker (Table 2.4). If it is possible to

modify microbrill cellulose (cellulose molecule) for regeneration (cellulose solid to liquefication for spinnerette), it will be possible to produce a continuous filament with no issue for aspect ratio to yarn production. So cellulose's chemical and physical properties need to be discussed for the feasibility of further chemical modification.

2.3 Cellulose

Cellulose is therefore also the most abundant polysaccharidec and is a constantly renewable resource [80]. By treating different vegetable materials successively with nitric acid, ammonia, water and alcohol, the French chemist Anselme Payen [81]always obtained a fibrous material as a final product: he named its cellulose. In 1842 French chemist Anselme Payen first published the elemental composition of cellulose [82]. Cellulose consists of 44.0–45.0% carbon (C), 6.0–6.5% hydrogen (H), 48.5–50.0% oxygen (O). Glucose is the monomer of cellulose . In cellulose chemistry, cellulose (Average per unit molecular weight) molecular weight of anhydroglcose unit, AGU=162.1406 mol/g.

Cellulose is a linear unbranched polysaccharide having a degree of polymerization (DP=number of AGUs in the chain) of 1000–15000 according to the biological origin.. Several hundred to many thousands of glucose units are linked with (1,4) β linkage. Every unbranched long chain cellulose molecule   is linked to each aother firmly together by hydrogen bonds [15]
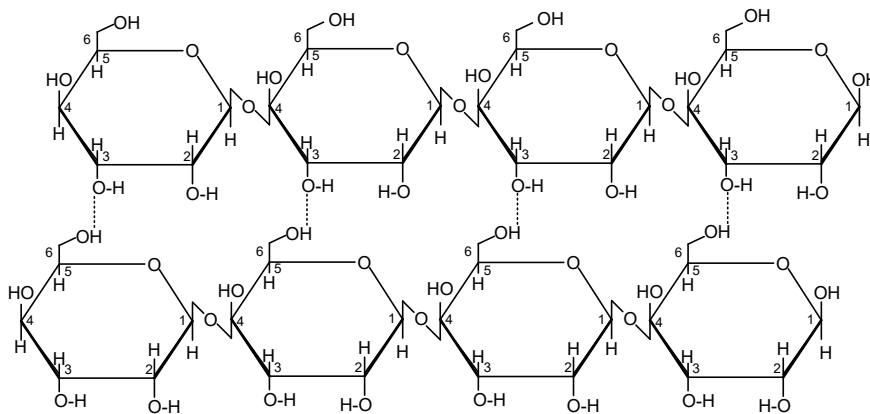
Figure 2.17: Hydrogen bonds in cellulose molecule (represent by dotted line "…")

The length of the chain differs from the origin of the cellulose. Wood pulps consist of chains of 300–3300 glucose monomers. The processing of cellulosic materials via conversion into fibers reduces the average degree of polymerisation, DP. For example , DP of natural cellulose is >10000 [83] whereas cotton pulp DP is 300-6500 [84]. The most reactive funtional group in cellulose is hydroxyl groups which is responsible for the chemical modification. The hydrophilicity of cellulose is mostly due to the hydroxyl groups that form hydrogen bonds among themselves and absorb water. [85]. Not all the hydroxyl groups are linked each other to form the long cellulosic chain, but few left over which are responsible to absorb water. To reduce the water absorbency of cellulose it is required to increase the crystallinity because water can only penetrate through the amorphous region. However, some free hydroxyl groups are necessary to obtain the reactive sites intact for chemical reactions[86].
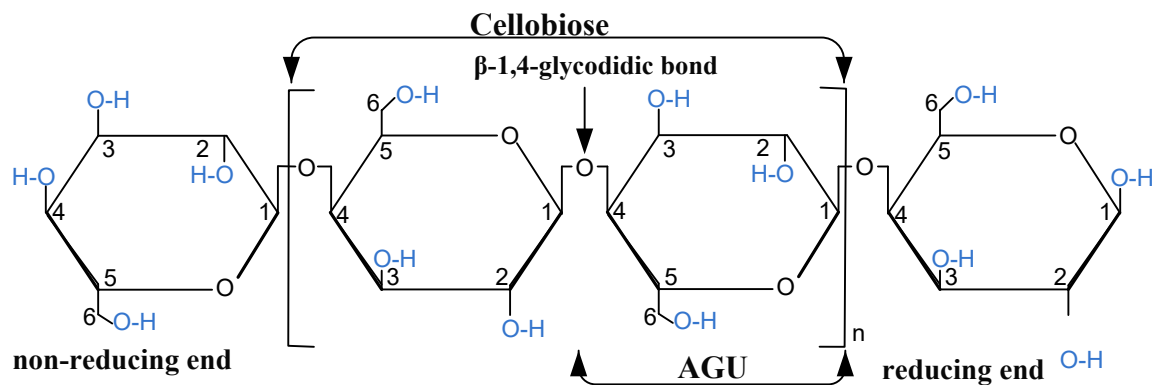
Figure 2.18: Representation of cellulose constituted of cellobiose units or AGU [87]

Every AGU unit remains 3 functional (-OH) groups, and as per the previous discussion -OH groups of amorphous region are more reactive than the crystalline area of cellulose chain polymer. Hence it is challenging to identify mole conversion of the cellulose polymer. For that in cellulose chemistry degree of substitution has been used instead of mole conversion. If one (-OH) group of AGU cellulose takes part in a reaction, then 1/162.14 mol/g or 6.167 mmol/g cellulose takes part in the reaction, and it provides degree of substitute is one (DS=1). If all three (-OH) groups of AUG cellulose take part in the reaction, then 18.50 mmol /g cellulose take part in the reaction, and its DS is 3.

The accessibility of the ─OH groups in cellulose has been the subject of considerable study, especially from the production of regenerated cellulosic fibers. After the reaction to the cotton cellulose with diethylaminoethyl (DEAE) chloride, DEAE cellulose is then hydrolyzed to form the substituted glucoses and glucose. Using gas chromatography analysis, the relative amounts of OH-2, OH-3, and OH-6 DEAE glucose are calculated and it is found that OH-2 is the most reactive hydroxyl at basic conditions. The proportion of OH-2 's overall reactivity is 11 times that of OH-3, and more than twice that of primary OH-6 hydroxyl [88, 89]. So, in this case, hydroxyl groups' availability follows the order: OH-2 > OH-6 >>OH-3. The accessibility depends on the pretreatment process employed, and the methods can be used to determine such accessibility, the results obtained vary according to the method employed [88, 90-92].

Although, cellulose swells in water, it does not dissolve even in dilute acidic solution. In cocentrated acids, dissolution of cellulose can be achieved – but at the cost of severe degradation of the cellulose chain. Caustic solutions cause extensive swelling and dissolution of low molecular mass portions (DP 200). Hydroxyl groups of cellulose are sensitive to the oxidizing agents. Fortunately, lignins react faster with oxidizing agents, which is important for the bleaching of cellulose pulps.

The hydroxyl functions of cellulose behave like alcohol functions and react with the concentrated mineral or organic acids to give esters. Cellulose remains inactive, and swelling agents of cellulose are also used to increase the accessibility to hydroxyls [93]. For this reason, the alkali-celluloses are common starting materials for the production of cellulose ethers. Cellulose is non-melting, and thermal decomposition of pure native cellulose starts at temperatures above 180 °C (356 °F).

2.4 Source of cellulose and their pulping process

It is estimated that nature produces a mass of 500–1000 billion tons of pure cellulose [94] per year. If all the cellulose molecules produced daily were strung together, they would cover a distance of 2.62×10^{10} km. This length is equivalent to about 175 times the distance between the sun and the earth [95]. This massive amount of cellulose production makes it the most abundant organic

compound on earth. Cellulose remains as a mass fraction of 40–50% of wood and 90% or more of cotton fiber. The presence of cellulose is often accompanied by several other natural substances including numerous saccharides, e.g. maltose and xylose; polysaccharides hemicellulose and lignin [96].

Table 2.5: Chemical composition of some natural cellulose sources[96]

Source	Composition, mass fraction (%)			
	Cellulose	**Hemicellulose**	**Lignin**	**Extract**
Hardwood	43-47	25-35	16-24	2-8
Softwood	40-44	25-29	25-31	1-5
Cotton	95	2	1	0.4
Bagasse	40	30	20	10
Coconut fiber(coir)	32-43	10-20	43-49	4
Corn cobs	45	35	15	5
Corn stalks	35	25	35	5
Chaina grass(ramie)	76	17	1	6
Flax (unretted)	63	12	3	13
Flax (retted)	71	21	2	6
Hemp	70	22	6	2
Jute	73	14	13	2
Sisal	73	14	11	2
Kenaf	36	21	18	2
Sunn	80	10	6	3
Wheat straw	30	50	15	5

For the industry production of cellulose derivatives, the cellulose is usually introduced into the industrial process in form of pulps. Pulp suppliers are the renewable resources tree wood and cotton linters. There there are several types of pulping process to get cellulose source as pulp.

2.5. Pulping process:

Plant fibers have about 40-50% cellulose—only renewable sources of available cellulose for pulp production. The pulp is a lignocellulosic fibrous material produced by chemically treated followed by mechanical commutation separating cellulose fibers from wood. The main purpose of pulping

is to break down the bulk structure of wood fiber source, remove lignin and hemicellulose, reduce the crystallinity of cellulose and increase the porosity of the lignocellulosic materials.
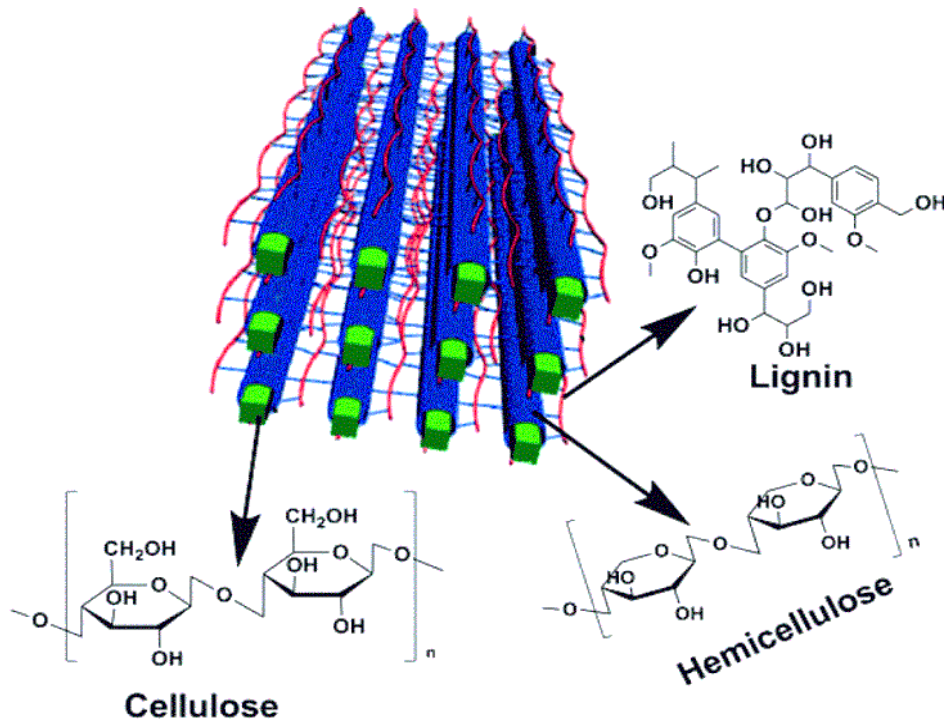
.**Figure 2.19:** Basic chemical composition of wood, Source:https://chembites.wordpress.com

The presence of lignin and hemicellulose in lignocellulose materials leads to a protective barrier of cellulose fibrils that prevents plant cell destruction by the weather. Hemicellulose is similar to cellulose and it is arranged in five (xylose, pentose) or six (mannose, galactose) carbon sugars of short chains (DP 10-100) [86]. For that, hemicellulose is soluble in water [85]. Hardwoods contain more hemicelluloses than softwoods. On the other hand, lignin is a complex organic phenolic polymer, and it is insoluble in water and alcohol but soluble in weak alkaline solutions. Softwoods have a more amount of lignin than hardwoods[97, 98]. Lignin and hemicellulose removed via pulping process are usually lignin burned as fuel and separated hemicellulose sometimes used for further biorefinery processing.

Mechanical pulping, chemi-mechanical pulping, semi-chemical and chemical pulping are the four basic categories of pulping processes. These are in order to reduce the mechanical energy needed to separate fibers and increase dependence on chemical action. Chemical pulping methods

therefore rely on the effect of chemicals to separate fibers, while mechanical pulping methods rely entirely on physical action [99].

Mechanical comminution is combination of chipping, grinding, and/or milling to reduce cellulose crystallinity to size usually 10-30 mm after chipping and 0.2-2 mm after milling or grinding[100]. if the final particle size is held to the range of 3-6 mm, the energy input for comminution can be kept below 30 kWh per ton of biomass[101]. On the other hand, the more chemicals are used, the lower the pulp yield as a chemical reaction will degrade and will solubilize important wood components other than lignin. Paper mills primarily are engaged in manufacturing wood pulp for papermaking, various paper-based products, and other pulp fiber. Though woods are used for different purposes nowadays and only 10% of total wood is consumed in pulp processing shown in figure 2.19 a.

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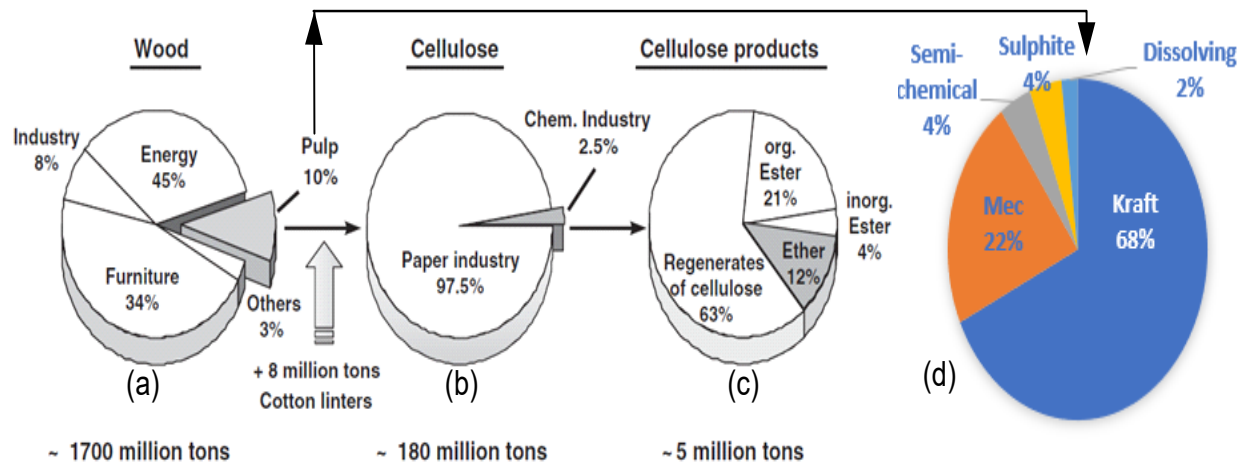
Figure 2.20: Global use of wood for cellulose ether and pulp production [82, 102]

Any wood pulp production process can be divided into seven sub-processes: raw materials processes; wood-yard; fiber line; chemical recovery; bleaching; products and recycling. Depending on product (cellulose) purity pulping process can be divided into two catagories and it is paper grade pulping and dissolving pulping process.

2.5.1. Paper grade pulping :

Paper grade pulping aims to separate cellulose fibers from the wood structure by removing lignin. Here, hemicelluloses are considered a part of the pulp, and pulp yield is up to average 48 % [103]. The paper grade pulping process is low-cost pulp compared to dissolving pulp. Paper grade pulp is usually used paper and packaging purposes. Some of the paper grade pulping processes are discussed here.

Kraft pulping:

Kraft Pulping Sulfate or Kraft pulping was once invented in Germany in 1884 and remains the dominating technological know-how these days, and about 70 % of whole pulping is kraft pulping[102] . Better pulp strength, a more comprehensive range of wooden species, can also be used and extra effective at removing impurities like resin are the advantages of the process. The disadvantage of the pulp yield is low. Kraft pulping process dominates worldwide as a producer of paper and board pulp grade. In the kraft pulping process, wood chips are cooked in a digester in a solution of sodium hydroxide, and sodium.
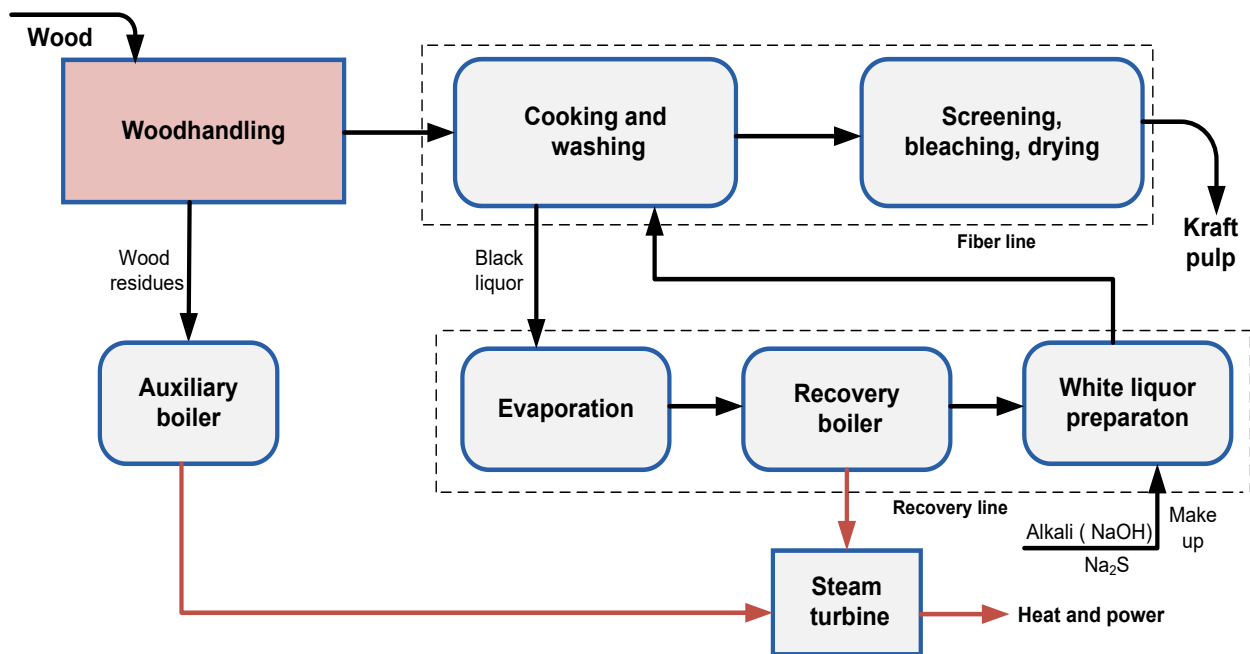

Figure 2.21 : Process flow diagram of Kraft pulping [104]

sulphide called white liquor [105, 106] . The wood chips are cooked in water maintaining temperature 140–170°C . The filtrate from this washing is called black liquor, which is sent to the chemical recovery system. Spent cooking liquor and the pulp wash water form a weak black liquor, which is concentrated through evaporation from 16% to 60-80% solids in a multiple-effect evaporator system.

The chemical reaction takes place in the kraft pulping process that degrades and dissolves the lignin of wood and cellulose is separated from the wood structure [107] . An important step of kraft pulping is a treatment of biomass with sodium hydroxide and sodium sulfide to cleave ether linkage by sulfide and bisulfide ions [108] . In order to remove color associated with the remaining residual lignin bleaching step is introduced. The bleached kraft pulp is white, and it is used for printing and writting purposes.

Sulfite pulping: Sulfur dioxide (SO_2) is used to react with water to form sulfonic acid, and bases such as calcium, sodium, magnesium, or ammonium at 140 oC with time 1-5 hours [105, 109]. Under these conditions, the process of sulfite delignification leads to the cleavage of lignin's α-ether (α-O-4') and β-ether (β-O-4') linkages, which is an acid-catalyzed method. The introduction of polar sulfonic acid groups into the lignin backbone allows for hydrolysis and dissolution, while the cellulose remains in solid-state and is easily separated from wood stucture [106, 110] .

Soda pulping: Soda pulping is typically used for the treatment of non-wood material, including grass, straw, and sugarcane bagasse, which accounts for 5% of the total pulp production [106, 111]**.** The oldest pulping method and solubilization mechanism of wood biomass are similar to the kraft process where uses sodium hydroxides as the chemical reagents of the pulping process at 140-170 °C. The obtained soda lignin is difficult to separate by filtration and has no sulfur.

Organo solvent pulping: An organic or aqueous organic solvent of formic acid, acetic acid, ethanol, and so forth is utilized to delignification the wood cellulose. In this process, mixture inorganic acid as catalysts (HCl or H_2SO_4) is used, and the temperature is maintained 170-190 °C

[106, 112, 113]; involve simultaneous pre-hydrolysis and delignification of lignocellulosic biomass. The solvent needs to be drained from the reactor and recycled after having evaporated and condensed that increases cost a lot.

Steam explosion process: Wood biomass can be treated with high-pressure saturated steam for delignification. The wood chips were steam heated at a very high temperature, about 285°C, and at a pressure of 3.5 MPa for about 2 min. The pressure increased rapidly to about 7 MPa for about 5 s, and the chips exploded at atmospheric pressure into a pulp [114]. The factors that affect the steam-explosion process are residence time, temperature, chip size, and moisture content [115]. Compared to other processes, lignin is removed only to a limited extent, but cellulose and hemicellulose degradation increase the potential fiber loss.

Dilute acid hydrolysis: The pulp can be separated from lignin and hemicellulose by the pre-treatment of dilute H_2SO_4 or HCl. After a water wash, wood biomass is cooked in dilute sulfuric acid (0.5-1.4%) at high temperature 165-195 ^{0}C for 3-12 min [116, 117] . Hemicellulose and low DP cellulose are hydrolyzed to glucose monomar sugar in this step resulting in loss of fiber biomass.

2.5.2   Dissolving pulping :

Dissolving pulp is a high-grade cellulose pulp, with low contents of hemicellulose, lignin, and resin where cellulose content (> 90%) [103] with low yield (30-35%) after pulping. This pulp is excessive degree of brightness (>80) and uniform molecular-weight distribution[120] with high chemical purity. Wood based dissolving pulps generally are manufactured through two processes: the acid sulfide (AS) technique and pre-hydrolysis kraft (PHK) pulping process. At the end of 2014 data confirmed that the PHK procedure was used for 56% of the world dissolving pulp production, whilst the AS procedure accounted for 42% [118, 119] .

The acid sulfide process is a very old process for dissolving pulp production and has been used for many years. In this process, ammonia-based sulfite process uses, and lignin, hemicelluloses, and other extractives are removed from the wood then dissolved in the spent sulfite liquor.

Dissolving pulp is found from the brown stock after further purification of bleaching or hot alkali extraction steps. Biomass collected from spent sulfite liquor (SSL) is converted to value-added products like lignosulfonates, vanillin, xylitol, and ethanol [120, 121].

The PHK system is a sort of aggregate of acid hydrolysis and kraft pulping. After the acid hydrolysis, the kraft cooking manner is introduced, and for that, this technique is referred to as pre-hydrolysis kraft cooking .Hydrolysis process, hemicelluloses are extracted from the wood chips, so after dissolving hemicellulose and a portion of lignin Kraft cooking (Figure 2.22) process unit is removed most
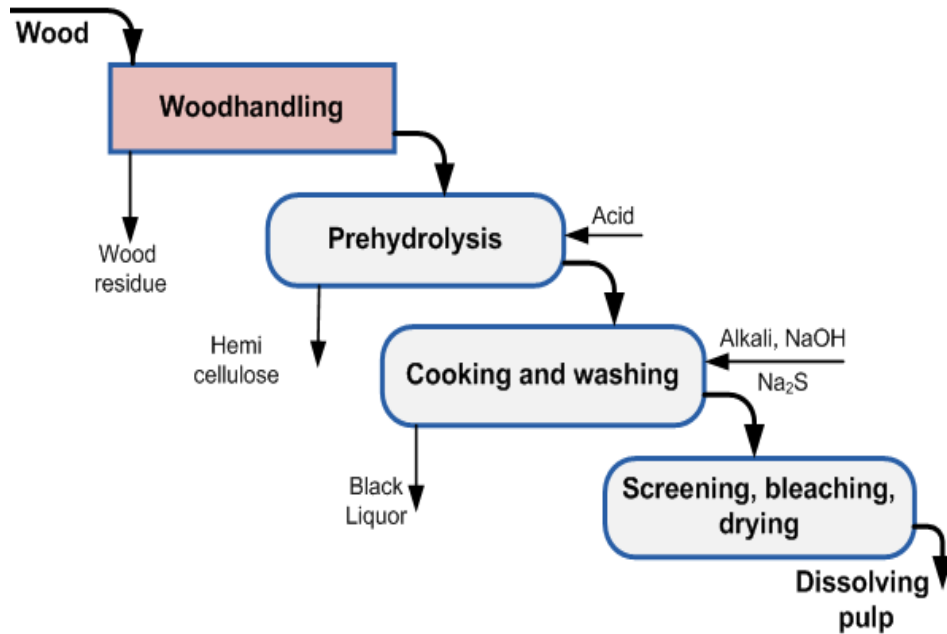
Figure 2.22 : Schematic diagram of pre-hydrolysis kraft pulping, PHK [103]

of the lignin. Then a multi-stage bleaching process is employed to reach the desired purity of the dissolving pulp[122] .

Most of the hemicelluloses and a portion of lignin are eliminated from the wood chips using the auto-hydrolysis initiated and generating acetic acid throughout the pre-hydrolysis stage. Again, Kraft cooking is disposing of the majority of lignin present in the wood chips, and in the same process, greater hemicelluloses, and a fraction of cellulose are additionally dissolved. After Kraft

cooking, the residual lignin is similarly eliminated from the pulp by way of subsequent bleaching stages

Dissolving pulp has a large proportion of alpha-cellulose (> 90 % w/w), a tiny amount (3 to 6 % w/w) of hemicellulose content, and a trace amount of lignin and other impurities[122] making it unique.Cellulose content, alkali solubility, degree of polymerization (DP), uniform molecular weight distribution (MWD), and reactivity are the crucial top-notch parameters for dissolving pulp.

Table 2.6: Difference in between paper grade pulp and dissolving pulp [103, 123, 124]

Paper grade pulp	Dissolving pulp
High yield (up to avg 48 %) as hemicelluloses are considered as a part of pulp. Low cost pulp compared to dissolving pulp.	Low yield (30-35 %) as hemicelluloses are limited by less than 4% with cellulose purity 90-99 %
Contains around 80 % α-cellulose and less brightness compared to dissolving pulp	Higher brightness and more uniform molecular weight distributions with >90 % α-cellulose
This kind of pulp shows less reactivity (for example pulp derived from birch cellulose's reactivity is 40-50 %	Dissolving pulp (from birch) cellulose's reactivity[2] increased to approx. 60-70%
Paper-grade pulps have higher viscosity than dissolving pulp (approx. 700-800 dm3/kg)	The viscosity of dissolving pulp is lower than paper grade pulp (approx. 500-700 dm3/kg)
Paper grade pulp is produced by pulping (kraft, sulfide.) process	Dissolving pulp is produced by integrating pre or post hydrolysis in pulping (Kraft, sulfide etc.) process where hemicelluloses are removed.

2.6 Application of cellulose

Cellulose is used to produce paperboard and pulp and paper making industries. A small amount of cellulose is chemically converted into a wide variety of value-added derivative products in biomedical, health care, food, and other sectors. The biorefinery uses cellulose as biomass to

generate biobased products such as biofuel (biobutanol & bioethanol), bioenergy (heat & power), and chemicals .The bulk amount of applications in the areas of tissue, board, painting additives, and especially paper manufacturing. Value products like textiles, apparel, and other products from dissolving pulp include viscose rayon, cellulose nanofiber (CNF), and others.

Cellulose derivative- cellulose acetate, cellulose nitrate, cellulose ether, and others produced from dissolving pulp [125] . Industrial products such as textiles, tires, coating, paints and tobacco products, and food and pharmaceutical products. Cellulose-based nanocomposite for eclectic, electronic, and biomedical applications. The emerging area of dissolving pulp application is in printing of three–dimensional (3D) objects[103].
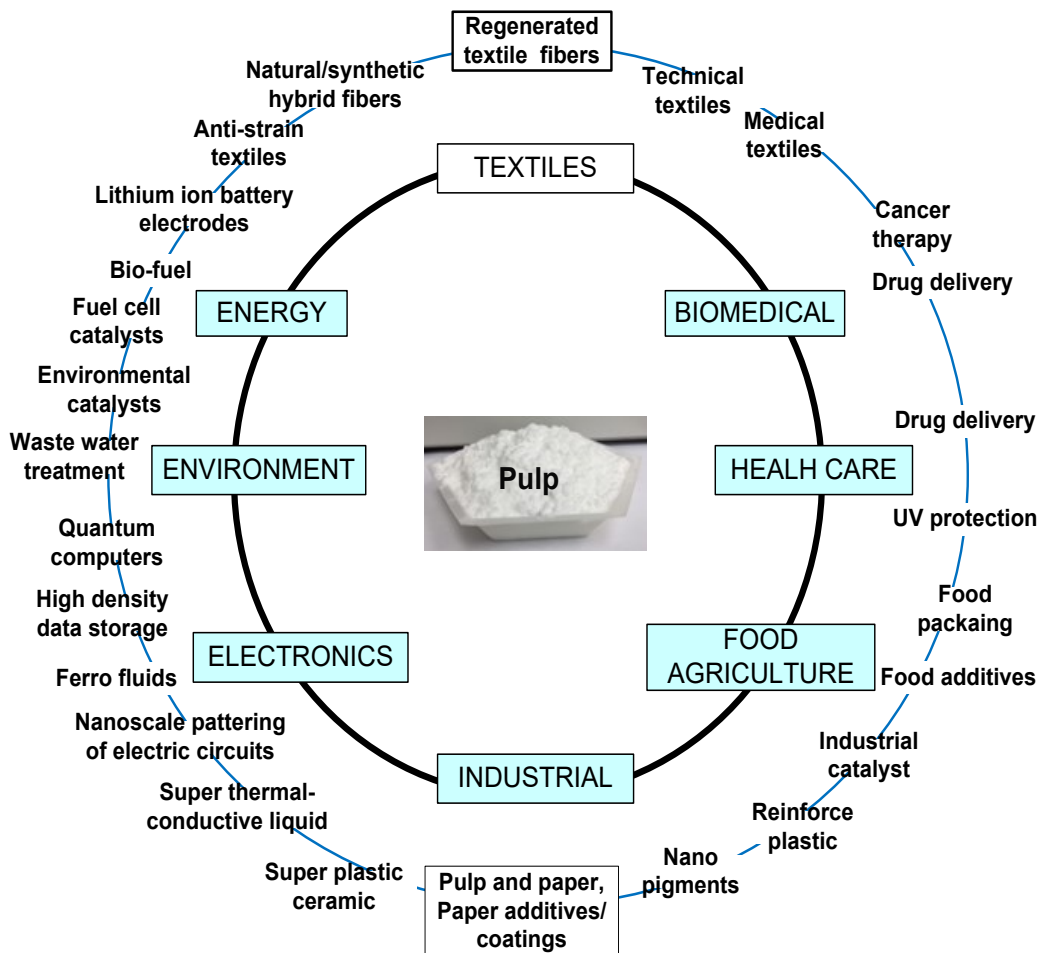
Figure 2.23: Application of cellulose (reproduced: http://people.forestry.oregonstate.edu)

Pulp and paper is the primary bulk user of cellulose under the industrial sector. However, nowadays, using paper decreasing for digitalization, and hence for that, we have an opportunity to use the pulp and paper sector's cellulose in other sectors. On the other hand, regenerated textile fiber can be a potential bulk user of cellulose among the other sectors. Figure 2.23 shows that cellulose has diversified applications wherein paper and pulp industries dealt with a bulk amount of kraft pulp as cellulose. This cellulose needs modification chemically in order to utilize this natural resources Kraft pulp into the textile sector.

2.7 Chemical modification of cellulose

From the cellulose molecule structure, 1-4 positions are occupied by β-linked that form an unbranched long-chain polymer. Other 2,3 and 6 positions have three '-OH' functional group [94]. These three functional groups can take part in a chemical reaction [8, 126]. The necessary hassle in chemical modification of cellulose is that cellulose is pretty inert and does no longer right away follow the normal rules of organic chemistry (For example, '-OH' groups of cellulose are alcohols,
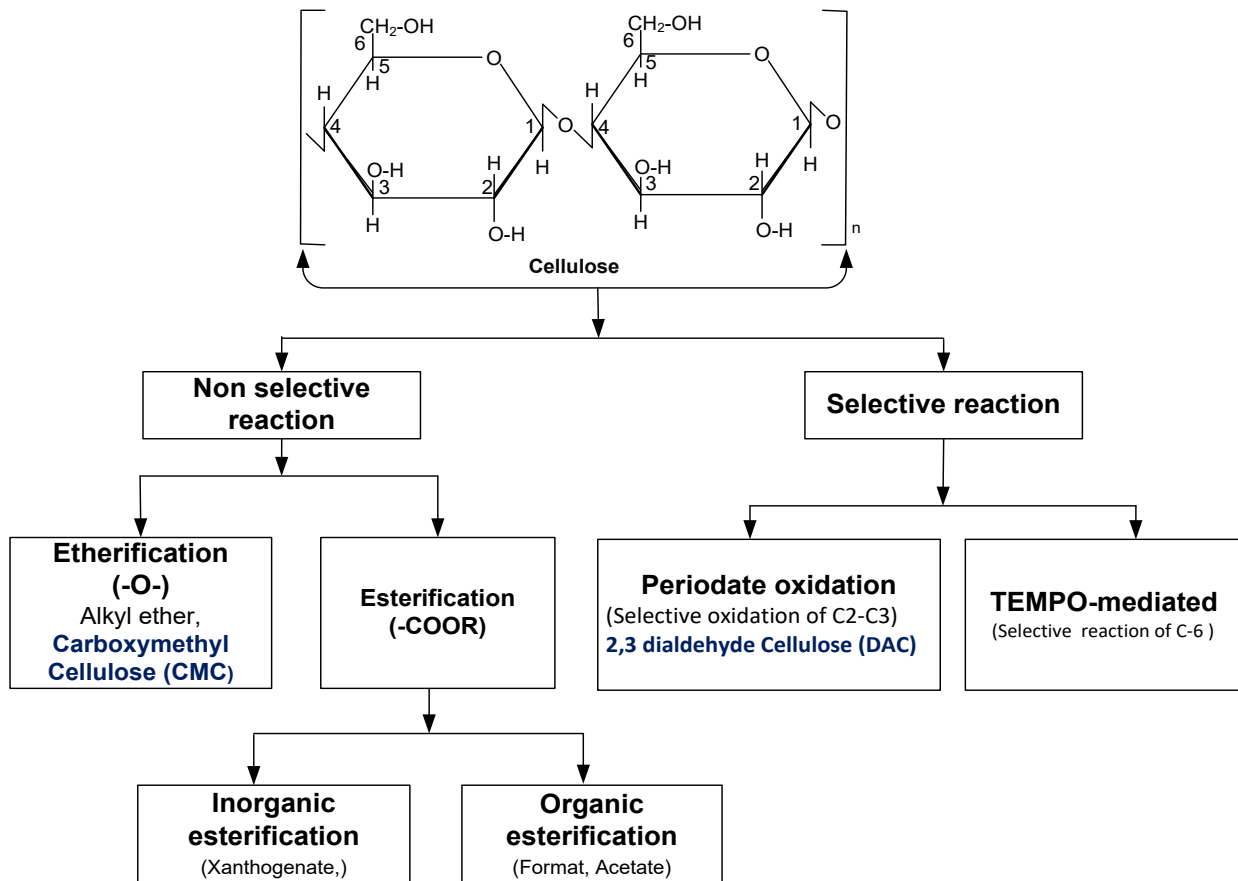
Figure-2.24: Classification of cellulose modification reaction

however, they do not produce esters with carboxylic acids under ordinary conditions) [130].First, cellulose molecules need to be chemically active then allow them a particular reaction environment to take part in the reaction. Depending on the reaction environment and reaction with these three functional group cellulose modifications, the chemical reaction can be divided into two main categories: Selective reaction and Non Selective reaction.

Selective reaction : When the reaction environment in such that only a 2-3 position or 6-position hydroxyl group takes part and produces cellulose derivatives, then the reaction mechanism is called cellulose selective reaction. For example, the cellulose molecule reacts with sodium meta periodate in a periodate oxidation reaction and produced 2-3 dialdehyde cellulose (DAC), and here both secondary 2-3 positions '-OH' group take part in the reaction [127-129]. Similarly, in TEMPO mediated reaction, only primary 6-positions '-OH' group take part in reaction [21]

Non selevtive reaction:
The reaction environment at which any position of 2,3 and 6 position functional group '-OH' or all of three functional '-OH' group take part in a chemical reaction is called non-selective reaction. For example, in the presence of sodium hydroxide and sodium mono-choloaceted, cellulose etherification reaction occurred and formed carboxymethyl cellulose (CMC). Here substitution reaction can take place either or all of 2,3 and 6 '-OH' positions of cellulose molecule [130]

2.8 Cellulose fiber modification process

Cellulose has extended the hydrogen bond community, and for that, it is neither meltable nor soluble in the common organic solvents. So, in order to dissolve cellulose, it is wished to weaken the cellulose inter- and intramolecular interactions [131]. The shaping of cellulose for fiber production, distinctive techniques have to employ. There are two strategies to gain this. One is to

make cellulose derivatives, e.g., the method used in the viscose process. The different alternative is to dissolve cellulose directly in some specific solvents, e.g., NMMO used in the Lyocell process [53]. Some of the present cellulose modification for textile yarn manufacturing are described below (figure 2.25)
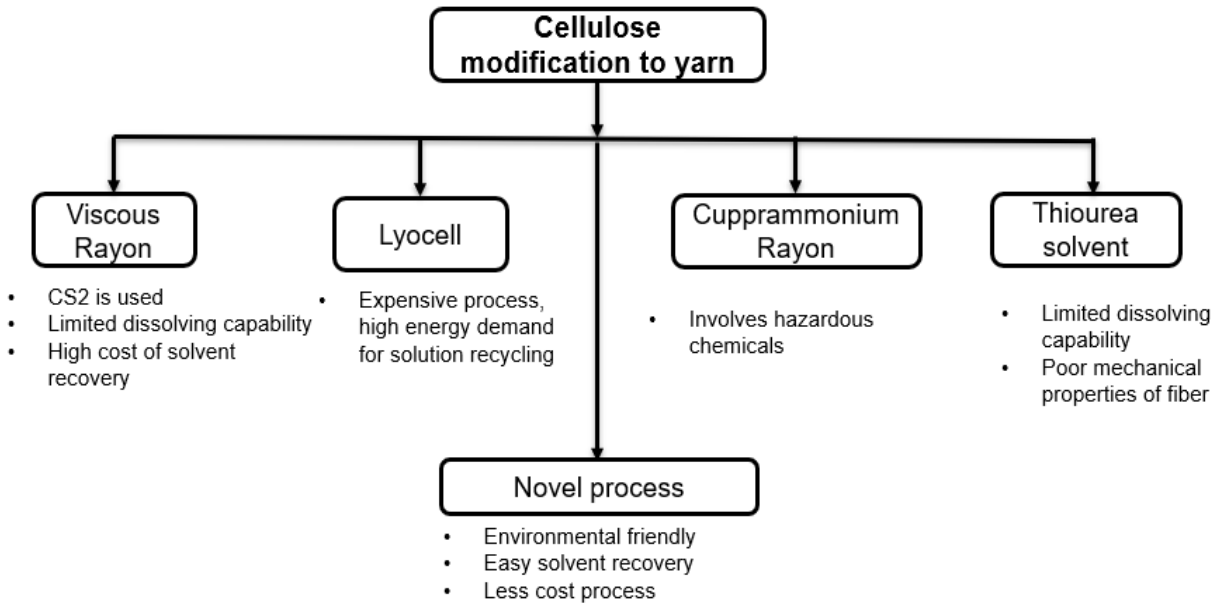
Figure 2.25: Existing process of cellulose modification to yarn.

2.8.1 Viscous Rayon:

Being more than 100 years old and the Viscous Rayon process was developed early 20th century. This process is still dominating cellulose fiber production with an annual output of more than 2 million tons [8]. Gel for this wet-spinning process, cellulose xanthogenate is prepared by chemical treatment of pressed alkali cellulose and liquid carbon disulfide. This derivative is soluble in alkali and forms thick and a viscous like liquid resembling honey in both color and consistency. After a certain period of ripening, the viscose is spun into an acidic coagulation bath, where the xanthate groups are cleaved off the polymeric chains. The pure cellulose is regenerated in fiber form, called rayon, viscose rayon or viscose fiber. A brief discussion on the unit operation is given below.

Process description: In viscous rayon production facility involves dissolving pulp as feedstock. Dissolving pulp content higher brightness and more uniform molecular weight distributions with >90 % α-cellulose polymer. Cellulose pulp is solid, and the reaction required more time to take place. So here, every step is considered as a batch process. Reference: PFD [figure 2.26], [2, 132-134]

Steeping process, V-201

Dissolving pulp and aqueous caustic soda (17-20% w/w) are put in a steeping unit where the temperature is maintained 40-50 °C and slurry containing 5% finely dispersed pulp. Highly polymerized cellulose (DP 1000) of the dissolving pulp is converted into Na-cellulose. These cellulose are allowed to soak the solution until they become dark brown, and it takes about 1-4 hours. In this unit, there is an option to drain off excess caustic soda solution though stream number 2. Here pulp sheets are pressed out by a hydraulic press to squeeze excess caustic soda solution called pressing fluid

Shredding, V-202:

The pressed soda-cellulose is mechanically shredded to yield finely divided, fluffy particles referred to as "crumbs". This step provides good mixing soda cellulose. Soda and cellulose become fine crumbs within 2-3 hours.

Aging, V-203:

Oxidative de-polymerization happens during aging. The temperature is kept 18-30°C for 48 hours to get the optimum degree of polymerization . Here DP is reduced to a factor of 2-3 from 800 to about 30
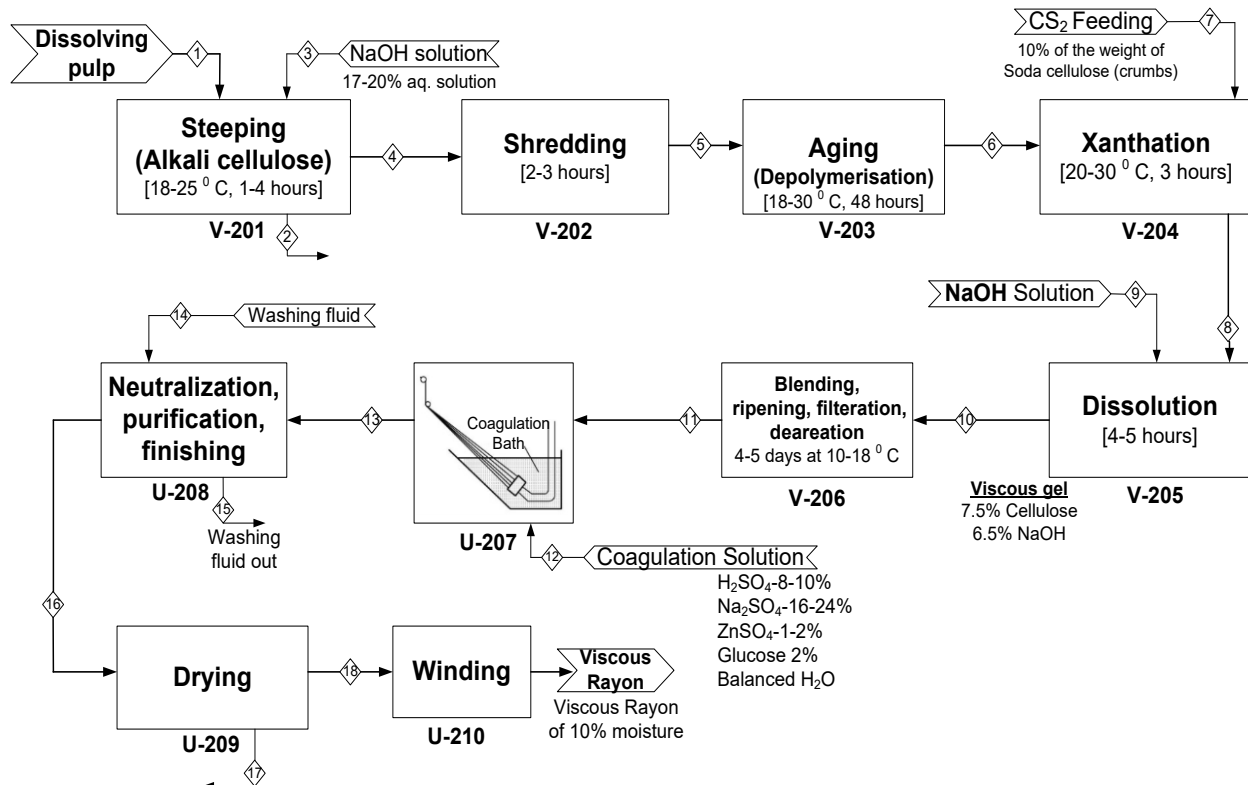
Figure 2.26: Process flow diagram of Viscous Rayon manufacturing [132, 133].

Chemical Reactions: [Reference figure 2.26]

Unit	Reactants		Products
V-201:	$[C_6H_{10}O_5]_n$ +	$nNaOH$	$\rightarrow$ $[C_6H_9O_4\text{-}ONa]_n$ + nH_2O
	Cellulose	Caustic Soda	Soda Cellulose
V-204:	$[C_6H_9O_4\text{-}ONa]_n$ +	nCS_2	$\rightarrow$ $[C_6H_9O_4\text{-}OCS_2Na]_n$
	Soda Cellulose		Sod. Cellulose Xanthate
U-207:	$[C_6H_9O_4\text{-}OCS_2Na]_n$ + ½ H_2SO_4 $\rightarrow$		$[C_6H_{10}O_5]_n$ + CS_2 + ½ Na_2SO_4
	Sod. Cellulose Xanthate		Viscose Rayon

Xanthation, V-204:

Upon maturity, soda cellulose crumbs are moved to revolving, airtight, a hexagonal drum known as churner. Carbon disulfide is applied to the churner for around 10 per cent of the weight of the crumbs by spinning the mixers at a slow speed of 2 rpm to obtain xanthate sodium cellulose

Dissolving, V-205:

The color of sodium cellulose xanthate is yellow, and its shape is like a ball. This ball falls into a mixer, and this unit is called the dissolution unit. In this unit, dilute sodium hydroxide (caustic soda) is added to get viscous concentration 6.5% w/w caustic soda and 7.5% w/w cellulose. Cellulose xanthate dissolves by stirring about 4-5 hours to get clear brown thick liquor. This thick liquor is like honey called viscous gel.

Ripening, V-206:

In order to get the best spinning qualities, the viscose solution is required to do blending, ripening, and finally, filtration —all processes, including aging, need 4-5 days. The temperature is maintained here about 10-18°C.

Spinning process, U-207:

The filtrate viscose solution (gel) is pushed through a spinneret, with several tiny holes of 0.05-0.1 mm diameter. The spinneret is immersed in a solution tub called a coagulation bath. The coagulation bath solution contains the chemicals sulphuric acid (8- 10%), sodium sulphate (16-24%), zinc sulphate (1-2%), glucose 2%, and the rest water. The coagulation bath temperature is maintained 40-45 C. Washing step, U-208 involves washing out all chemical adhering with viscous filament, and this filament is run through the Drying unit, U-209 to get moisture off. Finally, the filament is winding up for sale.

2.8.2 Lyocell:

The Lyocell process developed in the 80s, and it is a direct method that utilized the NMMO (N-methylmorpholine-N-oxide/water mixture) [135]. Direct dissolving the pulp fibers include the disintegration of fibers and mixing an aqueous system containing NMMO to form a dope of high viscosity. Then dope is filtered to remove coarse components. Filtered high viscous dope is extruded through an orifice spinneret into an air gap and then regenerated in a coagulation bath. Finally, lyocell fibers are washed, and the residual NMMO is recovered and recycled but high energy demand

2.8.3 Cuprammonium rayon:

Cuprammonium rayon is another type of regenerated cellulose filament produced with the use of hazardous chemicals (ammonium), and Cuprammonium solution was making progress as early as the 1850s–1880s. Cuprammonium solution is another chemical that can dissolve cellulose directly[136]. It is also a direct dissolution method like lyocell. However, here tetra-ammonium copper hydroxide solution is used for dissolving cellulose gel preparation and then put into spinning by spinneret, and sulphuric acid is used in the coagulation bath. This process generates heavy metal salts that are difficult to dispose of [129]

2.8.4 Thiourea solution:

In recent years, a green process for regenerated cellulose textile fibers was developed via direct dissolution of cellulose in a NaOH/thiourea solution at sub-zero temperatures[137]. The NaOH/thiourea solvent has two significant limitations: 1) limited abilities to dissolve cellulose with a high degree of polymerization (DP), and 2) the cellulose concentrations in this solvent cannot exceed 10% w/w. Furthermore, the process is energy-intensive and produces fibers with poor mechanical properties that are not suitable for textile applications [129].

2.8.5 Ionic liquid (IL):

Nowadays, ionic liquids (ILs) as a kind of cellulose solvent combined with other solvents or additives have been widely discussed worldwide, both industrially and academically [134]. ILs refers to salts with low melting points usually less than 100 C and contain large volume cations and anions. EMIMAc is one of the most popular ILs for dissolving cellulose. Ionic liquid (IL), EMIMAc (1-ethyl-3-methyl-imidazolium acetate), which can potentially be a new type of environmentally friendly cellulose direct dissolution solvent. Novel fibers with similar properties to the Lyocell fibers. It needs to be overcome to establish a large-scale, multi-filament. The IL-based wet spinning process is reusability but costly and toxic.

2.8.6 Novel Process:

The above-described methods for producing cellulose-based textile fibers all suffer certain techno-economic, and environmental drawbacks mainly dominated viscous rayon process has a severe environmental issue [62, 135] . A new technique will be introduced that is a cost-effective and environmentally sustainable (CS2-free) process to resolve current technologies' limitations. It is also a called novel process because this method will use green chemicals but use the existing technology of the viscous rayon process. Instead of using hazardous chemical carbon disulfide, food-grade chemical sodium mono chloroacetate will be utilized for carboxymethyl cellulose (CMC) production. Later for crosslinking of this CMC, di-aldehyde cellulose (DAC) will be produced. By mixing of CMC and DAC as per predetermined ratio (composition) and the filament will be made through wet spinning. Finally, this filament will be characterized by the standard method

Chapter 3

Materials and Methods

3.1 Materials

Bleached softwood kraft pulp (BSWK) was obtained from the Resolute Forest Products pulp mill in Thunder Bay, Ontario Canada. Sodium (meta) periodate ($NaIO_4$), sodium chloride (NaCl), sodium chloroacetate or monochloroacetate "MCA" ($Cl-CH_2COONa$), zinc sulfate ($ZnSO_4$), sodium sulfate (Na_2SO_4), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH) standard solution (0.5 N), hydrochloric acid (HCl) standard solution (0.1 N), and hydroxylamine-hydrochloride ($NH_2OH.HCl$) were purchased from Sigma-Aldrich (Mississauga, Ontario). Sodium hydroxide (NaOH, 98% pure), hydrochloric acid (HCl, 36 wt. %), methanol (CH_3OH), ethanol (C_2H_5OH, 95% pure) and isopropyl alcohol "IPA" (C_3H_7OH) were supplied by Fisher Scientific (Whitby, Ontario). All chemicals were used as received. Deionized water (DI water) was used throughout all experiments.

3.2 Experimental Procedures/Methods

3.2.1 Production of textile filaments:

Figure 3.1 describes the filament preparation process. In short, BWSK pulp powder is chemically modified to CMC and DAC (Di-aldehyde cellulose) through carboxymethylation and periodate oxidation reaction, respectively. The different compositions of CMC and DAC are then dissolved in water in a NaOH solution to prepare a gel for the wet spinning process where the modified cellulose fibers are regenerated in a coagulation bath. Following the spinning process, the regenerated cellulose fibers are washed with hot water, and rinsed with ethanol and acetone. Finally, the produced filaments are dried with hot air and stored at room temperature for further evaluation of the properties.
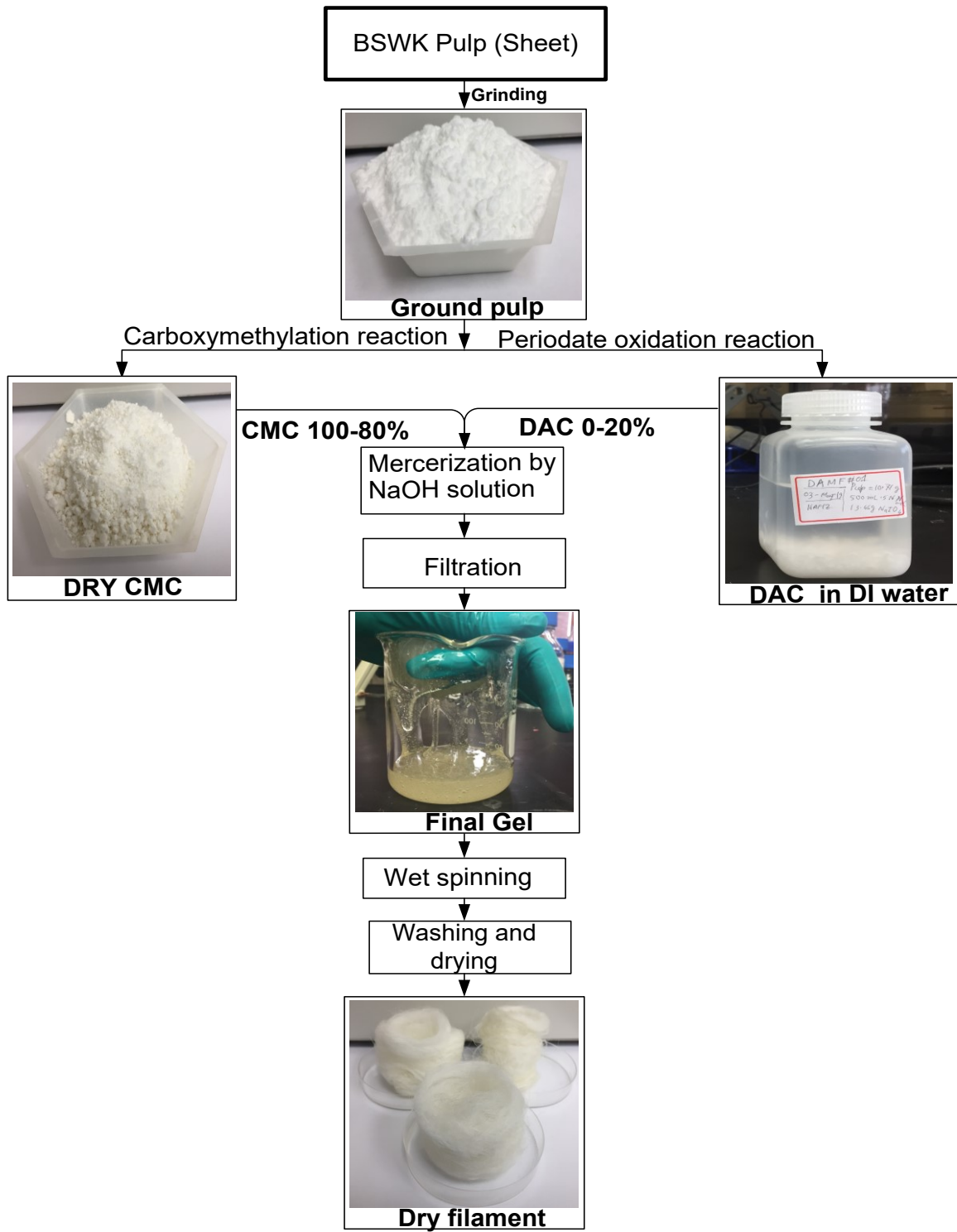
Figure 3.1 Process steps for production of cellulose filaments.

The overall experiment process was divided into five major steps, as follows:

1. Production of low-substituted carboxymethyl cellulose (CMC)

2. Dialdehyde cellulose (DAC) preparation

3. Gel preparation

4. Preparation of textile filaments by wet spinning

5. Washing and drying of filaments

3.2.2 Preparation of low-substituted CMC fibers:

The low-substituted CMC fibers were produced from BSWK pulp fibers. The BSWK pulp sheets were cut into small pieces and fed into a grinding machine to reduce the fiber size to 200-300 μm. A desired mesh size screen was used to collect the pulp powder. The CMC preparation method is a two-stage process. In the first stage, 100 g of dry pulp powder was mixed with 880 g of IPA (880 g). This mixture was pre-heated to 40°C using the hot water circulation bath. A different amount of NaOH (Table 3.1) was mixed with 70 mL of DI water, which was slowly added to the slurry mixture. The reaction mixture was maintained at 40°C for 1 hour with continuous stirring (approximately 200 rpm). The MCA solutions were prepared with 50 mL of DI water (Table 3.1) and was slowly added to the reaction mixture. The reaction mixture temperature was then raised to 60°C and maintained at 60°C for another 2 hours with continuous stirring at 200 rpm. The MCA and NaOH amounts were changed to acquire the desired carboxylic content of the final CMC products, and the ratio of IPA and water were always maintained at 88:12 for all reaction conditions. The detailed experimental setup and conditions are displayed in Figure 3.2 and Table 4.1, respectively. After completing the reaction, the mixture was filtered and washed several times with 70% (v/v) ethanol/water mixture to remove unreacted chemicals (MCA and NaOH), by-products (sodium chloride), and solvent (IPA). The final products of low-substituted CMC were dried at room temperature (25°C).
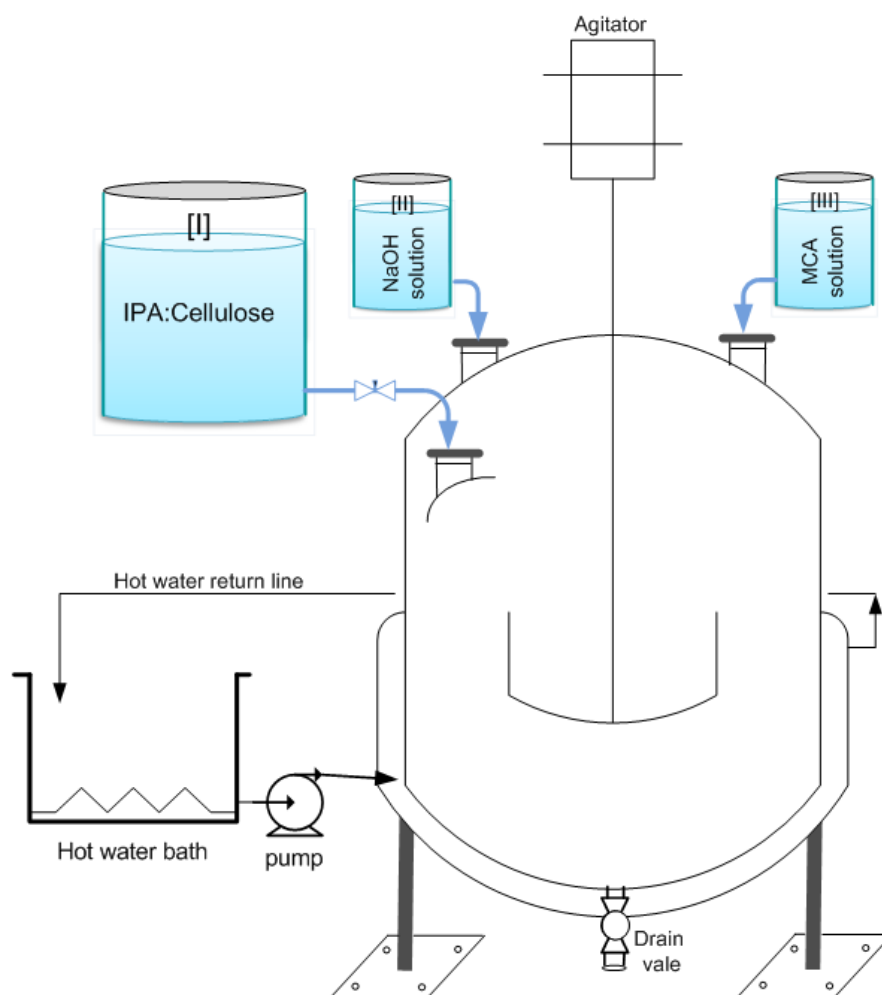
Figure 3.2: Experimental setup for CMC preparation from pulp fibers.

3.2.3 Preparation of dialdehyde cellulose (DAC):

DAC was also prepared from the same BSWK pulp powder by the selective periodate oxidation reaction [129]. For this experiment, the cellulose was partially oxidized. Briefly, 10 g of pulp powder and certain amount of sodium meta periodate were mixed with 500 ml of 0.5 N sodium chloride solution in a closed reactor equipped with a mechanical mixer; the entire reactor was covered with aluminum foil to prevent any source of light. The reaction mixture was kept in the dark for 12 hours at room temperature. It was then filtered and washed with deionized water several

times to remove the salt and the unreacted periodate. The reaction scheme and the stepwise experimental procedure are shown in Figures 3.3 and 3.4, respectively.

Figure 3.3: Periodate oxidation reaction of cellulose with periodate forming a dialdehyde cellulose (DAC).

Figure 3.4: Dialdehyde cellulose (DAC) preparation steps from pulp fibers.

3.2.4 Gel preparation:

Two types of gel were prepared for spinning. First, a gel was prepared from only pure low-substituted CMC pulp fibers where a certain amount of low-substituted CMC (16 g) was dispersed in DI water (176 g) to make a slurry mixture, which was then mercerized with 24 g of NaOH solution (50 w/w%) to prepare the gel. The mixture was stirred by an overhead stirrer for 10 minutes at 1000 rpm to produce a homogenous gel. The gel was passed through the 40-micron

wire mesh to remove undissolved cellulose particles in order to prevent clogging during the wet spinning process. Another gel was prepared with low-substituted CMC and DAC together. In this case, different ratios of low-substituted CMC (95-80%) and DAC (5-20%) were mixed with NaOH solution and the gel was prepared to form a 8 w/w% cellulose solution in 6 w/w% NaOH by weight (however the DAC was added prior to the NaOH solution). Figure 3.5 outlines the gel preparation procedure for CMC gel (A-C-D), and CMC with DAC gel (B-C-D). In both cases, the resulting gels were 8% cellulose and 6% NaOH.
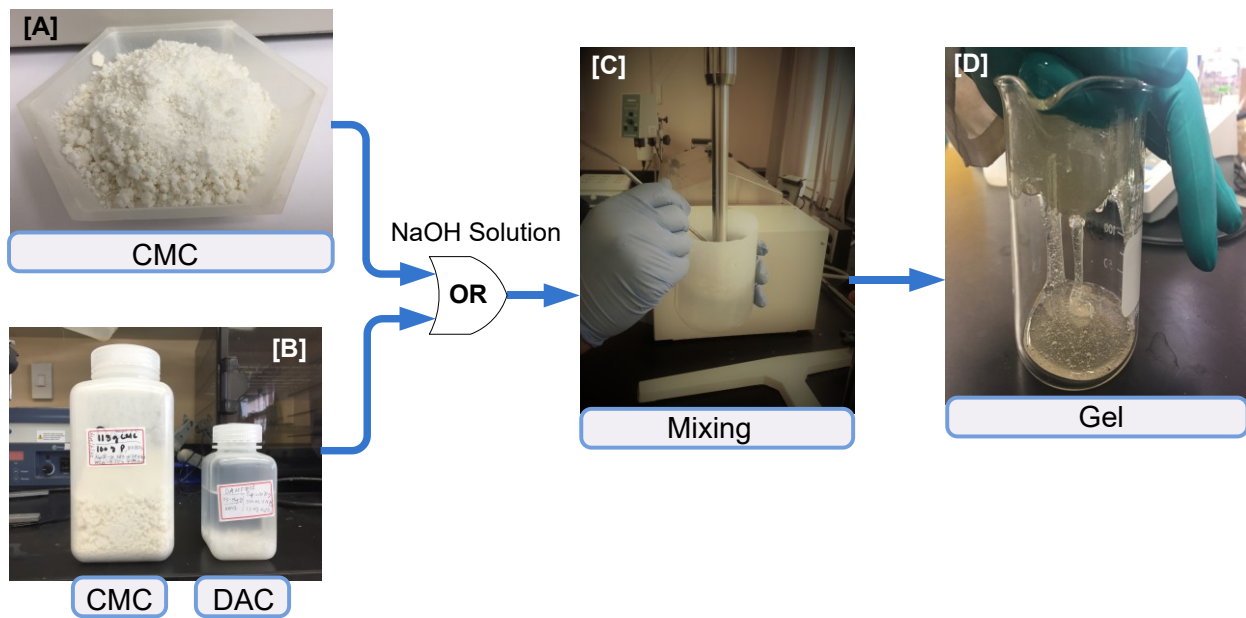
Figure 3.5: Gel preparation steps for CMC (A-C-D), and CMC with DAC gel (B-C-D).

3.2.5 Preparation of textile filaments:

The prepared gels were extruded with a laboratory spinneret (10-jet, 200-micron hole) at a constant speed of 5-10 m/min. The gels were poured into a 500 mL cylinder and gels were extruded via air driven pressure at 25-30 psi into the acid coagulation bath containing 5 (w/w%) $ZnSO_4$, 25 (w/w%) Na_2SO_4 and 13 (w/w%) H_2SO_4 solution. The bath was pre-heated to 50-55°C and kept at that constant temperature during the extrusion process. The rotor speed remained between 80 and 120

rpm, depending on the amount of air pressure that was applied. The wet spinning process and their steps are shown in Figure 3.6.
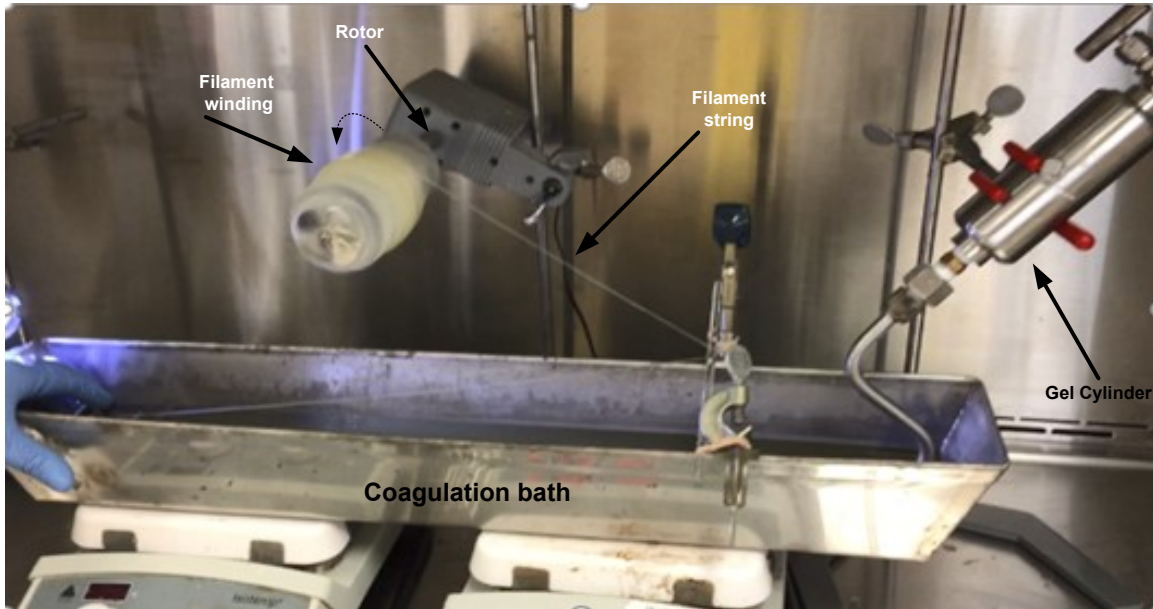
Figure 3.6: Laboratory spinning process with coagulation bath for preparation of textile filaments.

3.2.6 Washing and drying of filaments:

The extruded filaments were washed with hot water (50-60°C) for removing the coagulation bath chemicals and acids. There were then washed repeatedly with a mixture of 70% (v/v) ethanol and water until the pH was neutral (pH ≈ 7). Before drying, the filaments were rinsed with acetone to remove excess water and ethanol. Finally, they were dried with forced hot air flow (80-90°C). The washing steps are detailed in Figure 3.7.
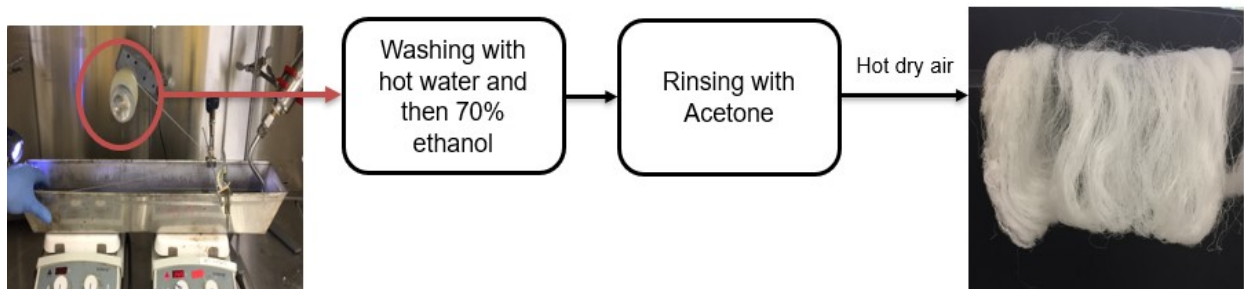
Figure 3.7: Washing and drying steps for the preparation of filaments after wet spinning.

3.3 Characterization

3.3.1 Determination of carboxylic acid groups content:

The carboxylic acid (R–COOH) content was calculated by conductrometric titration, whereby we used a METTLER TOLEDO (InLab-731 ISM, Switzerland) tiltrotor. The carboxyl content of low-substituted CMC was determined according to a previous study[138, 139] . We diluted 0.2-0.3 g of dry CMC sample with 150 ml of DI water, which were thoroughly stirred to obtain a well-dispersed solution. 2.5 ml of NaCl (0.02 M) was added to the mixture in order to attain ionic stability of the titrate solution. We then adjusted the pH of solution to 3 by adding 0.1 N HCl. The titration was then carried out with 0.05 N NaOH standard solution until the solution pH reached close to 11. The carboxyl content was calculated using Eq. 3.1 from the conductivity curve (Figure 3.8b), which represents the weak acid titration.

$$\text{COOH content (m mol/ g cellulose)} = \frac{(V_C \ \text{X} \ N_C)}{W_c} \ \text{………………..} \ \text{Eq. 3.1}$$

Where,

V_C = Volume of NaOH (mL) required for the deprotonation of carboxylic groups

N_C = Molar concentration of NaOH (N)

W_C= Amount of dry CMC used (g)
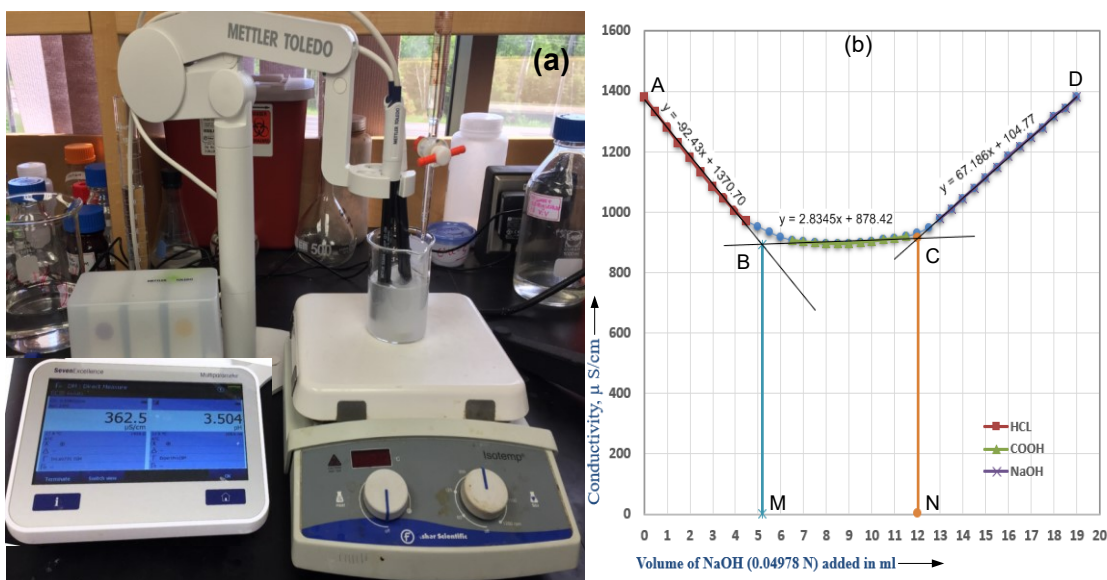
Figure 3.8: (a) Conductimetric titrator; (b) carboxylic acid content determination graph

3.3.2 Determination of aldehyde groups content:

The aldehyde groups content of the periodate oxidize cellulose was calculated using the hydroxylamine-hydrochloride ($NH_2OH.HCl$) titration method [139, 140] in which the HCl was released and titrated with a specific concentration of NaOH standard solution. An OHRUS pH meter (Model-ST5000, USA) was used to measure the pH for the determination of the content of aldehyde groups, as shown in Figure 3.9. The following reaction was carried out and released HCl from the reaction of cellulose aldehyde and $NH_2OH.HCl$.

Cellulose-CHO   + $NH_2OH.HCl$ $\longrightarrow$ Cellulose-CHNOH   +   HCl

In this study, 0.25 g of produced dialdehydes cellulose (DAC) was suspended in 50 ml of isopropanol/water mixture (1:1, v/v) and stirred with a magnetic stirrer at 200 rpm for 20-30 minutes to prepare a well-dispersed solution. The pH of the mixture was carefully adjusted to 3.5 by using HCl (0.1N) acid; 2.5 mL of $NH_2OH.HCl$ (10 wt.%) solution was then added to the suspension mixture. The reaction mixture was left to react for approximately 10 minutes at room temperature. The pH of this mixture dropped due to the HCl released from the reaction of aldehyde and $NH_2OH.HCl$, which was titrated with a specific concentration of NaOH (0.5 N) standard solution until it returned to pH 3.5.

The aldehyde content of DAC was calculated in Eq. 3.2 below:

$$Ac = \frac{(V_A \ X \ N_A)}{W_C}$$ ………………………………………….. Eq. 3.2

Where,

Ac = Aldehyde content of DAC (m mol/g DAC)

V_A = Volume of NaOH (mL) required for the titration

N_A = Concentration of NaOH (N) standard solution

Wc = Weight of dry DAC (g) initially dissolved

Figure 3.9: Titration for aldehyde group content determination.

3.3.3 Mechanical properties measurements:

Tenacity testing of the filaments was conducted to determine fiber strength. Tenacity of the filaments produced by wet spinning process was measured from the tensile strength and the liner density. We used a TMI instrument to measure the diameter of the filaments; we then input that data into the INSTRON instrument software prior to testing for tensile strength, for which we used an INSTRON (MINI 44, USA) instrument. The 50 mm filaments were attached to both jaws where the strain rate of 5 mm/min was applied. Each set of experiment was conducted three times, after which the mean and standard deviation were calculated.

3.3.4 Water absorbency calculations:

The water absorption value was measured by dispersing 0.5 g of filaments in deionized water, soaking for 12 hours. The filaments were then centrifuged (Sorvall RT1, Thermo Scientific, German) at 1000 g (around 2300 rpm) at 4ºC for 10 minutes in a tube with a porous screen so that the excess water was removed from the filaments [129]. All samples were analyzed in three

different pH conditions (pH 3, pH 7 and pH 9). Water absorption was calculated by measuring the wet weight (after centrifuge) and dry weight (after drying in a hot oven at 105°C for 4 hours) of each sample using Eq. 3.3, as follows:

$$\text{Water uptake}, \frac{g}{g} = \frac{(Y_w - Y_d)}{Y_d} \dots\dots\dots\dots\dots\dots\dots\dots\dots \text{Eq. 3.3}$$

Where,

Y_w = wet weight of filaments (after centrifuged)

Y_d = dry weight of filaments (after dried)

Figure 3.10: Sorvall RT1 Centrifuge for water uptake calculations.

3.3.5 Fourier Transform Infrared Spectroscopy (FTIR):

FTIR of the samples was measured using the Bruker Tensor 37 (Bruker, Germany) with a PIKE MIRacle Diamond Attenuated Total Reflectance (ATR) accessory. Dry samples were placed on the ATR crystal, where we applied maximum pressure by using a Zinc Selenide (ZnSe) clutch-type mechanism. All data from 64 scans were collected and recorded for each sample; the wavelength averaged between 600 and 4000 cm-1, with a resolution of 4 cm-1.

3.3.6 X-ray diffraction (XRD) analysis:

The crystalline nature and crystal type of the filaments were identified by XRD (X'Pert Pro X-ray diffractometer, PANalytical, Netherlands) with a PIXcel detector and Kα radiation (λ = 1.54 Å). The X-ray diffractograms were acquired with a current of 40 mA and a voltage of 45 kV, using a copper X-ray tube with a range of 6°-40° at a scan speed of 0.005 deg sec^{-1}.

3.3.7 Scanning Electron Microscope (SEM):

The morphological properties of the cellulose filaments were examined using a Hitachi SU-70 field emission scanning electron microscope (SEM, Hitachi, Japan) with operating voltage of 5 kV. The samples were mounted with double-sided carbon tape on aluminum stubs and sputter-coated with gold to make them conductive prior to SEM observation.

4.1. Filament Production from Low-substituted CMC Fibers

The low-substituted CMC fibers were produced from the chemical modification of cellulose (pulp) fibers. The significant advantages of these modified fibers are that they are easy to prepare, inexpensive, and their anionic functional groups can be utilized to produce a wide range of new high-value cellulose-based products. In this study, the carboxymethylation reaction was used to produce the low-substituted CMC fibers where introduced a small amount of negatively charged cellulose derivative -- mainly carboxyl groups (-COOH) on to the cellulose fibers. The carboxyl groups had a strong water affinity and were able to create a gel solution in the water with a minimum amount of shared forces. This cellulose gel can be used for fabrication of cellulose-based filaments through wet spinning. It was not possible to produce a gel solution from the unmodified cellulose due to the high interaction between the -OH groups among the cellulose chain. The entire carboxymethylation reaction for both stages is illustrated in Figure 4.1.
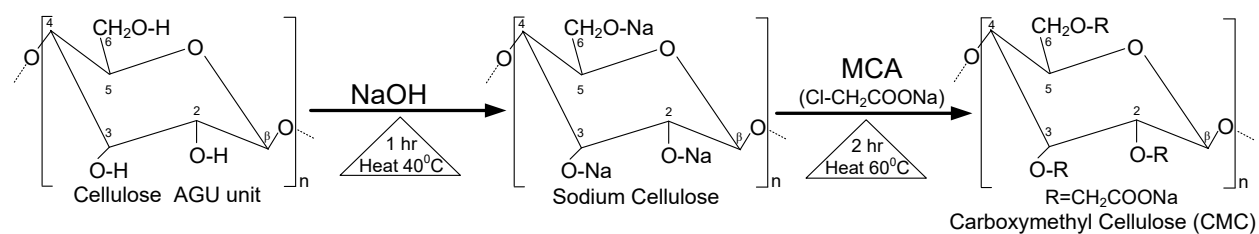
Figure 4.1: CMC formation between hydroxyl groups of cellulose and MCA.

The modification reaction of cellulose fibers involved two steps: a reaction of unmodified cellulose with NaOH, and a reaction of the product (obtained from the first step) with MCA ($ClCH_2COONa$). The content of -COOH groups, which were also related to the degree of substitution (DS) in the modified cellulose, depends on the reaction conditions (Table 4.1) such as reactant concentration (NaOH and MCA), reaction temperature, reaction time, and solvent type.

Earlier research suggested that higher DS (0.4-1.6) in cellulose filaments were capable of absorbing water up to 33 g/g. [141], which was suitable for producing absorbent materials. On the other hand, strong water absorption was not desirable for textile applications. For this reason, we modified the cellulose in low DS of CMC fibers, which we named low-substituted CMC fibers. Table 4.1 represents the carboxylic content of all samples (1-5).

Table 4.1: Optimization of experimental conditions and carboxyl group contents for CMC preparation.

Recipe	Cellulose, g	IPA	NaOH(g)	MCA (g)	COOH content (m mol/g)	Degree of substitute (DS).
1	100	880	30	12	0.85	0.14
2	100	880	30	15.6	0.98	0.16
3	100	880	30	20	1.2	0.19
4	100	880	30	22.5	1.31	0.21
5	100	880	30	25	1.43	0.23

Table 4.1 portrays the gradually increasing DS with the increase in carboxylic content. The DS and carboxylic content were maintained in such way that the dissolution of CMC was desired for the spinning process. The low-substituted CMC derivative with various -COOH content (0.85 to 1.43 mmol/g cellulose) were used to produce gel for fabricating filaments through the spinning process (Table 4.1). Due to the lower carboxylic content, the CMC with -COOH groups content of 0.85 - 1 mmol/g cellulose (recipe 1-2) was unable to form a gel for spinning. The CMC with a -COOH group content of 1.2, 1.31 and 1.43 mmol/g cellulose (recipe 3-5) were able to form gels; however, the gels with a -COOH group content of 1.2 and 1.3 mmol/g cellulose were highly viscous, which was likely due to the high interaction created by hydrogen bond formation among the -OH groups residing in the cellulose chain, and was therefore not suitable for spinning either. It became possible to create a perfect and uniform gel with a -COOH group content of 1.43 mmol/g cellulose (recipe# 5, Pulp: IPA: NaOH: MCA = 5 : 4 4 : 1.5   : 1.25) for the filaments production. Therefore, the COOH group content of 1.43 mmol/g cellulose was selected for the production of

filaments in this study. The prepared filaments were then analyzed to investigate their physical and chemical properties. The FTIR spectrum (Figure 4.5) of filaments with CMC only (0% DAC) shows that the formation of ester bond at 1730 cm^{-1} occurred during the regeneration process, which indicates that intra cross-linking is occurring between the CMC -COOH groups and cellulose -OH groups. For this reason, a significantly low amount of water absorption (2.39 g/g at pH 7) was observed for the filaments with CMC only (0% DAC) in Figure 4.4. However, this water absorbency value was still high for the commercial applications of textile fibers. To achieve a further reduction of water while maintaining satisfactory filament strength (major objectives of this study), the CMC was cross-linked with various amounts of DAC (periodate oxidized cellulose) during the spinning and drying cycles.

4.2 Crosslinking of filaments with DAC

Cross-linking between the cellulose chains plays an important role in the formation of the filaments, and their properties can vary depending on the amount of cross-linker. The cross-linking reaction between the unmodified hydroxyl groups of cellulose and the modified aldehyde groups of cellulose is presented in Figure 4.2. Periodate oxidation of cellulose fibers reduces the number of hydroxyl groups in cellulose molecules due to the partial conversion of hydroxyl groups to aldehyde groups, which diminishes the hygroscopicity of the DAC [129]. The prepared CMC fibers with a large number of unreacted OH groups (CMC contain 1.43 mmol COOH group per g cellulose, and the rest contain approximately 17 mmol OH groups remain unchanged - out of a total of 18.5 mmol OH groups per 1g of anhydrous glucose unit "AGU") was cross-linked with DAC containing -CHO groups of 1.4 mmol/g. During cross-linking, a hemiacetal and acetal bond was formed between the aldehyde and hydroxyl group of cellulose. As a result, the strength of the filaments increased nearly 30% with 5% DAC cross-linked (Figure 4.3), along with a significant reduction of water absorption (Figure 4.4). No catalyst or activator was required for this reaction, and no extra purification was required because water was the only by-product.

$$\text{Cell}-\overset{\displaystyle O}{\underset{\displaystyle H}{C}} \;+\; \text{Cell}-\text{OH} \longrightarrow \text{Cell}-\underset{\displaystyle O-\text{Cell}}{\overset{\displaystyle OH}{C}}-H \;\xrightarrow[\text{drying}]{\text{Cell}-\text{OH}}\; \text{Cell}-\underset{\displaystyle O-\text{Cell}}{\overset{\displaystyle O-\text{Cell}}{C}}-H \;+\; H_2O$$

Cellulose-aldehyde   Cellulose-hydroxyl   hemiacetal   acetal
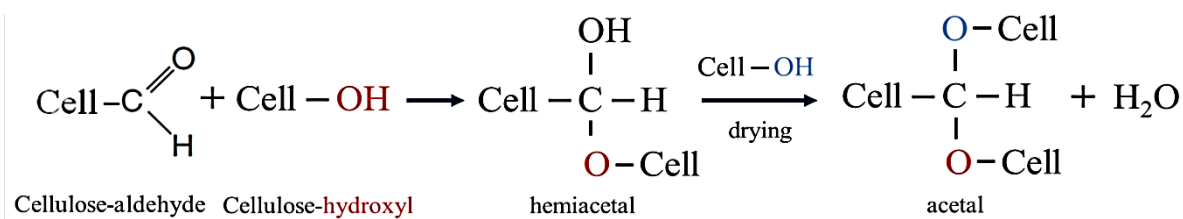
Figure 4.2: Cross-linking reaction of hemiacetal and acetal bond formation during the preparation of filaments.

4.3 Mechanical Properties of Filaments

Fiber tenacity indicates the mechanical strength of textile fibers. In this study, the air-dried fiber samples were analyzed for tenacity (see results in Figure 4.3). The tenacity of the control filaments sample (100% CMC and 0%DAC) was 0.65 cN/dtex (Figure 4.3), whereas the addition of 5% cross linker (DAC) significantly increased it to 28% more (0.83 cN/dtex) compared to without DAC (Figure 4.3). The filaments having higher tenacity are better suited for the textile applications. The best results in terms of tenacity were obtained with 5% DAC. This can be explained with the state of the macromolecular network formed in the cellulose molecules. However, further addition of DAC (Figure 4.3) decreased the strength of the filaments and resulted in increased brittleness, which was expected because higher cross-linking density created a denser macromolecular network with less flexibility in the cross-linked filaments. The FT-IR spectra (Figure 4.5) also confirmed the peak at 1733 and 887 cm⁻ for hemiacetal bonds between the hydroxyl groups and aldehyde groups. The tenacity of the filaments was comparable with the regenerated rayon fibers (0.9 cN/dtex) [142]. In this study, we observed slightly lower tenacity due to the partially regenerated filaments. In addition, the modified functional groups were unable to create a hydrogen bond between the cellulose molecules.
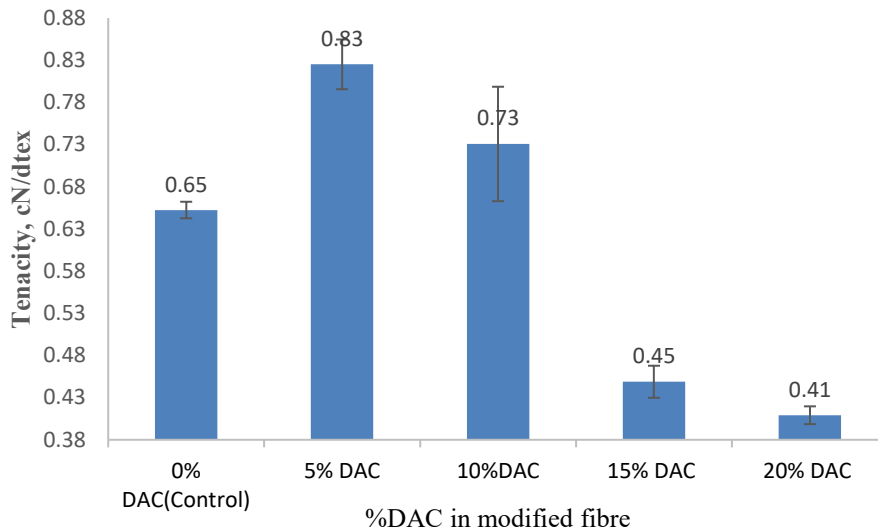
Figure 4.3: Tenacity of filaments with different amounts of modified cross-linker (DAC).

4.4 Swelling Property of Filaments

In this study, the filaments were produced by adding a different amount of DAC cross linker (5% to 20% DAC in terms of total CMC). Water absorption is one of the most important properties of filaments for textile applications. In this experiment, Figure 4.4 represents the water absorption of different filament samples. The control filaments (0% DAC) show higher water absorption; whereas water absorption decreased with an increased amount of DAC (the filaments become less hydrophilic). This is because the cross-linked network structures shield the interior of the filaments structure (denser network), thus preventing swelling of the cellulose molecules. As a result, lower water absorption was observed with the DAC cross-linked filaments (Figure 4.4). The water absorption properties of the filaments were strongly dependent on the pH, as well as on the types of salt that were present in the solution. To investigate the pH sensitivity of the produced filaments, we kept them in acidic (pH=3), neutral (pH=7) and basic (pH=9) solutions (refer to Figure 4.4). The amount of water absorption was very minimal in an acidic solution, whereas it drastically

increased in a basic solution, which is attributed to the fact that the PH increase in pH induced deprotonation of the ionization functional groups which were bound to the cellulose molecules network, causing the increase in the osmotic pressure and thus, enhancing the hydration of the fibers [143]. When the fibers were dipped into the basic solution, the ionization of -COOH increased, which in turn increased the osmotic swelling pressure as a result of the relaxation of the fibers cross-linking networks due to the repulsion forces among the carboxylic groups [144]. The addition of DAC into the filaments resulted in the formation of cross-linking network, which increased, which also decreased the H-bond interactions resulting in significantly-reduced water absorption [145]. Adding 5% DAC decreased water absorption by nearly 52%, and to 65% at pH 7 and pH 9, respectively, compared to the control filaments (100% CMC). In the previous study [129], the cross-linked cellulosic fibers were produced from DAC and chitosan and absorbed approximately 2 g/g of yarn, which is almost double than that of our filaments. Morton and Hearle (2008) reported that rayon fibers absorbed around 2-4 g/g of yarn, and cotton absorbed 1.1-1.2 g/g of yarn [5]. In this study, the water absorption values of the filaments cross-linked with DAC were around 1-2 g/g, which were very comparable to the commercial rayon and cotton fibers.
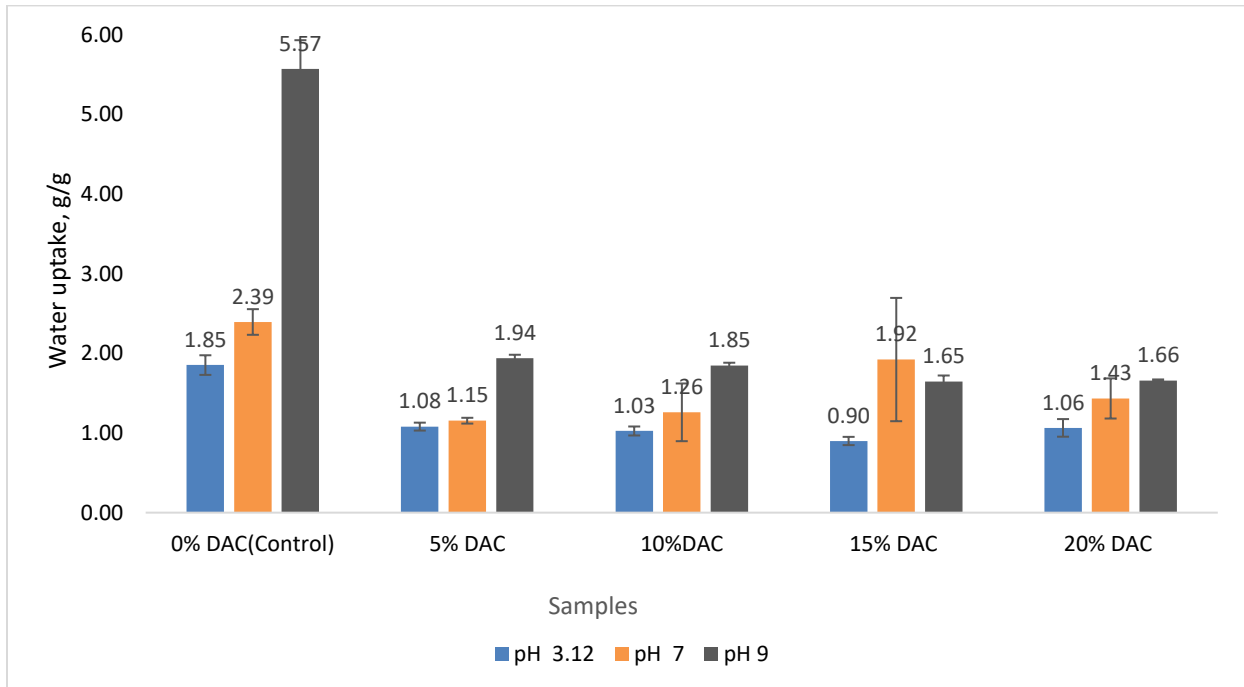
Figure 4.4: Water absorption of the modified filaments on different pH conditions.

4.5 Analysis of Filaments Cross-linking Bonds

The FTIR was conducted to analyze the cross-linking bonds between the carboxylic, aldehyde and hydroxyl groups. The broad peak at 3292 cm-1 indicates the stretching vibrations -OH groups [129]. The intense peak at 2375 cm^{-1} is for CO_2 due to direct diamond press, which is a common peak found during analysis [146]. A clear intense peak in CMC at 1591 cm^{-1} represents the carbonyl (C=O) stretching for COO- ions, which attributes the $–COO^-Na^+$ rather than in the acid form [147]. This is due to the use of sodium instead of chloroacetic acid chloroacetate. The broad band region between 1400 and 1300cm^{-1} can be ascribed for the vibrations of C-H, C-O-H stretching and bending for CMC. The peak intensity at 1591 cm^{-1}, as well as the 1300-1400 cm^{-1} region, diminish significantly due to cross-linking during the spinning process. On the other hand, after adding DAC, cross-linking between the aldehydes and the -OH groups formed hemiacetal bonds that can be attributed to the peak forms at 887 cm^{-1}[129]. The constant peak at 1733 cm^{-1} for all regenerated filaments can be ascribed for the carbonyl group (C=O) of ester bond [148]. Moreover, a slight intensity increased in the 1300 cm^{-1} band in the modified fibers (DAC+CMC), which can be attributed to C–O–C stretching; this is indicative of hemiacetal and acetal bond formation [147].
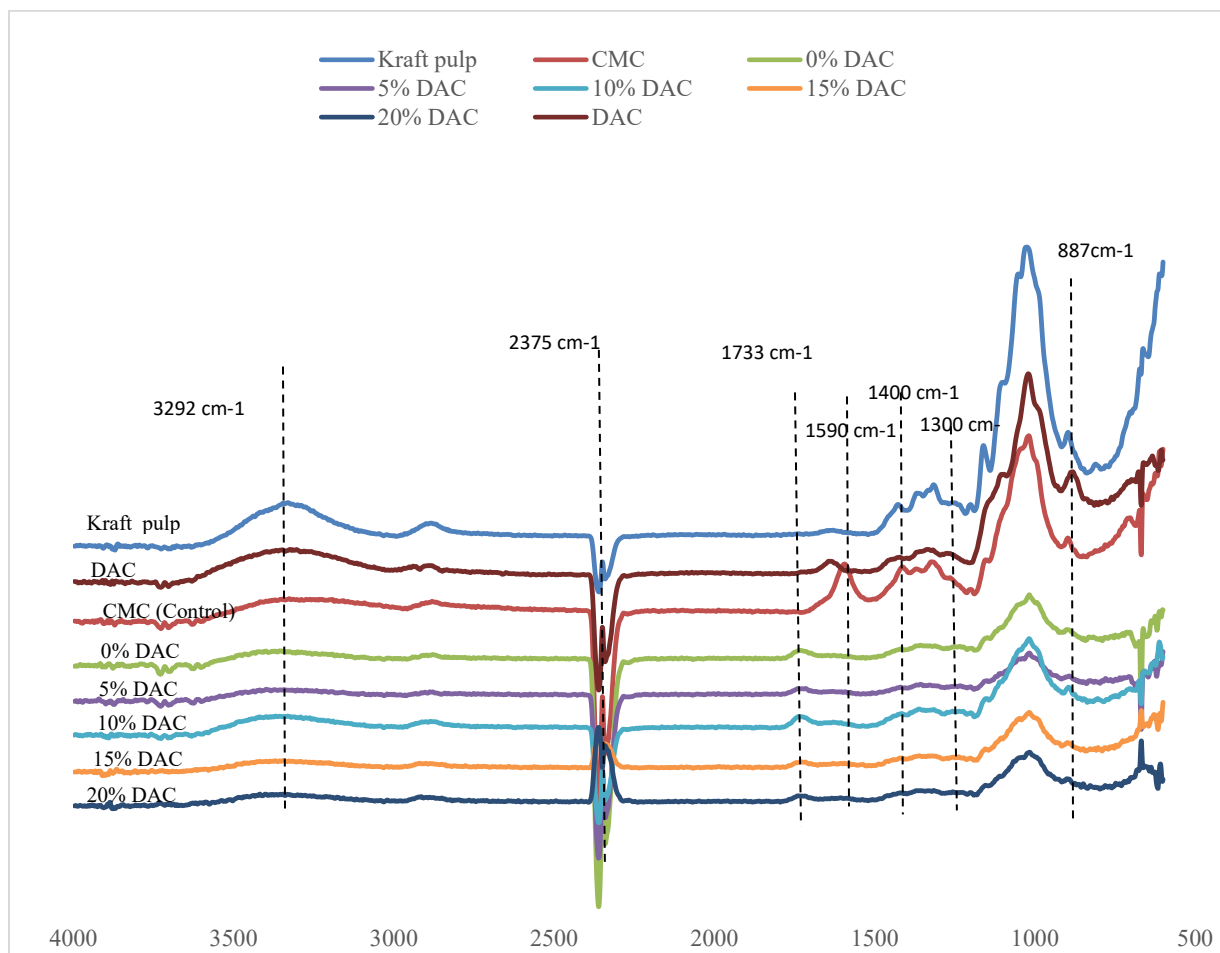
Figure 4.5: FTIR spectra of the different fibers and the modified crosslinked filaments.

4.6 Morphological Properties of Filaments

The morphological properties of the filaments were presented in Figure 4.6, where the SEM images of control filaments (100% CMC) and 5% DAC (cross-linked) filaments were displayed. The control filaments in Figure 4.6A represent the filaments produced without cross-linking DAC. It is clear that the prepared filaments were well packed together, and that the filaments are covered with cellulose chains and small pores. The magnified SEM images of the filaments' surface can be observed in Figure 4.6 (A2 and B2). The filaments with DAC (Figure 4.6 B2) were of a highly porous structure compared to the control (CMC only) filaments (Figure 4.6 A2). This suggests unreacted native cellulose (cellulose I) was present in the filaments due to the partial conversion

of cellulose during DAC preparation. The unmodified cellulose (cellulose I) is also apparent from the XRD analysis Figure 4.7. As seen in the cross-sectional view, the DAC filaments were homogenously cross-linked with others cellulose chains. Previous studies suggested that the porous structure is also important for filament tuning in textile and yarn manufacturing[129].
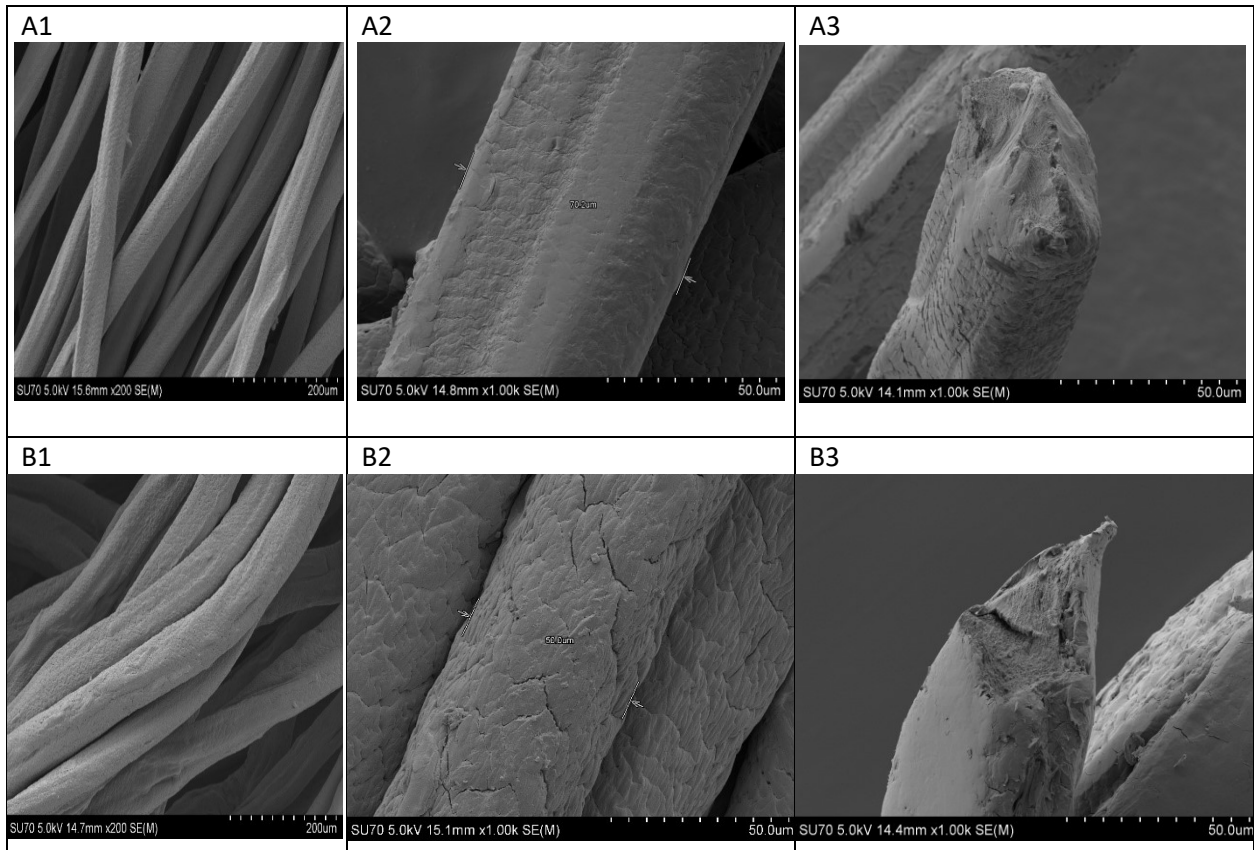
Figure 4.6: SEM images of filaments surface without cross-linker DAC (A1, A2), with 5% cross-linker DAC (B1, B2) and their cross-sectional view (A3, B3).

4.7 Crystalline Properties of Filaments

The crystallinity of the filaments was investigated by X-ray diffraction (XRD), and the XRD profile of unmodified, modified cellulose (CMC and DAC) and cross-linked filaments with 5% DAC are presented in Figure 4.7. The typical cellulose peaks were assigned according to

Nishiyama et al. [149] and Isogai et al. [150]. The diffraction angles (2θ) of 15°, 16.5°, and 22.6° correspond to the 110, $\underline{1}$10, and 200 peaks, respectively, which were the main crystalline regions of native cellulose (cellulose I). The native form of cellulose was found in nature (e.g., wood fibers, cotton, agriculture waste, linen, etc.), where the orientation of all cellulose molecules are parallel to the crystal plane [151, 152]. On the other hand, cellulose-II is the regenerated form of cellulose-I, where the structure of the cellulose molecules' orientation was changed (anti-parallel), and increased the number of hydrogen bonds over cellulose-I [152].

The crystallinity index (C.I.) of cellulose was used to describe the relative amount of crystalline material in the cellulose, which provides a clear indication of cellulose structure degradation (cellulose-I or cellulose-II) after chemical or biological treatments.

The crystallinity index (C.I.) was calculated as [153]:

C.I. = $100(I_{200} - I_{AM})/I_{200}$ .... (Eq. 4.1)

Here, I_{200} is the intensity of the 200 planes reflection located (2θ) at 22.6°, and I_{AM} is the intensity at 16.5°.

Using Eq. 4.1 in Figure 4.5, the C.I. of the unmodified cellulose was 75%. After DAC modification, the C.I. slightly decreased to 67%, which was obviously due to the partial conversion of some of the hydroxyl groups to aldehyde groups (periodate oxidation). This result is consistent with the experiments that were previously conducted [154], which discovered that the crystalline index of cellulose decreased with periodate oxidation level.

Following cellulose modification to CMC and the formation of filaments, the peaks of modified CMC and regenerated filaments look very similar (Figure 4.7); however, there was a slight left shift left of both peaks from the peak of the unmodified cellulose and modified DAC. The C.I. also decreased to 53% and 50%, respectively, which suggests that some crystalline regions in the cellulose were also modified during the carboxymethylation reaction and periodate oxidation of cellulose in addition to the amorphous region.
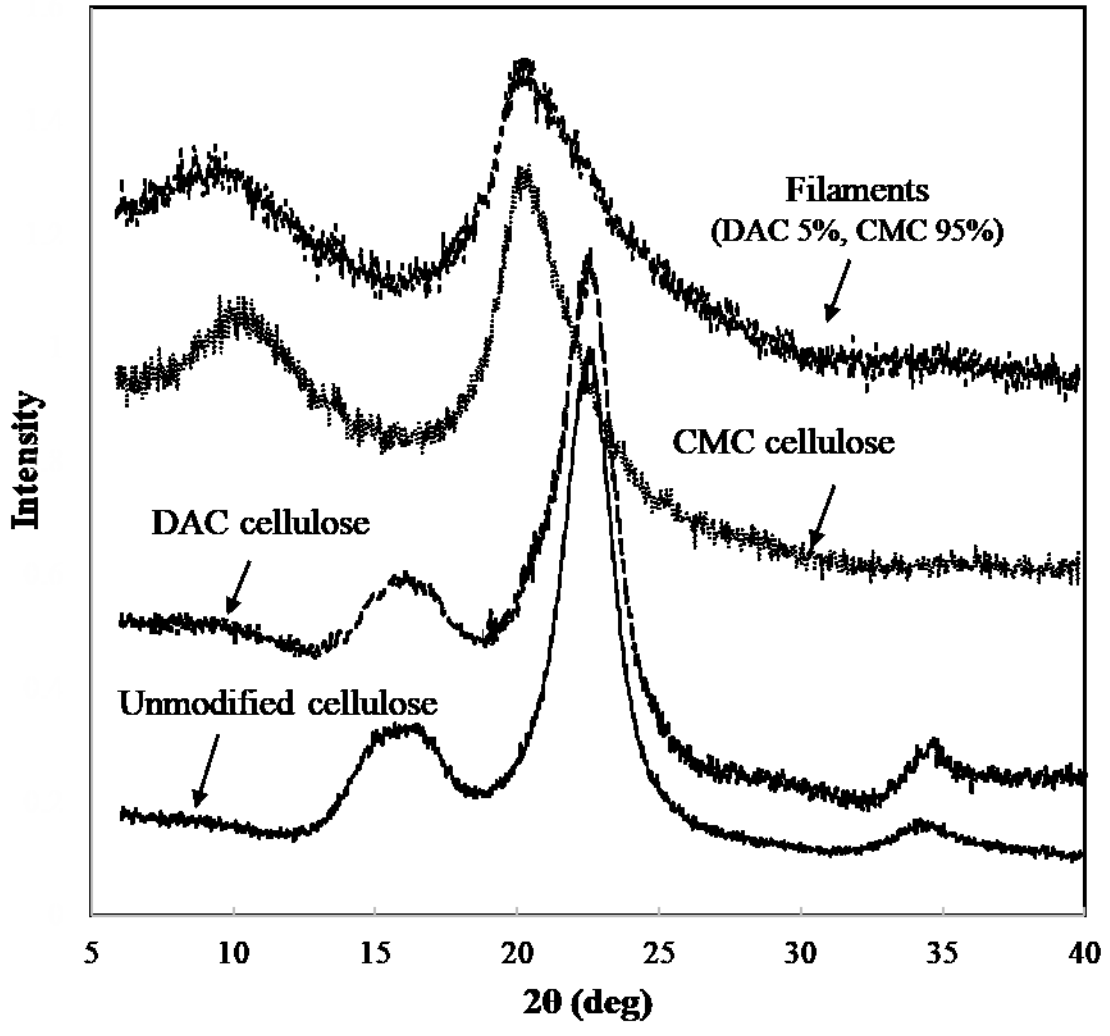
Figure 4.7: XRD of unmodified cellulose, DAC cellulose, CMC cellulose, and filaments with 5% DAC and 95% CMC.

Chapter 5

Conclusions

5.1 Conclusion

In this study, we successfully produced cross-linked textile filaments with CMC and DAC. The produced filaments had significant lower water absorption properties with a high degree of mechanical strength. The carboxylic content of 1.4 mmol per g of the modified CMC fibers was selected for the homogenous gel formation for the production of the filaments. However, less than 1.3 mmol per g carboxylic content of CMC fibers were not suitable for spinning process. In order to reduce water absorption, DAC was used for the cross-linking reaction with modified cellulose gel. The results showed that the cross-linking reaction increased the hydrophobicity of the filaments during the filament formation process. The addition of DAC significantly reduced water absorption by nearly 50% in all pH conditions and improved the mechanical properties. The cross-linking reaction with DAC improved filament strength by up to 28% by adding 5% DAC due to the formation of hemiacetal and acetal bonds between the -OH and -CHO groups. The FTIR data also supported the ester bond formation during the cross-linking reaction with DAC. The morphological properties of the modified fiber indicated that the modified cellulose fiber (95% CMC and 5% DAC) is comparable with cotton and commercial rayon. Furthermore, XRD analysis suggests that the C.I. of modified filaments significantly decreased compared to unmodified cellulose due to chemical modification of cellulose (carboxymethylation and periodate reaction). The XRD analysis also revealed that the filaments contain cellulose-1 due to a partial conversion of cellulose I to cellulose II during the chemical modification and regeneration processes. Finally, the partially regenerated cellulose filaments were produced from softwood kraft pulp fibers, which could expand the current cellulosic fiber market.

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