

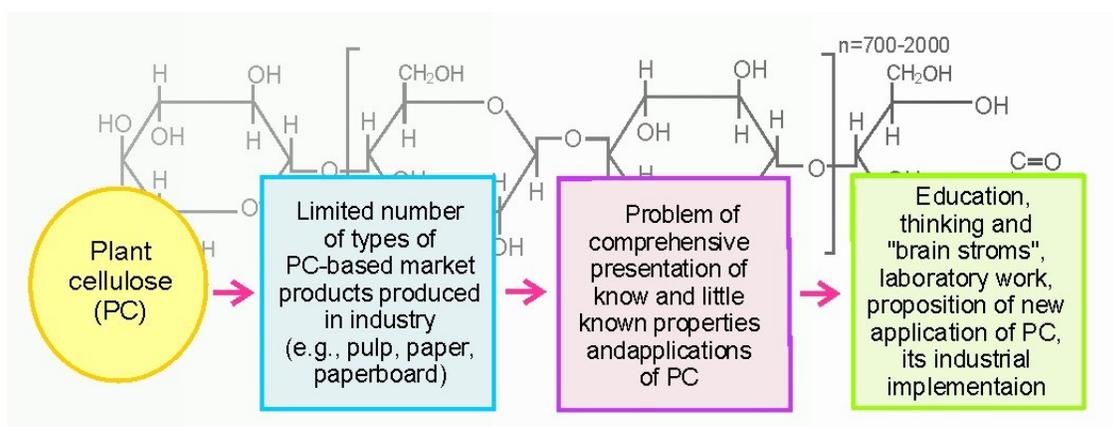
# Plant Cellulose – An Attempt at General Characterization of Properties and Application of the Material

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## GRAPHICAL ABSTRACT



# Plant Cellulose – An Attempt at General Characterization of Properties and Application of the Material

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This paper attempts to provide a general characterization of the properties and applications of plant cellulose (PC) based on literature data regarding its sources, discovery, fractional composition and cell dimensions, the microphysical structure of the fibrous component, its content in wood and non-woody plants, functional properties, traditional uses, and selected contemporary opportunities to expand the use of this material in the production of new types of industrial products. This topic can be useful from systematic, informational, and practical perspectives for engineers involved in teaching plant cellulose technology, for researchers and practitioners searching for substitute materials as alternatives to synthetic polymers and fossil-fuel-derived chemicals, and for paper mills seeking opportunities to mitigate the effects of declining demand for printing papers through the development of other PC-based products. The issues discussed in this article may serve as a starting point for the development of an expanded version of this study, supplemented with additional PC properties and applications not identified by the author, and ultimately for the preparation of a book that would include a comprehensive discussion of specific PC applications.

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*Keywords: Plant cellulose; Sources; Definition and presentation; Discovery; Fractional composition; Cell dimensions; Content in wood and nonwoods; Properties; Applications*

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## INTRODUCTION

Fibrous plants have existed on Earth for millions of years, performing both oxygen-generating and broader environmental functions. More recently, they have served as sources of building materials, food, medicines, fuel, and raw materials for the production of crafts and industrial products needed by people (Dilantha Fernando 2012). Their global reserves are vast and virtually inexhaustible due to their natural photosynthetic regeneration, rendering them renewable resources (Wandelt 2015). Plants are composed of five main groups of chemical components. The most important of them is cellulose, which, unlike the others (*i.e.*, hemicelluloses, lignin, extractives, and inorganic substances), has a distinct form that can be described as fibrous. This form of cellulose, which in this work is termed plant cellulose (PC), exists in nature in the form of chemically near-pure (cotton seed fibres), semi-pure (bast tissues), and composite (lignocellulosic) forms (Surewicz 1971).

Some of the most important applications of these forms of PC today include textile fibres and fabrics, paper and paperboard products, cellulose derivatives, and products from solid wood or engineered wood materials (plywood, oriented strandboard, particleboard,

medium-density fibreboards, *etc.*) (Wandelt 1996; FAO 2024). In many of these applications, PC exists as a composite material with hemicelluloses (*e.g.*, bleached papermaking pulps), residual lignin and hemicelluloses (*e.g.*, unbleached kraft and sulphite pulps, high-yield kraft and sulphite pulps), and native lignin and hemicelluloses [*e.g.*, wood, TMP papermaking pulps, or HT-TMP (high-temperature thermomechanical pulp for medium-density fibreboard)]. The variety of industrial uses for the purest forms of PC therefore appears to be relatively limited in relation to current needs. It would be beneficial for the environment if the PC had much wider industrial applications than today. This could help many industrial products be recognized as products made partially or entirely from renewable natural resources. In this regard, considerable work still remains to be done. A comprehensive understanding of the fundamentals of PC – including its content in plants, microphysical structure, key properties, traditional and potential applications, and even the history of its discovery in condensed form —can be helpful in achieving this goal.

In light of this, the present study attempts to provide a general characterization of PC by presenting information about its origins, discovery, fractional composition, and microstructure, as well as its content in wood and non-woody plants, functional properties, traditional uses, and other potential uses based on a review of the relevant literature, much of which has been published in print journals. This article does not attempt to address issues related to the chemical structure of PC, nor does it provide an extensive discussion of any of its specific applications, such as *e.g.*, those in health care, as considered by some authors (*e.g.*, Klemm *et al.* 2005; Moon *et al.* 2011; Chandel *et al.* 2023).

It is, however, intended as a study presenting the principal properties and applications of PC, which may serve as a starting point for the development of an expanded version of this work, either in response to suggestions from peers or through collaboration with them. Such future work could be supplemented with additional PC properties and applications not considered in the present study, potentially culminating in the preparation of a book that would include a comprehensive discussion of the specific PC properties and applications.

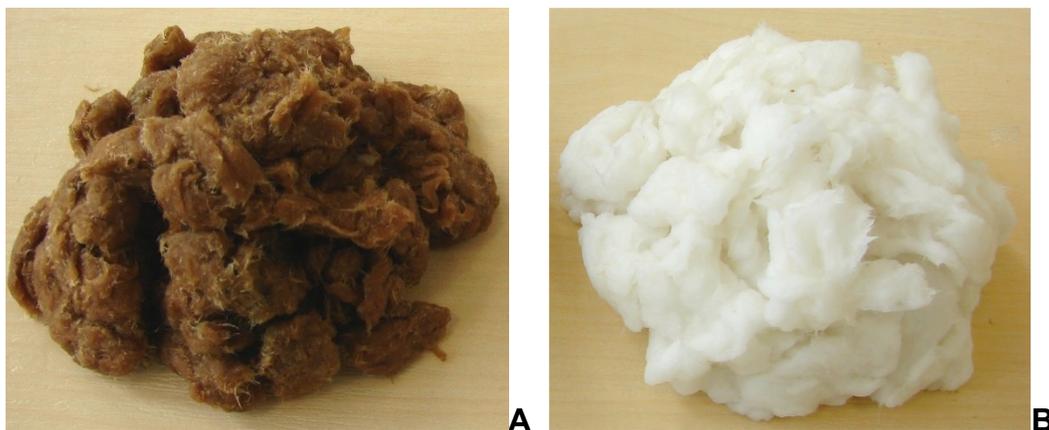
## RESULTS OF THE REVIEW

### Sources, Definition, and Presentation

Plant cellulose (PC) that can be used industrially occurs in nature mainly in the form of cells within the anatomical parts of plants. In these parts, it occurs primarily in highly lignified and hemicellulose-rich woody tissues, less frequently in slightly lignified bast (*e.g.*, industrial hemp and flax) and leaf tissues (*e.g.*, leaves of *Musa textilis* and *Agave sisalana*), and least frequently in the form of seed fibres (as *e.g.*, cotton lints and linters) (Douglas 1950). It should also be noted that cellulose, albeit in a non-fibrous form, is also produced by non-plant organisms including *Acetobacter xylinum* bacteria (Surma-Ślusarska *et al.* 2008), green algae (*Valonia ventricosa*), and tunicates (Brown 2004; Kamel *et al.* 2008; Moon *et al.* 2011).

PC can be defined as a fibrous pulp with a 0 to 10% lignin content, obtained by the light chemical purification of fibres (*e.g.*, cotton fibres) or light (for bast and leaf fibres) or advanced (for wood) chemical delignification (chemical pulping), possibly supplemented with additional mild mechanical refining in a disc refiner (sack and board grade kraft and sulphite pulps). The largest sources of PC today are the cotton industry, the textile industry, and, above all, papermaking pulp mills, in which plant fibrous raw materials (mainly wood)

are chemically pulped, mainly using the sulphate (kraft pulp mills), sulphite (sulphite pulp mills), and soda methods (non-wood pulp mills), producing kraft, sulphite, or soda pulps, respectively. In industry, these pulps are commonly called “cellulose,” despite the fact that they contain a certain amount of other chemical substances typically present in wood, such as lignin, hemicelluloses, and resinous compounds (Fig. 1) (Douglas 1950).



**Fig. 1.** Examples of plant cellulose. A – unbleached softwood kraft/sulphate pulp (wet state), B - bleached softwood kraft/sulphate pulp (wet state)

Pulp mills should be regarded as the primary source of PC for industrial purposes. This is because the most rational use of cotton and bast fibres is in textile production, especially considering the specific agronomic requirements of cotton (Vitale *et al.* 2024), the relatively low global production volumes of hemp and flax globally (Grégoire *et al.* 2021; Scheibe *et al.* 2023), and the growing demand from the textile and other industries for sustainable, eco-friendly, biodegradable, and renewable fibres with lower environmental impact than synthetic alternatives (Anon. 2024).

Assuming that PC is obtained mainly from woody plants, and considering the massive and difficult-to-estimate global biomass of these plants produced annually globally (approximately  $0.8 \cdot 10^{11}$  tons), the vast resources of PC (approximately  $9.2 \cdot 10^{11}$  tons), and the average cellulose content in such biomass of about 40%, it can be stated that PC is a material occurring on Earth in immense quantities (Duchesne and Larson 1989; Hon 1994; Chiellini *et al.* 2004; Kamm and Kamm 2004). Interestingly, the majority of this resource remains largely unexploited, as the wood and paper industries use only a small fraction of the PC synthesized by plants on Earth. According to Wandelt (2015), the paper industry utilizes only 0.2 to 0.3% of the PC available globally. This indicates that PC can be regarded as an almost inexhaustible source of raw material for industrial products, biofuels, and biochemicals.

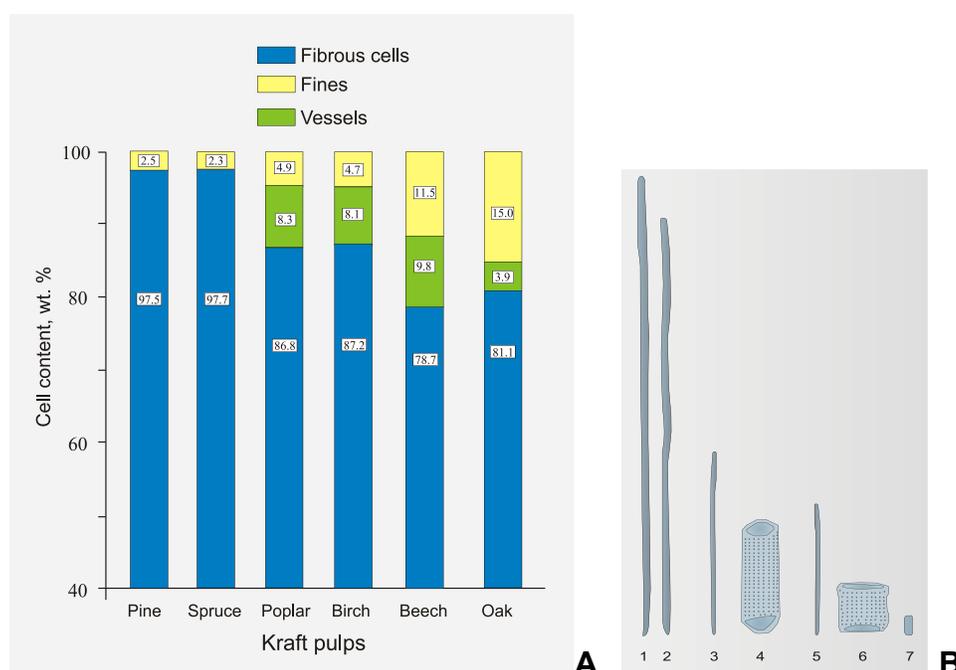
## Discovery

The French chemist Anselme Payen is considered the discoverer of PC. Between 1837 and 1842, he subjected the straw of various plants and their anatomical parts to the action of a nitric acid solution, followed by extraction with ammonia, alcohol, and ether. As a result of these experiments, he found that these raw materials contained a primary substance forming their structure (Mark 1980; Hon 1994), having a fibrous form, which he named “cellulose”. It is worth mentioning that the presence of a substance in plants that was resistant to delignifying agents, previously called “xyloidin,” had been noticed by H.

Braconnot. However, it was A. Payen who gave the substance its current name. This name derives from the fact that it is the main building component of plant cell walls, and in Latin, a plant cell is called *cellula* or *cella* (Sarnecki 1970; Mark 1980; Hon 1994).

### Fractional Composition and Cell Dimensions

The main components of PC obtained from coniferous wood (e.g., pine kraft pulp) and deciduous wood (e.g., birch or eucalyptus kraft pulps) are, respectively, tracheids and wood fibers (fiber fractions) (Fig. 2). According to Surma-Ślusarska (1989), well-pulped kraft pulps from pine, spruce, as well as from poplar, birch, beech, and oak, contain, by weight, 97.5% to 97.7% tracheids and 78.7% to 87.2% libriform fibers, respectively (Fig. 2A). The tracheids are accompanied by parenchymal cells (primary fines fraction), while the wood fibers occur in the wood of deciduous trees alongside vessel cells (vessels fraction), in addition to parenchymal cells (Fig. 2).



**Fig. 2.** Weight share of individual cell types in the kraft pulps from different wood species (A) and cells of plant cellulose (B). 1- spruce tracheid, 2 – pine tracheid, 3 – birch wood fibre, 4 – birch vessel cell, 5 – eucalyptus fibre, 6 – eucalyptus vessel cell, 7 – ray cell

According to the aforementioned author, the weight fraction of parenchymal cells (defined as the fine fraction passing through a 150-mesh sieve) in kraft pulps from Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) averages 2.3 to 2.5%. In contrast, this content in kraft pulps from aspen, silver birch, common beech, and oak averages 4.9%, 4.7%, 11.5%, and 15.0%, respectively. Furthermore, the weight fraction of vessels in these hardwood pulps was 8.3%, 8.1%, 9.8%, and 3.9%, respectively.

Regarding dimensions, Lehtonen and Lehtonen (2004a) categorize the average length of tracheids from 25 softwood species into three groups: 2.0 to 3.3 mm, 2.5 to 3.5 mm, and >3.5 mm in the case of some types of PC. Meanwhile, the average length of wood fibres from 35 different hardwood species studied by Lehtonen and Lehtonen (2004b) are divided into groups of 0.6 to 0.8 mm, 0.8 to 1.0 mm, and >1.0 mm.

According to Nyrén and Back (1959) as well as Hasvold and Lund (1974), the average length of parenchymatous ray cells in *Pinus sylvestris* ranges from 0.030 to 0.180 mm, while in *E. tereticornis*, *E. saligna*, birch, and beech, it ranges from 0.051 to 0.080 mm. Furthermore, Heintze (2007) and Hasvold and Lund (1974) report that vessel lengths in several hardwood species range from 0.025 to 0.610 mm.

The values mentioned above represent averages. Within the pulp components of a given wood species, the lengths of fibers, parenchymal cells, and vessels typically fall within specific ranges. This is well-illustrated by Tiikaja (1999) and Danielewicz and Surma-Ślusarska (2010), whose data on fiber length distribution show that kraft pulps papermaking softwood and hardwood species contains fibers ranging from 0.2 to 7.0 mm and 0.2 to 1.7-3.0 mm, respectively.

In papermaking, fiber width is of significant importance, as it affects factors such as minimum paper basis weight, fiber susceptibility to flattening, and fibre stiffness. According to Tiikaja (1999), the average fiber widths for Northern pine, Southern pine, birch, and eucalyptus are 31.2  $\mu\text{m}$ , 27.2  $\mu\text{m}$ , 18.7  $\mu\text{m}$ , and 14.8  $\mu\text{m}$ , respectively. Somewhat larger fiber widths for European hardwood species—21.0 to 22.6  $\mu\text{m}$  for birch, beech, hornbeam, oak, and poplar, and 17.2  $\mu\text{m}$  for acacia—were reported by Danielewicz and Surma-Ślusarska (2010). However, in reality, these values fall within broader ranges of 7–70  $\mu\text{m}$  (pine), 7–37  $\mu\text{m}$  (birch), and 7–27  $\mu\text{m}$  (eucalyptus). Furthermore, the width of parenchymal cells in *Pinus sylvestris*, *Eucalyptus tereticornis*, and *Eucalyptus saligna* ranges from 12 to 40  $\mu\text{m}$  and from 18 to 22  $\mu\text{m}$ , whereas vessel diameters in *Eucalyptus tereticornis*, *Eucalyptus saligna*, birch, beech, *Quercus alba*, *Betula lutea*, *Betula papyrifera*, *Populus deltoides*, and *Populus grandidentata* range from 44 to 246  $\mu\text{m}$  (Marton and Agarwal 1965).

## Physical Structure in Micro Scale

### *General features of the plant cellulose (PC) structure*

The main element of PC *i.e.*, fibres are formed in woody plants as a result of the maturation of elongated, polyhedral living precursor cells (Bannan 1957). This process involves the ordered (fibrillar) deposition of cellulose layers from the inner side of these cells in a precisely defined pattern, leading to their final cell wall form. Furthermore, in lignified plants, the free spaces between these cellulose fibrils are filled with other structural substances—primarily lignin and hemicelluloses. In many cases, this occurs to a large extent, depending on the programmed degree of lignification and hemicellulose deposition. This results in the formation of a highly complex composite material constituting PC cell walls (Nečesany 1957; Duchesne and Larson 1989; Vincent 1999; Brown 2004).

Important features of the PC microstructure include bundles, bands, and layers. The bands result from the longitudinal joining of elementary fibrils into strings (elementary nanofibrils) through the coalescence of amorphous regions at their ends (Sullivan 1968; Ioelovich 2008). On the other hand, bundles relate to the supramolecular structure of plant cellulose. This involves the transverse aggregation of cellulose macromolecules into clusters called elementary fibrils and the transverse joining of several elementary fibril strings into microfibrils. This process occurs *via* lateral “co-crystallization,” which is facilitated by a relative shift between fibrils enabled by plant-produced lubricants, such as xyloglucans and rhamnogalacturonans (Brown 2004). Bands and bundles are also evident in the way microfibrils combine to form macrofibrils. Furthermore, the term “layers” refers

to the morphological structure of the PC cell wall, which consists of several membranes. Among these, two types can be distinguished: the primary wall (P) and the secondary wall (S).

#### *The primary (P) wall of PC fibres*

The primary wall, also known as the cambial wall, is the very thin, outermost layer of the fiber. It has a thickness of approximately 0.03  $\mu\text{m}$  (30 nm) in the dry state—roughly the thickness of three microfibrils—and about 0.1  $\mu\text{m}$  in the wet state (Lange 1959). It consists of a loose, flexible, and irregular mesh with large voids, formed by interconnected cellulose microfibrils. Initially, these spaces are filled primarily with pectins (approximately 40 to 60%), proteins, galactan, araban, and glycoproteins (Winczakiewicz 1955; Kremers 1964; Westermark *et al.* 1987). Subsequently, upon the formation of the S<sub>1</sub> layer (the first layer of the secondary wall), other components begin to appear in the primary wall. These include lignin and “proper” wood hemicelluloses, such as glucomannans (GM), glucuronoarabinoxylans (GAX), xyloglucans (XG), and mixed-linkage glucans (MLG) (Von Koeppen 1964; Vogel 2008; Joseleau and Perez 2024), along with small amounts of pectins and proteins (Westermark *et al.* 1986; Vogel 2008).

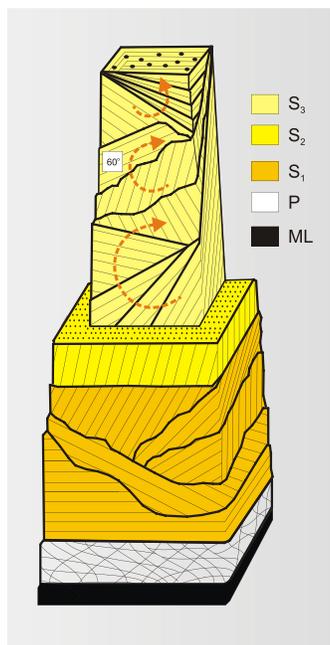
#### *The secondary (S) wall of PC fibres*

The primary wall (P) surrounds the secondary wall. It is characterized by low swelling capacity due to its isotropic structure, likely higher porosity than the middle lamella (ML) (Westermark *et al.* 1987), and greater resistance to cellulolytic enzymes than the remaining cellulose in the cell wall (Lange 1959). During the mechanical and chemical treatment of wood or papermaking pulps, the primary wall tends to separate partially or completely from the rest of the cell wall. This separation occurs in various forms, such as ribbons (the entire primary wall spirally detached from the fiber), flakes, lamellae (primary wall fibrils), or fibril sheets. These elements constitute a portion of the fines fraction in mechanical and chemical pulps or contribute to their external fibrillation. Subsequently, these fragments either deposit onto the fiber surfaces during the formation of the paper web on a paper machine or enter the process water (Winczakiewicz 1955; Norberg 1969, 1970; Asplund 1958; Jurbergs 1960b; Jayme 1963; Polcin *et al.* 1967; Talmadge *et al.* 1973; Westermark *et al.* 1987; Suurnäkki *et al.* 1996).

The secondary wall (S) of plant cellulose in normal wood consists of three sublayers: the outer layer (S<sub>1</sub>), the middle layer (S<sub>2</sub>), and the inner layer (S<sub>3</sub>). These layers differ in thickness, the number of fibril lamellae composing them, the orientation of cellulose fibrils relative to the fiber axis, density, and the concentration of individual chemical components. The majority of the cellulose is concentrated in the middle layer (S<sub>2</sub>) of the secondary wall, which is the thickest and is characterized by a relatively small microfibril angle (MFA) relative to the fiber axis, ranging from 5° to a maximum of 30°. Some studies indicate that in this sublayer, cellulose, lignin, and hemicelluloses are not distributed uniformly throughout S<sub>2</sub> of untreated fibers. Instead, they are broadly divided into minilayers that form two different patterns: concentric and radioconcentric, with the former being the most frequently reported. The cohesive force of these layers protects the fiber from disintegration even if the P and S<sub>1</sub> layers are removed (Emerton 1957; Winczakiewicz 1955; Kallmes 1960; Stone 1964; Stone and Scallan 1965; Dunning 1969; Norberg 1970).

The S<sub>1</sub> and S<sub>3</sub> sublayers are much thinner than the S<sub>2</sub> layer and are composed of several cellulose macrofibril lamellae with variable orientation of the macrofibrils. These

layers exhibit a much greater variation in the orientation angle of the fibrils relative to the fiber axis than the S<sub>2</sub> layer (Fig. 3). For example, research by Dunning (1969) has shown that in the latewood fibers of longleaf pine (*Pinus palustris*), the S<sub>1</sub> sublayer going into the center of fibre consists of a lamella of transversely oriented fibrils, a left-hand helix lamella, a right-hand helix lamella, and transitional lamellae that provide a gradual, stepwise shift toward the fibril orientation of the S<sub>2</sub> layer (Fig. 3). The S<sub>3</sub> sublayer was found to include at least 12 lamellae. These lamellae do not alternate between right- and left-hand orientations; instead, they demonstrate an extended progression of gradual, stepwise orientation transitions from the angle of the S<sub>2</sub> macrofibrils to the angle of the macrofibrils on the lumen surface. If one imagines a line segment moving from the S<sub>2</sub> toward the lumen surface, parallel to the fibrils of each lamella it passes through, this line rotates incrementally in a clockwise manner (as viewed from a point in the S<sub>2</sub>). Beginning at the S<sub>2</sub> orientation, the line rotates more than 270°, ending in a left-hand helix at approximately 60° to the fibre axis. Subsequently, a reversal in the direction of rotation occurs; the line moves counterclockwise through a few additional lamellae and finally stops at the surface lamella, where the fibrils are oriented nearly perpendicular to the fiber axis. Thus, these S<sub>3</sub> lamellae display such a wide variety of orientations that the concept of an “average angular orientation” becomes meaningless (Fig. 3) (Dunning 1969).



**Fig. 3.** Longleaf-pine cell wall structure (Dunning 1969)

The transverse physical and chemical diversity of PC can significantly impact its suitability for specific industrial applications. For example, it has been found that the alternating orientation of macrofibrils in the S<sub>1</sub> layer and the increased lignin concentration in its outer regions [due to its proximity to the primary wall (P) and the middle lamella (ML)] limit the swelling capacity of PC (Jurbergs 1960b; Kallmes 1960). These factors also impair the bonding ability of the S<sub>1</sub> sublayer compared to the S<sub>2</sub> sublayer (Polcin *et al.* 1967). Partial disruption (fibrillation) of the S<sub>1</sub> sublayer or its partial detachment from the fiber (known as “skinning”) has proven beneficial for achieving higher tensile strength in paper produced from papermaking pulps. This process is facilitated by the relatively weak

bond between the S<sub>1</sub> and S<sub>2</sub> layers and the high internal cohesion of the S<sub>1</sub> layer itself (Lange 1959). The detachment of S<sub>1</sub> from S<sub>2</sub> has been observed in several processes, including the production of high-yield kraft pulps (85 to 90% yield), where wood is subjected to chemical pulping followed by mechanical action (Polcin *et al.* 1967). It is also seen in chemically treated cotton fibers (Jurbergs 1960a); during long-term intensive mixing of sulfite pulp slurry in laboratory pulpers (Kallmes 1960); during the beating of sulfate pulps (Polcin *et al.* 1967); and during the production of thermomechanical pulps (Cisneros *et al.* 1995). In the wood fibers of certain hardwood species (*e.g.*, *Betula papyrifera*, *Quercus rubra*, *Acer saccharum*, and *Eucalyptus viminalis*), fibrillating the S<sub>1</sub> sublayer during beating to facilitate the swelling of the S<sub>2</sub> layer can be more difficult. This is due to the thickness of the S<sub>1</sub> layer in these species, which is two to three times greater than that of Norway spruce earlywood fibers (Marton *et al.* 1979). Furthermore, it must be considered that in areas where the primary wall and S<sub>1</sub> sublayer are completely removed, and the fiber is broken or subjected to intense mechanical forces, it can undergo total fibrillation—resulting in the complete disintegration of the fibrillar structure, as demonstrated by Asplund (1958).

As for the S<sub>3</sub> sublayer, it performs a function similar to the S<sub>1</sub> wall; its denser structure and the substances encrusting the fiber interior protect the S<sub>2</sub> layer against the harmful effects of microorganisms that might be present within the lumen (Winczakiewicz 1955; Nečesany 1957; Lange 1959; Jurbergs 1960b). Lange (1959) and Von Koeppen (1964) report that the PC arrangement in spruce and birch fibers is densest around the lumen which likely impedes the diffusion of pulping and impregnating chemicals through the cell walls toward the lignin-rich middle lamella. Such challenges are addressed in chemical pulping technologies, which emphasize the critical importance of thoroughly impregnating wood chips with these chemicals to ensure optimal results when processing wood into papermaking pulps. However, this density decreases toward the outer layers of the fiber (Robertsen *et al.* 1996; Wedin *et al.* 2012).

### Plant Cellulose (PC) Content in Wood

The PC content in plant fibrous raw materials depends on the plant species, its origin, age, and anatomical part. Furthermore, results vary depending on the type of cellulose being measured and the analytical method employed. For example, the wood of European coniferous species, such as pine and spruce, is reported to contain 43.8% to 45.6% PC when determined by the Seifert method. In contrast, European deciduous species (birch, poplar, oak, beech, alder, and hornbeam) contain 37.2% to 42.7% PC according to the Seifert method, and 44.1% to 48.9% when using alternative determination methods (Wandelt *et al.* 1976a,b,c; Pustelnik *et al.* 1963; Rutkowski and Mróz 1972; Danielewicz and Surma-Ślusarska 2010). The cellulose content of softwood and hardwood species from other global regions used in papermaking typically falls within similar ranges: 38% to 45% and 38% to 50%, respectively (Sjöström 1993; Naffzinger *et al.* 1959; Pereira *et al.* 2013; Pauly and Keegstra 2008). However, it seems that certain species may exhibit a higher cellulose content. *Eucalyptus globulus* is a notable example; this wood likely contains slightly more cellulose than other tree species, with values ranging from 45% to 53% (Sjöström 1993; Cotterill and Macrae 1997; Pereira *et al.* 2013).

Wood bark also contains PC. Its concentration in this anatomical element depends on the tree species and the bark layer. According to a study by Samuels and Glennie (1958), the  $\alpha$ -cellulose content in Douglas fir bark and wood is 27.4% and 56.7%, respectively. In contrast, Erickson *et al.* (1970) report that in *Populus grandidentata*, the bark contains an

average of 50.4% cellulose. Values more consistent with the nature and properties of bark, and correlating with the data from Samuels and Glennie (1958), were also presented by Tripathi *et al.* (2020). According to these authors, the cellulose content in a 70:30 mixture of Indian eucalyptus and poplar bark was  $31.8 \pm 0.7\%$ , compared to  $52.8 \pm 0.4\%$  in the wood mixture of these species. Lower cellulose values in bark compared to wood are more credible due to the high content of lignin and substances soluble in 1% NaOH, which were reported as 55.4% and 36.8%, respectively, for southern pine bark (Sproull and Pierce 1963). A lower cellulose content than in normal wood fibers can also be expected in wood ray cells—due to their higher lignin content—and in the fibers and ray cells of compression wood (the reaction wood of softwoods) (Hoffman and Timell 1972). On the other hand, tension wood (the reaction wood of deciduous trees) contains more of this biopolymer than normal wood fibers (*e.g.*, 57.3% vs. 44.0% in *Eucalyptus goniocalyx*) (Timell 1967).

### Plant Cellulose (PC) Content in Non-wood Plants

The PC content in wheat, oat, barley, rye, and rice straw ranges from 34.0% to 53.7% (Naffzinger *et al.* 1959; Edelmann *et al.* 2000; Vargas *et al.* 2012; Rodriguez *et al.* 2008; Ateş *et al.* 2015). Esparto grass and switchgrass (*Panicum virgatum*) contain 33.0% to 47.8% (Foster 1967; Nieschlag *et al.* 1960; Nadji *et al.* 2006) and 32.9% to 43.4% cellulose, respectively (Radiotis *et al.* 1999; Ververis *et al.* 2004; Keshawani and Cheng 2009; Madakadze *et al.* 2010). Meanwhile, reeds such as *Phragmites* and *Arundo donax* contain 29.3% to 52.6% of this substance (El-Taraboulsi 1961; Rodriguez *et al.* 2008; Nieschlag *et al.* 1960; Ateş *et al.* 2015). A broad range of cellulose content, from 36.5% to 49.2%, is also reported for bagasse (Knapp *et al.* 1957; Dugal 1976; Prieto *et al.* 1987; El-Sakhawy *et al.* 1995; Edelmann *et al.* 2000; Fišerová *et al.* 2006), and bamboo (26% to 54%) (Foster 1967; Fišerová *et al.* 2006; Khristova *et al.* 2006).

Oilseed flax straw contains 37.7% PC (Naffzinger *et al.* 1959), while kenaf contains 36.0% to 59.5% of it (Clark *et al.* 1962; Bajwa and Toor 1979; Saikia *et al.* 1997; Khristova *et al.* 1998; Ververis *et al.* 2004). Hemp exhibits a PC content of 43.0% to 60.1% in stalks, 31.5-47.3 in woody-core and 53.2 to 69.7% in bast (Kovacs *et al.* 1992; Danielewicz and Surma-Ślusarska 2010; Fišerová *et al.* 2013; Danielewicz 2023).

*Miscanthus* is an example of a plant cultivated for energy purposes that is also being considered for use in papermaking. The most extensively studied varieties are *Miscanthus x giganteus* and *Miscanthus sinensis* (Arnoult *et al.* 2015). The reported PC content in the stalks of these plants ranges from 35.5% to 52.1% (Nieschlag *et al.* 1960; Cappelletto *et al.* 2000; Ververis *et al.* 2004; Marin *et al.* 2009; Villaverde *et al.* 2010; Brosse *et al.* 2012; Garcia *et al.* 2014; Joachimiak *et al.* 2019).

In the textile, plastics, and papermaking industries, fibers extracted from specific anatomical parts of certain non-woody plants are often used to produce specialty papers. These include bast fibers from flax, hemp, jute, and ramie, as well as abaca and sisal leaf fibers. Between 2003 and 2005, the global production of these fibers amounted to approximately 0.08, 0.09, 2.7, 0.15, 0.08, and 0.3 million tons, respectively (Siqueira *et al.* 2010). These technical fibers contain significantly more PC than wood or the whole stems of non-woody plants, with contents of 64.1% to 81.0%, 65.0% to 78.0%, 58.0% to 72.0%, 68.6% to 86.0%, 52.4% to 70.0%, and 65.8% to 73.0%, respectively (Timell 1957; Popa and Breaban 1995; Peralta 1996; Bledzki and Gassan 1999; Cuissinat and Navard 2008). The highest amount of PC among all papermaking raw materials—ranging from 79% to 99%, depending on the purity of the raw material—is found in cotton seed fibers. These

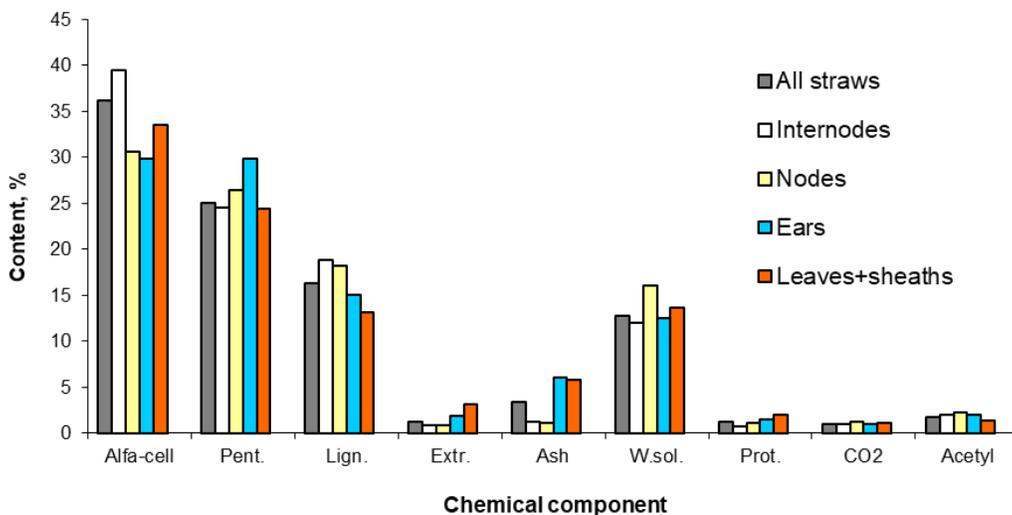
occur in two forms: lint and linters (Omar *et al.* 1960; Popa and Breaban 1995; Bledzki and Gassan 1999; Cuissinat and Navard 2008).

The wide ranges of PC content in the fibrous raw materials listed above, beyond differences inherent to the plant species, may also result to a significant extent from the analytical methods used to determine this component and its degree of purification from hemicelluloses and ash. For this purpose, several methods can be employed, including the Kürchner-Hoffer, Cross-Bevan, Seifert, monoethanolamine,  $\alpha$ -cellulose, peroxyacetic acid, and nitric-acetic acid methods (Wright and Walls 1998).

For example, Knapp *et al.* (1957) report that for the bamboo varieties *Oxytenanthera abyssinica* and *Bambusa vulgaris*, the cellulose content determined by the Kürchner-Hoffer method was 47.0% to 62.4%. In contrast, results obtained using the Cross-Bevan and monoethanolamine methods were 65.6% and 56.7% to 70.7%, respectively, which are considered quite high.

The results obtained by the Seifert method are typically lower than those from the other mentioned methods because, as noted by Wright and Walls (1998), this procedure yields one of the purest forms of cellulose. For instance, these authors report that the cellulose content in *Eucalyptus nitens* determined by the nitric-acetic acid method (a modification of the Kürchner-Hoffer method) is 46.7%, whereas the Seifert method yields a value of 40.0%. The lowest reported PC values in non-wood raw materials, such as approximately 35%  $\pm$  2%, likely correspond to the  $\alpha$ -cellulose content, determined using methods such as TAPPI T 203 om-88 (formerly sm-44) following prior conversion to holocellulose (Knapp *et al.* 1957; Fišerova *et al.* 2006).

Such low values of  $\alpha$ -cellulose content—averaging 36.2% in the whole stalks of rye, oat, and wheat straw (indicated by the grey “all straws” bar in Fig. 4)—may result from the low concentration of this biopolymer in the nodes (30.6%) and spikes (29.8%). Additionally, this can be attributed to the higher content of ash, extractives, and insoluble proteins in the spikes (panicles) and leaves/sheaths compared to the internodes and nodes of these straws (Fig. 4) (Muller 1960).



**Fig. 4.** Average content values of  $\alpha$ -cellulose, pentosans, lignin, ether extractives, insoluble ash, water-soluble substances, insoluble proteins, carbon dioxide (representing uronic acids), and acetyl groups for various straws and their anatomical parts (internodes, nodes, spikes/panicles, leaves + sheaths). The data include tetraploid rye, rye grown on sandy and peaty soils, oats grown on sandy, silty, and peaty soils, as well as spring and winter wheat (Muller 1960).

Such low concentrations of these chemical components in non-wood raw materials can result in lower pulp yields when conventional pulping methods are used. In such case, it is common practice to separate anatomical parts with low  $\alpha$ -cellulose content—such as the spikes (panicles), leaves, and sheaths of cereal straws, or the pith in the case of bagasse.

Nevertheless, non-wood fibrous raw materials can be distinguished into four basic groups based on their cellulose content:

- Group 1: Straw from grasses and reeds, exhibiting the lowest PC content.
- Group 2: Whole stalks (straw) from bast plants, showing a slightly higher cellulose content than that of group 1.
- Group 3: Technical bast fibers (extracted from bast plants) and leaf fibers, with a PC content ranging from 58% to 86%.
- Group 4: Cottonseed fibers, which possess the highest PC content (79% to 99%).

### Properties

The versatility of PC for various industrial applications can be attributed to the following attributes (Surewicz 1971; Duchesne and Larson 1989; Kamel *et al.* 2008; Kalia *et al.* 2009):

- It is a renewable biopolymer derived from sustainable biological sources and is biodegradable under natural conditions.
- It is relatively inexpensive.
- It is typically white or brown/beige in unrefined form; it is naturally opaque but can become more transparent after advanced modification.
- It is odorless and generally biologically neutral.
- It has a semi-crystalline (crystalline–amorphous) polymeric structure.
- It possesses the ability to bind together through wetting, pressing, and drying.
- It is structurally modifiable.
- Its mechanical properties depend on its physical form (e.g., fiber length or cellulose particles of reduced size generated from fibrous PC).
- Although it is opaque in its normal state, it can be relatively easily modified to increase its translucency.
- While naturally hydrophilic, it can be chemically or physically modified to achieve water resistance.
- Its surface activity allows for easily deposition and anchoring of various solid particles.
- It is insoluble in water, dilute acids, dilute alkalis, and most organic solvents, yet it can be dissolved in strong acids and certain specific solvents.
- It is chemically and surface-modifiable.
- It can be readily converted into monomeric form.
- It has limited resistance to elevated temperatures and is inherently flammable.
- In its dry state, it exhibits excellent electrical insulation properties.

#### *Dissimilarity to synthetic polymers*

One of the most significant characteristics of PC is its natural origin, renewability through plant growth, and wide global availability. These attributes make it a crucial resource for future industrial applications within a sustainable economic framework. Other properties that distinguish PC from synthetic polymers include its relatively lower cost in

many cases; lower density, and its availability in the form of thick sheets, which can be readily converted into aqueous suspensions, in contrast to synthetic polymer granulates. Moreover, PC is compatible with substances of natural origin, fully biodegradable, and does not emit as large an amount of harmful gases during disposal as synthetic polymers. The features that distinguish PC from synthetic polymers are also its internal structure stabilized by hydrogen bonding, broader possibilities for modification in particle form, its non-thermoplasticity, and much greater ability to stain (Surewicz 1971).

#### *Similarity to synthetic polymers*

Plant cellulose (PC) is one of the few natural materials that exhibits a polymeric (macromolecular), semi-crystalline structure similar to that of synthetic polymers. According to Ioelovich (2008), the degree of crystallinity of PC in kraft pulps is approximately 62 to 65%, while in unrefined and refined chemically cotton fibers it is about 68 to 69% and 70 to 72%, respectively. These values show similarities to some synthetic polymers, such as polyethylene, polypropylene, polyamide, and polyethylene terephthalate (PET). For example, Kaczmarek *et al.* (2017) reported the degree of crystallinity of polypropylene to be approximately 55%. PC also shows similarities to synthetic polymers in terms of color. After production, it is typically brownish-beige or white. Similarly, many synthetic polymers are naturally white or milky [*e.g.*, polyethylene, polypropylene, polystyrene, polytetrafluoroethylene (Teflon), and PVC] or may exhibit slightly creamy or yellowish hues (*e.g.*, polyamides), yellowish-brown to dark brown coloration (*e.g.*, phenolic resins), pale yellow tones (*e.g.*, polyurethanes), or yellow to amber shades (*e.g.*, epoxy resins).

#### *Good felting/matting ability*

As mentioned above, PC fibers have a natural ability to bond with each other through wetting, pressing, and drying. This property significantly facilitates the manufacturing of industrial products using this fibrous intermediate. The strength of created inter-fiber bonding depends on the fiber flexibility, hemicellulose content, susceptibility to cell wall collapse, and the development of the external surface area (Rance 1953; Chase 1960). For example, cotton linter fibers, rag pulp fibers, and unbeaten virgin papermaking pulps tend to bond with relatively low strength (Rance 1953; Centola *et al.* 1961; Fišerová and Gigac 2011). In its most common commercial form—paper—PC exhibits a tensile index in the range of 20 to 100 N·m/g, which corresponds to a tensile strength of approximately 15 to 73.5 MPa (Fišerová and Gigac 2011; Latka 2024). These values are limited by the presence of voids within the paper network (bulk of paper structure) and the individual strength of the fibers (McKenzie 1978).

#### *Structural modifiability*

Although the spindle-shaped, tubular morphology and heterogeneous internal structure of PC make it well suited for the production of paper, cardboard, and various insulating or absorbent materials, these characteristics can pose significant challenges in other industrial sectors. Many applications require materials with higher density, greater structural uniformity, improved surface finish, and greater strength. These requirements can be met by exploiting the inherent densification capability of PC through pressing its sheets (*e.g.*, as in the production of pressboards from single-layer board) and by utilizing the ability of PC to undergo vulcanization (as in the production of vulcanized fiber materials); as well as its ability to be mechanically or chemomechanically fragmented into

particles with dimensions on the order of several parts of a millimeter (microcrystalline cellulose, MCC), several thousandths parts of a millimeter (microfibrillated cellulose, MFC), and even millionths parts of a millimeter (nanofibrillated cellulose, NCF, and cellulose nanocrystals, CNC).

Pressboard materials are produced from wet PC sheets by drying them in continuous or batch drying presses at pressures of 150 kgf/cm<sup>2</sup> or higher and temperatures of 120 to 140 °C, resulting in densities of, for example, 1.15 to 1.35 g/cm<sup>3</sup> (Sawicki 1952). Treatment of PC sheets (e.g., 120 g/m<sup>2</sup>) with a concentrated aqueous ZnCl<sub>2</sub> solution (e.g., 68% concentration, 30 to 60 °C) for 30 s, followed by stacking, pressing, removal of ZnCl<sub>2</sub> by rinsing, and drying at 80 °C, yields a strong and rigid industrial material. The physical properties of this material in many respects resemble those of plastic laminates based on resin–paper systems (Lee 1964; Scholz *et al.* 2016).

For fragmenting of PC into finer particles hydrolytic–mechanical methods are particularly noteworthy; however, their application is typically associated with a significant reduction in the degree of polymerization (DP) of PC, which leads to a decrease in its overall mechanical strength, as for example in the case of MCC and cellulose powders (Caulfield and Steffes 1969). Interestingly, the strength of materials produced from PC can increase markedly—reaching approximately 100–1000 MPa—after its conversion into nanofibrillated cellulose (NFC), also known as cellulose nanofibers (CNF), or nanocrystalline cellulose (NCC), more commonly referred to as cellulose nanocrystals (CNC) (Duchesne and Larson 1989; Henriksson *et al.* 2008; Chamberlain 2017; Shaghaleh *et al.* 2018; Meng and Wang 2019).

### *Modifiable opacity*

Historically, paper technologists addressed the unfavorable for various application opacity of paper—offering vegetable/genuine parchment paper or pergament; natural tracing paper; imitation parchment, pergamin or glassine paper; vellum paper or prepared tracing paper; cellophane, oiled papers, and waxed papers (Van der Reyden 1992; Danielewicz 2025a).

In the case of production of vegetable/genuine parchment paper a mixture of nine parts concentrated H<sub>2</sub>SO<sub>4</sub> and one part H<sub>2</sub>O was typically employed. To prevent complete disintegration of the PC, the process was brief—usually lasting 3 to 12 seconds—followed immediately by rapid washing. This treatment converted the outer layers of the PC fibers into a viscous mass, historically referred to by some researchers as “amyloid.” This substance binds the fibers and fills the interfiber voids within the sheet, resulting in airtight vegetable/genuine parchment paper upon drying (Marchlewska-Szrajderowa 1953). It is now established that “amyloid” consists of weakly crystallized cellulose II (Cartier *et al.* 1984) and that the dehydrating properties of concentrated H<sub>2</sub>SO<sub>4</sub> play a key role in compacting the paper structure (Clark 1984). The term “amyloid” appears to have been borrowed from the starch-like granules component of many dicotyledonous plants to describe the pore-filling substance in vegetable parchment (Schreuder *et al.* 1966). The pulp used for the production of natural tracing paper is, in turn, so highly refined that the material virtually exhibits no fiber structure in cross-section. Imitation parchment, pergamin, or glassine paper is produced from pulp that is highly fibrillated and partially “gelatinized” through prolonged beating and subsequently highly compressed by calendaring. Vellum paper and prepared tracing paper are produced from cotton pulp, to which translucency is imparted by filling or coating with transparentizing agents. The transparency of PC can also be increased by impregnation with oils and waxes.

Regarding transparentizing agents for PC, Van der Reyden describes aromatic solvent-based synthetic resins, styrene, and cellulose esters as examples of substances that can be used for this purpose. A number of these substances were tested by Vaurio (1960). For example, the introduction of chemicals from the groups of dioctyl phthalate-tricresyl phosphate, tricresyl phosphate, and cresyl diphenyl phosphate enabled paper light transmittance values of 69 to 78%, 79 to 82%, and 77 to 80%, respectively.

Although abovementioned PC-based materials are more transparent than the conventional paper products, nevertheless, they exhibit several significant drawbacks that often limit their application. These include susceptibility to mechanical damage and creasing, hygroscopicity (*i.e.*, the absorption of water vapor and liquid water) (Van der Reyden 1992), surface irregularities, and a porous structure (Zhu *et al.* 2014). One possible solution to these issues is the use of PC in nanoscale form, such as nanofibrillated cellulose (NFC), for the production of transparent paper. However, in this case, the main challenge lies in the difficulty of rapid industrial-scale manufacturing of such materials, resulting from the fine dimensions of its particles as well as their slow dewatering rate on the special wire.

#### *High hydrophilicity*

The hydrophilicity of PC results from its physical structure—specifically the presence of capillaries (El-Hosseiny *et al.* 1979)—as well as its chemical characteristics, namely the abundance of polar hydroxyl groups and their ability to form hydrogen bonds with water molecules. This feature is beneficial for absorbent paper products and microcrystalline cellulose (Steege *et al.* 1978). However, it is disadvantageous for the production rate (due to slow drying) of products made from PC suspensions and negatively affects the strength of these products when they are used in high-humidity conditions or in direct contact with water. It also impacts resistance to microorganisms, the maintenance of low thermal conductivity, and the use of PC in hydrophobic composites with thermoplastics, where cellulose swelling within the matrix remains a challenge (Kalia *et al.* 2009). To address this issue, various methods have been developed to reduce the water absorption of PC. These include the deposition of sizing agents (*e.g.*, rosin) on its surface or the blocking of hydroxyl groups with reactive sizing agents such as alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA). Despite these treatments, traditional protection is often insufficient for advanced applications. Consequently, new methods are being developed to render PC superhydrophobic, mimicking natural surfaces such as butterfly wings or lotus leaves (Song and Rojas 2013). On such materials, the water contact angle exceeds 150°. These advanced techniques include coating PC with waxes, silicones, or fluorinated organic compounds, as well as applying nanoparticles (SiO<sub>2</sub>, ZnO, Ag, CaCO<sub>3</sub>, TiO<sub>2</sub>) followed by treatment with silicones (*e.g.*, octyltriethoxysilane) or fluorinated compounds (*e.g.*, perfluorodecyltrichlorosilane). Another approach involves the partial substitution of hydroxyl groups in amorphous regions (*i.e.*, chemical grafting) with silicone polymers, hydrocarbon polymers, fluorinated substituents, maleated polypropylene (MAH-PP), or isocyanate groups (Sawatari *et al.* 1998; Jiang *et al.* 2005; Kalia *et al.* 2009; Song and Rojas 2013).

#### *Surface charge and absorption*

An interesting aspect of PC that offers numerous possibilities for its modification is its ability to be finely dispersed in water and to enable the coating of all dispersed particles (fibres) with various substances by manipulating its surface charge, in order to

achieve electrostatic attraction. This phenomenon arises from the presence of hydroxyl groups and negatively charged carboxyl groups of hemicelluloses in PC, as well as from its ability to shift its surface charge—the so-called zeta potential—to more positive values through the adsorption of cationic polymeric substances onto the surface. This feature of PC is extensively utilized to reduce paper production costs *via* “filling”—the incorporation of inexpensive mineral fillers into the paper matrix. Furthermore, this mechanism can be leveraged to impart specialized properties to PC by depositing chemically, biologically, or electrically active substances onto cellulose fibers (Chase 1960; Jakobson and Schmut 1964; Hubbe *et al.* 2009; Credou and Berthelot 2014).

### *Solubility*

Despite its high content of hydrophilic hydroxyl groups, PC does not dissolve in water. This behavior is attributed to the strong hydrogen bonding between cellulose macromolecules within its crystalline regions and the hydrophobic nature of part the glucose pyranose rings.

The low solubility of PC in dilute solutions of specific acidic and alkaline substances [*e.g.*,  $\text{Ca}(\text{HSO}_3)_2$ ,  $\text{Mg}(\text{HSO}_3)_2$ ,  $\text{NaHSO}_3$ ,  $\text{Na}_2\text{SO}_3$ ,  $\text{NaOH}$ ,  $\text{Na}_2\text{S}$ ] enables its separation from plant fibrous raw materials during pressurized cooking. Although PC is poorly soluble in dilute acidic and alkaline solutions, it can undergo significant physical and chemical changes when exposed to these media. Physical changes include swelling under the influence of alkalis (Denoyelle 1959)—sometimes resulting in the formation of characteristic “balloons” (Jurbergs 1960b; Kallmes 1960)—and color alterations. Chemical changes involve alkaline and acidic degradation, which reduces the degree of polymerization (DP) of the macromolecules through the hydrolysis of glycosidic bonds and the “peeling” reaction of monomeric end residues. While the depolymerization of cellulose in dilute acids and alkalis is generally unfavorable—as it compromises strength properties (dry cellulose becomes brittle at  $\text{DP} < 125$ )—it is highly beneficial for specific applications. These include the production of cellulose powders, where depolymerization facilitates processing, and the total hydrolysis of cellulose into glucose (Douglas 1950; Steege *et al.* 1978; Zhu *et al.* 2011). Glucose can then be converted into several important chemicals, such as lactic acid (LA), levulinic acid (LevA), sorbitol, and 5-hydroxymethylfurfural (5-HMF), may serve as bio-based platform chemicals for polymer synthesis (Shaghaleh *et al.* 2018).

PC can be transformed into solution when exposed to 72%  $\text{H}_2\text{SO}_4$ , 40%  $\text{HCl}$ , or 85%  $\text{H}_3\text{PO}_4$ ; however, this is primarily due to the severe degradation of cellulose macromolecules into glucose, possibly accompanied by substitution reactions (Marchessault and Rånby 1959; Schweiger 1974).

While PC dissolves in certain substances and their aqueous solutions, most of these solvents are unsuitable for industrial use due to their toxicity and environmental impact, as well as their high cost. The most well-known cellulose solvents include Schweitzer’s reagent  $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$ , cuoxam, zincoxene, nioxam, cadoxene, and cupriethylenediamine (CED) (Kleinert 1958). Other solvent systems capable of dissolving PC include (Heinze and Koschella 2005; Klemm *et al.* 2005):

- Inorganic solutions:  $\text{NaOH}$ ,  $\text{NH}_3/\text{NH}_4\text{SCN}$ , and  $\text{NaOH}/\text{CS}_2$ .
- Inorganic/organic mixtures:  $\text{N}_2\text{O}_4/\text{DMF}$ ,  $\text{LiCl}/\text{DMAc}$ , *N*-methyl-2-pyrrolidinone/ $\text{LiCl}$ ,  $\text{NaOH}/\text{urea}$ ,  $\text{NaOH}/\text{thiourea}$ , and  $\text{NaOH}/\text{ZnO}$ .
- Organic solvents: *N*-methylmorpholine *N*-oxide (NMMO).

More recently, certain ionic liquids—salts that remain in a liquid state at ambient conditions—have been shown to effectively dissolve PC (Zhu *et al.* 2006).

#### *Chemical and surface modifiability*

PC is also capable of chemical and surface modification (Madhushree *et al.* 2024). For example, the action of concentrated hydroxide solutions (8% to 20%) on PC either purifies it by removing low-molecular-weight carbohydrates (alkaline refinement), activates it, or transforms its native cellulose I structure into cellulose II—a process known as mercerization (Sarko 1978). As a result, the cellulose becomes more hygroscopic, shows better dye affinity, and is more accessible to chemical reagents reacting with hydroxyl groups. Conversely, mercerized cellulose is extremely resistant to mechanical refining—a phenomenon known as passivation—and exhibits poor solubility after acetylation (Centola *et al.* 1961).

For many years, the ability of PC to bind chemical modifiers through covalent bonds—enabled by the three hydroxyl groups in the  $\beta$ -D-glucopyranose residue—has been of immense practical importance. This reactivity allows for the production of several widely used cellulose derivatives with unique properties. Notable examples include:

- Methylcellulose [world production (WP) in 2001: 150,000 t/y]
- Ethyl cellulose (WP: 4,000 t/y)
- Carboxymethyl cellulose (WP: 300,000 t/y)
- Nitrocellulose (WP: 200,000 t/y)
- Hydroxyethyl cellulose (WP: 50,000 t/y)
- Cellulose acetate (WP: 900,000 t/y)

Additionally, numerous other lesser-known derivatives with specific functional properties have been developed (Goheen 1958; Ward 1960; Rahn *et al.* 1996; Heinze and Libert 2001; Kamel *et al.* 2008; Kuznetsov *et al.* 2015; Moral *et al.* 2017; Patil *et al.* 2022; Aziz *et al.* 2022; Etale *et al.* 2023; El Bourakadi *et al.* 2024; Madhushree *et al.* 2024). Some of these derivatives can also be obtained by grafting synthetic polymer chains onto PC or paper products to impart advanced functionalities (Phillips *et al.* 1972).

Regarding the surface modification of PC, both conventional and advanced methods can be employed. Conventional methods include the above-mentioned treatments with concentrated sulfuric acid, concentrated  $ZnCl_2$ , and surface deposition. As for advanced methods, for instance, it has been reported that jute fibers subjected to hot water immersion followed by a 10 min corona discharge treatment exhibited an approximately 34% increase in adhesion strength compared to untreated fibers. This corona pretreatment improves fiber-matrix adhesion by activating the surface and increasing fiber roughness (Campomori *et al.* 2024). Furthermore, inert argon plasma treatment of oxidized cellulose induces significant changes in the chemical composition and morphology of its surface layers. Importantly, such modifications maintain or even enhance the antibacterial properties and hemostatic functions of the oxidized cellulose (Vosmanska *et al.* 2014). Similarly, UV irradiation improves the dye absorption and surface polarity of PC fibers (Madhushree *et al.* 2024), while gamma irradiation can positively affect the properties of PC composites with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) (Lenfeld *et al.* 2020). Some authors also indicate the possibility of a significant increase in the tensile strength of kenaf PC—rising from approximately 300 to 500 MPa—as a result of thermal treatment in a vacuum heater at 140 °C for 10 h (Cao *et al.* 2007). Another study highlights the potential of biological pretreatment using laccase (*e.g.*, Maximize 2540, Buckman) to

enhance the strength of recycled PC, increasing the Concora Medium Test (CMT) and Ring Crush Test (RCT) indices by 4.1% and 9.6%, respectively (Denowski 2012).

#### *Controlled depolymerization*

PC is a substance that can be broken down into its monomer substance, i.e. glucose, in a controlled manner under relatively mild conditions. In the natural environment, this undergoes through enzymatic hydrolysis. Under industrial conditions, this degradation can be initiated similarly *i.e.*, by the action of these biocatalysts or by exposure to concentrated mineral acids. This susceptibility to degradation is a significant advantage for the biorefinery industry, as it enables the transformation of PC into a solution of monosaccharides (glucose), which can then serve as a versatile feedstock for the production of biochemicals and biofuels (Douglas 1950; Alvira *et al.* 2010; Palme *et al.* 2016; Antczak *et al.* 2019).

#### *Thermal stability and breakdown*

PC is a material with limited resistance to elevated temperatures and is relatively flammable. The effect of heating cellulose at relatively low temperatures (*e.g.*, 100 °C) depends significantly on the exposure time. Short-term heating does not cause immediate degradation but leads to a decrease in the absorbed water content and a slight reduction in brightness (Croon *et al.* 1966). Heating also reduces its swelling capacity, leading to a phenomenon known as hornification, which reflects distinct changes in its capillary structure (Weise 1998). Prolonged heating at temperatures above 100 °C can result in a reduction in the degree of polymerization (DP), the loss of chemical water (*e.g.*, through the transformation of hydroxyl groups into keto groups), and darkening of the material (Matsuo *et al.* 2012). While these changes progress relatively slowly, visible signs of PC decomposition, such as slight darkening and brittleness, can be observed at approximately 120 °C. At temperatures exceeding 150 °C, chemical water begins to slowly dissociate from the cellulose chains—a process that peaks around 300 °C (Scheirs *et al.* 2001; Xing *et al.* 2023). Under these conditions, PC is converted into “dehydrocellulose.” Gašparik *et al.* (2024) reported that the overall cellulose content in beech wood heated between 140 and 210 °C does not decrease. However, examining the DP of cellulose after heating, they found a slight increase at 140 to 150 °C (from 2762–3006 to 3029–3303). This may be attributed to the hydrolysis of shorter cellulose chains, likely within the amorphous regions. This hypothesis is supported by an increase in the crystallinity index (CrI/LOI). When the temperature was further increased to 160 to 190°C for beech PC, its DP significantly decreased to a range of 1535 to 1747, dropping further to the range of 427 to 962 after heating at 210 °C.

PC heated to above 300 °C begins to undergo rapid thermal degradation, resulting in the formation of tar (a mixture of liquid compounds), gas (a gaseous mixture), and char (solid residues) (Yang *et al.* 2007; Wang *et al.* 2022). In addition to carbon, charred cellulose contains cross-linked carbon skeletons with a high concentration of aromatic rings (Nomura *et al.* 2021). The liquid substances formed by the thermodecomposition of PC, known as pyrolysis oil or bio-oil, primarily consist of levoglucosan, 5-hydroxymethylfurfural (5-HMF), furfural, hydroxyacetone, hydroxyacetaldehyde, and various C<sub>1</sub>–C<sub>2</sub> compounds, along with other organic substances in smaller quantities. Conversely, the primary products of cellulose gasification are CO, CO<sub>2</sub>, C<sub>x</sub>H<sub>y</sub>, and H<sub>2</sub> (Arseneau 1971; Broido and Nelson 1975; Shen and Gu 2009). According to a study by

Shen and Gu (2009), the following yields of tar, char, and gas can be produced by heating PC at 420 to 730 °C for a residence time of 0.44 s.

**Table 1.** The Yield of Tar, Char, and Gas from the Gasification of Cellulose Under the Different Temperature and Residence Time 0.44 s

Component	420 °C	470 → 530 °C	580 → 730 °C
	wt. %		
Tar	30.60	60.90 → 68.90	72.20 → 56.60
Char	47.44	13.51 → 7.34	2.55 → 1.03
Gas	20.10	24.80 → 26.40	27.30 → 42.50

It has also been established that the optimal temperature for bio-oil production from cellulose is approximately 500 °C. Furthermore, studies have shown that cellulose contributes more significantly to bio-oil and CO formation than hemicelluloses, whereas the latter are the primary contributors to biogas and CO<sub>2</sub> formation. Regarding the composition of the liquid fraction, cellulose-derived bio-oil is characterized by unique saccharides and a higher concentration of furans, while hemicellulose-derived bio-oil contains higher levels of acids and ketones (Zhao *et al.* 2017).

Pyrolysis of PC typically occurs with limited oxygen access. However, if oxygen is available in sufficient quantities, the primary products of combustion are CO<sub>2</sub> and H<sub>2</sub>O. This clean combustion profile is considered a significant environmental advantage over synthetic polymers, which often release toxic by-products.

The relatively low thermal stability of PC limits its use in various applications, particularly as a reinforcing component in thermoplastic composites that require processing temperatures exceeding 250 °C. However, its thermal resistance can be enhanced through chemical modifications, such as phosphorylation (Madhushree *et al.* 2024), cyanoethylation and hydroxyethylation (Ward *et al.* 1969), benzylation and esterification (Agustin *et al.* 2018), grafting with TiO<sub>2</sub>@SiO<sub>2</sub>-alkyl-NH<sub>2</sub> (Torkian *et al.* 2024), or silylation (Zhang *et al.* 2016; Madhushree *et al.* 2024).

#### *Electrical conduction*

From an electrical perspective, PC is classified as an excellent insulating material. Electrical conduction in PC-based paper typically results from electron mobility within the aqueous phase (the content of which may vary widely), ionic conduction from residual ions (Buck and Winczakiewicz 1959; Vittins 1960; Hanneson *et al.* 1971), or space-charge buildup within the bulk material, leading to space-charge-limited leakage currents (Hanneson *et al.* 1971). For example, a capacitive PC tissue (with a sample thickness of 0.35 mm) conducts a steady-state current of only 10<sup>-12</sup> to 10<sup>-10</sup> A (Hanneson *et al.* 1971). A sheet of paper made from loblolly pine latewood fibers exhibits conductivity values of 1.74×10<sup>-11</sup> and 1.07×10<sup>-6</sup> mho/cm at moisture contents of 4.6% and 15.7%, respectively (Lowe and Baum 1979) [(mho/cm is an older unit of electrical conductivity, equivalent to S/cm (Siemens per centimeter)]. In contrast, bond paper made from sulfite pulp at 12% and 60% relative humidity shows a surface resistance of 37,500 MΩ/sq and 18.8 MΩ/sq, respectively (Vaurio and Fird 1964). Interestingly, the conductivity of individual PC fibers is higher than that of the paper produced from them (*e.g.*, 1.03×10<sup>-7</sup> mho/cm vs. 6.37×10<sup>-9</sup> mho/cm) (Lowe and Baum 1979). Consequently, paper conductivity increases with density—for instance, through pressing—as demonstrated by Josefowicz and Landhear (1981).

## Applications

### *Conventional uses of PC*

Historically, the earliest use of PC involved the production of textiles from flax and hemp, followed by cotton fibers (Ranalli and Venturi 2004). After approximately 100 AD, the large-scale use of PC for papermaking became widespread as the art of papermaking diffused through Asia, North Africa, and eventually to Europe and later America. The volume of PC utilized for this purpose increased drastically with the invention of chemical pulping methods in XIX<sup>th</sup> century—soda, sulfite, and kraft—which enabled the industrial conversion of wood into papermaking pulps on a large scale.

Later, human ingenuity and advancements in the purification of PC from accompanying hemicelluloses (refining) facilitated its application in the production of regenerated fibers (*e.g.*, viscose), microcrystalline cellulose (Płonka *et al.* 1980), and various cellulose derivatives. Notable examples include carboxymethyl cellulose (Cell–O–CH<sub>2</sub>COONa, CMC), methylcellulose (Cell–O–CH<sub>3</sub>, MC), ethylcellulose (Cell–O–CH<sub>2</sub>CH<sub>3</sub>, EC), hydroxypropyl methylcellulose (HPMC), and cellulose acetate (Cell–O–CO–CH<sub>3</sub>, CA) (Barber and Ware 1957; Goheen 1958).

Common features of these cellulose derivatives include full biodegradability and non-toxicity to humans, even upon ingestion. Derivatives such as CMC, MC, HPMC, and CA are characterized by excellent film-forming abilities but exhibit poor water resistance. In contrast, EC films demonstrate significant hydrophobicity and moisture resistance (Elfawal *et al.* 2025).

PC derivatives that have been known for many years and are used commercially also include:

- Nitrocellulose, utilized as an explosive (gun cotton) and a high-performance film-forming agent in lacquers and coatings.
- Hydroxyethyl methylcellulose (H<sub>3</sub>C–O–Cell–O–CH<sub>2</sub>CH<sub>2</sub>OH, HEMC) (Klemm *et al.* 2005; Kamel *et al.* 2008; Madhushree *et al.* 2024), which efficiently thickens and provides critical water retention in construction materials such as plasters and mortars.
- Hydroxypropyl cellulose (Cell–O–CH<sub>2</sub>CH(OH)CH<sub>3</sub>, HPC), used as a thickener, emulsifier, and stabilizer in cosmetic formulations, including shampoos, conditioners, and lotions (Selvaraj *et al.* 2024).
- Phosphorylated cellulose (Cell–O–PO(OH)<sub>2</sub>), applicable in diverse fields such as orthopedics, biomedicine, textiles, and biochemical separation (Rol *et al.* 2020; Etale *et al.* 2023).

Another significant achievement in the utilization of PC was the development of form-molded pulp products (FMPP) at the beginning of the 19<sup>th</sup> century—three-dimensional structures are manufactured directly from fibrous pulp and serve as sustainable substitutes for numerous synthetic polymer products (Debnath *et al.* 2022; Danielewicz 2025b), with the most ubiquitous example being egg trays.

The advancement of PC production and refining methods, coupled with rising global paper consumption, led to a significant increase in demand for it. By 2010, 130.4 million tons of PC (as chemical pulp) were produced from lignocellulosic raw materials. The vast majority was utilized for paper and paperboard manufacturing, while approximately 5 million tons were dedicated to chemical processing (Bride 2012; Björkman 2014).

### *Alternative applications of PC for expanding its the economic utilization*

The types and applications of PC listed above represent conventional uses. Its alternative applications aimed at expanding the economic utilization of PC include:

- Thermoformed and injection-molded FMPPs, including those engineered for resistance to oil and water penetration through the application of biodegradable barrier materials (Debnath *et al.* 2022; Danielewicz 2025b).
- Novel cellulose derivatives.
- Advanced composites incorporating PC and natural substances and synthetic materials.
- PC immobilized with a range of functionalizing agents, including metal and metal oxides particles, semiconductor nanocrystals (quantum dots), carbon nanoparticles, biomolecules, and polymers.
- Lightweight porous materials offering high surface area, shock-absorbing, and insulation properties.
- Micro- and nano-structured materials, including those produced using shredded PC into cellulose powders, microfibrillated cellulose (MFC), nanofibrillated cellulose (CNF), or nanocrystalline cellulose (CNC) forms, as well as composites reinforced with these particles.
- Bio-refinery products, specifically bio-oil and glucose derived from the controlled degradation of cellulose for the production of platform chemicals and second-generation biofuels.

### *Advanced FMPPs*

The advancement of thermoforming and injection molding techniques represents a significant breakthrough in the production of FMPPs. These methods enable the manufacturing of thinner products with higher geometric complexity and well-defined edges. Furthermore, the application of various bio-based coating formulations, derived from natural substances, ensures that these refined FMPPs remain fully biodegradable while gaining the necessary barrier properties (Debnath *et al.* 2022; Danielewicz 2025b).

### *Specialized derivatives*

Regarding other specialized PC derivatives, the following are of increasing research and industrial interest:

- Aminated cellulose (Cell-NH-R) (El Bourakadi *et al.* 2024; Madhushree *et al.* 2024).
- Benzylated cellulose (Cell-O-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>) (Goheen 1958; Patil *et al.* 2022).
- Carbanilated cellulose (Cell-O-CO-NH-R) (Aziz *et al.* 2022; El Bourakadi *et al.* 2024).
- Cationized cellulose (Cell-O-R<sup>+</sup>) (Moral *et al.* 2017; Etale *et al.* 2023).
- Cyanoethylated cellulose (Cell-O-CH<sub>2</sub>CH<sub>2</sub>CN) (Goheen 1958).
- Oxidized cellulose (Kamel *et al.* 2008).
- Organosulfonated cellulose (*e.g.*, sulfoethyl cellulose, p-toluenesulfonated cellulose) (Rahn *et al.* 1996).
- Silylated cellulose (Cell-O-SiR<sub>3</sub>) (El Bourakadi *et al.* 2024).
- Sulfated cellulose (Cell-SO<sub>3</sub>Na) (Kuznetsov *et al.* 2015).
- Thiolated cellulose (Cell-O-CO-CH(SH)-CH<sub>2</sub>-COOH) (Etale *et al.* 2023).

- Polymer-grafted cellulose incorporating various synthetic or natural side chains (Etale *et al.* 2023; Madhushree *et al.* 2024).
- other derivatives.

These PC derivatives are characterized by a wide range of specific properties. For instance, aminated cellulose imparts alkaline, hydrophilic, and cationic characteristics to the material. These modifications enhance its structural diversity and reactivity, enabling various functional applications in adsorption products, antibacterial materials, catalysis, and proton conduction (Zhang *et al.* 2024). The introduction of benzyl groups makes the cellulose surface hydrophobic by creating hydrophobic zones (benzyl groups) within the hydrophilic matrix (hydroxyl groups and the cellulose backbone). This modification improves the material's compatibility with synthetic polymers and reduces its thrombogenicity (Patil *et al.* 2022). Furthermore, benzylated cellulose exhibits enhanced elasticity and thermoplasticity (Goheen 1958). Cellulose carbamate is recognized as a bio-based, environmentally friendly alternative to petroleum-based polymers. It features excellent solubility in aqueous alkali and possesses high spinnability, making it suitable for fibers production (Xiong *et al.* 2017). In contrast, cellulose tricarbamate (CTC) has emerged as the preferred derivative for determining the molecular weight distribution (MWD) of cellulose *via* high-performance size exclusion chromatography (HPSEC) due to its high stability (Aziz *et al.* 2022). The cationization of cellulose introduces a positive charge to its surface, significantly improving its accessibility to anionic molecules and facilitating targeted functionalization for various applications (Negi 2025). Cyanoethylated PC is reported to show no loss in strength even after 12 weeks of soil burial, alongside improvements in heat resistance, acid resistance, and dyeability (Goheen 1958). Kamel *et al.* (2008) noted that oxidized fabrics (such as gauze and cotton) swell and become translucent and gelatinous upon contact with blood. These materials are utilized in various surgical procedures through direct application to oozing surfaces to achieve a hemostatic effect. Due to its enhanced acidity, oxidized cellulose is used in medicine to create unfavorable conditions for the growth of bacteria and fungi, such as *Staphylococcus epidermidis*, *Bacillus licheniformis*, *Rhizopus oryzae*, *Candida albicans*, and *Candida tropicalis* (Vytrasova *et al.* 2008; Zhang *et al.* 2008). It was also established that a 150% increase in fiber charge due to the oxidation of PC enhanced the dry and wet tensile indices of paper handsheets (made from bleached hardwood kraft pulp) by 30% to 200% (Saito and Isogai 2005). Furthermore, these celluloses can form thixotropic aqueous dispersions, making them suitable for novel film-forming systems. Such systems serve as carriers for bioactive compounds in cosmetic, pharmaceutical, agricultural, and consumer applications (Kamel *et al.* 2008). Sulfoethyl cellulose is a water-soluble and strongly acidic cation exchanger. It is used as a chromatographic adsorbent for inorganic ions, in the preparation of polyelectrolyte–surfactant complex membranes, and as an additive in gypsum and cement compositions. Additionally, it serves as a major component in aqueous formulations for the surface treatment of paper and paperboard or as a superabsorbent material (Zhang *et al.* 2011). Silylated cellulose exhibits increased hydrophobicity, enhanced tensile strength, higher absorption capacity for certain organic solvents and oils, and improved thermal resistance (Madhushree *et al.* 2024). Finally, cellulose sulfates find applications across various industries as thickeners, sorbents, and ion-exchange materials, particularly in biotechnological and medical fields (Kazachenko *et al.* 2023).

### *PC-based composites*

Composites of PC with thermoplastic polymers, such as PE, PP, and PVC (Kalia *et al.* 2009) [often referred to as biocomposites, ecomposites, or natural fiber-reinforced composites (NFRCs)], composites of PC (microfibrillated) with mineral fillers (GCC, PCC, talc, kaolin) (Skuse *et al.* 2018), and all-cellulose composites” (ACCs) (Wittmar *et al.* 2025), are subjects of extensive research aimed at developing materials with novel characteristics.

Regarding the challenges in the field of composites of PC with thermoplastic polymers, it has been established that a lack of strong interfacial adhesion, the low thermal stability of fibers, and poor moisture resistance can limit the attractiveness of NFRCs. However, it was found that the pretreatment of natural fibers prior to composite fabrication significantly enhances their performance by cleaning the fiber surface, introducing chemical modifications, reducing moisture absorption, and increasing surface roughness. Among various pretreatment techniques, graft copolymerization and plasma treatment have yielded particularly promising results. For instance, graft copolymerization of natural fibers with vinyl monomers significantly improves the interfacial adhesion between the synthetic polymer matrix and the fibers, leading to enhanced mechanical properties (Kalia *et al.* 2009).

PC/filler composites are produced when pulp and mineral fillers are co-processed in an aqueous suspension. In this process, the mineral acts as a grinding aid within industrial milling equipment, facilitating the cost-effective production of cellulose fibrils. Research indicates that the integration of mineral-microfibrillated cellulose (MFC) composites into fiber-based applications generally enhances both wet and dry mechanical properties. This approach offers significant opportunities for cost reduction, properties optimization, and the development of high-performance paper grades (Skuse *et al.* 2018). Similarly, composites of precipitated calcium carbonate (PCC) and cellulose nanofibrils (CNF) obtained through a co-refining process have shown remarkable results. It was reported that the tensile index of cellulosic paper containing a PCC/CNF composite increased by 44.5% compared to paper filled with PCC alone (Song *et al.* 2022).

As for the ACCs, the following fabrication methods can be used (Wittmar *et al.* 2025):

- Wet-mixing cellulose particles with PC pulp, followed by sheet formation and hot pressing.
- Partial dissolution of the PC reinforcement matrix, cellulose regeneration, and finally hot pressing to form the final composite.
- The complete dissolution of cellulose or a similar biopolymer in an adequate solvent system, followed by the impregnation of a cellulose reinforcement material (fibers or fabrics), cellulose regeneration, and finally hot pressing.

Wittmar *et al.* (2025) report that very high tensile modulus values of ~2.8 GPa and ~3.3 GPa were recorded for the composites obtained by the impregnation of a cotton textile with pure ionic liquids 1-ethyl-3-methylimidazolium acetate. In comparison, composites obtained by the impregnation of the reinforcement textiles with a diluted solution of a similar cellulose biopolymer, namely chitosan, were less hydrophilic.

### *Deposition of functional materials onto PC*

There is also a significant perspective for developing novel commercial products by the deposition/immobilization of functional substances onto PC, including (Credou and Berthelot 2014; Agarwal and Csóka 2018):

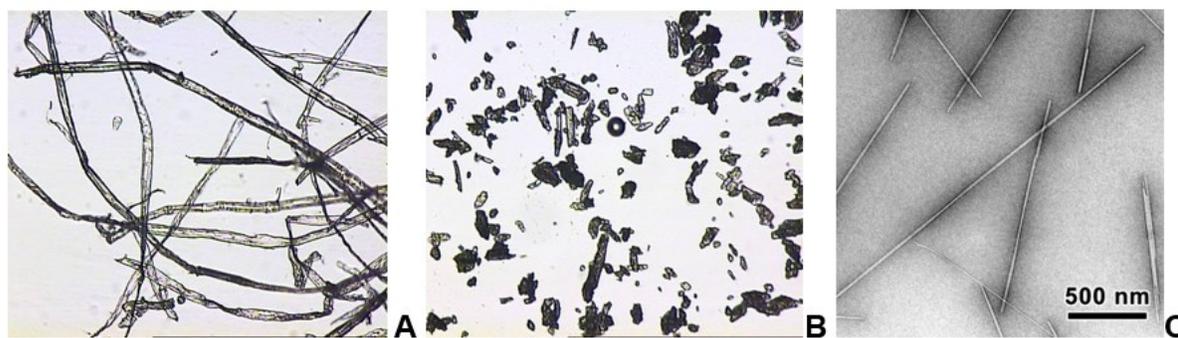
- Metallic nanoparticles: such as silver (Ag), gold (Au), platinum (Pt), palladium (Pd), copper (Cu), and cobalt (Co).
- Metal oxides nanoparticles: including oxides of titanium (TiO<sub>2</sub>), zinc (ZnO), iron (Fe<sub>x</sub>O<sub>y</sub>), and silicon (SiO<sub>2</sub>).
- Carbon nanomaterials: such as carbon nanotubes (CNTs), fullerenes, graphene, and graphene oxide (GO).
- Quantum dots and other semiconductor nanocrystals.
- Biomolecules: including enzymes, antibodies, bacteriophages, aptamers, and various protein-ligand complexes.
- Functional polymers: such as polypyrroles, polyethyleneimine (PEI), poly(methyl methacrylate) (PMMA), polystyrene, and polyaniline (PANI).

These modifications of PC enable the development of highly innovative products across various sectors:

- Antimicrobial materials: for applications such as advanced wound dressings and accelerated-healing scaffolds (Mirgorod *et al.* 2019).
- Catalytic and photocatalytic systems:
  - Chemical catalysts: *e.g.*, PC coated with MnO<sub>2</sub> nanoparticles for the catalytic decomposition of formaldehyde (Zhou *et al.* 2011).
  - Photocatalysts: *e.g.*, TiO<sub>2</sub> nanoparticle-loaded carbon fibers deposited on PC for the degradation of methyl orange (Zhang *et al.* 2013).
  - Biocatalysts: *e.g.*, biocatalytic fibers produced by the covalent immobilization of glucose oxidase from *Aspergillus niger* onto PC fiber surfaces (Vega Erramuspe *et al.* 2016).
- Adsorbents for environmental remediation: used for the removal of heavy metal ions, such as Pb<sup>2+</sup> and Cu<sup>2+</sup>, utilizing PC immobilized with TiO<sub>2</sub> (Li *et al.* 2015).
- Electronic and energy storage devices: including paper-based photoconductive ultraviolet (UV) sensors (Gimenez *et al.* 2011), piezoelectric strain sensors (Gullapalli *et al.* 2010), glucose sensors (Li *et al.* 2015), rechargeable batteries (Ferreira *et al.* 2010), and supercapacitors (Liu *et al.* 2012).
- Advanced sensing technologies:
  - Physical sensors: *e.g.*, paper-based humidity sensors (Han *et al.* 2012) and pressure sensors (Tao *et al.* 2017).
  - Electrochemical sensors: *e.g.*, amperometric glucose sensors (Kuek *et al.* 2014).
  - Bio-detection: immunosensors (Sun *et al.* 2015), biosensors (Li *et al.* 2015), and biomarkers (Wu *et al.* 2015).
- Diagnostic and analytical tools: including immunosorbents (Peng *et al.* 2016) and immunoassays (Credou and Berthelot 2014) designed for the detection of various targets such as trinitrotoluene (TNT) vapors, cancer cells, prostate-specific antigen (PSA), cyanotoxins, and immunoglobulin G (IgG).
- Selective absorption materials: utilized for the immune-capturing of *Salmonella* bacteria using bound antibodies (Bodelon *et al.* 2014) or the recovery of copper, nickel, and cadmium ions from aqueous solutions (Alekseeva *et al.* 2015).
- Chemical indicators: such as colorimetric sensors for the detection of acids and bases (Gonçalves 2016).

*Micro- and nano-fragmented PC*

As previously mentioned, innovative applications are being developed for PC in forms even more finely divided than classical product obtained by PC disintegration *i.e.*, microcrystalline cellulose. These include microfibrillated cellulose (MFC; particle size 4 to 250  $\mu\text{m}$ ), nanofibrillated cellulose (NFC; 50 to 1000 nm), and cellulose nanocrystals (CNC). The latter typically exhibit a width and height of 3.5 to 10 nm, while their length depends on the specific cellulose source (Moon *et al.* 2011) (Fig. 5).



**Fig. 5.** Morphological comparison of cellulose forms: (A) plant cellulose fibers (bleached kraft pulp), (B) Avicel microcrystalline cellulose (MCC) particles, and (C) commercial nanocellulose (Nanografi 2025)

The literature on the subject demonstrates that nanocellulose can be utilized for several advanced applications, including:

- Enhancing mechanical properties. Improvement of the strength of paper and paperboard produced from low-quality fibrous pulps or those containing a high filler content (Rice *et al.* 2018).
- Barrier performance. Reduction of the permeability of gases (*e.g.*, air, oxygen) and liquids through paper structures (Aulin *et al.* 2010).
- Surface modification. Improvement of the quality of paper coatings to enhance printability, surface smoothness, and stiffness (Brodin *et al.* 2014).
- Nanopaper production. Manufacturing “nanopaper,” which exhibits superior durability, stretchability, and porosity compared to conventional paper (Henriksson *et al.* 2008; Lee *et al.* 2011).
- Barrier films. Production of foil-like barrier materials for high-end packaging applications (Bessonoff and Paltakari 2015).
- Green composites. Serving as a reinforcing agent in natural polymer matrices to create environmentally friendly composites (Mikkonen *et al.* 2011).
- All-cellulose composites (ACCs). Production of composites from various types of cellulose particles, where both the matrix and reinforcement are cellulose-based (Magalhaes *et al.* 2011; Huber *et al.* 2012; Shaghaleh *et al.* 2018).
- Synthetic polymer additives. Reduction of the basis weight and improving the mechanical properties of synthetic polymers, while simultaneously increasing the biodegradability of the resulting composites (Peresin *et al.* 2010).
- Cellulose aerogels. Manufacturing ultra-lightweight, highly porous aerogels for insulation or absorption (Yu *et al.* 2018).

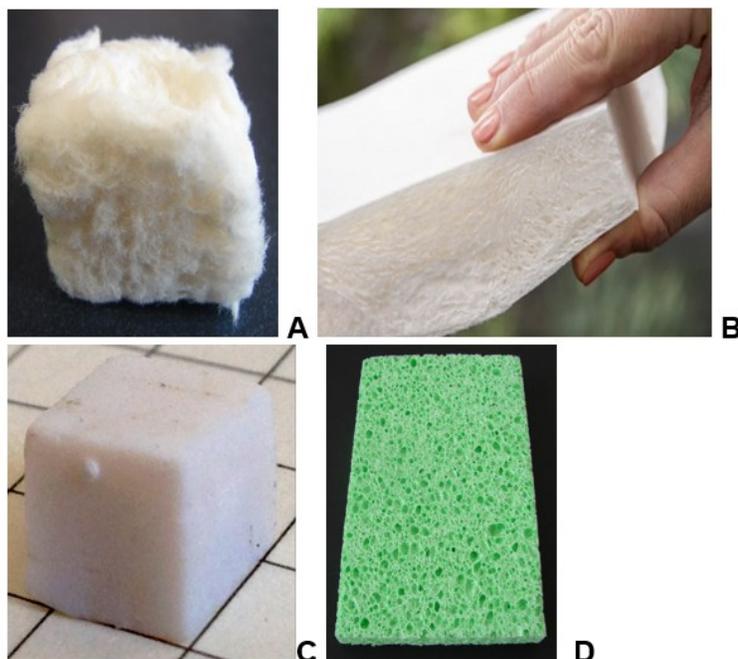
- Biomedical and pharmaceutical applications. Serving as a filler and carrier for unstable chemical compounds in pharmacology, as hydrogel wound dressings in medicine, and as scaffold for periodontal tissue repair in dentistry (Kamel *et al.* 2008; Lu *et al.* 2014).

#### *Insulating, cushioning, and absorbent PC products*

The possibility of producing of such lightweight materials from a foamed suspension of PC fibers, a foamed viscose solution and drying the cellulose solution under supercritical conditions—such as wadding/wool-like materials, expanded styrofoam-like materials, aerogels, and cellulose foams, respectively—is also interesting (Fig. 6).

The production of PC wadding- or wool-like materials (Fig. 6A) involves the filtration of pre-foamed cellulose suspension. This is achieved by adding surfactants or air-capturing and stabilizing agents—such as carboxymethyl cellulose (CMC) and sodium dodecyl sulfate (SDS)—combined with high-shear mechanical mixing. In this process, the foam bubbles act as “spacer particles” between the fibers, effectively preventing their flocculation. Such lightweight materials can be utilized in construction (as sustainable alternatives to glass wool, expanded polystyrene, or polyurethane boards), horticulture (as substrates for hydroponics), and acoustic insulation due to their excellent sound absorption properties (Jahangiri *et al.* 2014; Orzan 2025).

By precisely modifying the PC fiber characteristics, foaming conditions, and dewatering parameters, and by incorporating specialized additives, it is possible to manufacture cellulose products with structural and protective properties comparable to those of expanded polystyrene (EPS). Papira® (Fig. 6B) is a prime example of such an innovation, designed primarily as a sustainable intra-package insert to protect fragile goods during transport (Nechita and Nâstac 2022).



**Fig. 6.** Advanced porous plant cellulose-based materials: (A) wadding/wool made from bleached kraft pulp (sample courtesy of Dr. P. Pospiech, CPP, Poland), (B) Papira™ – bio-based Styrofoam-like material (Stora Enso 2025), (C) cellulose aerogel (Walczak 2016), and (D) lightweight, thick cellulose foam

Cellulose aerogel is a highly porous, ultra-lightweight solid material. Its preparation typically involves three main stages: dissolving or dispersing PC (or its derivatives), forming a cellulose gel *via* the sol–gel process, and drying the gel while carefully maintaining its three-dimensional porous architecture. The specific surface area (10 to 975 m<sup>2</sup>/g), porosity (84.0 to 99.9%), and density (0.0005 to 0.35 g/cm<sup>3</sup>) of cellulose aerogels are comparable to those of traditional silica or synthetic polymer aerogels. However, cellulose aerogels offer significantly higher compressive strength (5.2 kPa to 16.67 MPa) and superior biodegradability. Consequently, they represent an environmentally friendly, multifunctional class of materials with immense potential in applications such as liquid adsorption, oil/water separation, thermal insulation, biomedical scaffolds, carriers for metal nanoparticles or oxides, as well as precursors for carbon aerogels (Long *et al.* 2018).

Cellulose foams are materials with a highly porous structure similar to that of bath sponges (Fig. 6C). To obtain this type of product, PC is first dissolved—for example, in a CS<sub>2</sub>/NaOH (viscose process) or a urea/NaOH solvent system. The resulting solution is then foamed, regenerated in an acidic bath to precipitate the solid cellulose structure, and subsequently dried. For example, Meng *et al.* (2020) achieved such effect by adding CaCO<sub>3</sub> as a pore-forming agent to a cellulose solution (dissolved in urea/NaOH), followed by regeneration in 1 M HCl and freeze-drying to preserve the open-pore network.

#### *Conversion of PC to glucose and related chemical products*

In the future, PC may become a primary feedstock for the large-scale production of glucose, which serves as the ideal monomer for bioethanol synthesis and the manufacture of various organic chemicals. The main challenge with this biopolymer lies in its recalcitrance, because it forms robust crystalline structures stabilized by an extensive network of inter- and intramolecular hydrogen bonds. These bonds afford PC high chemical stability and render it insoluble in most common solvents, including water. Consequently, the critical technical hurdle is the efficient and selective degradation of this persistent polymer. Extensive research has been dedicated to the hydrolysis of cellulose into glucose, with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) being a traditional catalyst for this reaction. However, this process is hampered by the corrosive nature of the acid, the complexity of product separation, and the environmental burden of neutralizing acidic waste. While cellulase enzymes can selectively convert cellulose to glucose under ambient conditions, this method is limited by high enzyme costs, slow reaction kinetics, and the difficulty of recovering enzymes from the reaction mixture (unless immobilized). Given these constraints, heterogeneous (solid) catalysts are considered highly favorable for cellulose conversion due to their ease of separation, reusability, and stability under diverse reaction conditions. In particular, supported metal catalysts represent a promising group of solid catalysts, as their properties can be finely tuned by varying the active components and the preparation methods (Kobayashi *et al.* 2011; Galadima *et al.* 2022).

Methods for the depolymerization of cellulose into glucose open up a wide range of new possibilities for obtaining bulk cellulose-derived platform chemicals (such as ethanol, lactic acid, 5-hydroxymethylfurfural (5-HMF), levulinic acid, sorbitol, and itaconic acid). These, in turn, serve as precursors for various polymerizable monomers, including ethylene, 1,3-butadiene, propylene glycol, lactide, furan-based monomers (*e.g.*, BHD and FDCA), isosorbide, sorbitan, propylene, 2-methyl-1,4-butanediol, and acrylic or methacrylic acids. These monomers are essential for the production of a diverse array of sustainable bio-based polymers (Shaghaleh *et al.* 2018).

As previously mentioned, PC can also serve as a substrate for thermochemical conversion, particularly through the pyrolysis process. It is well-established that the pyrolysis of raw lignocellulosic biomass yields a bio-oil containing a complex, heterogeneous mixture of numerous chemical species with diverse functional groups. The complex composition and suboptimal physicochemical properties of such bio-oil, combined with the low concentration of most components, often conflict with the requirements for liquid fuels and industrial chemicals. Consequently, the upgrading process remains laborious and expensive. To mitigate these challenges, an integrated bioprocessing approach has been developed. This strategy involves the fractionation of biomass into its primary lignocellulosic constituents, followed by the selective pyrolysis of the recovered fractions (*e.g.*, including PC) to produce a “specialized” bio-oil that is rich in specific chemical components. Catalytic pyrolysis is another effective approach, where various catalytic materials are employed to enhance selectivity toward desired products. To date, several selective pyrolysis schemes—including feedstock pretreatment and catalytic pathways—have been proposed for the production of high-value bio-based chemicals. The primary product of PC pyrolysis is levoglucosan (LG), which can reach concentrations as high as 70 wt% in bio-oil derived from pure cellulose. Furthermore, the degradation mechanism of PC into LG is well-characterized, and its separation and recovery from the pyrolytic liquid are relatively straightforward (Hakeem *et al.* 2021).

Such levoglucosan (LG) provides a viable route for the production of monomeric sugars—primarily glucose *via* hydrolysis—which is a critical precursor for biochemically derived fuels. The unique chemical structure and properties of LG—including its inherent chirality, an internally protected primary hydroxyl group at the C-6 position, and a 1,6-anhydrobridge that opens under mild acidic conditions—render it a multifunctional C6 molecule and a highly valued platform chemical. LG serves as an attractive building block with significant commercial potential for the synthesis of pharmaceuticals, specialty polymers, surfactants, resins, additives, and green solvents. Beyond synthesis, LG is utilized as a key tracer compound (biomarker) in environmental science to monitor bioaerosols generated during biomass burning, particularly during wildfires and bushfires (Hakeem *et al.* 2021).

## AN ATTEMPT AT A GENERAL CHARACTERIZATION OF THE PROPERTIES AND APPLICATIONS OF PLANT CELLULOSE

### Fractional Composition and Cell Dimensions

#### *Fractional composition*

- Softwood pulp: Relatively homogeneous, *e.g.*, approximately 97.5 wt% tracheid fibers, with a low content of parenchymal cells (approximately 2.5 wt%).
- Hardwood pulp: More heterogeneous. In addition to fibers (approximately 79 to 87 wt%) and parenchymal cells (approximately 5–15 wt%), it also contains vessels (up to approximately 10 wt%).

### Form of the Main Element and Geometry of a Fiber

- **Form:** Needle-like, slender, elongated, and cylindrical, tapering at the ends, with a hollow interior (lumen) and a cell wall several micrometers thick.
- **Length:** Softwood fibers average 2.0 to 3.5 mm, whereas hardwood fibers average 0.6 to 1.1 mm (approximately 2 to 6 times shorter than softwood fibers).

- **Width:** Softwood fibers are approximately 1.2 to 2.2 times wider than hardwood fibers.

### Form of Additional Elements and Geometry

- **Parenchymal cells:** Mainly brick-like and short, *e.g.*, 0.030 to 0.180 mm (softwood PC) and 0.050 to 0.080 mm (hardwood PC); the average width and height of these cells in softwood and hardwood PC are similar (approximately  $20\ \mu\text{m} \pm 8$  and  $20\ \mu\text{m} \pm 2\ \mu\text{m}$ , respectively).
- **Vessels:** Barrel-shaped, with a wide range of lengths (*e.g.*, approximately 0.025 to 0.610 mm) and widths (*e.g.* approximately 44 to 246  $\mu\text{m}$ ).

### Structural Hierarchy of PC Fibers

- **Elementary fibrils:** Lateral assembly of cellulose macromolecules into bundles known as elementary fibrils.
- **Microfibrils and macrofibrils:** Longitudinal and lateral aggregation of elementary fibrils into microfibrils, which subsequently organize in a similar manner into macrofibrils.
- **Lamellae:** Periodic deposition of macrofibrils at specific angles, resulting in groups of structurally similar lamellae.
- **Cell wall layers:** Four main layers (P, S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub>) are distinguished due to the characteristic pattern of macrofibril deposition in the lamellae in the XY and XZ planes, as well as differences in the content of cellulose and encrusting substances within these layers.

### Content in Plant Materials

- **$\alpha$ -cellulose content (the purest form of PC):** In wood, it typically begins at approximately 37%, whereas in non-wood plant anatomical parts it usually ranges from about 29% to 33%.
- **Seifert cellulose content:** In wood, this value is usually a few percentage points higher than the  $\alpha$ -cellulose content.
- **Other PC determination methods:** These often yield even higher values of PC content in fibrous raw materials because they measure progressively less pure forms of cellulose.

### Sources with Higher Contents of Pure PC Include:

- **Bast of bast plants:** *e.g.*, hemp bast (cellulose content of 61 to 67%)
- **Long technical fibers:** *e.g.*, flax, hemp, jute, ramie, abaca, and sisal fibres (53 to 81% of PC)
- **Cotton seed fibers:** The highest chemical purity (even 99%).

### Properties

- **Ecological:** renewable; biodegradable in nature; capable of being sourced sustainably.
- **Economic:** Inexpensive due to its high natural abundance.
- **Sensory:** Fragrance-free and tasteless.

- **Optical:** White or brown/beige in refined and unrefined forms, respectively; inherently opaque, although capable of being transformed into less opaque or even fully transparent forms.
- **Chemical:** Polymeric in nature; often chemically contaminated; chemically modifiable; convertible to glucose; and thermochemically convertible into compounds other than glucose.
- **Physicochemical:** Having a semi-crystalline structure; highly hydrophilic; biologically neutral (inert); surface-active; non-thermoplastic.
- **Physical:** Relatively lightweight; insoluble in water, dilute acids, alkalis, and most traditional organic solvents; soluble in concentrated acids and certain specific solvents or solvent systems.
- **Mechanical:** Its strength depends on its morphological form.
- **Technical:** Capable of binding together simply as a result of wetting, forming, and drying; structurally, mechanically, and superficially modifiable; non-conductive when dry; possessing moderate thermal resistance.
- **Other properties:** Not considered in this study.

## Applications

Traditional applications of PC—including paper, tissue, paperboard, packaging materials, disposable tableware, basic molded pulp products, vulcanized paperboard, pressboard, cellophane, cellulose varnish, explosives, textiles, cellulose derivatives, and microcrystalline cellulose—can be classified as first-generation PC diversification products.

In the modern economy, these applications are often considered insufficient to replace fossil-based raw materials and synthetic polymers or to significantly improve the economic situation of pulp and paper mills producing graphical papers. Consequently, the industry is increasingly shifting toward second-generation PC diversification products, which include:

- **Advanced molded papermaking products:** Thermoformed and injection-molded PC fiber-based molded products (FMPPs) intended to replace synthetic polymer packaging.
- **Novel derivatives:** Unconventional PC derivatives designed for specialized high-tech sectors.
- **Insulating materials:** Lightweight waddings/wools; EPS-like products; PC-based PU-like foams; and ultra-light aerogels.
- **Next-generation composites:** PC homocomposites, synthetic polymer–PC composites, and PC/mineral filler composites *etc.*
- **Functionalized cellulose:** Chemically modified PC with active chemical, optical, or biological properties.
- **Nanotechnology:** Utilization of MFC, NFC, and CNC derived from PC to enhance material performance.
- **Biorefinery sector:** Conversion of PC into high-value biochemicals and biofuels using advanced thermochemical and biochemical processes.
- **Other applications:** Not included in this study.

## Summary

The aim of this work was to characterize plant cellulose (PC) with respect to its properties and its applications in the production of industrial products, based on an analysis of its fractional composition, cell dimensions, microphysical structure of the fibrous component, content in wood and non-woody plants, functional properties, traditional uses, and selected contemporary opportunities for expanding the use of this material in the production of new of industrial products.

The description of these elements of PC characterization was based on data from approximately 250 sources and is presented within a manuscript of ~27 pages. In the final section of the work, the reviewed source literature is summarized in special subsections corresponding to the individual aspects of PC characterization discussed in the paper.

This work may be useful for engineers involved in teaching PC technology, for researchers and practitioners seeking substitute materials as alternatives to synthetic polymers and fossil-fuel-derived chemicals, and for paper mills exploring ways to mitigate the effects of declining demand for printing papers by developing alternative PC-based products. It can also serve as a foundation for the development of an expanded version of such a characterization, supplemented with additional PC properties and applications not identified here, and potentially culminating in a book providing an extensive discussion of specific PC properties and applications.

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