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Recent Developments in Biodegradable Cellulose-Based Plastics

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8.1 General Introduction

The abundance of carbohydrates like cellulose and starch, combined with their specific properties, makes them very suited for the development of bio-based and biodegradable plastics. This has been recognized in the past as cellulose esters are among the oldest plastics found in industrial applications. With the development of environmentally benign plastics, including plastics from bio-based origin and plastics that have a lower potential to accumulate in the natural environment, there is a renewed interest in carbohydrate-based plastics. A requirement for plastic behavior of polymers is that the melting temperature be lower than the degradation temperature [1]. Pure (dry), unmodified cellulose does not melt and cellulose needs extensive chemical modification to allow thermal processing. Despite the abundant availability of functional groups, cellulose cannot be easily modified. Cellulose is insoluble in water and most organic solvents. The crystalline structure of cellulose limits accessibility of solvents and reagents, and highly pure cellulose (dissolving pulp) is needed as a raw material [2]. The most commonly used cellulose plastic is cellulose acetate (CA). Its main application is in cigarette filters, and moreover it is used in durable applications where the excellent optical properties, hypoallergenic nature, and high toughness are beneficial. Examples include spectacle frames, tool handles, and liquid crystal displays (LCDs). Cellophane films are used in packaging applications, but these regenerated cellulose materials (hydrolyzed version of a CS_2-modified cellulose) are not true plastics as they do not melt or flow and require different conversion processes. This book chapter summarizes the latest developments in biodegradable cellulose-based plastics with an emphasis on developments from 2015 onwards. The main focus is on applications that apply cellulose as a matrix material and as fiber reinforcement rather than as a filler. Cellulose plastics discussed are typically cellulose esters and cellophane as these are most commonly used in plastic applications.

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8.2 Cellulose

Cellulose is the most abundant polymer on earth. It is estimated that annually 10^{11}–10^{12} tonne cellulose is produced via photosynthesis. It is a structural component of the primary cell wall of plants. It is also found in various algae and produced by some species of bacteria and fungi. Cellulose for industrial use is most commonly obtained from wood pulp and cotton. Plant-derived cellulose is found in a composite structure with hemicellulose, lignin, pectin, and other substances [3]. The cellulose content of cotton fiber is about 90%, whereas that of wood is typically 40–50% [4].

Cellulose is a linear polymer where the glucose units are linked together via an β-1,4 linkage [5], see Figure 8.1. The typical length of cellulose from wood pulp ranges between 300 and 1700 glucose units, whereas cotton displays a degree of polymerization (DP) ranging from 800 to 10 000. Cellulose consists of fibrils with crystalline and amorphous regions. A high crystallinity together with extensive hydrogen bonding explains its stiffness, high tensile strength, and insolubility in water and most organic solvents.

The main industrial uses of cellulose are paperboard, paper, and textiles. The global annual production volume of cellulose pulp has exceeded 400 million tonnes [6]. Only about 2% is used for the production of cellulose derivatives like cellophane, viscose, and cellulose esters [5]. More recent is the development of industrial processes to convert cellulose into biofuels like ethanol, and this boosts cellulose utilization.

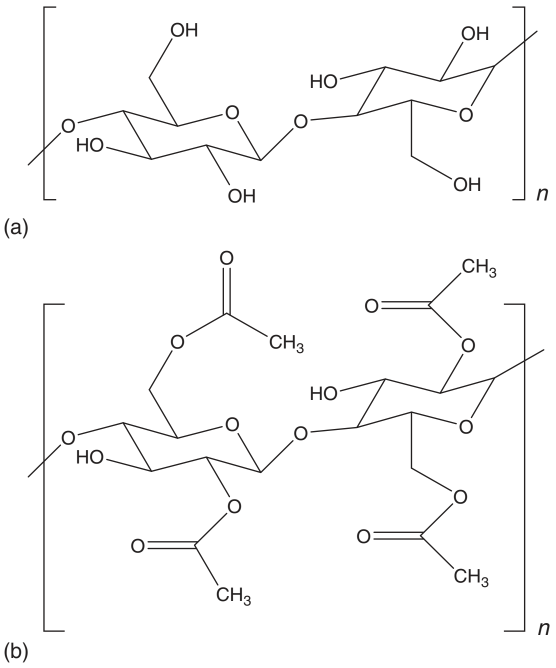

Figure 8.1 Chemical structure of (a) cellulose, (b) cellulose acetate with a degree of substitution of 2.

8.3 The Development of Cellulose Plastics

Cellulose-based plastics are of historical importance, as the development of the plastics industry started with the discovery and production of bio-based plastics like cellulose nitrate, celluloid, viscose, and cellulose acetate [7]. These plastics were used to replace expensive and scarce materials like ivory, and allowed the development and production of cars and aircrafts [8]. The production of cellulose-based plastics originates in the nineteenth century. Cellulose nitrate was first used as guncotton and in 1862 cellulose mononitrate film was patented under the tradename Parkesine. It was produced by treating cellulose with nitric acid and a solvent. A few years later it was discovered that cellulose nitrate could be plasticized with camphor, an oil extracted from wood, to produce celluloid. Celluloid is a highly flammable material that was used in photographic films and lacquers. The most widely used process to manufacture regenerated cellulose (cellophane film and viscose fibers) originates from 1891 when it was discovered that treatment of cellulose with alkali and carbon disulfide generated a soluble cellulose derivative that could be regenerated to cellulose by immersion in a bath containing dilute acid. Regenerated cellulose is chemically identical to cellulose and combines the advantages of natural cellulose (biodegradable, high strength, and stiffness) with the uniformity of man-made materials. The production of cellophane film was patented in 1912 by Brandenberger, and in the same year it was introduced as candy wrapping [9]. Cellulose acetate films, lacquers, and yarns were developed in the early twentieth century. Reacting cellulose with acetic anhydride resulted in the production of cellulose triacetate (CTA) and, via selective partial hydrolysis, cellulose diacetate was produced with an improved solubility in organic solvents which extended application opportunities. The development of new fossil-based plastics produced from building blocks like ethylene, propylene, butadiene, benzene, and toluene started just before the World War II, and cheaper fossil-based plastics replaced most bio-based plastics [10] (see Chapter 4, tutorial on polymers). Still, cellulose-based plastics regained a fair market share based on their specific properties. The increasing demand for bio-based and biodegradable plastics has led to a renewed interest in cellulose-based plastics. An asset of cellulose-based plastics is that they are produced from feedstocks that are not in direct competition with food.

Important topics related to the development and production of cellulose-based plastics include the cellulose source and cellulose purification, the derivatization process, and the extent and type of derivatization. Originally cotton was used as feedstock for the production of cellulose derivatives, the development of new purification and bleaching processes enabled the use of soft wood as the main source. New purification and derivatization processes also aim to reduce the environmental footprint of regenerated celluloses and cellulose derivatives. A well-known example is the development of the Lyocell process for the production of textile fibers [11]. In this process regenerated cellulose fibers are spun from a solution of cellulose in *N*-methyl morpholine *N*-oxide (NMMO). Lyocell fibers are stronger than viscose fibers, also when they are wet due to an improved orientation of cellulose.

8.3.1 Cellulose Feedstock and Dissolving Pulp

At present wood is the most important source for the recovery of cellulose. As wood contains about 15–35% lignin and 20–30% hemicellulose, extensive purification is needed to extract clean cellulose fibers. Most effective are chemical pulping processes that rely on chemical reactants and heat to dissolve lignin, and on subsequent mechanical refining to separate the cellulose fibers. The annual production volume of paper-grade pulp amounted to 178 million tonnes in 2018. Additional purification is needed to produce "dissolving-grade" cellulose pulps that are needed as raw material for the manufacture of cellulose derivatives. The cellulose content of dissolving-grade cellulose pulp needs to be higher than 90% [12]. Moreover, a low hemicellulose content is required as it is chemically similar to cellulose and can interfere during derivatization. The lignin content in dissolving pulp is generally very low, around 0.05%. The global annual production volume of dissolving pulp in 2020 is about 8.5 million tonnes of which 80% is used to produce textile fibers (viscose) [11].

Typical processes used to produce dissolving pulp are the sulfite process and the prehydrolysis kraft pulp process. In the sulfite process wood chips are treated with an aqueous solution of hydrogen sulfite and sulfur dioxide at elevated pressure and temperature. The bonds between cellulose and lignin components are cleaved, and lignin is converted to lignosulfonates that are soluble and can be removed. Prehydrolysis kraft pulping involves treatment of wood chips at acidic conditions to remove hemicelluloses and a subsequent treatment with an aqueous solution of sodium hydroxide and sodium sulfide to remove lignin [4]. A drawback of this process is the required pH switch that contributes to the chemical use and costs.

Cotton linters are an alternative feedstock to produce dissolving pulp. Cotton linters are a by-product of the production of staple cotton for textile applications. They can be used to manufacture high-quality dissolving pulps with a high cellulose content, high degree of polymerization (DP), and are free of lignin [13].

There is an increasing interest in the recovery of cellulose from non-wood plant sources [14], agricultural residues, and waste streams [15]. Non-wood plant sources like sisal, hemp, and flax have the advantage of a higher cellulose content and lower lignin content as compared to wood, and thus require less chemicals during pulping. Non-wood fibers require pre-treatments to prevent deterioration during storage. During the production of dissolving pulp from non-wood fibers typically a highly viscous black liquor is formed that is difficult to remove. This is an important drawback of non-wood fibers [16].

Agricultural residues like rice straw, wheat straw, sugarcane bagasse, and corn cobs are widely available because they are associated with the increasing production of sugar for biofuels [17]. Commonly agricultural residues have a low cellulose content and a high ash content, and this complicates cellulose recovery.

8.3.2 Cellulose Derivatization

The large number of free hydroxyl groups along the polymer chain (3 per glucose unit, see Figure 8.1) offers plenty of opportunity to derivatize cellulose and change the properties of the material. These hydroxyl groups can react with alcohols and acids to form ether and esters, and can be oxidized to ketones, aldehydes, and carboxylic groups [18]. The maximum number of substituent groups per glucose is referred to as the degree of substitution (DS) and is equal to the amount of hydroxyl groups per glucose unit. Typically, cellulose ethers are water soluble and commonly used as rheology modifiers or thickeners, adhesives, film formers, and water-retention agents. Cellulose esters are soluble in organic solvents and used in cigarette filter tow, membranes, coatings, and plastics. The enhanced solubility and thermoplastic behavior can be explained by the disruption of the crystalline structure of cellulose and the inhibition of hydrogen bond formation.

Both heterogeneous (cellulose in a solid phase) and homogeneous (cellulose completely dissolved) reaction paths can be applied to modify cellulose. Dissolution of cellulose in DMAc/LiCl allows a homogeneous reaction with for example anhydrides or acyl chloride. Industrial production of cellulose acetate is initially a heterogenous process and cellulose is present in a solid phase. Cellulose is treated with a mixture of acetic acid, acetic anhydride, and mineral acid catalyst in the presence of an organic solvent. Successive layers of cellulose react and the produced CTA is “peeled of” as it is soluble in the reaction mixture. At the end of the reaction, the reaction mixture is homogeneous and free of undissolved cellulose [19]. Cellulose esters with a DS lower than 2.9 cannot be produced directly as this will lead to an inhomogeneous product that is not evenly modified. The DS in amorphous regions will be higher than in crystalline regions, and this will lead to issues like gel formation. The required lower DS is obtained by partial hydrolysis of the fully substituted product.

Important research and development topics in cellulose derivatization are:

✓ Activation of cellulose to make it more susceptible for dissolution and derivatization [19–21]
✓ Controlling the molecular mass (depolymerization) during dissolution and derivatization [22–24]
✓ Novel derivatization agents and derivatives [25, 26]
✓ The properties of derivatives and the influence of the DS and regularity of substitution [27–29]

8.3.3 Cellulose Acetate and Cellulose Esters

The most important group of cellulose derivatives in thermoplastic applications are cellulose esters. Cellulose acetate (CA, see Figure 8.1) is the most commonly used cellulose ester and is known from its application in Lego bricks until 1967, when it was replaced by poly acrylonitrile butadiene styrene (ABS). Less common cellulose esters include cellulose acetate butyrate (CAB) and cellulose propionate [30].

The synthesis of cellulose esters is a three-step process: activation of cellulose by solvents or heat, functionalization and dissolution of cellulose, and hydrolysis to obtain the desired DS [31]. The pre-treatment process aims to accelerate the acetylation process and the most used method is exposure to glacial acetic acid [30]. The acetylation mixture contains three components: the acetylation agent, a catalyst, and a diluent. A common diluent is acetic acid that can be used in combination with methylene dichloride. The most common catalyst is sulfuric acid. Anhydrides are used as reactants. Hydrolysis with water and dilute acid can be performed to partially reverse the acetylation reaction without isolation of CTA. During the production of both dissolving pulp and cellulose acetates the molar mass of cellulose is reduced. Usually cellulose acetates have a degree of polymerization (number of glucose units) of 100–360 [19].

The DS determines the solubility and thermal properties of cellulose acetate and the desired DS depends on the application [30]:

- Cellulose acetate with a DS of 2.2–2.3 is soluble in acetone and suitable for injection molding
- Cellulose acetate with a DS of 2.3–2.4 is used in films
- Cellulose acetate with a DS of 2.4–2.6 is used in lacquers
- Cellulose triacetate with a DS of 2.8–3.0 is soluble in chloroform and used in triacetate film or fibers.

The T_g of cellulose acetates decreases with an increasing DS [1]. CTA tends to crystallize because of its highly symmetric structure. This behavior is shown by Teramoto [1] by measuring the T_g of cellulose acetates with a DS ranging from 1.8 to 2.95 (See Figure 8.2).

Commonly, plasticizers are used to lower the melting temperature and simultaneously reduce the melt viscosity. The most frequently used plasticizers are diethyl phthalate and triacetin (glycerol triacetate). Properties like the heat distortion temperature (HDT), stiffness, and strength can be tuned by varying the plasticizer content. Cellulose acetate propionate and cellulose butyrate have longer side chains, and this results in a lower stiffness, lower HDT, lower density, and improved processability (flow).

Cellulose esters are used for their excellent toughness and appearance (high gloss and clarity). These properties are beneficial in injection-molded articles, e.g. tool

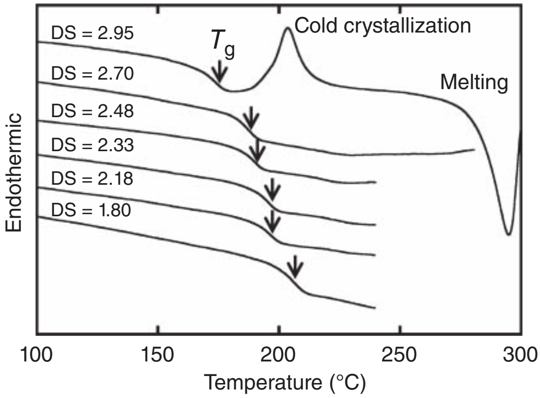

Figure 8.2 Differential scanning calorimetry (DSC) thermograms showing the T_g as a function of the DS. DSC thermograms obtained during the second heating scan. Arrows indicate Tg positions taken as midpoints of heat flow discontinuity. Source: Teramoto [1] / MDPI./ CC BY 4.0.

handles, spectacle frames, and ophthalmics (also see Chapter 9 on microbial polysaccharides and their applications). Moreover, cellulose acetate films are used in adhesive tapes, lamination films, and labels.

Since 1990 there is an increased interest in biodegradable cellulose acetate compounds for the production of packaging and disposables. Typically cellulose acetates with a DS below 2.5 are biodegradable [32–34]. Biodegradation is enhanced by the presence of plasticizers and is faster for cellulose acetates with lower DS. Cellulose propionates are biodegradable when the DS is below 1.85.

Besides the potential biodegradability and the bio-based origin, important advantages of cellulose acetates in packaging applications are the excellent water resistances, high transparency and gloss, and the high HDT. Comparative life-cycle assessments that include cellulose acetates are not available [35]. Based on the high energy and chemical use during the production of dissolving pulp and cellulose acetates, it can be expected that the environmental footprint is high compared to other bio-based plastics. Strategies to lower this footprint include heat recovery and reduction of reaction times as well as recovery of solvents and reduction of the water usage.

8.3.4 Cellophane

Although regenerated cellulose films are not true plastics (they do not melt upon heating) they are considered an important class of cellulose-based bioplastics because of their excellent biodegradability in all natural environments [36]. Most commonly, cellophane is produced via the xanthate process. Cellulose is first activated with alkali and subsequently treated with carbon disulfide to produce sodium cellulose xanthate by converting a few –OH groups (DS ~0.5) to $-O-C(S)S^{(-)}$ [30]. Next the solution is dispersed into an aqueous caustic soda solution to ripen. The solution is then extruded through a slit into a bath of dilute sulfuric acid and sodium sulfate. This results in the complete hydrolysis of the xanthate and regeneration into a transparent cellulose film [36]. The brittleness of the cellulose film is reduced by blending ethylene glycol or glycerol that act as a plasticizer. Novel, more environment-friendly production routes are reported for regenerated cellulose fibers but not yet for cellophane films [30].

The cellulose films can be provided with lacquers or can be laminated with other thermoplastic films to improve the moisture barrier or to allow sealing. The use of the lacquers or other thermoplastic films can compromise the biodegradability of the film. Cellulose films are used in packaging applications typically for food (candy) and tobacco. Limited information is available on the environmental footprint of cellophane production. Starting from wood, extensive purification and modification is required. Most concerns are related to the use of highly toxic CS_2. Through the development of new production processes, the recovery of chemicals including CS_2 and the reduction of energy use the environmental footprint of regenerated celluloses and toxicity issues can be reduced [37]. CS_2 can be recovered to a great extent or alternatively converted to sulfuric acid. Futamura, one of the main producers of cellophane films, reports significant reductions of the environmental footprint of cellophane films over the past years. It is indicated that at present the global warming potential of cellophane is slightly higher compared to polyethylene terephthalate (PET) [38].

8.3.5 Cellulose Fibers in Thermoplastic Formulations

Cellulose fibers obtained from wood or annual plants can be used to produce biodegradable thermoplastic composites. Cellulose fibers are added to fossil-based, bio-based, and biodegradable plastics to improve mechanical properties like stiffness and strength, reduce costs but also to enhance the biodegradability or rather the disintegration rate [39–41]. Cellulose nanofibers are used as a nucleating agent, enhancing crystallization. Interaction between the polymer matrix and the cellulose fiber can be improved by chemical modification, and this generally results in improved mechanical properties.

Besides wood fibers a broad range of cellulose fibers from various parts of plants can be used including bast fibers (hemp, flax, kenaf), seed fibers (cotton, kapok), fruit fibers (coir, oil palm), leaf fibers (sisal, abaca, banana), and grass fibers (bamboo, bagasse, wheat, rice). Composites with a range of biodegradable and bio-based plastics are reported in the literature including polyhydroxyalkanoates (PHAs), polylactic acid (PLA), polybutylene succinate (PBS), and starch-based plastics. "All cellulose composites" (ACCs) are reported in which both the matrix and the fibers are produced from cellulose [42]. Typically cellulose (nano-)fibers are then dispersed in a regenerated cellulose film.

Typical applications include packaging and disposables, automotive (interior parts), building, and furniture [43]. Advantages of natural fibers over glass fibers are low costs, low weight, low abrasion, and high a specific stiffness. Moreover, at end-of-life incineration of natural-fiber-reinforced composites are more advantageous compared to glass-containing composites.

The development of nanocellulose has boosted research related to cellulose fibers and composites [44, 45]. A common classification of nanocellulosic material includes cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), and bacterial nanocellulose (BNC) [46]. CNCs are rod-like structure that can be acquired via acid hydrolysis of lignocellulosic fibers, removing the amorphous regions of the cellulosic source. CNFs are produced via a combination of mechanical and chemical techniques and have a complex fiber structure with thin fibrils in a web-like structure. Target applications range from composites, paper applications, membranes to biomedical applications [47].

8.4 Recent Developments in Thermoplastic Cellulose Derivatives

This section lists the developments related to thermoplastic cellulose derivatives from 2015 onwards. Many developments are driven by the aim to improve sustainability of cellulose derivatives and to reduce costs. Developments are related

Table 8.1 Summary of the research and development topics.

Topic	Development
Feedstock use and dissolving pulp production	Characterization of biomass feedstock Alternative feedstocks
Derivatization processes	Novel solvents Alternative processes
New derivatives and formulations	Plasticizers Mixed esters Blends New derivatives
Processing and properties and applications	Foaming Flame retardancy Anti-microbial properties
Products and applications	Biosensors Drug delivery All cellulose composites Nano-fibers
End-of-life	Biodegradability

to the feedstock and use of alternative biomass feedstocks, the development of more environment-friendly production processes up to materials that are more sustainable at end-of-life. The research topics are summarized in Table 8.1.

8.4.1 Characterization Methods for Lignocellulosic Biomass

Incentives for using and producing biofuels and bioenergy has resulted in a renewed interest in lignocellulosic biomass. New deconstruction strategies are developed to maximize yields and improve recovery of cellulose from biomass [48]. Improved and advanced analysis techniques are needed to characterize lignocellulosic biomass and allow the use of alternative biomass sources.

Lupoi et al. reviewed the opportunities of Raman spectroscopy to analyze lignocellulosic biomass and its derivatives, and for downstream process monitoring [49]. As Raman imaging techniques allow the real-time evaluation of deconstruction strategies and provide fundamental insights into how specific reagents affect the morphology of the biomass, the technique is valuable for future developments in cellulose chemistry and production of cellulose plastics for instance for the development of dissolving celluloses. As shown in Figure 8.3 Raman spectroscopy can show the distribution of cellulose and lignin in cellulose fiber bundles [50].

Another valuable new technique to analyze the recalcitrant nature of lignocellulosic biomass is infrared photo-induced force microscopy (IR PiFM) [51]. IR PiFM has a spatial resolution comparable to transmission electron microscopy (TEM) and

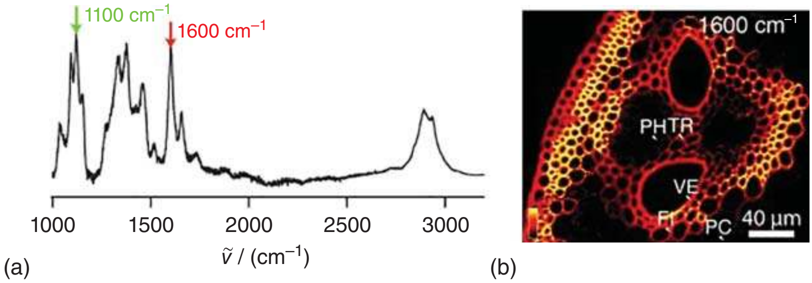

Figure 8.3 Raman spectroscopy and Stimulated Raman Scattering (SRS) imaging of corn stover. (a) Raman spectrum of raw corn stover. The peak at 1600 cm^{-1} (red arrow) corresponds to the lignin distribution, and the peak at 1100 cm^{-1} (green arrow) corresponds to cellulose. (b) SRS image of the vascular bundle including the edge of the stem in raw corn stover at 1600 cm^{-1}, showing the lignin distribution. Labeled structures are discussed in the text: parenchyma (PC), phloem (PH), vessel (VE), tracheid (TR), fiber (FI). Source: Reproduced with permission from Saar et al. [50].

more than 50 times higher than Raman imaging. An additional benefit of IR PiFM is that it can resolve structures based on their chemical composition. This allows nanoscale analysis of the physical and chemical structure of plant cell walls.

A third technique that needs to be mentioned is scanning near-field optical microscopy (SNOM) [52]. SNOM images provide chemical information on the spatial distribution of the cell wall components in secondary cell walls at a resolution similar to atomic force microscopy (AFM) and TEM.

8.4.2 Alternative Feedstocks for Dissolving Pulp and Production Routes

Whereas wood and cotton remain the most important sources for dissolving pulp and cellulose derivatives, various studies are found using alternative feedstocks typically from waste streams (sawmill) or non-wood plants like bamboo [23, 53, 54]. High-quality dissolving pulps were obtained from *Eulaliopsis bininata* (grass) feedstock, the *Acacia farnesiana* L. Willd. plant (huizache), jute, banana plant stem, palm empty fruit bunch, and bamboo willow [55–60]. Other developments with respect to dissolving pulp production include the conversion of paper grade pulp to dissolving pulp, and the valorization of by-products from the pulping process (like hemicellulose) to value-added products [54].

Developing dedicated processes to produce dissolving pulp from lignocellulose waste is important to achieve high purities. Using a pre-hydrolysis potassium hydroxide pulping process, dissolving pulp suitable for the production of viscose fibers could be produced from rice and wheat straws, corn stalk, dhaincha, and jute stick [61]. Steam explosion at 190 °C for 15 minutes combined with oxygen-assisted alkaline delignification was used to simultaneously produce oxidized lignin and cellulosic pulp from sugarcane bagasse [62]. Oxidation using oxygen and ozone followed by an alkaline extraction proved to be an effective additional purification process to produce dissolving grade pulp from sawdust and sugarcane bagasse [63].

8.4.3 Ionic Liquids and Deep Eutectic Solvents for Cellulose Regeneration and Modification

Dissolution of cellulose and accessibility of cellulose for derivatization in ionic liquids is a rather new topic. Ionic liquids are a combination of bulky organic cations with mostly inorganic anions, resulting in salts that are liquids at temperatures below 100 °C. The cellulose dissolution in ionic liquids is controlled by the anion selection, since its size and geometry plays an important role in cellulose dissolution. The chlorine ion is one of the most promising anions, but other halides, carboxylates, or phosphates anions can also be used for cellulose dissolution. Other parameters that affect cellulose dissolution in ionic liquids include the presence of water (that negatively influences cellulose dissolution), the dissolution temperature, and the cellulose source. Advantages of ionic liquids include the relatively mild dissolution conditions, easy processability, low volatility, and the environment-friendly nature. This makes them promising solvents to apply in industrial processes for biomass processing [23, 64, 65]. A review by Yuan et al. aims to provide an improved understanding of the mechanism of cellulose dissolution in ionic liquids [66]. To allow cellulose dissolution, the native hydrogen-bonding network in cellulose needs to be disturbed or destroyed and ionic liquids have this ability. The authors conclude that there are three interacting modules that determine the mechanisms of cellulose dissolution in ionic liquids: (i) the structure of elementary fibrils; (ii) the solvation of cellulose in ionic liquids by interaction of cation, anion, and cellulose on different length scales, and (iii) solution structure of cellulose solubilized in ionic liquids.

The practical application of ionic liquids for the manufacture of regenerated cellulose fibers is reviewed by Mendes et al. [23]. Advantages in fiber spinning are the ability to dissolve cellulose in high concentrations and to recover the solvent after the regeneration of the cellulose film or fiber. Moreover, water pollution is moderate and sometimes a higher fibrillation resistance is obtained. Drawbacks include the slow rate of dissolution, high costs of the solvents, difficulties to reuse or recycle the solvents, and some ionic liquids are toxic and non-biodegradable. Imidazolium ionic liquids with chloride anions are suitable for cellulose spinning, but can induce cellulose degradation at temperatures above 90 °C [67]. Regenerated cellulose fibers with a strength comparable to Lyocell could be produced using 1,5-diazabicyclo[4.3.0]non-5-enium acetate [22]. This solvent allowed high cellulose concentrations at moderate temperatures (60–100 °C) while cellulose degradation was limited.

Pang et al. report the properties of regenerated cellulose films fabricated from different cellulose feedstocks using ionic liquids [68]. Feedstocks studied included pine, cotton, and bamboo and the ionic liquid used was 1-ethyl-3-methylimidazolium acetate. Using X-ray diffraction (XRD) it was confirmed that the transition of cellulose I to cellulose II had occurred due to dissolution and regeneration. The films prepared from cotton linter and pine exhibited excellent thermal stability and mechanical properties.

The use of ionic liquids allows the homogenous production of CTA [69]. CTA with a DS of 2.98 was prepared by transesterification of lignocellulosic biomass with isopropenyl acetate in 1-ethyl-3-methylimidazolium acetate. Homogenous esterification of cellulose pulp was also achieved using 1,5-diazabicyclo[4.3.0]non-5-ene acetate as a solvent. A recyclable system with low boiling by-products was demonstrated [70].

With an increased use of ionic liquids, their regeneration, recovery, and recycling becomes even more important [71]. Filtration and rotary evaporation to recover 3-butyl-1-methylimidazolium chloride (BMIM Cl) from corn stover hydrolysate enabled at least 10 reuse cycles. Also, recovery using vacuum distillation was reported with an efficiency higher than 95%. Alternative methods include electrodialysis and in some cases this ionic liquid can be recovered by washing with water. Although various procedures are proposed in literature there are still a very limited number of methods for the direct reuse or regeneration of ionic liquids. Extensive studies on procedures regarding the reuse of ionic liquids are needed.

Another class of promising solvents that are currently studied for cellulosic biomass dissolution and biomass conversions are deep eutectic solvent (DESs). These solvents are formed by a hydrogen bond acceptor (commonly an ammonium salt) and a hydrogen bond donor (e.g. amines and carboxylic acids), linked by hydrogen bonds at a certain molar ratio. Advantages of DES in biomass pre-treatment are lower production costs, higher biodegradability, low vapor pressure, safety, and innocuous nature [23, 24]. Cellulose solubility in DES is limited as compared to ionic liquids, due to the strong hydrogen bond network in DES that results in a decrease of interactions between cellulose and the DES solvents. A review on the use of DES for lignocellulosic biomass fractionation and subsequent conversion to bio-based products is prepared by Tan et al. [24]. Studies indicate a DES based on choline chloride and urea is an effective plasticizer for cellulose leading to soft materials having enhanced elongation [72].

8.4.4 New Derivatization Routes

Apart from the use of new solvents (ionic liquids) there is little progress in the development of new derivatization routes. A new strategy to produce thermoplastic cellulose oleate involved ball milling [73]. Cellulose oleates with a high DS (1.29–2.55) were produced using a low dosage of oleic acid (6 mol per anhydro glucose unit) and no additional solvents. Materials with a high DS (2.34–2.55) could be processed into homogeneous flexible transparent films via compression molding at 160 °C.

8.4.5 Plasticizers

Several publications study the interactions of cellulose acetates with plasticizers [74–76]. Glycerine, triethyl citrate, and dioctyl phthalate were found to significantly enhance crystallization of CTA. Dioctyl phthalate was the most effective plasticizer leading to a T_g depression of 46 °C at an addition level of 25 wt%. Related to this effect, the compounds with dioctyl phthalate had the lowest E-modulus [74]. Bao studied the miscibility of cellulose diacetate with diethyl phthalate. At a diethyl phthalate content higher than 25% phase separation occurred [75]. Alternative plasticizers include essential oils (EO) [77]. Essential oils containing limonene and pinenes (e.g. from lime and nutmeg) gave the strongest plasticizing effect. Essentials oils containing fatty acids (e.g. from coffee) were the weakest plasticizers. When essential oils were added to cellulose acetate the water barrier was improved. Most of the essential oils decreased the transparency of the films. Eugenol, pimento berry, and anise were notable exceptions. In an earlier study essential oils (EO) from lemongrass, rosemary pepper, and basil were found to plasticize cellulose acetate, cellulose acetate propionate, and CAB [78]. Li studied the thermal behavior of cellulose diacetate melts, using ionic liquids as a plasticizer aiming to develop a melt-spinning process. At higher shear rates and at higher concentrations the thermal stability was found to decrease [76].

8.4.6 Mixed Cellulose Esters

A detailed analysis of the thermoplastic behavior of cellulose derivatives is published by Teramoto [1] (Figure 8.2). The review includes the effect of single-substituent derivatization, derivatization with multi-substituents, blending of simple derivatives with synthetic polymers, and graft copolymerization.

Multi-substitution offers the opportunity to develop new cellulose-based thermoplastic polymers that combine excellent thermal processability with tunable mechanical performance. It allowed the development of the first melt-spun cellulosic fiber by Toray Industries. Derivatization of cellulose diacetates with modified cardanol (phenolic compound extracted from cashew nutshell liquid) was presented as an alternative to the use of plasticizers [79]. Mixed cellulose acetate oleate esters demonstrate promising properties including an improve oxygen and water vapor barrier. In this mixed ester the oleate functions as an internal plasticizer [80]. A wide range of cellulose mixed esters was synthesized through homogeneous acylation of cellulose diacetate (DS 2.45), by using a series of commercially available aliphatic acid chloride modifiers (fatty chains with different length, ramified, bulky, aliphatic, or aromatic rings disposed more or less near to cellulose backbone) [81]. The covalent introduction of the acyl moieties leads to a significant lowering of T_g, as a consequence of the enhancement of the overall mobility of the macromolecular chains. Acylating reagents composed of bulky moieties at the extremity of a soft linear chain led to an efficient plasticization. The water transport properties of casted films were evaluated and were decreased by the presence of apolar side groups. The effects of long acyl chain structures on mechanical and thermal properties are reported by Tanaka et al. [82]. The study focused on two types of renewable long acyl chains for mixed cellulose esters: the aromatic 3-pentadecylphenoxy acetyl (PA) group derived from cardanol extracted from cashew nutshells and the aliphatic stearoyl (St) group made from vegetable oils. Mixed substitution of long and short acyl chains (acetate) prevented the crystallization of the long acyl chain moieties in mixed cellulose esters. Materials with the PA group had a slightly higher bending strength and glass transition temperature than those with the St group but showed

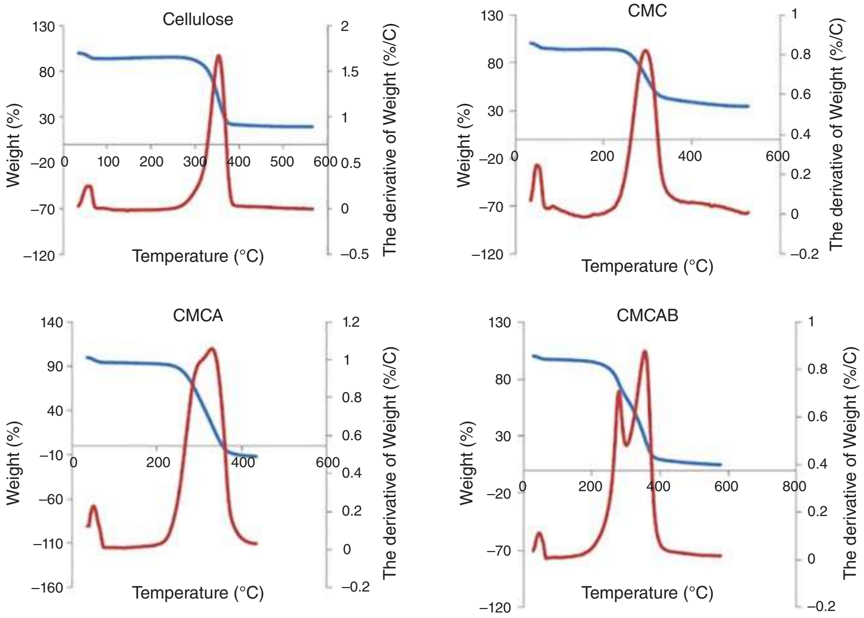

Figure 8.4 Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of cellulose, CMC, CMCA, and CMCAB [83]. Source: Reproduced by permission of Romanian Academy Publishing House, the owner of the publishing rights.

low impact strength. Materials with the St group showed remarkably improved impact strength with sufficient balanced mechanical properties for use in durable products.

Grafting caprolactone and lactic acid onto cellulose diacetate resulted in a transparent thermoplastic material that could be processed at 200 °C without the use of an additional plasticizer [72].

Carboxymethyl cellulose acetate (CMCA) and carboxymethyl cellulose acetate butyrate (CMCAB) are glassy thermoplastic materials with T_g of 138.35 °C and T_m of 200 °C [83]. From Figure 8.4 (weight loss in blue, differential weight loss in red) it can be seen that the CMCAB demonstrates an increased thermal stability compared to those of cellulose, carboxymethyl cellulose (CMC), and CMCA.

New thermoplastic cellulose stearate and laurate esters were prepared by Krasnou et al. [84]. The authors indicate that more development is needed to improve the properties of these cellulose esters.

Synthesis of cellulose acetate propionate with controllable contents and distributions of acetyl and propionyl in the C2, C3, and C6 positions was studied by Meng et al. [85]. The reactivity as well as selective hydrolysis of the different OH-positions of the anhydro glucose unit was determined.

8.4.7 Cellulose–Polymer Blends

Various studies focus on blending as a route to avoid the use of plasticizers. Polyvinyl pyrrolidone forms a miscible blend with cellulose acetate [86]. Of specific interest however are biodegradable blends with aliphatic polyesters like polycaprolactone (PCL, see Chapter 7). The miscibility of cellulose acetates with PCL depends on the type of cellulose derivative and the DS, and the most commonly used cellulose acetates are immiscible with PCL [87]. CAB and PBS can form miscible blends. It was found that PBS acts as a plasticizer for CAB, lowering the E-modulus and enhancing elongation [88]. Cross-linked blends of cellulose acetate and starch acetate were claimed to combine the advantages of these two materials while reducing their disadvantages [89]. The films displayed improved mechanical properties as compared to fragile starch acetate films, and the strength and strain at break increased at higher cellulose acetate contents. Specifically films with higher starch acetate were more readily biodegradable in soil as compared to cellulose acetate. Blends of plasticized CAB and PLA were studied by Kunthadong et al. [90]. Limited compatibility of the materials negatively influenced the mechanical properties of the blend.

8.4.8 (New) Properties and Processing Routes

Extrusion foaming of cellulose palmitate with a DS of 1.0 was studied by Rokkonen et al. [91]. The blowing agents isobutane, carbon dioxide, and nitrogen all enable foam formation. Foams with the lowest density were obtained using isobutane; nitrogen resulted in the most uniform cell morphology. Further studies are needed to improve the quality of the foams. Extrusion foaming of cellulose acetate with various co-blowing agents was studied by Hendriks et al. [92]. It was found that the effect of the co-blowing agent depended on its solubility in the melt. Ethyl acetate gave optimal results at low addition levels, while isopropanol and acetone gave improved foaming at higher addition levels. Further research is needed to study the effect of co-blowing agents on cell nucleation.

Development of flame-retardant cellulose acetate foams was not successful [93]. The flame retardants had a strong effect on the processing behavior, especially on the rheological properties. The higher viscosity of the flame-retardant compounds negatively influences processing and foaming.

Cellulose acetate with antimicrobial activity was achieved by embedding molybdenum trioxide particles [94].

8.4.9 New Applications

Development of new cellulose and cellulose acetate products for biomedical applications is frequently reported [95–98]. Cellulose acetate fibers produced via electrospinning are biocompatible and biodegradable and, hence, suitable for medical applications like tissue engineering, drug delivery, and wound dressings [99]. Wound dressings based on cellulose acetate/PCL blends are prepared via electrospinning [96]. Electrospun cellulose acetate nanofibers are studied for drug-delivery systems [97]. These electrospun fibers are also very suitable for application in biosensors including optical/colorimetric, and electrochemical-based sensing systems. The use of electrospinning to produce 3D nano-fiber stacks of cellulose acetate for biomedical and pharmaceutical applications such as tissue engineering, cell cultures, immobilization of bioactive substances, and drug delivery is discussed by Cheng et al. [100]. Cellulose-based hydrogels have promising properties for application in various biomedical applications including drug delivery, tissue engineering, wound dressing, bioimaging, and wearable sensors [101]. The use of cellulose-based materials in sodium-ion batteries and capacitors is presented in an extensive review showing these have excellent opportunities in these applications [102].

Various publications can be found on the application of cellulose fibers in composite materials. These include review articles on the opportunities of natural composites, publications on specific fibers like bamboo, coir, abaca, and curaua, but also articles focusing on isolation and modification of cellulosic fibers and the properties of cellulose-fiber-based composites [103–109]. Various articles discuss “ACCs” [110–112]. These ACCs consist of a matrix of dissolved and regenerated cellulose reinforced by undissolved or partly dissolved cellulose. Two routes are applied to produce ACCs; the complete dissolution of a cellulose material followed by conventional impregnation methods of fibrous cellulose material, or partial dissolution of a cellulose fabric to form a matrix phase that bonds undissolved cellulose fiber cores together. This last method offers more opportunities for industrial upscaling. ACCs can be used in a wide range of applications including structural materials, biomedical engineering, photoelectric devices, electro-active paper, sensors, electrical displays, filtration materials, biodegradable food packaging materials, and mulching films for agriculture. Other biodegradable natural-fiber-reinforced composites are based on biodegradable polymers like starch, PBS, PCL, or polylactic acid [106, 113–118].

A clear trend is the development and use of cellulosic nano-fibers because of their outstanding mechanical properties. Commonly chemo-mechanical processes are used to produce nano-fibers [119]. Alternatives routes include biological synthesis of nano fibers via controlled hydrolysis of cotton fibers by purified cellulase enzymes [120]. Electrospinning is reported as a technique to convert both cellulose and derivatives like cellulose acetates into nanofibers [121]. Apart from composites for engineering applications, potential uses of cellulose nano-fibers include thickening agents, tissue engineering scaffolds, nucleation agent, dry-strength additive for paper and adsorbents [122, 123]. Another promising application field for cellulosic materials are liquid crystal polymers. This includes the use of cellulose nanocrystals that can form ordered structures leading to lyotropic liquid crystals [124].

8.5 Biodegradation of Cellulose Derivatives

Whereas natural cellulose and regenerated cellulose are readily biodegradable in all natural environments, there is still little fundamental understanding regarding the biodegradation mechanisms of cellulose esters. This is illustrated by contradictory literature and two review papers tried to clarify the biodegradation behavior of cellulose acetates [125, 126]. The aerobic biodegradation of cellulose acetates in soil is discussed by Polman, whereas Yadav reviewed the complicated interplay between structure, environment, and degradation. Both studies confirm that chemical modification negatively affects biodegradability of natural polymers and that the biodegradability of cellulose acetate largely depends on the degree of acetylation. At a DS <1.8, acetyl esterase enzymes are able to remove acetyl groups and this has a significant effect on the biodegradation rate, as deacetylation is the rate-determining step during biodegradation of cellulose acetate. Regio-selectively substituted cellulose acetate degrades faster than randomly substituted cellulose acetate with a similar DS. Other material modifications (like plasticizers and other additives) can enhance or further limit the degradability. The biodegradation rate is highly influenced by the actual degradation environment, and often a long lag phase is reported before the biodegradation process starts. Several biodegradable cellulose acetate grades are commercially available, and these are certified biodegradable at industrial composting conditions or even in the marine environment.

8.6 Conclusions

Although they are a fairly old class of plastics, there are still developments that increase the applicability and improve the environmental footprint of cellulose plastics like cellophane and cellulose acetates. Reducing energy use and chemical loads, for example by using novel solvents and new recovery processes, is demonstrated in textile applications and is under development for plastic applications. Optimized processing could also reduce the costs of cellulose plastics. This can be envisaged using new plasticizers that are less volatile or do not migrate from the plastic matrix, by developing new blends that do not need plasticizers or via the production of mixed esters with internal plasticization. Historically, cellulose plastics are used in durable applications. The applicability of these new plasticizer systems depends on the development of cost-efficient production routes. In recent literature new opportunities of cellulose plastics in biomedical applications are explored (drug delivery, biosensors). Moreover new cellulose acetate grades are developed that are biodegradable in the natural environment. Typically, these grades have a relatively low DS and additives including plasticizers are used to enhance biodegradation. These new materials can be of interest in agricultural applications and in fishing nets where littering cannot be avoided and where the excellent mechanical properties of cellulose plastics are beneficial. Biodegradability is also an important asset of cellulose based (nano-)fibers that are studied for a wide range of applications.

As compared to other bio-based plastics, cellulose plastics have a rather large (historical) market share. Still, they are rather expensive and this limits applicability in bulk applications like packaging. Exploiting the biodegradability in the natural environment could help to obtain market shares in new applications.

References

1 Teramoto, Y. (2015). Functional thermoplastic materials from derivatives of cellulose and related structural polysaccharides. *Molecules* 20 (4): 5487–5527.

2 Kennedy, J.F. and Hasamudin, W.H.W. (1995). Cellulose: structure, accessibility and reactivity, edited by H. A. Krassig. Gordon & Breach, Pennsylvania, 1993. Pp. xvi + 376, price £169.00, US$260.00. ISBN 2-88124-798-9. *Polymer International* 36 (1): 101–101.

3 Abe, M.M., Martins, J.R., and Sanvezzo, P.B. (2021). Advantages and disadvantages of bioplastics production from starch and lignocellulosic components. *Polymers* 13 (15): 2484.

4 Heinze, T., El Seoud, O.A., and Koschella, A. (2018). Production and characteristics of cellulose from different sources. In: *Cellulose Derivatives: Synthesis, Structure, and Properties* (ed. T. Heinze, O.A. El Seoud and A. Koschella), 1–38. Cham: Springer International Publishing.

5 Ganster, J. and Fink, H.-P. (2013). Cellulose and cellulose acetate. In: *Bio-based Plastics* (ed. S. Kabasci), 35–62. Hoboken, NJ, USA: Wiley Online Library.

6 Chauhan, S. and Meena, B.L. (2021). Introduction to pulp and paper industry: global scenario. *Physical Sciences Reviews* 6 (5): 81–109.

7 Rasmussen, S.C. (2021). From Parkesine to celluloid: the birth of organic plastics. *Angewandte Chemie International Edition* 60 (15): 8012–8016.

8 Zhibitsky, J.T. (1943). Plastics and their application to aircraft construction. *Journal of the Roy Aeronautical Society* 47 (389): 138–143.

9 Carlisle, R.P. (2004). *Scientific American Inventions and Discoveries : All the Milestones in Ingenuity From the Discovery of Fire to the Invention of the Microwave Oven*. Hoboken: Wiley.

10 Geyer, R. (2020). A brief history of plastics. In: *Mare Plasticum – The Plastic Sea: Combatting Plastic Pollution Through Science and Art* (ed. M. Streit-Bianchi, M. Cimadevila and W. Trettnak), 31–47. Cham: Springer International Publishing.

11 Kallio, A.M.I. (2021). Wood-based textile fibre market as part of the global forest-based bioeconomy. *Forest Policy and Economics* 123: 102364.

12 Sixta, H. (2006). Pulp properties and applications. In: *Handbook of Pulp* (ed. H. Sixta), 1009–1067. Weinheim, Germany: Wiley.

13 Sczostak, A. (2010). Cotton linters: an alternative cellulosic raw material. *Macromolecular Symposia* 280: 45–53.

14 Kamoga, O.L.M., Byaruhanga, J.K., and Kirabira, J.B. (2013). A review on pulp manufacture from non wood plant materials. *International Journal of Chemical Engineering and Applications* 4: 144–148.

15 Nuruddin, M., Chowdhury, A., and Haque, S.A. (2011). Extraction and characterization of cellulose microfibrils from agricultural wastes in an integrated biorefinery initiative. *Cellulose Chemistry and Technology* 45 (5, 6): 347–354.

16 Hammett, A.L., Youngs, R.L., and Sun, X. (2001). Non-wood fiber as an alternative to wood fiber in Chinas pulp and paper industry. *Holzforschung* 55 (2): 219–224.

17 Ali, M., Saleem, M., and Khan, Z. (2019). The use of crop residues for biofuel production, Chapter 16. In: *Biomass, Biopolymer-Based Materials, and Bioenergy* (ed. D. Verma, E. Fortunati and S. Jain), 369–395. Woodhead Publishing.

18 Heinze, T., Koschella, A., and Liebert, T. (2012). Cellulose: chemistry of cellulose derivatization. In: *The European Polysaccharide Network of Excellence (EPNOE): Research Initiatives and Results* (ed. P. Navard), 283–327. Vienna: Springer Vienna.

19 Heinze, T., El Seoud, O.A., and Koschella, A. (2018). Principles of cellulose derivatization. In: *Cellulose Derivatives: Synthesis, Structure, and Properties* (ed. T. Heinze), 259–292. Cham: Springer International Publishing.

20 Yan, L., Li, W., and Qi, Z. (2006). Solvent-free synthesis of cellulose acetate by solid superacid catalysis. *Journal of Polymer Research* 13 (5): 375–378.

21 Matsumoto, T., Tatsumi, D., and Tamai, N. (2001). Solution properties of celluloses from different biological origins in LiCl DMAc. *Cellulose* 8 (4): 275–282.

22 Asaadi, S., Hummel, M., and Ahvenainen, P. (2018). Structural analysis of ioncell-F fibres from birch wood. *Carbohydrate Polymers* 181: 893–901.

23 Mendes, I.S.F., Prates, A., and Evtuguin, D.V. (2021). Production of rayon fibres from cellulosic pulps: state of the art and current developments. *Carbohydrate Polymers* 273: 118466.

24 Tan, Y.T., Chua, A.S.M., and Ngoh, G.C. (2020). Deep eutectic solvent for lignocellulosic biomass fractionation and the subsequent conversion to bio-based products – a review. *Bioresource Technology* 297: 122522.

25 Aly, A.A. and El-Bisi, M.K. (2018). Grafting of polysaccharides: recent advances. In: *Biopolymer Grafting: Synthesis and Properties* (ed. V.K. Thakur), 469–519. Elsevier Inc.

26 Hon, D.N.S. (2017). Cellulose and its derivatives: structures, reactions, and medical uses. In: *Polysaccharides in Medicinal Applications* (ed. S. Dumitriu), 87–105. CRC Press.

27 Suzuki, S., Hikita, H., and Hernandez, S.C. (2021). Direct conversion of sugarcane bagasse into an injection-moldable cellulose-based thermoplastic via homogeneous esterification with mixed acyl groups. *ACS Sustainable Chemistry & Engineering* 9 (17): 5933–5941.

28 Battisti, R., Hafemann, E., and Claumann, C.A. (2019). Synthesis and characterization of cellulose acetate from royal palm tree agroindustrial waste. *Polymer Engineering and Science* 59 (5): 891–898.

29 Niu, X., Liu, Y., and King, A.W.T. (2019). Plasticized cellulosic films by partial esterification and welding in low-concentration ionic liquid electrolyte. *Biomacromolecules* 20 (5): 2105–2114.

30 Gilbert, M. (2017). Cellulose plastics, Chapter 22. In: *Brydson's Plastics Materials*, 8e (ed. M. Gilbert), 617–630. Butterworth-Heinemann.

31 El Seoud, O.A. and Heinze, T. (2005). Organic esters of cellulose: new perspectives for old polymers. In: *Polysaccharides I*, Advances in Polymer Science (ed. T. Heinze), 103–149. Berlin/Heidelberg, Germany: Springer.

32 Buchanan, C.M., Dorschel, D., and Gardner, R.M. (1996). The influence of degree of substitution on blend miscibility and biodegradation of cellulose acetate blends. *Journal of Environmental Polymer Degradation* 4 (3): 179–195.

33 Edgar, K.J., Buchanan, C.M., and Debenham, J.S. (2001). Advances in cellulose ester performance and application. *Progress in Polymer Science* 26 (9): 1605–1688.

34 Sakai, K., Yamauchi, T., and Nakasu, F. (1996). Biodegradation of cellulose acetate by *Neisseria sicca*. *Bioscience, Biotechnology, and Biochemistry* 60 (10): 1617–1622.

35 Foroughi, F., Rezvani Ghomi, E., and Morshedi Dehaghi, F. (2021). A review on the life cycle assessment of cellulose: from properties to the potential of making it a low carbon material. *Materials* 14 (4): 714.

36 McKeen, L.W. (2017). Environmentally friendly polymers, Chapter 13. In: *Permeability Properties of Plastics and Elastomers*, 4e (ed. L.W. McKeen), 305–323. William Andrew Publishing.

37 Shen, L., Worrell, E., and Patel, M.K. (2010). Environmental impact assessment of man-made cellulose fibres. *Resources, Conservation and Recycling* 55 (2): 260–274.

38 Futamura. *Carbon Footprint*. 2021 [cited 2021 October 25th]. http://www.futamuragroup.com/jp/sustainability/carbon-footprint.

39 Mu, B., Tang, W., and Liu, T. (2021). Comparative study of high-density polyethylene-based biocomposites reinforced with various agricultural residue fibers. *Industrial Crops and Products* 172: 114053.

40 Morin, S., Dumoulin, L., and Delahaye, L. (2021). Green composites based on thermoplastic starches and various natural plant fibers: impacting parameters of the mechanical properties using machine-learning. *Polymer Composites* 42 (7): 3458–3467.

41 Rajeshkumar, G., Arvindh Seshadri, S., and Devnani, G.L. (2021). Environment friendly, renewable and sustainable poly lactic acid (PLA) based natural fiber reinforced composites – a comprehensive review. *Journal of Cleaner Production* 310: 127483.

42 Nishino, T. and Peijs, T. (2013). All-cellulose composites. In: *Handbook of Green Materials* (ed. K. Oksman, A.P. Mathew and A. Bismarck), 201–216. World Scientific.

43 Peças, P., Carvalho, H., and Salman, H. (2018). Natural fibre composites and their applications: a review. *Journal of Composites Science* 2 (4): 66.

44 Khalid, M.Y., Al Rashid, A., and Arif, Z.U. (2021). Recent advances in nanocellulose-based different biomaterials: types, properties, and emerging applications. *Journal of Materials Research and Technology* 14: 2601–2623.

45 Zhang, L., Guo, L., and Wei, G. (2021). Recent advances in the fabrication and environmental science applications of cellulose nanofibril-based functional materials. *Materials* 14 (18): 5390.

46 Zinge, C. and Kandasubramanian, B. (2020). Nanocellulose based biodegradable polymers. *European Polymer Journal* 133: 109758.

47 Sharma, A., Thakur, M., and Bhattacharya, M. (2019). Commercial application of cellulose nano-composites – a review. *Biotechnology Reports* 21: e00316.

48 Liao, Y., Op de Beeck, B., and Thielemans, K. (2020). The role of pretreatment in the catalytic valorization of cellulose. *Molecular Catalysis* 487: 110883.

49 Lupoi, J.S., Gjersing, E., and Davis, M.F. (2015). Evaluating lignocellulosic biomass, its derivatives, and downstream products with Raman spectroscopy. *Frontiers in Bioengineering and Biotechnology* 3: 50.

50 Saar, B.G., Zeng, Y., and Freudiger, C.W. (2010). Label-free, real-time monitoring of biomass processing with stimulated Raman scattering microscopy. *Angewandte Chemie International Edition* 49 (32): 5476–5479.

51 Kesari, K.K., O'Reilly, P., and Seitsonen, J. (2021). Infrared photo-induced force microscopy unveils nanoscale features of Norway spruce fibre wall. *Cellulose* 28 (11): 7295–7309.

52 Keplinger, T., Konnerth, J., and Aguié-Béghin, V. (2014). A zoom into the nanoscale texture of secondary cell walls. *Plant Methods* 10 (1): 1.

53 Choudhury, M.J. and Khan, G.M.A. (2015). Utilization of sawmill by-product for making cellulose and its valuable derivatives. In: *Biomass and Bioenergy: Applications* (ed. K.R. Hakeem, M. Jawaid and U. Rashid), 165–186. Springer International Publishing.

54 Kumar, H. and Christopher, L.P. (2017). Recent trends and developments in dissolving pulp production and application. *Cellulose* 24 (6): 2347–2365.

55 Harsono, H., Putra, A.S., and Maryana, R. (2016). Preparation of dissolving pulp from oil palm empty fruit bunch by prehydrolysis soda-anthraquinone cooking method. *Journal of Wood Science* 62 (1): 65–73.

56 Das, A.K., Nakagawa-Izumi, A., and Ohi, H. (2016). Quality evaluation of dissolving pulp fabricated from banana plant stem and its potential for biorefinery. *Carbohydrate Polymers* 147: 133–138.

57 Nayeem, J., Sarkar, M., and Quadery, A.H. (2017). High purity dissolving pulp from jute. *Nordic Pulp and Paper Research Journal* 32 (4): 623–629.

58 Wu, C.J., Zhang, J.C., and Yu, D.M. (2018). Dissolving pulp from bamboo-willow. *Cellulose* 25 (1): 777–785.

59 Casillas, R.R., López, M.C.L., and Aguilar, B.B. (2019). Obtaining dissolving grade cellulose from the huizache (*Acacia farnesiana* L. Willd.) plant. *BioResources* 14 (2): 3301–3318.

60 Wu, G., Zhang, Y., and Yuan, B. (2019). Production of dissolving pulp from *Eulaliopsis binata* with the concept of integrated biorefinery. *Cellulose* 26 (3): 2087–2097.

61 Sarkar, A.M., Nayeem, J., and Rahaman, M.M. (2021). Dissolving pulp from non-wood plants by prehydrolysis potassium hydroxide process. *Cellulose Chemistry and Technology* 55 (1, 2): 117–124.

62 Rocha, G.J.M., Andrade, L.P., and Martín, C. (2020). Simultaneous obtaining of oxidized lignin and cellulosic pulp from steam-exploded sugarcane bagasse. *Industrial Crops and Products* 147: 11227.

63 Ehman, N.V., Rodriguez Rivero, G.E., and Area, M.C. (2017). Dissolving pulps by oxidation of the cellulosic fraction of lignocellulosic waste. *Cellulose Chemistry and Technology* 51 (9, 10): 863–870.

64 Cao, Y., Zhang, R., and Cheng, T. (2017). Imidazolium-based ionic liquids for cellulose pretreatment: recent progresses and future perspectives. *Applied Microbiology and Biotechnology* 101 (2): 521–532.

65 Michud, A., Hummel, M., and Sixta, H. (2016). Influence of process parameters on the structure formation of man-made cellulosic fibers from ionic liquid solution. *Journal of Applied Polymer Science* 133 (30): 43718.

66 Yuan, X. and Cheng, G. (2015). From cellulose fibrils to single chains: understanding cellulose dissolution in ionic liquids. *Physical Chemistry Chemical Physics* 17 (47): 31592–31607.

67 Michud, A., Tanttu, M., and Asaadi, S. (2015). Ioncell-F: ionic liquid-based cellulosic textile fibers as an alternative to viscose and lyocell. *Textile Research Journal* 86 (5): 543–552.

68 Pang, J., Wu, M., and Zhang, Q. (2015). Comparison of physical properties of regenerated cellulose films fabricated with different cellulose feedstocks in ionic liquid. *Carbohydrate Polymers* 121: 71–78.

69 Suzuki, S., Shibata, Y., and Hirose, D. (2018). Cellulose triacetate synthesis via one-pot organocatalytic transesterification and delignification of pretreated bagasse. *RSC Advances* 8 (39): 21768–21776.

70 Kakko, T., King, A.W.T., and Kilpeläinen, I. (2017). Homogenous esterification of cellulose pulp in [DBNH][OAc]. *Cellulose* 24 (12): 5341–5354.

71 Dołżonek, J., Kowalska, D., and Maculewicz, J. (2020). Regeneration, recovery, and removal of ionic liquids. In: *Encyclopedia of Ionic Liquids* (ed. S. Zhang), 1–9. Singapore: Springer Singapore.

72 Müller, K., Zollfrank, C., and Schmid, M. (2019). Natural polymers from biomass resources as feedstocks for thermoplastic materials. *Macromolecular Materials and Engineering* 304 (5): 1800760.

73 Hou, D.-F., Li, M.-L., and Yan, C. (2021). Mechanochemical preparation of thermoplastic cellulose oleate by ball milling. *Green Chemistry* 23 (5): 2069–2078.

74 Azadimanesh, F. and Mohammadi, N. (2015). A plasticizer index to universally correlate the normalized work of fracture and elastic modulus of plasticized cellulose triacetates. *Carbohydrate Polymers* 130: 316–324.

75 Bao, C.Y., Long, D.R., and Vergelati, C. (2015). Miscibility and dynamical properties of cellulose acetate/plasticizer systems. *Carbohydrate Polymers* 116: 95–102.

76 Li, Z., Liu, N., and Yao, Y. (2015). Thermal behavior of cellulose diacetate melt using ionic liquids as plasticizers. *RSC Advances* 5 (2): 901–907.

77 Biswas, A., do Socorro Rocha Bastos, M., and Furtado, R.F. (2020). Evaluation of the properties of cellulose ester films that incorporate essential oils. *International Journal of Polymer Science* 2020: 1–8.

78 do Socorro Rocha Bastos, M., Da Silva Laurentino, L., and Canuto, K.M. (2016). Physical and mechanical testing of essential oil-embedded cellulose ester films. *Polymer Testing* 49: 156–161.

79 Iji, M., Moon, S., and Tanaka, S. (2011). Hydrophobic, mechanical and thermal characteristics of thermoplastic cellulose diacetate bonded with cardanol from cashew nutshell. *Polymer Journal* 43 (8): 738–741.

80 Tedeschi, G., Guzman-Puyol, S., and Paul, U.C. (2018). Thermoplastic cellulose acetate oleate films with high barrier properties and ductile behaviour. *Chemical Engineering Journal* 348: 840–849.

81 Boulven, M., Quintard, G., and Cottaz, A. (2019). Homogeneous acylation of cellulose diacetate: towards bioplastics with tuneable thermal and water transport properties. *Carbohydrate Polymers* 206: 674–684.

82 Tanaka, S., Iwata, T., and Iji, M. (2017). Long/short chain mixed cellulose esters: effects of long acyl chain structures on mechanical and thermal properties. *ACS Sustainable Chemistry & Engineering* 5 (2): 1485–1493.

83 El-Sakhawy, M., Tohamy, H.A.S., and Salama, A. (2019). Thermal properties of carboxymethyl cellulose acetate butyrate. *Cellulose Chemistry and Technology* 53 (7–8): 667–675.

84 Krasnou, I., Tarasova, E., and Märtson, T. (2015). Thermoplastic cellulose stearate and cellulose laurate: melt rheology, processing and application potential. *International Polymer Processing* 30 (2): 210–216.

85 Meng, C., Cao, G.P., and Yan, Y.Z. (2017). Synthesis of cellulose acetate propionate with controllable contents and distributions of acetyl and propionyl in the C2, C3 and C6 positions. *Reaction Kinetics, Mechanisms and Catalysis* 122 (2): 1031–1047.

86 Ohno, T. and Nishio, Y. (2007). Estimation of miscibility and interaction for cellulose acetate and butyrate blends with *N*-vinylpyrrolidone copolymers. *Macromolecular Chemistry and Physics* 208 (6): 622–634.

87 Kusumi, R., Inoue, Y., and Shirakawa, M. (2008). Cellulose alkyl ester/poly(ε-caprolactone) blends: characterization of miscibility and crystallization behaviour. *Cellulose* 15 (1): 1–16.

88 Wang, X., Huang, S., and Wang, Y. (2017). Eco-friendly cellulose acetate butyrate/poly(butylene succinate) blends: crystallization, miscibility, thermostability, rheological and mechanical properties. *Journal of Polymer Research* 24 (2): 16.

89 Fei, Z., Huang, S., and Yin, J. (2015). Preparation and characterization of bio-based degradable plastic films composed of cellulose acetate and starch acetate. *Journal of Polymers and the Environment* 23 (3): 383–391.

90 Kunthadong, P., Molloy, R., and Worajittiphon, P. (2015). Biodegradable plasticized blends of poly(ʟ-lactide) and cellulose acetate butyrate: from blend preparation to biodegradability in real composting conditions. *Journal of Polymers and the Environment* 23 (1): 107–113.

91 Rokkonen, T., Willberg-Keyriläinen, P., and Ropponen, J. (2021). Foamability of cellulose palmitate using various physical blowing agents in the extrusion process. *Polymers* 13 (15): 2416.

92 Breuer, R., Zhang, Y., and Erdmann, R. (2018). Extrusion foaming of thermoplastic cellulose acetate sheets with HFO-1234ze and co-blowing agents. *Polymer Engineering & Science* 58 (S1): E182–E188.

93 Breuer, R., Zhang, Y., and Erdmann, R. (2020). Development and processing of flame retardant cellulose acetate compounds for foaming applications. *Journal of Applied Polymer Science* 137 (28): 48863.

94 Shafaei, S., Dörrstein, J., and Guggenbichler, J.P. (2017). Cellulose acetate-based composites with antimicrobial properties from embedded molybdenum trioxide particles. *Letters in Applied Microbiology* 64 (1): 43–50.

95 Liu, J., Willför, S., and Xu, C. (2015). A review of bioactive plant polysaccharides: biological activities, functionalization, and biomedical applications. *Bioactive Carbohydrates and Dietary Fibre* 5 (1): 31–61.

96 Suteris, N.N., Misnon, I.I., and Roslan, R. (2020). Synthesis and characterization of polycaprolactone/cellulose acetate by electrospinning for wound dressing applications, Chapter 3. In: *Materials Science Forum* (ed. A.G.E. Sutjipto, F.H. Zulkifli and I.I. Misnon), 291–295. Trans Tech Publications Ltd.

97 Khoshnevisan, K., Maleki, H., and Samadian, H. (2018). Cellulose acetate electrospun nanofibers for drug delivery systems: applications and recent advances. *Carbohydrate Polymers* 198: 131–141.

98 Baharifar, H., Honarvarfard, E., and Malek-Kheili, M.H. (2017). The potentials and applications of cellulose acetate in biosensor technology. *Nanomedicine Research Journal* 2 (4): 216–223.

99 Suwantong, O. and Supaphol, P. (2015). Applications of cellulose acetate nanofiber mats. In: *Handbook of Polymer Nanocomposites. Processing, Performance and Application: Volume C: Polymer Nanocomposites of Cellulose Nanoparticles* (ed. J.K. Pandey, H. Takagi, A.N. Nakagaito and H.-J. Kim), 355–368. Berlin/Heidelberg: Springer.

100 Cheng, M., Qin, Z., and Hu, S. (2017). Use of electrospinning to directly fabricate three-dimensional nanofiber stacks of cellulose acetate under high relative humidity condition. *Cellulose* 24 (1): 219–229.

101 Fu, L.H., Qi, C., and Ma, M.G. (2019). Multifunctional cellulose-based hydrogels for biomedical applications. *Journal of Materials Chemistry B* 7 (10): 1541–1562.

102 Zhang, L., Guo, L., and Wei, G. (2018). Recent advances of cellulose-based materials and their promising application in sodium-ion batteries and capacitors. *Small* 14 (47): e1802444.

103 Abdul Khalil, H.P.S., Alwani, M.S., and Islam, M.N. (2015). The use of bamboo fibres as reinforcements in composites. In: *Biofiber Reinforcements in Composite Materials* (ed. O. Faruk and M. Sain), 488–524. Elsevier Inc.

104 Agarwal, J., Sahoo, S., and Mohanty, S. (2020). Progress of novel techniques for lightweight automobile applications through innovative eco-friendly composite materials: a review. *Journal of Thermoplastic Composite Materials* 33 (7): 978–1013.

105 Ferreira, D.P., Cruz, J., and Fangueiro, R. (2018). Surface modification of natural fibers in polymer composites. In: *Green Composites for Automotive Applications* (ed. G. Koronis and A. Silva), 3–41. Elsevier.

106 Gutiérrez, T.J. and Alvarez, V.A. (2017). Cellulosic materials as natural fillers in starch-containing matrix-based films: a review. *Polymer Bulletin* 74 (6): 2401–2430.

107 Panthapulakkal, S., Raghunanan, L., and Sain, M. (2017). Natural fiber and hybrid fiber thermoplastic composites: advancements in lightweighting applications. In: *Green Composites: Waste and Nature-based Materials for a Sustainable Future*, 2e (ed. C. Baillie and R. Jayasinghe), 39–72. Elsevier Inc.

108 Ramamoorthy, S.K., Skrifvars, M., and Persson, A. (2015). A review of natural fibers used in biocomposites: plant, animal and regenerated cellulose fibers. *Polymer Reviews* 55 (1): 107–162.

109 Souza, S.F., Ferreira, M., and Sain, M. (2015). The use of curaua fibers as reinforcements in composites. In: *Biofiber Reinforcements in Composite Materials* (ed. O. Faruk and M. Sain), 700–720. Elsevier Inc.

110 Sarasini, F. (2017). Fully biodegradable all-cellulose composites. In: *Handbook of Composites From Renewable Materials* (ed. V.K. Thakur, M.K. Thakur and M.R. Kessler), 303–322. Wiley.

111 Baghaei, B. and Skrifvars, M. (2020). All-cellulose composites: a review of recent studies on structure, properties and applications. *Molecules* 25 (12): 2836.

112 Fujisawa, S., Saito, T., and Isogai, A. (2018). All-cellulose (cellulose-cellulose) green composites. In: *Advanced Green Composites* (ed. A. Netravali), 111–133. Wiley.

113 de Oliveira Sousa Neto, V. and Do Nascimento, R.F. (2017). Recent progress in biocomposite of biodegradable polymer. In: *Handbook of Composites from Renewable Materials* (ed. V.K. Thakur, M.K. Thakur and M.R. Kessler), 61–94. Wiley.

114 Dufresne, A. and Castaño, J. (2017). Polysaccharide nanomaterial reinforced starch nanocomposites: a review. *Starch/Staerke* 69 (1, 2): 1500307.

115 Espinach, F.X., Méndez, J.A., and Granda, L.A. (2017). Bleached kraft softwood fibers reinforced polylactic acid composites, tensile and flexural strengths. In: *Natural Fiber-Reinforced Biodegradable and Bioresorbable Polymer Composites* (ed. A.K. Lau and A.P.-Y. Hung), 73–90. Elsevier Inc.

116 Khosravi, A., Fereidoon, A., and Khorasani, M.M. (2020). Soft and hard sections from cellulose-reinforced poly(lactic acid)-based food packaging films: a critical review. *Food Packaging and Shelf Life* 23: 100429.

117 Mokhena, T.C., Sefadi, J.S., and Sadiku, E.R. (2018). Thermoplastic processing of PLA/cellulose nanomaterials composites. *Polymers* 10 (12): 1363.

118 Nazrin, A., Sapuan, S.M., and Zuhri, M.Y.M. (2020). Nanocellulose reinforced thermoplastic starch (TPS), polylactic acid (PLA), and polybutylene succinate (PBS) for food packaging applications. *Frontiers in Chemistry* 8: 213.

119 Jonoobi, M., Oladi, R., and Davoudpour, Y. (2015). Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: a review. *Cellulose* 22 (2): 935–969.

120 Vigneshwaran, N., Satyamurthy, P., and Jain, P. (2015). Biological synthesis of nanocrystalline cellulose by controlled hydrolysis of cotton fibers and linters. In: *Handbook of Polymer Nanocomposites. Processing, Performance and Application: Volume C: Polymer Nanocomposites of Cellulose Nanoparticles* (ed. J.K. Pandey, H. Takagi, A.N. Nakagaito and H.-J. Kim), 27–36. Berlin/Heidelberg: Springer.

121 Abdul Khalil, H.P., Davoudpour, Y., and Bhat, A.H. (2015). Electrospun cellulose composite nanofibers. In: *Handbook of Polymer Nanocomposites. Processing, Performance and Application: Volume C: Polymer Nanocomposites of Cellulose Nanoparticles* (ed. J.K. Pandey, H. Takagi, A.N. Nakagaito and H.-J. Kim), 191–228. Berlin/Heidelberg: Springer.

122 Boufi, S. (2015). Nanofibrillated cellulose: sustainable nanofiller with broad potentials use. In: *Biomass and Bioenergy: Applications* (ed. K.R. Hakeem, M. Jawaid and U. Rashid), 267–305. Springer International Publishing.

123 Jorfi, M. and Foster, E.J. (2015). Recent advances in nanocellulose for biomedical applications. *Journal of Applied Polymer Science* 132 (14): 41719.

124 Joseph, K., Sandhya, K.Y., and Saritha, A. (2015). Liquid crystalline polymers from renewable resources: synthesis and properties. In: *Liquid Crystalline Polymers: Volume 1-Structure and Chemistry* (ed. V.K. Thakur and M.R. Kessler), 273–306. Springer International Publishing.

125 Polman, E.M.N., Gruter, G.-J.M., and Parsons, J.R. (2021). Comparison of the aerobic biodegradation of biopolymers and the corresponding bioplastics: a review. *Science of the Total Environment* 753: 141953.

126 Yadav, N. and Hakkarainen, M. (2021). Degradable or not? Cellulose acetate as a model for complicated interplay between structure, environment and degradation. *Chemosphere* 265: 128731.