

Self-assembly Fundamentals in the Reconstruction of Lignocellulosic Materials: A Review

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This review article considers processes by which the main components of wood have been reported to arrange themselves into various kinds of organized structures, at least to a partial extent. The biosynthesis of wood provides the clearest examples of such self-organization. For example, even before a cellulose macromolecule has been completely synthesized in a plant organism, the leading parts of the polymer chains already will have assembled themselves into organized crystals, *i.e.*, nano-fibrils. This review then considers a challenge that faces industrial engineers: how to emulate the great success of natural systems when attempting to achieve favorable materials properties, process efficiency, and environmental friendliness when developing new engineered wood structures, barrier films, and other desired products composed of lignocellulosic materials. Based on the reviewed literature, it appears that the main chemical components of wood, even after they have been isolated from each other, still have a remnant of their initial tendencies to come back together in a somewhat non-random fashion, following mechanisms that can be favorable for the production of engineered materials having potentially useful functions.

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INTRODUCTION

Self-assembly can be defined as a tendency of molecules or other substructures to come together in an organized fashion, ideally resulting in a structure that embodies desired characteristics and behaviors. The actions of the DNA molecules, and indeed of life itself, can be regarded as the world's premier example of self-assembly. Remarkably, a set of DNA molecules has the potential to direct the assembly of an entire living organism – not just for a single generation but also for the second generation, and then the next. Numerous other examples of self-assembly take place in a wide variety of existing processes, and in many cases they may be under-appreciated. For instance, when cellulose is formed into a solution and then rendered insoluble again by changing the solvent mixture, it has a strong tendency to form fiber-like structures (Fink *et al.* 2001; Zhang *et al.* 2018). Thus, engineers who work with lignocellulosic materials may ask themselves what they can do to take advantage of such a powerful principle in the manufacture of materials and products for usage in modern society. The goal of this review is to consider both the opportunities and constraints when self-assembly is considered as a potential tool for development and production of items based on the components of lignocellulosic source materials. This article focuses on fundamentals. A series of future articles are planned to go more deeply into literature findings related to self-assembly phenomena involving lignin, cellulose, hemicellulose, and wood extractives.

Motivations

This review article aims to discuss basic concepts related to self-assembly strategies and to envision ways in which such strategies are or can be applied in biomass-related technologies, which can include papermaking, composites, and the formation of bio-based films. As should become clear from articles cited in this review, there are many challenges associated with such efforts. Accordingly, it makes sense to consider a simple question, “Why should a modern engineer, involved with product development, even consider self-assembly as a possible tool to use in preparing new materials and products from lignocellulosic resources?” Four reasons, to be described below, can be briefly labeled as “eco-friendliness,” efficiency,” “performance,” and “tailored properties”.

Eco-friendly

There is not necessarily a direct correlation between self-assembly and eco-friendliness. But on the converse, many of the preparation steps used presently in present industry yield large proportions of wasteful and often harmful byproducts and emissions, even when utilizing bio-based materials (Weiss *et al.* 2012; Hahladakis *et al.* 2018; Ramesh *et al.* 2020). Production of steel requires, for example, large amounts of fuel to reduce the ore to iron, leaving behind tons of low-valued slag (Norgate *et al.* 2007; Olmez *et al.* 2016). Traditional organic synthesis of drugs requires multiple procedural steps, many of which have relatively low yields, with the generation of toxic solvent-containing mixtures (Jahangirian *et al.* 2017). Plastic beverage containers are a prime example when considering products that compete with cellulose-based products. In addition to inherent inefficiencies and environmental harm associated with the initial production (Hahladakis *et al.* 2018), the proportion of recycled plastics is relatively low (Ragaert *et al.* 2017), and their remnants as litter and microparticles contaminate the environment and fail to decompose in practical lengths of time (Horton *et al.* 2017).

The term “biomimicry,” *i.e.*, the imitation of nature, describes a promising strategy to achieve environmental compatibility. The logic is that nature itself has evolved a balanced, self-sustaining cycle of production, decay, and reutilization of byproducts. A modern engineer can choose to take advantage of some aspects of this self-sustaining web of processes in the production of items used by society. For instance, wood can be utilized as lumber, as oriented strands for strandboard, or as particles in the preparation of particleboard (Chen *et al.* 2020). At the same time, the engineer may choose to avoid toxic or non-biodegradable components or to avoid processing aids that do not fit with natural degradative and regenerative cycles (Hemmila *et al.* 2017; Hubbe *et al.* 2018).

An approach based on self-assembly may be expected to contribute to eco-friendly outcomes if and when the inherent self-organizing characteristics of the substances and procedures make it possible to decrease the usage of energy, toxic materials, or the generation of waste materials during preparation of an item needed by society. Consider, for example, the preparation of particleboard. In conventional practice, particleboard is made by coarse grinding of either freshly cut or used wood, followed by gluing it all back together in the presence of formaldehyde-containing resins, heat, pressure, and time (Owodunni *et al.* 2020). There has been extensive research aimed at finding conditions of pressing and formulation to allow the production of “binderless” board (Hubbe *et al.* 2018; Owodunni *et al.* 2020). This can include reliance on natural binder-like materials (*e.g.* tannins or lignin itself) that are already present in the plant materials (Tajuddin *et al.* 2016; Nasir *et al.* 2019). Such binderless or natural-binder approaches can be called self-assembly if and when the woody particles or resinous substances have an inherent tendency to organize themselves into a desired structure upon application of suitable processing conditions.

Efficient

Enzymes can be regarded as premier examples of self-assembly tools. They can direct chemical reactions toward preferred pathways. For example, the enzyme amylase can be used to convert starch to sugar at room temperature and with very high yield (van der Maarel *et al.* 2002). Likewise, it was shown recently that the lipase enzyme can be used for surface esterification of cellulose nanocrystals (CNC) with palmitoyl groups, thus providing a hydrophobic surface that is more compatible with a hydrophobic polymer matrix (Yin *et al.* 2020). Enzymes often can direct chemical reactions toward a single desired outcome, thus minimizing the generation of unwanted byproducts.

An inherent challenge faces modern engineers when considering the use of approaches based on the principles of self-assembly. While enzymes and other self-assembly processes are known from nature, the resulting cellulose, hemicellulose, or lignin materials, in the form that they are readily available to the modern industrialist, may be lacking in key features that may have been present at an earlier stage of biosynthesis or freshness of those materials. Some of the biosynthesis steps in the natural generation of lignocellulose have at least partially irreversible character. For instance, once cellulose chains come together as crystals, during their biosynthesis, there are relatively few solvent conditions capable of separating them (Rosenau *et al.* 2001; Chen *et al.* 2019; Verma *et al.* 2019). Likewise, when technologists attempt to dissolve lignin through pulping technologies or other isolation methods, the created substructures often undergo partial condensation reactions, leading to substantial differences in chemical structure relative to native lignin (Kim and Kim 2018).

Performance

One of the first well-known efforts in nanotechnology involved the one-by-one placement of atoms onto a crystal surface, thus spelling out the initials of a corporation (Bayda *et al.* 2020). Though such an outcome was noted as a great achievement, it is clear that different approaches need to be employed to achieve rates of production suitable for mass production. Ideally, the building blocks of the desired product would be capable of organizing themselves. And even if the spelling of a corporate logo by placement of atoms remains a CEO's dream, one also can aim for more practical goals, such as using self-assembly principles to create barrier films for packaging (Gokhale and Lee 2014; Hubbe 2021).

Oriented monolayer formation on smooth surfaces is achievable by optimized treatment with suitable surface-active compounds in solution (Senaratne *et al.* 2005). The contrasting affinities of the head groups and tail groups of the surfactant molecules drive the well-known adsorption tendency for such compounds. As shown in Fig. 1, there are often three main contributions to the stability of contiguous adsorbed monolayers in aqueous systems: between a hydrophobic tail group and the solid material; between adjacent hydrophobic tail groups; and between a hydrophilic head group and the aqueous solution. A main contribution to the so-called hydrophobic effect is the dominant effect of hydrogen bonding among water molecules (Tanford 1980). Those forces favor systems in which non-polar entities self-associate and thereby get out of the way of potential hydrogen bonding. In this way, self-association among non-hydrogen-bonding groups and compounds contributes to the free energy of the system. As suggested in Fig. 1, the interactions between the head groups and the aqueous phase can include not only hydrogen bonding but also the polar forces associated with optional ionized groups (Martinez *et al.* 2011). When the amount of surface-active molecules is less than what is needed for a fully compressed monolayer, as shown on the left of the figure, thermodynamics is likely to favor a conformation in which the molecules' hydrophobic groups associate with a cellulosic surface. Though the latter can be described as "hydrophilic," it is less so compared to an aqueous phase. The hydrophobic effect, having hydrogen bonding as its key factor, also benefits from the van der Waals-London component known as dispersion forces (Bowen and Jenner 1995).

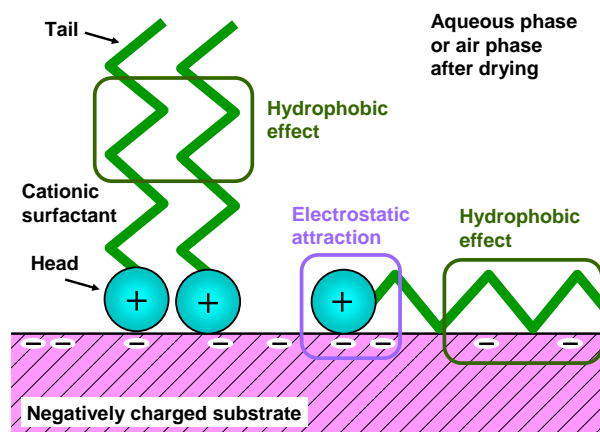


Fig. 1. Illustration of three main contributions to the stability of certain surfactant monolayer films self-assembled onto solid surfaces from aqueous solution

Oriented multilayer formulations also can be assembled. Layer-by-layer structures can achieve a certain degree of regularity because of their opposite charge in comparison to the net charge of each preceding layer (Xiong *et al.* 2017a; Kramer *et al.* 2019). By alternating the application of cationic and anionic polyelectrolyte solutions, with each such application separated by a rinsing (and optional drying) step, it is possible to prepare highly regular multilayer structures (Tong *et al.* 2012; Ariga *et al.* 2014; Keeney *et al.* 2015). Though the process is very slow, it is possible to achieve practical effects in the laboratory such as increases in the fiber-to-fiber bonding strength within paper structures (Aulin *et al.* 2010b). In addition, the knowledge gained in forming such multilayers may lead to more practical strategies for forming paper with large gains in bonding strength at commercially competitive speeds of formation (Hubbe 2014a).

Engineered materials with tailored properties

To compete in the current marketplace, a manufactured material or product needs to accurately fulfill many requirements simultaneously. Likewise, natural materials, all of which are developed through biological self-assembly processes, display a high level of complexity (Sanchez *et al.* 2005; Mendes *et al.* 2013). These considerations imply that extensive trial and error may be needed when one's goal is to use self-assembly as a tool in product development.

One promising approach by which to achieve a moderate level of complex structuring, while at the same time not exceeding what can be reasonably expected in terms of reliance on self-assembly, consists of three-dimensional printing, which is also called additive manufacturing (Mitchell *et al.* 2018; Ee and Li 2021). For example, Greenhall and Raeymaekers (2017) employed 3D printing to achieve a general placement of substances; ultrasonic vibrations were then used to enable the microscale self-organization of particles. Likewise, researchers have 3D-printed living biological cells into desired shapes or films, then relying on their natural self-organizing ability to finish the job of forming a biological tissue (Marga *et al.* 2012).

Reasons to be cautious

While the potential advantages of eco-friendliness, efficiency, performance, and tailoring of properties provide reasons for researchers and industrialists to consider production strategies based on self-assembly, there are also reasons to be cautious. Some of these already have been mentioned. A more complete list is as follows:

- The amazing self-assembly capabilities associated with DNA and life itself have taken very long spaces of time to evolve.
- The biosynthesis of lignocellulosic matter involves some steps that are at least partly irreversible.
- The chemical pulping of wood, which is an example of a process that separates lignocellulose into its main components, is expected to involve irreversible changes to those components.
- The organizing principles of self-assembly, such as charge attractions, hydrogen bonds, and differing affinities, may provide insufficient strength and durability of the prepared structures relative to their intended uses.
- Industrial processes such as papermaking often involve the recirculation of water, which will be contaminated with diverse substances that may interfere with various details of self-assembly.

Some Definitions Related to Self-assembly

Self-assembly

The definition of self-assembly provided at the very beginning of this article is not the only one. The textbook by Pelesko (2007) considers such definitions in detail. The book also provides numerous examples of self-assembly research, including both of ultra-simple and complex systems, ranging all the way to living organisms and ambitious philosophical questions. Pelesko (2007) has proposed the following general definition, in an attempt to encompass both the simple and the much more complex examples of self-assembly: “Self-assembly refers to the spontaneous formation of organized structures through a stochastic process that involves pre-existing components, is reversible, and can be controlled by proper design of the components, the environment, and the driving forces.” By the term “driving forces,” Pelesko is emphasizing the fact that self-assembly usually requires work to be done, and a completely static system, with no force fields or gradients in levels of energy, will lack a reason to become organized.

Fortunately, except at an absolute zero temperature, thermal energy can be relied upon to cause diffusion, *i.e.*, Brownian motion (Li *et al.* 2008). The random motions can often be sufficient motivation, acting together with other features, to allow the components to sample different possible patterns of organization on the way to finding a favorable self-assembled pattern. Accordingly, the next definition given by Pelesko is “static self-assembly,” meaning that the random process has reached a stable equilibrium. The converse is a “dynamic self-assembly,” which means that the resulting structure is stuck in a non-equilibrium state, which is determined by kinetic factors. Also there is programmed self-assembly, in which the components each embody some form of instructions regarding how they are supposed to ultimately fit together. Lindsey (1991) uses the term “strict self-assembly,” which appears to be the same as what Pelesko (2007) would call “static self-assembly,” with the further stipulation by Pelesko that there is no human intervention. This is consistent also with a definition used by Whitesides and Grzybowski (2002). In contrast, one can define “directed self-assembly” to cover cases of interest in which the human influences the outcome by adjusting various conditions as a self-assembly process is taking place, such as to favor a certain outcome (Lindsey 1991). The cited authors also notes that the main interest is often in forming a higher-order structure in comparison to the level of complexity of the initial molecules or substructures. In its most highly developed form, one might apply an ultimate definition for self-assembly as having “stunning features” such as convergence, control of disassembly and reassembly, error-checking and recovery, and high accuracy (Lindsey 1991). From the foregoing discussion it should be clear that the definition of self-assembly can be fashioned in diverse ways to describe many different situations.

Bio-inspired

By carefully observing certain processes associated with living systems, scientists may gain insight into what is possible to achieve. Such a focus is especially appropriate when considering ways to manufacture products such as biodegradable packaging items. Biological materials having a lignocellulosic nature are well known for such attributes as toughness, high strength-to-weight ratio, and biodegradability (Bond *et al.* 1995). In addition, rather than breaking in a catastrophic fashion, woody materials often fail in a graceful manner, meaning that the loss of strength is gradual (Bond *et al.* 1995). However, the same authors note that some of the premier biobased structures, including bone, wood, and insect cuticles, have highly refined low-density structures that would be inherently

difficult for a modern engineer to replicate in an industrial process. Although one might consider preparing the detailed structure of wood by means of three-dimensional printing, a recent article suggests that such a goal still remains beyond the capabilities of current 3D printing technology (Aydin and Yilmaz Aydin 2022). It remains an unresolved question as to whether developers will be able to match the properties of wood when using just the components, *e.g.*, cellulose, hemicellulose, and lignin in non-native forms. Gradwell *et al.* (2004) showed that at least part of such an effort could be achieved. They utilized pullulan abietate – roughly representing lignin and polysaccharide, according to those authors – as a matrix phase in the presence of cellulosic fibers. The amphiphilic pullulan abietate adsorbed strongly onto the cellulose, as a purported first step in making a wood-like material.

Bottom-up preparation of nanomaterials

When discussing different ways to obtain nanomaterials, especially in the case of cellulose nanomaterials, the term “bottom-up” means that fibril-like materials are assembled by biosynthesis (Mendes *et al.* 2013). One can envision other nanomaterials, such as colloidal silica particles, being formed as a result of sticking collisions among primary particles, followed by their fusion into persistent structures (Iler 1979). It has been shown that, by careful adjustment of both pH and concentrations of the starting materials, the primary particles will experience a relatively high probability of sticking collisions only to the ends of chains, rather than onto the sides of existing chains or groups of such primary particles. Thereby, chain-like growth may be preferred. The resulting particles have been called “gels.” In contrast, the unchained “sol” form of such particles will form under conditions in which there are sufficiently strong electrostatic repulsions between particles such that they grow individually (Iler 1979). The mechanism is illustrated in Fig. 2.

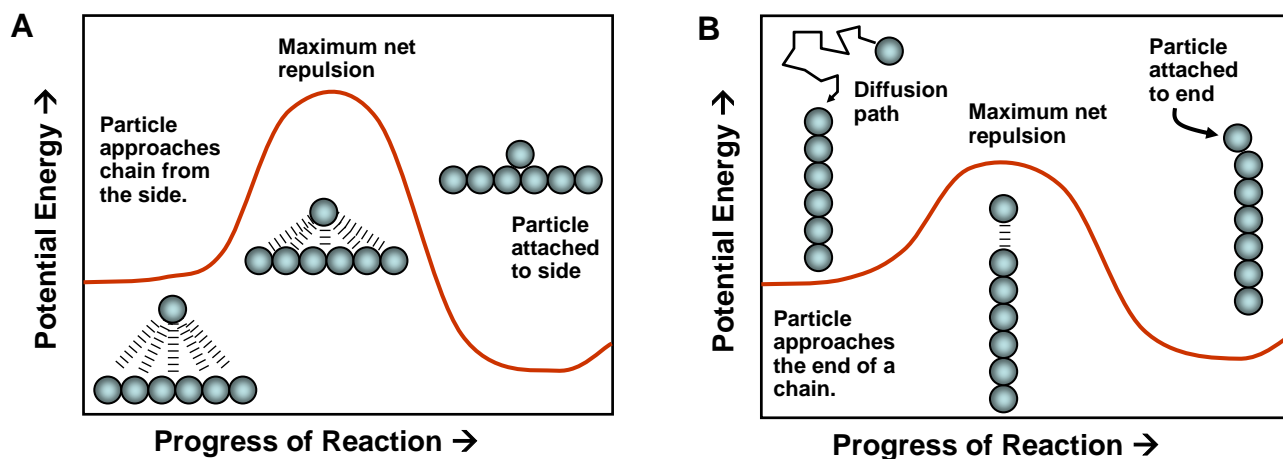


Fig. 2. Mechanism to explain preferential end-wise deposition of primary colloidal silica particles, thus leading to chain formation in the presence of an intermediate level of electrostatic component of repulsive forces between the surfaces. A: A higher energy barrier is encountered when approaching from the side; B: A lower energy barrier is encountered when approaching from the end.

When a primary particle of colloidal silica (typically about 1 to 5 nm in diameter) approaches the side of a chain of such particles (as illustrated in part A), the approaching particle is affected by electrostatic repulsion originating at the surfaces of several particles

in the chain simultaneously. By contrast, if the individual particles approaches from the end, it experiences repulsion mainly from just one particle, and therefore a successful collision is much more likely. Once the particles stick together, the chain essentially becomes sintered together due to ongoing interactions at the molecular scale. Such a bottom-up self-assembly could be considered for the components of lignocellulosic materials, and possibly such behavior might be demonstrated in the future.

GUIDING HYPOTHESIS

Hypothesis One:

It is proposed that the essentially irreversible character of certain sub-processes in both the biosynthesis of woody materials and in the isolation of woody materials provides barriers to full implementation of self-assembly procedures during attempted re-assembly of the components. In other words, it is proposed, for instance, that the mixing of cellulose, hemicellulose, lignin, and minor components of wood will not be able to re-create material with properties corresponding to those of wood.

Irreversible attributes of cellulose

Various research findings can be cited in general support of this first hypothesis. The insolubility of cellulose in most solvent systems is well known (Rosenau *et al.* 2001; Chen *et al.* 2019; Verma *et al.* 2019). The explanation for cellulose's reluctance to dissolve in most solvents apparently has to do with a two-fold mechanism involved in its crystallization. First, it is well known that cellulose undergoes highly regular and extensive intra- and intermolecular hydrogen bonding (Bergenstrahle *et al.* 2010). In addition, in the 1-10 crystal plane, the dominant interaction appears to be van der Waals attractions (Yamane *et al.* 2006). Any solvent system for cellulose needs to deal with both issues at once, or alternatively, it needs to form a derivative of cellulose (Medronho *et al.* 2012; Medronho and Lindman 2015). Thus, it is valid to say that cellulose's initial crystallization and insolubilization during its biosynthesis are essentially irreversible.

Drying of cellulosic materials can lead to irreversible changes, especially in cases where lignin and some of the hemicelluloses have been removed by pulping (Stone and Scallan 1966; Weise and Paulapuro 1999; Pönni *et al.* 2012). The effect, which is often called hornification, appears to involve the closing up of gaps between cellulosic surfaces (Pönni *et al.* 2012). Such closing up is favored by strong capillary forces as water is being evaporated (Campbell 1959; Page 1993). The effect occurs to a minor degree even during the wet-pressing of cellulosic pulp fibers (Maloney *et al.* 1997). One could say that as the tiny gaps between cellulosic surfaces become healed (Pönni *et al.* 2012), larger sizes of crystals are achieved, though one can expect there to be defects in such coalesced crystal structures (Scallan 1998).

Irreversible attributes of hemicellulose

Hemicelluloses, despite their tendency to swell in water, are mainly insoluble in aqueous media. This insolubility is achieved despite the molecules' somewhat irregular molecular structures (having side groups) and having two or three –OH groups per sugar monomeric unit. Based on these considerations, it can be concluded that a pattern of multiple, simultaneous hydrogen bonds is sufficient to keep hemicelluloses in solid form within a lignocellulosic or holocellulosic structure in the presence of water having

moderate pH values. Only at pH values greater than about 14 does the hemicellulose fully dissolve (TAPPI Method T 429). There appears to be a need for further research to clarify such irreversible tendencies in hemicellulose aqueous systems, including a fuller explanation of hemicelluloses' limited solubility in water.

Irreversible attributes associated with removal of lignin and hemicellulose

Another aspect of irreversibility can be blamed on the dominant pulping process that is being employed worldwide to liberate the cellulosic fibers from wood. The kraft pulping process not only breaks down and removes much of the lignin from the wood or nonwood lignocellulosic raw material, but it removes a substantial part of the hemicellulose as well (Fardim and Tikka 2011). It follows that one cannot expect the resulting cellulose fiber and directly reassemble as a wood-like material.

Irreversible attributes associated with lignin

Lignin, as it is being separated from lignocellulose in the course of pulping, is susceptible to condensation reactions (Schutyser *et al.* 2018). These reactions entail the essentially irreversible formation of carbon-carbon single bonds between aromatic groups. In principle, such condensed byproducts of lignin will be expected to have less ability to behave like native lignin. In an effort to minimize undesired condensation of lignin, researchers have developed a variety of strategies, often involving chemical derivatization of the starting material (Shuai *et al.* 2016; Renders *et al.* 2017; Schutyser *et al.* 2018). Such chemical details make it reasonable to question whether or not certain kinds of self-assembly, involving lignin moieties, may no longer be available after the completion of ordinary pulping and bleaching processes. Readers are encouraged to consult review articles for more details regarding pulping processes, the nature of the resulting lignin structures, and their possible modifications (Matsushita 2015; Trovagunta *et al.* 2021b).

Hypothesis Two:

It is proposed that developmental researchers and engineers will be able to improve their chances of achieving self-assembly due to the fact that they can select from a wide range of temperature, pressure, and chemical conditions, in comparison to the rather narrow ranges that are mandated by biological systems. Though living organisms have evolved to occupy niches in highly diverse environments, the aqueous conditions within the living cells generally are believed to approximate the salinity of an ancient ocean, in which the key initial steps of evolution presumably took place (Monnard and Deamer 2002). Under such conditions, DNA-based systems provide a high level of self-assembly in the perpetuation of life forms. But on the other hand, the modern developmental researcher does not have millions of years in which to wait for a desired evolutionary change to fully take place. As noted by Whitesides and Grzybowski (2002), a developmental researcher's motivation to employ some sort of self-assembly process may be greatest when considering the nano-scale of product development. As has been noted (Bayda *et al.* 2020), it is very difficult to manipulate a nano-scale object on an individual basis. Thus, the present review article will consider various evidence that more effective and efficient organization may be achieved by taking advantage of certain propensities of lignocellulosic components to organize themselves, especially if the engineer is able to prescribe the temperatures, pressures, aqueous conditions, and other factors. It is proposed that present and future engineers can widen their options by employing ranges of temperature and pressure that are not available during biosynthesis. They can also pre-plan various chemical conditions

and orders of addition. It is proposed that such options can provide opportunities for advances in materials processing that take advantage of self-assembly phenomena.

Some Key Sources

Table 1 provides a chronological listing, together with key themes and authors of review articles, other key articles, and one book dealing with self-assembly from various perspectives. Rather than going deeply into the subject matter of such articles, readers are encouraged to read the originals.

Table 1. Key Literature Related to Self-assembly

Doc. type	Main subject matter or insights	Citation
Review	Self-assembly as a means of synthesis at nano-scale	Lindsey 1991
Article	Molecular self-assembly and nanochemistry	Whitesides <i>et al.</i> 1991
Review	Forces that drive self-assembly at a nano scale	Suo & Lu 2000
Review	Membrane self-assembly and origins of life	Monnard & D, 2002
Review	Expansive, conceptual review: molecules to weather	Whitesides & G. 2002
Review	Evaporation-induced self-assembly	Brinker 2004
Review	Making things by self-assembly	Boncheva 2005
Review	Biomimicry and bioinspiration used as building principles	Sanchez <i>et al.</i> 2005
Review	Nanotechnology concepts for papermaking	Wegner & Jones 2006
Book	Systematic, thorough book with a focus on definitions	Pelesko 2007
Review	Self-assembly in bulk media and at interfaces	Ariga <i>et al.</i> 2008
Review	Colloidal interactions leading to self-assembly	Li <i>et al.</i> 2008
Review	Nanoscale forces and their use in self-assembly	Bishop <i>et al.</i> 2009
Review	Thermodynamic aspects of self-assembly	Grzybowski <i>et al.</i> 2009
Article	Self-winding in plant tendrils and cellulose liquid crystals	Godinho <i>et al.</i> 2010
Review	Directed self-assembly of nanoparticles	Grzelczak <i>et al.</i> 2010
Review	Cellulose nanocrystals and their nanocomposites	Habibi <i>et al.</i> 2010
Review	Bioinspired polymeric nanocomposites, <i>e.g.</i> , drawn silk	Stone & Korley 2010
Review	Cellulose and guest material self-assembly	Huang & Gu 2011
Review	Evaporation-induced self-assembly	Han & Lin 2012
Review	Biological tissues made with 3D printing	Marga <i>et al.</i> 2012
Review	Nano-scale coalescence of cellulose during processing	Pönni <i>et al.</i> 2012
Review	Self-assembly in nature and nanobiomaterials	Mendes <i>et al.</i> 2013
Review	Bio-inspired mineralization of polysaccharides	Wang <i>et al.</i> 2013
Review	Layer-by-layer self-assembly and architectures	Ariga <i>et al.</i> 2014
Review	Cellulose nanocrystals self-assembly	Lagerwall <i>et al.</i> 2014
Review	Biomedical applications of nanofibrous scaffolds	Wade & Burdick 2014
Article	Use of an acoustic field to align particles at a microscale	Collino <i>et al.</i> 2015
Review	Self-assembly mechanisms of plant cell walls	Murugesan <i>et al.</i> 2015
Review	Cellulose as a scaffold for self-assembly	Tian & He 2016
Review	3D printing in biological applications	Pekkanen <i>et al.</i> 2017
Review	3D printing and opportunities for self-assembly	Mitchell <i>et al.</i> 2018
Review	Self-bonding and natural binders for lignocellulose	Hubbe <i>et al.</i> 2018
Review	Liquid crystals and related self-organizing of CNC	Parker <i>et al.</i> 2018
Review	Self-assembly strategies for emerging nanomaterials	Percebom <i>et al.</i> 2018
Review	Cellulose nanomaterial self-assembly	Tayeb <i>et al.</i> 2018
Review	Bioinspired polymeric wood materials	Yu <i>et al.</i> 2018
Review	Nanoarchitectures achieved <i>via</i> self-assembly	Ariga <i>et al.</i> 2019
Review	Bio-inspired design and additive manufacturing	Li <i>et al.</i> 2019
Review	Self-assembly of lignin	Mishra & E. 2019a
Review	Self-assembly of surface-active compounds	Hubbe <i>et al.</i> 2020a

PRINCIPLES OF SELF-ASSEMBLY

As has already been noted, this article is about instances in which separated components of lignocellulose appear to self-arrange themselves. It is reasonable, in such cases, to consider a null hypothesis to the effect that the apparent self-organization is merely random or illusory. It has been suggested that humans have an inherent tendency to look for elements of organization in any situation that first appears to be chaotic (Whitesides and Grzybowski 2002). Thus, the first order of business is often to look carefully at each set of evidence.

In cases where evidence of self-assembly seems persuasive, the next step is to provide an explanation. In general terms, three things need to be present as a precondition for self-assembly to occur, namely some kind of information, some kind of interactive force, and some form of chaotic input, such as thermal diffusion or vibrations, *etc.* As discussed in the subsections below, all of these influences are required to follow the constraints imposed by thermodynamics.

Information

It has been proposed that organized assembly will require some form of information, which can take various forms. It can be embedded, for instance, in an amphiphilic nature of the parts to be assembled, such that they will prefer to go together in a certain manner. These tendencies could be based on shapes, on degrees of hydrophilicity, on the signs of electrical charge, or on details of molecular structure.

Amphiphilic character

Especially in aqueous media, a certain degree of self-organization can be expected when the dispersed entities (*e.g.*, molecules or particles) have hydrophilic parts and hydrophobic parts. Some examples are listed in Table 2. Of particular interest here are the findings that support the presence of different faces of native cellulose crystalline entities, giving rise to different affinities (Glasser *et al.* 2012; Khazraji and Robert 2013). Such affinities are important to keep in mind as potential contributing factors, even when researchers may be paying attention to different issues in their investigations.

Table 2. Publications Providing Examples in Which Amphiphilic Character Appeared to Promote Self-organization

Main subject matter or insights	Citation
Role of lipids (<i>e.g.</i> , fatty acids) in formation of biological membranes	Bond <i>et al.</i> 1995
Proposal that short-chain fatty acids were precursors of life	Monnard & Deamer 2002
Surface-modified cellulose exhibited surface-active behavior	Gradewell <i>et al.</i> 2004
Xylan self-assembly directed by different substituents	Westbye <i>et al.</i> 2007
Hydroxypropyl xylan self-assembly at cellulose surface	Kaya <i>et al.</i> 2009
Role of hydrophilic and hydrophobic interactions of cellulose	Glasser <i>et al.</i> 2012
Self-assembly of proteins and peptides for tissue regeneration	Hosseinkhani <i>et al.</i> 2013
Cellulose self-assembly affected by its amphiphilic nature	Khazraji & Robert 2013
Adsorption of proteins onto lignin controlled by wettability	Salas <i>et al.</i> 2013
Lignin hollow nanospheres having hydrophilic interiors	Xiong <i>et al.</i> 2017a,b
Fatty acid and wood pitch self-association	Hubbe <i>et al.</i> 2020a

Charges

The attraction between opposite electrical charges is well known to provide a driving force for various self-assembly phenomena. For example, the adsorption of cationic surfactants onto anionic substrates such as lignocellulosic material is known to benefit from such interactions (Biswas and Chatteraj 1997; Wågberg 2000; Szilagyi *et al.* 2014). Electrostatic forces between surfaces have been found to be especially prominent after oxidation of the cellulose to increase the amount of anionic groups on such surfaces (Soboyejo and Oki 2013).

Molecular structure

The fact that the details of molecular structure can affect organization at the nano-scale is already apparent from studies of DNA and its functions (Pelesko 2007). Another example comes from studies involving the partial modification of xylans (Kaya *et al.* 2009). The cited authors showed that different levels of hydroxypropylation of xylan influence its solubility in interesting ways. Although the hydroxypropyl groups are somewhat hydrophobic, low levels of hydroxypropylation favored water-solubility. At higher levels of substitution, the products of the reaction tended to agglomerate and separate themselves from water, as would be expected based on an increased hydrophobic character. It seems likely that the opposite effect at low substitution levels can be attributed to a break-up of regularity. This can be taken as evidence that the initial insolubility of the xylan is dependent on the regularity within its chain structure. Studies have shown that xylans, despite their strongly hydrophilic character, have a tendency to agglomerate in aqueous solution (Saake *et al.* 2001).

Shapes

Some of the most rudimentary empirical studies to confirm various aspects of self-assembly theories have involved the shapes of the yet-to-be-assembled items (Pelesko 2007). For instance, Li *et al.* (2008) showed that even monodispersed spheres tend to pack into neat face-centered cubic arrangements under the influence of gravity. Collino *et al.* (2015) showed that particle shape affected the organization of particles exposed to acoustic excitation. Rods, bricks, and bowtie-shaped objects yielded different types of “brick and mortar” structures having regular spacing.

For lignocellulosic materials, the most notable examples of shape-related organization are associated with cellulose nanocrystals (Habibi *et al.* 2010; Lavoine *et al.* 2019). Thus, Han *et al.* (2013) showed that a wide variety of CNCs and other forms of cellulosic nanomaterials could form various regular patterns in aqueous suspension, depending on the details. Lagerwall *et al.* (2014) explained such phenomena based on a competition between the formation of a glass-like organization and liquid crystal self-assembly. By adjusting various details, it is possible to achieve striking visual effects (Parker *et al.* 2018). Kawakatsu *et al.* (2006) used computer simulations to show the mechanistic feasibility of the initial self-organization of cellulose molecules shortly after their biosynthesis, which depends on their shape.

Forces

Some examples that already have been considered show that various types of self-organization can be achieved in the laboratory that do not involve close-range forces. This would be true, for instance, in the case of packing relatively large hard spheres in a gravity field (Li *et al.* 2008). But in many cases the subsequent usefulness of a self-organized

object depends on the action of forces of cohesion or adhesion. As indicated in the subsections that follow, these can involve van de Waals-type attractions, electrostatic forces, hydrogen bonding, and some related effects such as π -type bonding between aromatic groups associated with lignin structures.

Some general principles have become established regarding the relative magnitude of short-range forces relative to processes of self-assembly. Successful self-organization often requires that there be a suitable relationship between the magnitudes of attractive forces relative to the strength of chaotic effects such as Brownian diffusion or applied vibrations during the assembly process (Suo and Lu 2000). Especially if the aim is to create highly regular arrangements, it will be important for the aggregated system to have sampled a large number of arrangements. Each time, the structure is able to partially disassociate and then reassociate itself along a path leading to a more organized arrangement.

van der Waals forces

When the term “van der Waals forces” is used, it most often refers to the London dispersion component. This component arises due to mutually-induced momentary dipoles associated with the whirling motions of electrons in their orbits. In nature, such transient dipoles align themselves in such a way as to minimize free energy. Progress has been achieved in understanding such interactions in terms of electron density functions (Klimes and Michaelides 2012). Figure 3 presents a schematic illustration of three key components of force that are often involved with self-assembly in the absence of covalent bonding.

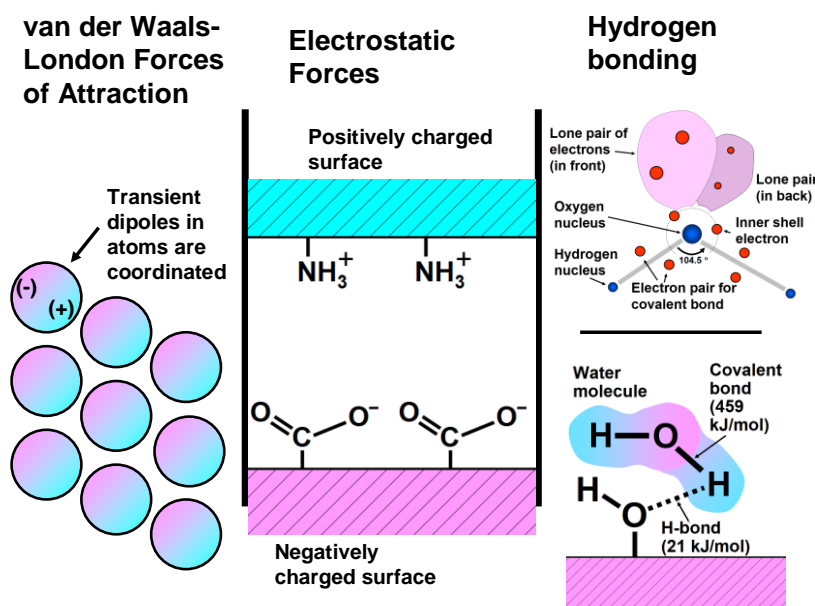


Fig. 3. Three key components of short-range interactive forces that are often involved with self-assembly phenomena that do not depend on the development of covalent bonds

For most systems of interest to scientists working with lignocellulosic materials, often in aqueous systems or in air media, the dispersion forces are attractive, acting to draw all objects – whether at the molecular level or larger – toward each other. Articles that have discussed the role of van der Waals (London) dispersion forces in the context of self-assembly are listed in Table 3. Of particular relevance for cellulosic systems are the articles

showing the dominance of dispersion forces relative to certain aspects of cohesion between adjacent cellulose chains (Saxena and Brown 2005; Khazraji and Robert 2013; Wang *et al.* 2013). In addition, Besombes and Mazeau (2005a,b) noted a tendency for the relatively hydrophobic lignin entities to adsorb onto the hydrophobic (200) crystalline face of cellulose.

Table 3. Publications Providing Examples in Which van der Waals Dispersion Forces Appear to be Involved with Self-assembly

Main subject matter or insights	Citation
Molecular modeling suggesting key role of dispersion forces	Besombes & Mazeau 2005a,b
Dispersion forces self-assemble “sheets” in cellulose synthesis	Saxena & Brown 2005
Review article focusing on self-assembly of colloidal particles	Li <i>et al.</i> 2008
Emphasizes the important of the relative strengths of forces	Bishop <i>et al.</i> 2009
Modeling showing importance of dispersion forces for cellulose	Khazraji & Robert 2013
Dispersion forces for cellulose chains at specified orientation	Wang <i>et al.</i> 2013

Electrostatic forces

Electrostatic forces were already mentioned in a previous subsection having to do with forms of information. Thus, the arrangements of charge on a molecule or on a particle could help to explain a resulting self-organizing arrangement. Table 4 lists some articles in which the action of electrostatic forces has been cited to explain self-assembled systems. A key advantage of electrostatic forces, from the standpoint of product development, is that one can envision strategies based on orders of addition. This is especially relevant when using polyelectrolytes, since the summative effect of multiple charge interactions can favor a stable adsorbed state (Dobrynin and Rubinstein 2005; Szilagyi *et al.* 2014). Such strategies are commonly employed in the paper industry, which will be considered near the end of this article.

Table 4. Publications Providing Examples in Which Electrostatic Forces Appear to be Involved with Self-assembly

Main subject matter or insights	Citation
Lignin adsorption onto cellulose facilitated by cationic polymer	Maximova <i>et al.</i> 2001
Review article focusing on self-assembly of colloidal particles	Li <i>et al.</i> 2008
Emphasizes the important of the relative strengths of forces	Bishop <i>et al.</i> 2009
Protein and peptide self-assembly for regenerative medicine	Hosseinkhani <i>et al.</i> 2013
Polyelectrolyte complexes formed with xylan and a cationic version	Vega <i>et al.</i> 2013

Hydrogen bonding

In view of the numerous and highly regular occurrence of hydroxyl groups in both cellulose and hemicellulose chains, there is reason to expect that hydrogen bonds will play a dominant role relative to the self-assembly that involves those components in aqueous systems. Table 5 lists articles in which hydrogen bonding was mentioned as a likely organizing factor in self-assembly.

Table 5. Publications Providing Examples in Which Hydrogen Bonding Appears to be Involved with Self-assembly

Main subject matter or insights	Citation
Role of hydrogen bonding shown in xylan aggregation	Mora <i>et al.</i> 1986
Molecular modeling suggests key role of dispersion forces	Besombes & Mazeau 2005
An additional hydrogen bond makes cellulose II more stable	Saxena & Brown 2005
Nano-scale coalescence of cellulose during processing	Pönni <i>et al.</i> 2012
Freeze-assembly of nanocellulose involves hydrogen bonding	Han <i>et al.</i> 2013
Suggests using solvents to turn hydrogen bonding off and on	Wang <i>et al.</i> 2013
Xylan self-assembly during oxygen delignification of pine	Grigoray <i>et al.</i> 2014
Lignin agglomeration can be brought about by hydrogen bonding	Ratnaweera <i>et al.</i> 2015

In addition to articles that attribute polysaccharide self-assembly effects to hydrogen bonding, there are additional articles that further bolster the accumulated evidence that such self-association has been broadly observed (Mora *et al.* 1986; Lang and Burchard 1993; Westbye *et al.* 2007; Grigoray *et al.* 2014). Whereas individual hydrogen bonds between polymers in an aqueous system can be easily displaced by water molecules, extensive and regular sheets of them can hold tenaciously together. Mora *et al.* (1986) demonstrated such effects through the usage of agents designed to disrupt hydrogen bonding.

Pi (π) bonding

A common variety of pi (π) bonding involves an attraction arising due to the delocalized electron cloud of an aromatic ring or rings. Figure 4 provides an illustration, based on a figure provided by Proteopedia (n.d.), using benzene as an example.

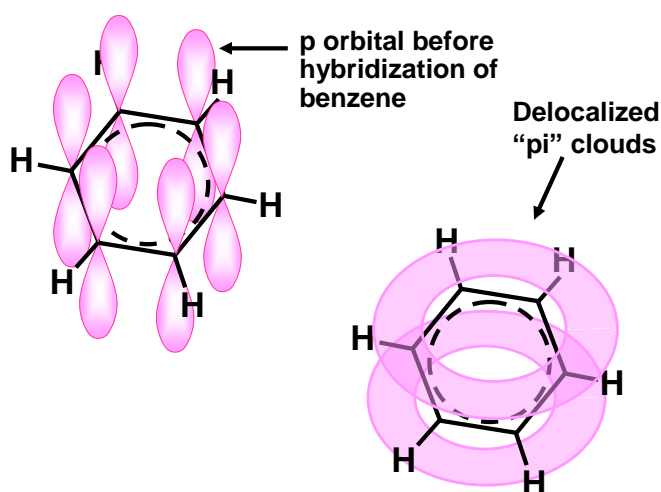


Fig. 4. Schematic illustration of the delocalization of electrons in an aromatic compound, which has been proposed to favor the plate-to-plate or other association of aromatic rings

The image at left shows the six p-type orbitals, in a hypothetical state prior to hybridization and formation of molecular orbitals. The image at right depicts the expected upper and lower parts of ring-like pi orbitals. These orbitals not only help to explain the

extra chemical stability of aromatic rings, but they also introduce the possibility of interactions between the molecular orbitals and other chemical entities such as cations or adjacent pi-type systems. Among other things, pi-bonding has been invoked to account for a tendency of certain aromatic compounds to form stacked arrangements (Small *et al.* 2004; Boltrushko *et al.* 2015). However, as discussed by Martinez and Iverson (2012) some related effects such as electrostatic attractions and polarization can be more important than the predicted effects due to the pi orbitals. Since lignin contains multiple aromatic rings, it makes sense to consider such bonding, whether or not it is defined as pi bonding, as a potential contributing factor. It also has been proposed that such aromatic groups in lignin are able to interact with polysaccharide surfaces (Asensio *et al.* 2013).

Pi bonding also has been suggested to contribute to interactions of lignin moieties, at least to the extent that the aromatic groups of lignin are accessible for such interactions (Contreras Sulbaran 2008; Ratnaweera *et al.* 2015). Xiong *et al.* (2017b) listed pi bonds among the important contributions to the formation of spherical lignin nanoparticles. Interestingly, in the work of Besombes and Mazeau (2005a,b), even though they were considering the “flat” adsorption of lignin onto cellulose, only hydrogen bonding and ordinary van der Waals interactions were considered. A possible reason is that pi bonding, as a source of inter-molecular forces, is predicted to be quite weak and too short-ranged to have an important effect. Also, the irregular structure of lignin may not facilitate the alignment of different aromatic groups.

Role of repulsive and relatively long-range forces

While most attention, in published articles, has been paid to attractive components of force associated with self-assembly processes, it is worth emphasizing that successful self-assembly is expected to require a well-tuned balance of forces. As noted by Bishop *et al.* (2009), to achieve a highly ordered system, at the colloidal scale, it is generally required to have relatively long-range forces that include a repulsive component. Electrostatic repulsive forces and depletion forces (due to the finite space occupied by certain non-adsorbing polymers) were listed in this category. Paananen *et al.* (2004) observed a long-range repulsive force of interaction between xylan and a mica surface. The authors attributed this to entanglement among the macromolecules. This is consistent with the agglomeration (*i.e.*, self-association) that has been observed by others (Mora *et al.* 1986; Lang and Burchard 1993; Westbye *et al.* 2007; Grigoray *et al.* 2014).

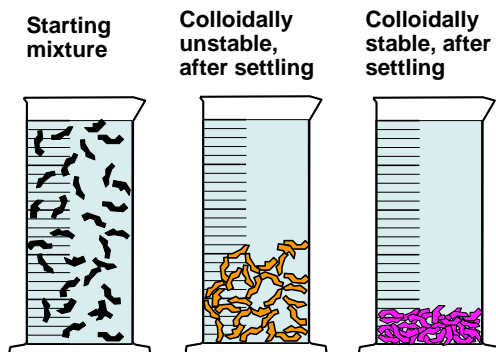


Fig. 5. Schematic illustration of how the presence of short-range repulsive forces between particles can facilitate progressive rearrangement, leading to a dense structure, especially after the material has been dried

As illustrated in Fig. 5, when particles are initially dispersed in an aqueous solution, they may appear to be well distributed throughout the volume, as in the image on the left. However, if the particles tend to stick irreversibly together upon each contact, then the resulting settled suspension may be as represented in the center image. Thus, a bulky, low-density suspension is expected when the interactions between surfaces are dominated by attractive forces. By contrast, when short-range repulsive forces are acting, for instance due to like charges or steric stabilization as a consequence of extended chains of water-loving polymer from each surface, then the particles will tend to slide relative to each other, rather than sticking initially. Thus, one can expect relatively dense sediment to form, as shown in the image on the right side of the figure (Martinez *et al.* 2005; Franks *et al.* 2006; Lerche and Sobisch 2014).

Thermodynamics

When considering whether or not a proposed explanation for a process is reasonable or not, thermodynamics can provide a useful perspective. Since self-assembly is a process, it is meaningful to look for thermodynamic reasons to explain why the system moves from its initial to its final, presumably self-assembled state. Table 6 lists some articles in which thermodynamic principles have been called upon to account for various aspects of self-assembly.

A key principle of thermodynamics is that processes take place spontaneously due to a balance between two factors – heats of reaction (or interaction) and a preference for maximization of randomness. Because self-assembly generally implies increased organization, a certain amount of enthalpy will be required to drive the process toward its conclusion (Lindsey 1991; Pelesko 2007; Grzybowski *et al.* 2009).

Table 6. Publications Using Thermodynamic Principles to Account for Observations Related to Self-assembly

Main subject matter or insights	Citation
Entropy cost of unscrambling vs. enthalpy of association	Lindsey 1991
A double-welled, composition-dependent free energy function	Suo & Lu 2000
Enthalpy differences not enough to determine patterns	Besombes & Mazeau 2005a
Energy minimization, binding forces, and applied forces	Pelesko 2007
Explains kT units of interaction for best self-assembly	Bishop <i>et al.</i> 2009
Self-assembly driven by both enthalpy and entropy	Grzybowski <i>et al.</i> 2009
Describes how modulations can direct thermodynamics	Grzelczak <i>et al.</i> 2010
Hypothesis to account for the cellulose I to II transition	Hubbe 2014b
Fatty acid self-assembly needs enough chain length (kT issues)	Hubbe <i>et al.</i> 2020a

Trapped non-equilibrium states

A critical problem can arise in self-association processes if the interactive forces and energies are not in an ideal range relative to the energy associated with chaotic factors such as Brownian motion (thermal diffusion) and ultrasonic waves, *etc.* These issues are illustrated schematically in Fig. 6.

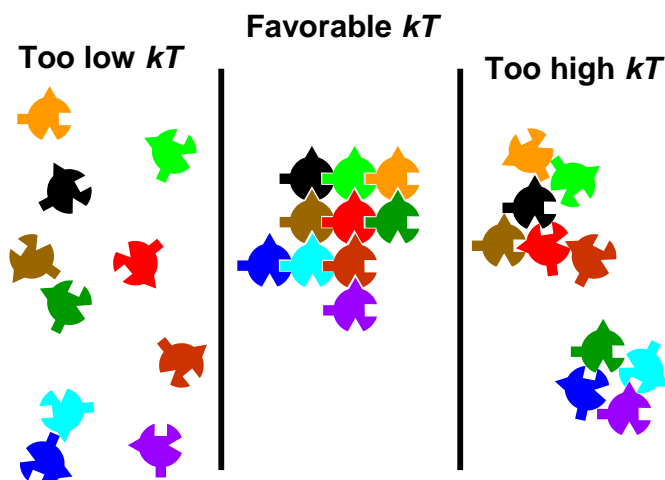


Fig. 6. Schematic illustration of how the free energy of interaction, in comparison to chaotic energy (such as Brownian motion) will affect outcomes of self-assembly

As illustrated in the figure, if the enthalpy of interaction is too low, then the entities may remain unconnected, essentially in a dissolved or well-dispersed state. The middle image depicts a supposedly favorable situation in which the entities are in the process of organizing themselves, based on their inherent tendencies, which are represented here by the shapes designed to fit together in a certain way.

If the interactive attractions are too large, in comparison to the chaotic energy (*e.g.*, associated with Brownian diffusion or vibrations), then one can expect the development of trapped non-equilibrium states (Bishop *et al.* 2009). In other words, though the system has not reached a minimum of free energy, the attachments that already have been established are sufficient to prevent further reorganization, at least within the time scale of interest. Such behavior is expected when an individual interaction has sufficient enthalpy such that the reverse action is slow. Once multiple contacts of that type have been established, as indicated in the right-hand frame of Fig. 6, the structure becomes essentially frozen.

An example suggesting such a non-equilibrium trapped state comes from a study of self-association of a xyloglucan having galactoxylose side chains (Lang and Burchard 1993). The authors observed strongly irreversible self-association, leading to thick bundles. Such agglomerates assembled themselves at first in a branch-like manner, and they eventually built up as larger agglomerates resembling spheres. Similar observations were reported by Saake *et al.* (2001) for a set of xylan samples. Because such chaotic associations might be expected to adversely affect events occurring during biosynthesis, it seems likely that enzymes and organelles within living cells are directing the assembly of such components of lignocellulose, *i.e.*, a form of directed self-assembly.

Chaotic energy

As illustrated in Fig. 7, one can envision a situation in which entities are initially joined together in a chaotic fashion. The initial attachments, though they may not represent the most favorable bonding options, are collectively strong enough to inhibit further rearrangement. In principle, such a situation can be overcome by the input of a favorable level of chaotic energy, such as thermal energy, eddies of flow, vibrations, *etc.*

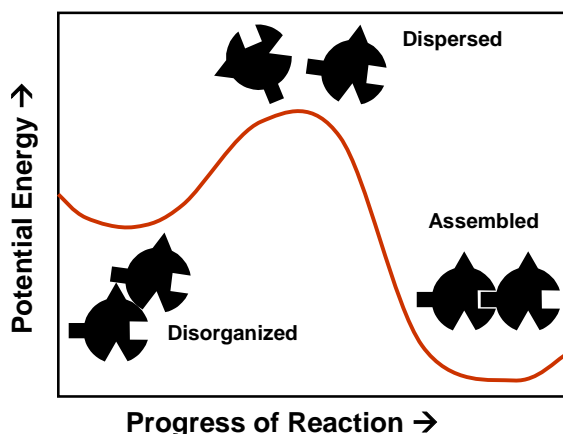


Fig. 7. Concept of an energy barrier that may stand in the way of local rearrangement of self-assembled structures, thus preventing the healing of trapped non-equilibrium states

The interplay among various forces, in collaboration with Brownian diffusion in the self-assembly of colloidal particles has been discussed by Li *et al.* (2008). These authors noted that the most successful instances of colloidal self-assembly generally have been associated with main reliance on relatively long-range forces, *i.e.*, van der Waals and electrostatic, as opposed to covalent or hydrogen bonding. By the involvement of flexible polyelectrolyte chains, the ranges of various forces can be extended beyond what can be achieved when relying upon forces originating at solid surfaces.

When the entities (such as suspended particles) to be self-assembled are sufficiently large, it becomes reasonable to consider various kinds of vibrations and flow impulses as a means to allow structures to form and reform multiple times on a pathway possibly leading to a preferred end structure. For example, Collino *et al.* (2015) employed acoustic vibrations to facilitate the organization of differently shaped particles into assemblies having characteristic structures. Greenhall and Raeymaekers (2017) used ultrasound to facilitate the rearrangement of nanoparticles in a polymer matrix. The chaotic energy was applied after the material was first applied in a pattern using 3D printing. Notably, these researchers used a pair of ultrasound transducers that were tuned a wavelength apart to induce the formation of a pattern.

Self-healing

A self-healing characteristic of self-assembled systems can be a desirable trait in many end-use applications (Wang *et al.* 2013). The issues related to self-healing are related to those of trapped non-equilibrium states and chaotic energy, as just described. According to Mitchell *et al.* (2018), self-healing can play an important role in the 3D printing of biological materials.

As illustrated in Fig. 8, the idea is that if the assembled materials remain exactly as they are placed *via* the relatively coarse method of printing, then one will not yet have achieved the degree of mutual association among neighboring cells to enable the repair and growth of tissues.

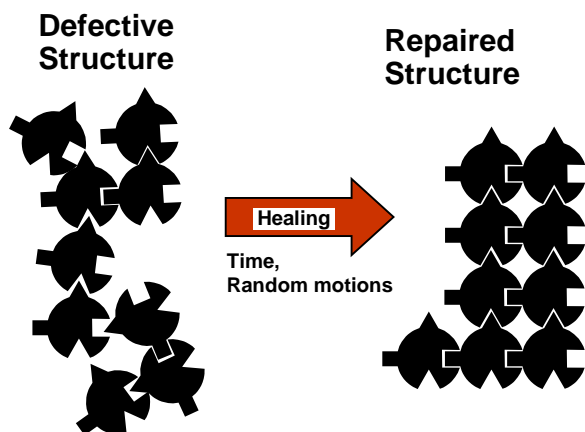


Fig. 8. Schematic illustration of the self-healing concept

Confined geometry

Issues related to confined geometries have implications in situations where templates are being considered as a means to direct the outcomes of self-assembly processes. Several researchers have focused on situations in which space constraints essentially force entities to arrange themselves in a certain pattern (Han and Lin 2012; Han *et al.* 2013). Figure 9 provides a conceptual schematic in which short-range repulsive forces are assumed to be acting between particles that are confined within two-dimensional spaces. Note that the particles have to line themselves up in order to minimize contact when they are constrained within a small space and have no alternative but to become close to each other or to the walls of the container. When considering cellulose nanocrystals, a premier example of confined geometry is represented by the striking iridescent colors that develop when the suspension is within a certain range of solids (Parker *et al.* 2018). The so-called chiral nematic organization of CNC can be attributed to the fact that mutual alignment is strongly favored when there is insufficient space in the system to allow chaotic orientations, especially when the particles are being mutually repelled by electrostatic forces having a certain effective range.

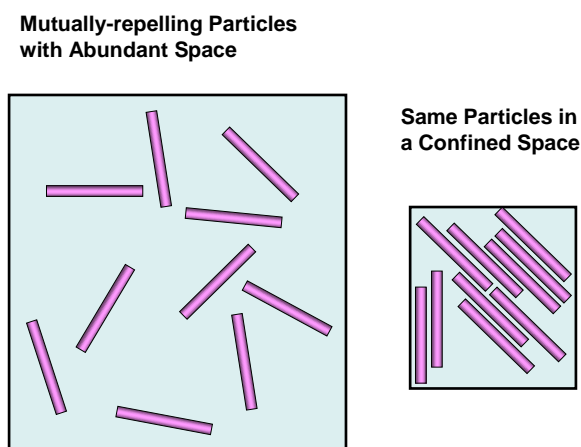


Fig. 9. Schematic illustration suggesting how confined geometries can be important as an influence for self-assembly

BIOSYNTHESIS-RELATED SELF-ASSEMBLY IN WOOD

Nature provides innumerable examples of self-assembly, most notably in the case of living organisms, but also in such domains as mineral formation, patterns of ripples in beach sand, and bubbles within natural layers of foam. Accordingly, this section considers processes related to the initial biosynthesis and assembly of woody materials. The idea is to be able to consider whether or not such processes might be pursued when the time comes to reconstitute the component parts of wood, namely cellulose, hemicellulose, lignin, and various extractive components, either singly or in various combinations. Mendes *et al.* (2013) provide a more complete description of ways in which self-assembly manifests itself in nature. More detailed background related to the biosynthesis of cellulose (O’Sullivan 1997; Glasser *et al.* 2012; Cosgrove 2014; Polko and Kieber 2019), hemicellulose (Scheller and Ulvskov 2010; Pauly *et al.* 2013), and lignin (Boerjan *et al.* 2003) is provided in review articles.

Characteristic Attributes of Natural Bio-materials

A common goal of efforts to self-assemble lignocellulosic materials can be described as “emulating wood.” A number of favorable attributes of wood have been mentioned with reference to self-assembly studies, and these include a high strength-to-density ratio, relatively high toughness, and a tendency to fail gracefully rather than always in a catastrophic fashion. Wood shares various attributes, such as having a hierarchical, porous structure, with various other biomaterials, including seashells, egg shells, bone, and insect cuticles (Bond *et al.* 1995).

Strength at relatively low density

As noted, an outstanding feature of wood is its high ratio of strength and modulus relative to density (Gradwell *et al.* 2004; Stone and Korley 2010; Yu *et al.* 2018). A likely explanation for such performance is a highly detailed structure, ranging from the molecular scale, through the nano-scale, and onward through microfibrils, fibrils, fibers, and larger wood structures. Features such as well-organized voids and triangular frame stiffeners are implemented at the nano-scale.

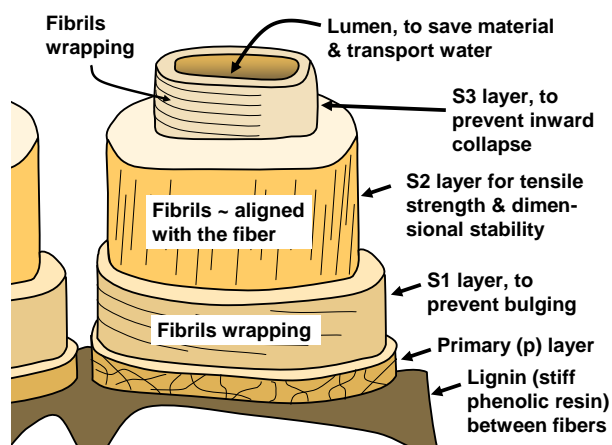


Fig. 10. Schematic illustration of key structures within lignocellulosic material that may explain its superior strength-to-weight characteristics

As illustrated in Fig. 10, ply construction is deeply involved in the structure of individual fibers, maximizing their strength in the longitudinal direction, while protecting them against bulging or the collapse of their lumens. Stone and Korley (2010) described wood as essentially being a composite with high-strength cellulose rods embedded in a softer matrix of lignin. Yu *et al.* (2018) compared wood's structure to that of a honeycomb.

Toughness

Figure 11 provides a working definition of “tough” as involving a combination of relatively high maximum stress to breakage and relatively high strain that can take place before the material experiences breakage. According to Bond *et al.* (1995), nearly all bio-based materials are noted for their high toughness. They used the term “graceful failure” to describe the manner in which wood and related materials often fail partially rather than all at once. Such behavior has an obvious potential value from an evolutionary standpoint. A partly broken tree sometimes is able to continue to grow in future years, often growing to maturity and releasing seeds to enable a future generation. Cheng *et al.* (2019) highlighted the desirability of toughness as an attribute in self-assembled films prepared from cellulose.

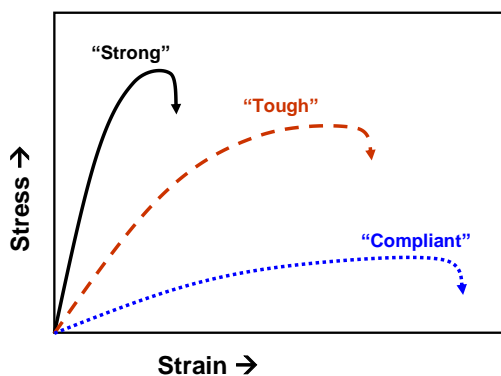


Fig. 11. Stress-strain relationships as a way to illustrate what is meant by toughness

Hierarchical

The strength-to-density and toughness attributes that generally characterize wood require a complex, hierarchical structure (Bond *et al.* 1995; Mendes *et al.* 2013). Therefore, a key question facing modern scientists and engineers is whether it is foolish to attempt to achieve comparable or better results by reassembling some of the components using mass production. Fortunately, some positive answers to such questions already exist in the form of widely available engineered wood products (Ding *et al.* 2022). Thus, materials such as oriented strand board are increasingly being used in construction, often substituting for and exceeding the mechanical properties of the solid wood. It might be argued, however, that such engineered wood products are still wood; no attempt is being made to reassemble the cellulose or other components of wood into a product; rather, strands or chips or fibers of wood are essentially being glued together. Questions remain regarding whether similar levels of success can be achieved with main reliance on self-assembly. As noted by Mendes *et al.* (2013), biological materials invariably are highly complex and highly precise, resulting from a detailed assembly process that integrates order and dynamics.

Mechanisms for Direction

As mentioned in the Introduction, successful self-assembly requires the participation of some form of information, along with some kinds of forces and chaotic energy, such that the entities will be able to assemble not as a jumbled mass, but as a useful structure of some sort. Some of the promising mechanisms by which self-assembly can be directed are discussed below.

Geometrical features

It has been found that geometrical features and constraints can offer an effective way to direct self-assembly. This is important because of the characteristic fibrillar or “flat” nature of cellulosic materials and their surfaces, when considering the simplest aspects (Besombes and Mazeau 2005a). The cited authors proposed that such geometrical forms are important relative to the arrangement of aromatic groups onto the crystal planes of cellulose in the course of biosynthesis. The flat and straight nature of cellulose has been proposed to favor its usage as a scaffold for the deposition of a wide range of adsorbates (Tian and He 2016). Micic *et al.* (2003) proposed that the carbohydrate matrix within plant cells can act as a template during the biosynthesis and formation of lignin structures. Figure 12 provides a conceptual depiction of monolignols diffusing into the spaces between recently-formed cellulose fibrils. Note that the figure suggests a dehydration step in the creation of a linkage within the incipient lignin structure. It would be expected that the resulting lignin nanostructure would be forced to take on the shapes of those limited spaces.

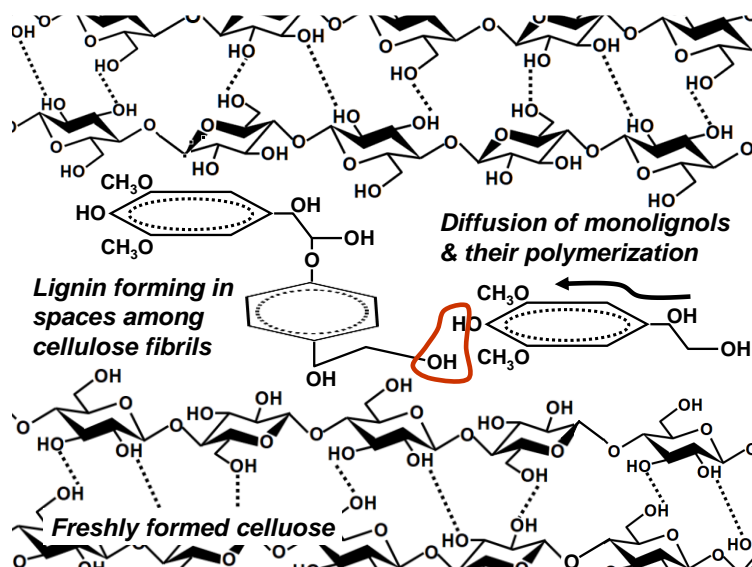


Fig. 12. Schematic illustration of the concept that a flat surface may help direct self-assembly

Chirality

Deviations from flatness may be important in some applications. Thus, Hosseinkhani *et al.* (2013) proposed that the chiral nature of some chemical structures may facilitate organization with unique features. Though the cited article does not mention cellulose, the concept would be relevant for the chiral nematic structures formed by cellulose nanocrystals at relatively high solids levels (Lagerwall *et al.* 2014; Parker *et al.* 2018; Tayeb *et al.* 2018).

Enzymes

In principle, by the usage of cultured and isolated enzymes, the modern engineer has a tool by which not only to replicate the action of living organisms, but also to achieve the same outcomes at a large scale. The participation of enzymes, including peroxidases and laccases, has been shown during the synthesis of lignin from monolignols (Dean and Eriksson 1994; Micic *et al.* 2003; Chiang 2006).

Cell wall processes

There is evidence that nano-scale structures within biological cells, *i.e.* organelles, play an essential role in the self-organization of molecules during biosynthesis. However, in the case of cellulose it is unclear whether or not such structures are involved. Figure 13 depicts key structures in the cell walls of plants that are associated with the biosynthesis of cellulose. As shown, the critical synthetic effects take place within proteinaceous “rosettes” within cell walls. Glucose, held within the cells, is transformed into cellulose as it passes through the rosette, and the nascent cellulose polymer chains are essentially extruded to the outside of the cells. Saxena and Brown (2005) suggested that the cellulose chains need to be properly oriented by some means. Haigler *et al.* (1980) observed the rosette features, which are involved in the formation of crystalline structures, by use of electron microscopy. The assembly of the cellulose was described as being “self-directed” rather than being associated with any observable structures in or on the cells. On the other hand, Matthyse *et al.* (1995) found that solid components of cell membranes needed to be present for cellulose synthesis. Cousins and Brown (1997a,b) envision a two-step process in which the cellulose chains first arrange themselves in sheets held together by van der Waals forces and that these sheets then are further assembled by hydrogen bonding. Saxena and Brown (2005) suggested that the spacing among the rosette-type enzyme structures responsible for cellulose chain synthesis helps to facilitate the self-assembly and initial crystal formation at the nanofibrillar level.

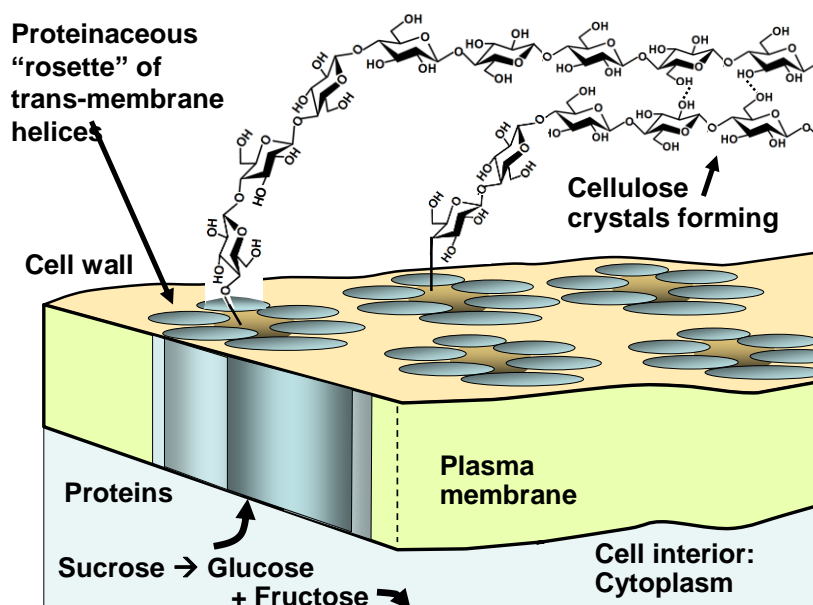


Fig. 13. Illustration of the cellular process of lignin biosynthesis, leaving open the question of whether or not structures within the cell help to direct the process

Multi-scale orchestration (cooperative)

It has been suggested that a multi-point interaction may be a key to successful self-assembly. Thus, Lindsey (1991) proposed that the formation of several bonds or non-covalent associations may be easier to achieve, in some cases, than a single attachment. Wang *et al.* (2013) likewise suggested that a cooperative effect is involved in the self-assembly of minerals with polysaccharides during biosynthesis, and that such effects might be employed for bio-inspired process development. This concept appears to be most relevant to the interactions among polysaccharides in aqueous environments, as illustrated in Fig. 14. The illustration suggests that whereas most monomer ions (especially monovalent ions) would remain in the bulk of solution, oligomers may be partially adsorbed, and that polymeric ions would tend to occupy almost all available sites on a typical solid substrate. As is clear from the nature of liquid water, the energy of an individual hydrogen bond is insufficient to create an attachment that lasts more than a picosecond (Rapaport 1983). However, dense patterns of hydrogen bonds attached to suitable polymer chains can lead to insoluble cellulose and other strongly associated compounds (Mora *et al.* 1986; Lang and Burchard 1993; Westbye *et al.* 2007; Grigoray *et al.* 2014).

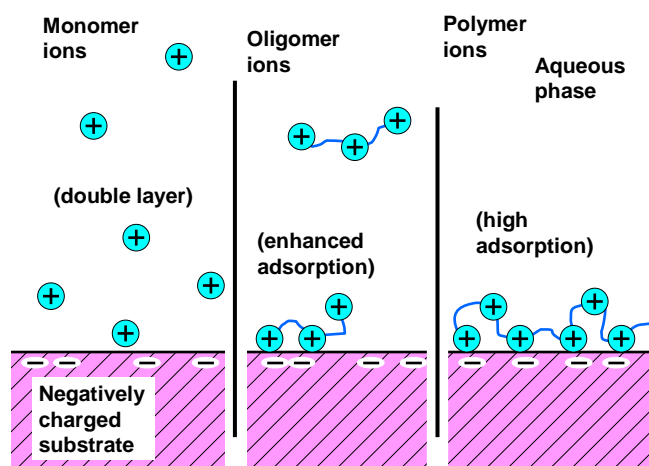


Fig. 14. Schematic illustration of multi-point collaboration in the formation of stable bonding between surfaces during self-assembly

Challenges in Attempting to Mimic Nature

Highly evolved systems

While nature provides numerous examples of self-assembly, it can be a challenge to mimic nature due to its complexity (Sanchez *et al.* 2005; Stone and Korley 2010). A further challenge resides in the irreversible nature of some of the key steps in biosynthesis. This irreversible nature is evident in the insolubility of cellulose and the fact that severe chemical conditions are needed to remove lignin from woody materials.

A further complication arises due to the presence of covalent bonds linking together the components of native wood – especially hemicellulose-to-lignin bonds (Meshitsuka *et al.* 1982; Lawoko *et al.* 2005; Westbye *et al.* 2007). These linkages, which are associated with lignin-polysaccharide complexes, might be viewed as a kind of cheating on the part of nature. Lignification, which involves *in-situ* polymerization (Mishra and Ekielski 2019a), mainly occurs after cellulose is already in place within lignocellulosic materials

during their formation (Boerjan *et al.* 2003). In principle, these covalent bonding events will tend to lock the component materials into place after the main biosynthetic self-assembly steps have been done. Figure 15 is a hypothetical structure illustrating common bonds to be expected within the lignin of woody plants. While one might visualize the possibility of employing a self-assembly scheme involving short-range forces such as van der Waals forces and electrical double-layer forces (Hubbe and Rojas 2008), it is a much bigger challenge to set up conditions favoring organized covalent bonding during the same (biosynthesis-like) process under conditions of mass production.

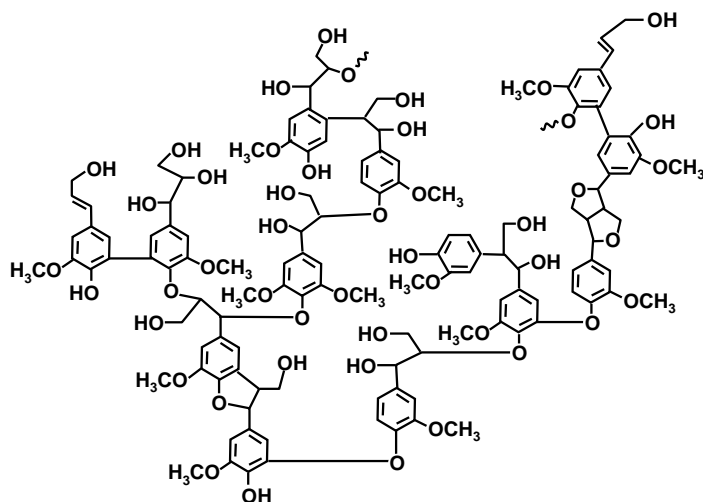


Fig. 15. Representation of some of the important functional groups and linkages within a lignin macromolecule within a plant

RECONSTRUCTION OF WOOD COMPONENTS BY SELF-ASSEMBLY

Having considered the motivating factors, having been inspired by the pervasive action of self-assembly in biosynthesis, and having considered some of the most challenging obstacles, this section will deal with some tools and strategies by which the engineer may induce self-assembly. The term “tool”, for the sake of this discussion, will include such things as selection of suitable building blocks, targeted modifications, taking advantage of propensities, selecting orders of addition, and the selection of ranges of operating conditions. The term “strategies” will deal with such issues as bio-based processes, dissolution and reprecipitation, liquid crystals, the application of fields, and self-assembly strategies based on adsorption, evaporation, drying, freezing, the use of templates, and finally the application of papermaking technologies.

The Engineer's Tools

Selection of suitable building blocks

Each time that a bio-based material is used to make products, there is an inherent advantage of using that material for its highest-value purpose. Often, in the case of wood from a large, well-formed log, that usage will be in the production of large-sized solid wood lumber. As illustrated in Fig. 16, one can envision a cascade, whereby the residues left over after making the preferred product can be utilized for such purposes as particleboard or pulp for paper production (Teuber *et al.* 2016). It has been argued that such utilization

of scraps and diversion of waste-wood streams is a way to minimize adverse environmental impacts (Sathre and Gustavsson 2006; Teuber *et al.* 2016; Jarre *et al.* 2020). In principle, if there is higher value when the material is in the form of relatively large pieces, it might be wasteful to convert it to fibers for the next phase of manufacturing. However, regardless of the details, progress in these directions can be expected to increase the demand for re-assembly of strands, chips, fibers, veneers, and other such pieces of lignocellulosic materials in the future, thus increasing the incentive to consider self-assembly strategies.

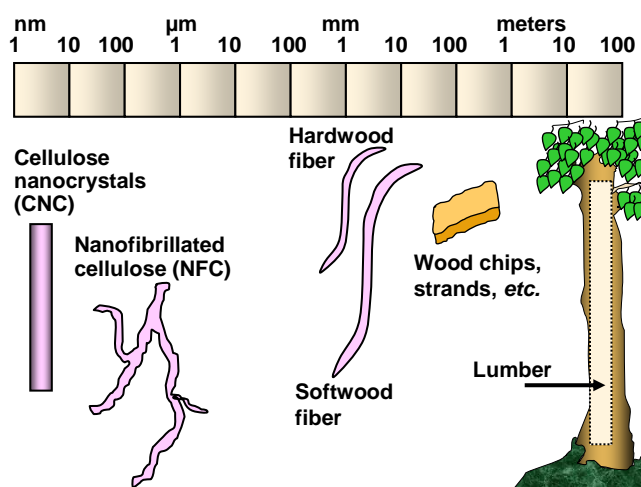


Fig. 16. Schematic illustration of contrasting types and sizes of possible building blocks that might be considered for self-assembly of plant-based materials

Another set of building blocks is available at a much smaller size range, consisting of the chemical components of wood. These are often available as byproducts from other industries, such as the pulping of wood for paper production. Though most of the lignin removed from wood during pulping is currently used as a fuel source in pulp and paper manufacturing facilities, the chemical byproducts have potential to be utilized for higher-valued purposes if and when other barriers to production can be overcome (Wenger *et al.* 2020; Poveda-Giraldo *et al.* 2021). A variety of products have been produced at a profit based on the utilization of lignin as an important component (Graichen *et al.* 2017). Presently the biggest impediments to the value-added usage of lignin lie in its molecular complexity and variability (Rahimi *et al.* 2014; Xu *et al.* 2014; Kim and Kim 2018; Argyropoulos *et al.* 2021). Fortunately, there are opportunities to decrease the variability by fractionation of industrial lignins (Li and McDonald 2014; Crestini *et al.* 2017).

Taking advantage of propensities

The favorable self-assembly tendencies of different components of biomaterials can be regarded as a tool that developers can employ as the basis for envisioning a self-assembly process. A premier example of such a propensity is the already-mentioned tendency of polysaccharides to form relatively durable hydrogen bonds. For example, a paper product can be readily formed by collecting the water-swollen fibers on a screen fabric, pressing out excess water, and then drying – usually with the application of heat (Rojas and Hubbe 2004). The structure thus formed can be expected to maintain its integrity until such time as it becomes fully wetted in an aqueous medium. There are numerous examples in which similar principles have been used to prepare well-bonded

films comprised of such biopolymers as hemicelluloses, starch products, *etc.* (Hansen and Plackett 2008; Zhao *et al.* 2020; Zhang and Rhim 2022). Figure 17 illustrates the concept that self-assembly can involve regions of a molecular or particle that have hydrogen bonding ability, cationic charge, anionic charge, hydrophobic character, ability to participate in common types of covalent bonding, or various enzymatic binding sites.

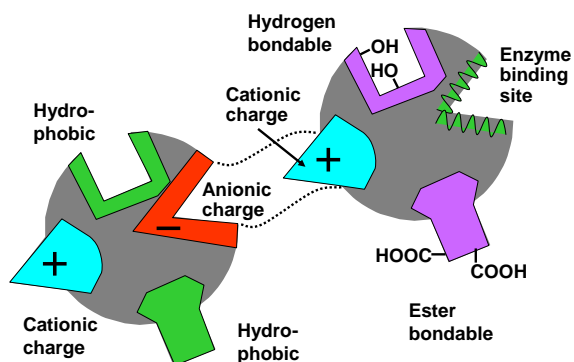


Fig. 17. Schematic illustration of favorable interactions that have the potential to direct local self-assembly directions (hydrophobic character, hydrogen bonding ability, and areas of net ionic charge)

An analogous set of self-affinity strategies can be envisioned based on various hydrophobic components of lignocellulose. Native lignin, due to its relatively high ratios of carbon to oxygen, as well as its content of aromatic groups, is more hydrophobic than cellulose or hemicellulose (Notley and Norgren 2010). In particular, lignin fragments become insoluble at pH values well below the pKa of phenolic groups (Hubbe *et al.* 2019). An example of where this tendency has been put to use in the self-assembly of a product is in the preparation of lignin nanoparticles (Qian *et al.* 2014; Ratnaweera *et al.* 2015; Salentinig and Schubert 2017; Mishra and Ekielski 2019a,b). Similarly, lignin can be prepared as a solution in tetrahydrofuran and ethanol (Qian *et al.* 2014; Xiong *et al.* 2017b; Ashok *et al.* 2018). Subsequent rapid dilution with water, which acts as an anti-solvent, causes the lignin to precipitate rapidly as tiny particles. Li *et al.* (2016) and Xiong *et al.* (2017a) optimized conditions so as to achieve hollow kraft lignin nanospheres by such an approach.

Selections of orders of addition

A developmental tool that could be called “selection of orders of addition,” follows logically from the previous item. In cases where the entities to be assembled have some known affinities, the developer of technology can employ the strategic placement of items, in a layer-like fashion. Examples of this approach can be found in processes where more than one material is adsorbed, sequentially, onto a substrate. Because of the inherent negative charge of most cellulosic materials, as they are produced commercially, the first additive often has a multivalent cationic charge, which encourages strong adsorption (Biswas and Chattoraj 1997; Maximova *et al.* 2001). Because the adsorption of a cationic material often reverses the charge of the substrate to positive, the next application can be an anionic polyelectrolyte of an anionic colloidal material (Hubbe 2014c). Ultimately, it is possible to alternatively expose the substrate to solutions of oppositely charged polyelectrolytes, thus building up a multilayer (Aulin *et al.* 2010b). Such a process is

illustrated schematically in Fig. 18. Some of these issues will be discussed in more depth near the end of this article when considering papermaking applications of self-assembly principles.

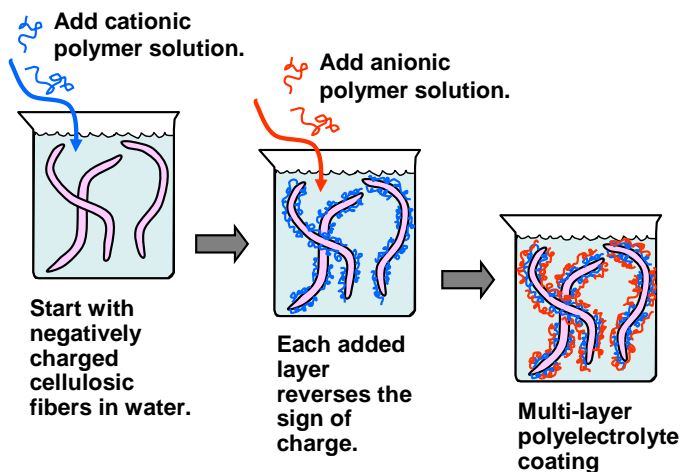


Fig. 18. Schematic illustration of how orders of addition can lead to layered structures at the nano scale. Note that the relative sizes require two major exaggerations: The fibers won't be so large compared to the beaker, and the macromolecules are extremely small relative to the size of the fibers.

Much wider range of conditions compared to natural processes

As was noted earlier, one can picture a biological cell as being nature's way of isolating weakly salty water having a composition resembling that of ancient seas that were present at the dawn of life (Tolstoguzov 2004). Such an environment is apparently ideal for processes involving DNA, RNA, and innumerable other factors associated with the propagation of life. Modern technologists don't necessarily need to be constrained by those rules, especially if they are not basing their work on viable bacteria or other forms of living matter. Figure 19 highlights some variables that the modern engineer can have opportunities to adjust within relatively wide ranges as a means to achieve various product goals.

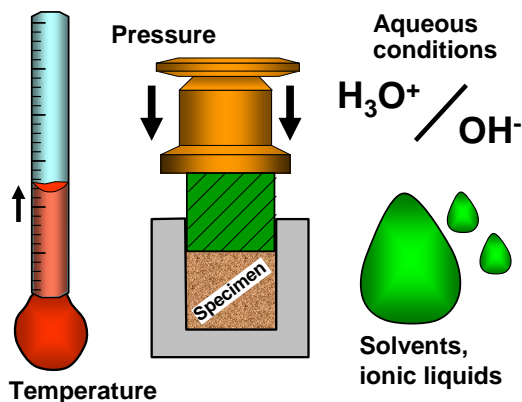


Fig. 19. Representation of the tools that developmental technologists can employ

Once the technologist breaks free of the constraint of depending on living biological systems, then a range of thermal conditions can be considered for the self-assembly of plant-based materials. For example, the plasticization of lignin, as well as various covalent reactions can be induced by heating, thus enabling the binderless assembly of engineered wood and other plant-based products (Hubbe *et al.* 2018; Nasir *et al.* 2019). At the other end of the spectrum, freezing strategies can be employed to direct aspects of self-assembly (Han *et al.* 2013; Yu *et al.* 2018).

The technologist can select among various aqueous conditions, well beyond those that could exist within a living cell. Thus, pH conditions well above 10 can be employed to solubilize lignin byproducts, and then those entities later can be precipitated under controlled conditions by further changes in the chemical environment (Hubbe *et al.* 2019). Further adjustment of the form of precipitated lignin can be achieved by adjusting the salt concentration (Li *et al.* 2016).

Especially when using combinations of solvents, selected temperatures, and various catalysts, the modern technologists can take advantage of a wide range of covalent reactions by which to form chemical derivatives of the surfaces of biobased materials. Of particular interest in this context are such reactions that can be carried out with a minimum of adverse environmental impact (Hubbe *et al.* 2015). For example, the aggregation behaviors of hemicelluloses can be modified by derivatization (Lang and Burchard 1993; Kaya *et al.* 2009; Vega *et al.* 2013).

Molecular dynamics simulations

In addition to the tools that can be utilized in a laboratory or industrial plant, the technologist may also learn by carrying out molecular dynamics simulations (MDS) (Bishop *et al.* 2009).

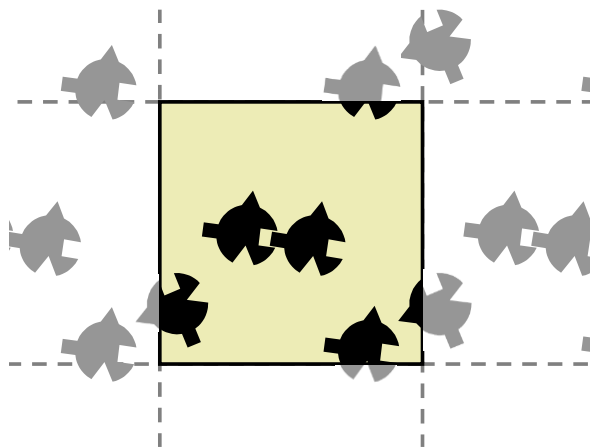


Fig. 20. Concept of infinitely repeating unit cells in a molecular dynamics simulation involving self-assembly phenomena of particles having a distinct fitting ability

Several researchers have reported MDS work related to the self-assembly of lignocellulosic materials. Suo and Lu (2000) focused on the general thermodynamics of such systems, with applications at the nanoscale. Khazraji and Robert (2013) modeled the intra- and inter-molecular associations of cellulose chains, with the formation of hydrogen bonds. Related work by Kawakatsu *et al.* (2006) predicted forms of crystallization of cellulose to form fibrillar structures, having fractal patterns. Bergenstrahle *et al.* (2010) employed related approaches to illustrate how a typical MDS procedure could be utilized

to simulate the self-assembly of particles having a distinct fitting ability. This principle is illustrated in Fig. 20, which represents a hypothetical two-dimensional molecular dynamics simulation of particles having a specific way of fitting together. Note that whenever an item diffuses in or out from the square (or cube) being considered, a copy of that item is migrating out or in from the opposite square (or cube) in the simulation.

Self-assembly by Dissolving and Re-precipitation

The precipitation of substances from solution can offer many opportunities for directed self-assembly. In principle, the developmental engineer will be able to tune the outcomes of such processes by selection and adjustment of factors responsible for the decreasing solubility that brings about precipitation.

Adding non-solvent

The strategy of using a non-solvent to destabilize a solution was introduced in an earlier section to illustrate how the hydrophobic nature of lignin can be used as a motivating factor to bring about conversion to a suspension of nanoparticles. To follow up on that introduction, there are some ways in which the process can be adjusted, depending on the desired outcome. For example, several works cited earlier involved a sudden addition of THF solutions of lignin into an excess aqueous solution (Qian *et al.* 2014; Li *et al.* 2016; Xiong *et al.* 2017a,b; Ashok *et al.* 2018). Under aqueous conditions that favored colloidal stability, such a sudden transformation was clearly capable of delivering nano-sized lignin particles that remained in suspension. In principle, a rapid separation of phases will tend to favor a high interfacial area of the separated phases, at least initially (Jung *et al.* 2012; Ma *et al.* 2019; Ilyas *et al.* 2020). As indicated in Fig. 21, the adding of an anti-solvent or the lowering of the pH would tend to decrease the repulsive forces acting between the dispersed substances, thus diminishing the energy barrier opposing their agglomeration. There is a question mark shown in the figure corresponding to the final condition at the right. Although lowering of the energy barrier opposing self-association can be expected to lead to increased agglomeration, whether or not it leads to organized self-assembly will depend on various conditions, including details of interactive forces and whether or not the entities become locked into non-equilibrium trapped states (not at a true thermodynamic equilibrium).

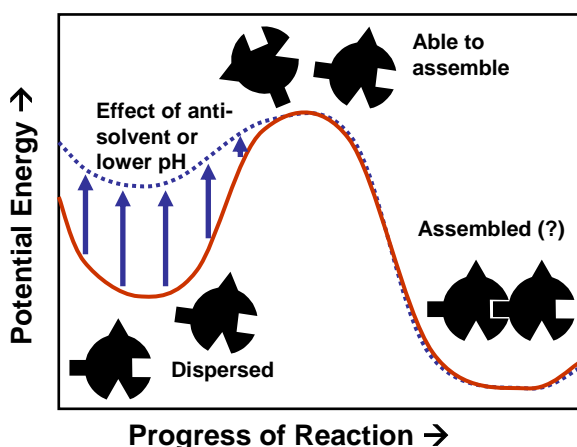


Fig. 21. Schematic illustration of the precipitation of cellulose by use of a non-solvent, leading to opportunities for self-assembly

There are further opportunities to tune the outcomes of phase separation in the regeneration of cellulose by its immersion in a non-solvent. In particular, Yamane *et al.* (2006) showed that the wettability characteristics of the produced cellulose II material were profoundly affected by the hydrophilic or hydrophobic characteristics of the regenerating liquid. Regeneration into a hydrophilic medium resulted in cellulose filaments that were hydrophilic, whereas regeneration into hydrophobic media yielded more hydrophobic cellulose surfaces. The results were attributed to changes in the relative amounts of different crystal phases of cellulose that were facing towards the outside of the filaments.

A further controlled self-assembly process can be achieved in cases where the lignocellulosic material is insoluble in a precipitating liquid. Li *et al.* (2016) showed that the precipitation of lignin, following the addition of water to a THF solution of lignin, tended to occur at the interface between the two liquid phases. Such a process can explain the formation of hollow spheres. The thickness of the walls of the hollow spheres could be adjusted by selecting the concentration of salt in the aqueous solution (Li *et al.* 2016). Related work by Xiong *et al.* (2017a) showed that such a separation resulted in hollow particles having a hydrophobic outside and a hydrophilic interior. The likely mechanism is that the lignin layer was functioning as the stabilizer (like a Pickering emulsion; Chevalier and Bolzinger 2013) for dispersed water droplets after phase separation; thus, the interior surfaces would have been initially in contact with a hydrophilic medium.

Changing the pH

It is well known that lignin moieties tend to become solubilized in aqueous media when the pH is high enough to deprotonate most of the free phenolic groups (Evstigneyev and Shevchenko 2019). Subsequently, the lignin can be precipitated out of the solution by the addition of such acids as carbon dioxide (for the formation of carbonic acid) and sulfuric acid (Hubbe *et al.* 2019). Such a process is illustrated schematically in Fig. 22. Under certain conditions, the lignin can be precipitated as nanoparticles (Mishra and Ekielski 2019a,b). By contrast, Salentinig and Shubert (2017) achieved a gel-like substance after decreasing of the pH, which caused lignin to initially precipitate as nanoparticles. In the reported system, nanoparticles were found to self-assemble into larger structures, depending on the pH and other variables.

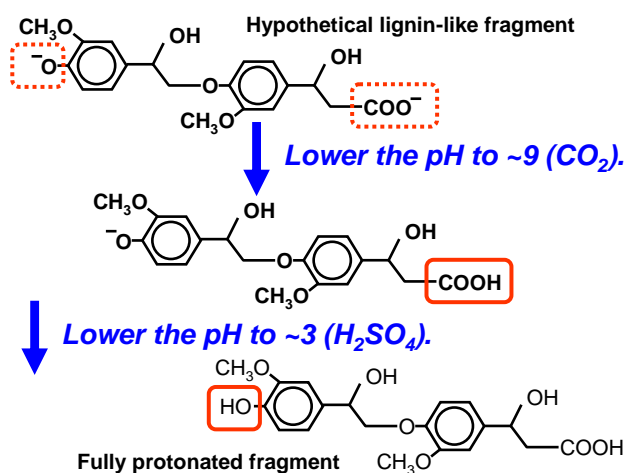


Fig. 22. Schematic illustration of phase separation of lignin from alkaline aqueous solution brought about by a reduction in pH, often giving rise to self-association, which might be limited by stabilizing agents or the presence of ionic charges

Decreasing pH also can be utilized as a means to precipitate certain hemicellulose components from an aqueous solution. Thus, Hansson and Hartler (1969) reported the precipitation of xylans onto cotton fibers. Birch xylans were first decreased in solubility by removal of uronic acids, thereby allowing them to adsorb onto the cotton. The completeness of the sorption was increased by decreasing the pH.

Polyelectrolyte complexes

Polyelectrolytes can be caused to precipitate from aqueous solution by mixing them with solutions of oppositely charged polyelectrolytes. Such precipitates generally obey stoichiometric rules for their self-assembly (Dautzenberg *et al.* 1996; Wang and Schlenoff 2014). However, the detailed behavior can depend on the order of addition and the final ratio of the components (Chen *et al.* 2003). The cited authors showed that different non-stoichiometric charge-stabilized polyelectrolyte complexes (PECs) could result, depending on the direction of titration. Thus, an excess of anionic polymer (polyvinyl sulfate) was observed in the PEC when a solution of it was gradually added, with mixing, to a solution of poly-diallyldimethylammonium chloride. The non-stoichiometric relationship became much more pronounced with increasing salinity of the solution. Similar results were obtained when the anionic polymer was carboxymethyl cellulose (Chen *et al.* 2001). By adjusting the ratios of additives during *in situ* preparation of PECs, it is possible to treat the surfaces of cellulose fibers with relatively large amounts of bonding agents, leading to strong increases in paper strength (Hubbe 2005; Hubbe *et al.* 2005).

Figure 23 illustrates such a process. In this schematic, a solution of a poly-anion, such as the sodium salt of carboxymethyl cellulose, is being poured from another beaker into a solution of a polycation, such as the chloride of chitosan. After the system has had time to mix and equilibrate, the PEC solids likely will have settled. Since the charges present on the macromolecules will be mostly occupied with “ion pair” associations, the counter-ions will be free to diffuse into the bulk of the solution. The increased freedom of the monomeric ions to diffuse within the bulk solution phase is a key factor in explaining the thermodynamic driving force favoring the complexation.

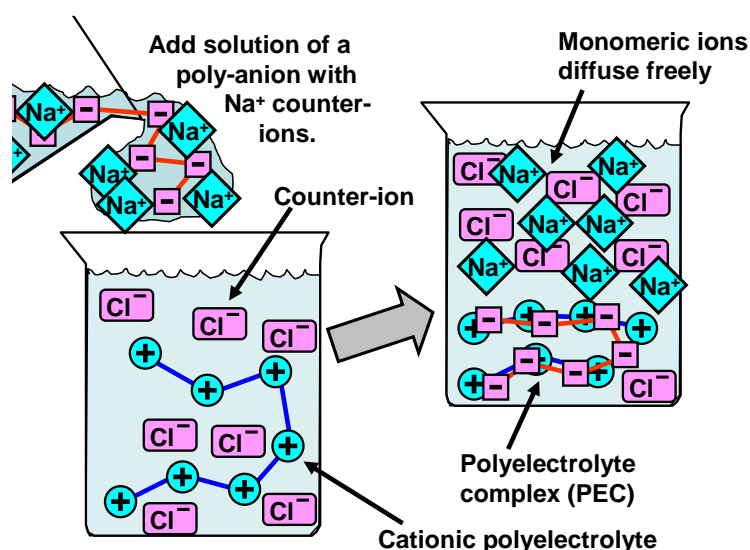


Fig. 23. Schematic illustration of polyelectrolyte complexation, showing a “latter” PEC structure

Because of the large gain in free energy associated with the formation of a PEC, there can be a significant danger that the formed structures may contain defects. In other words, the details of the structure might depend on kinetically-driven processes rather than a tendency to reach some kind of equilibrium condition. Figure 24 illustrates a mechanism by which such trapped non-equilibrium structures – such as the presence of fragmentation of the PEC structure – might be healed. A key requirement for such a healing process to be able to occur is the ongoing occurrence of intermittent detachments and reattachments of ion pairings within the PEC. For instance, the image at left shows some Na^+ and Cl^- counter-ions intermittently replacing pairings between ionic groups bound to the respective chains. Whether or not such a healing process will lead to a scrambled structure, a ladder-like structure, or some kind of crystalline structure may be hard to predict.

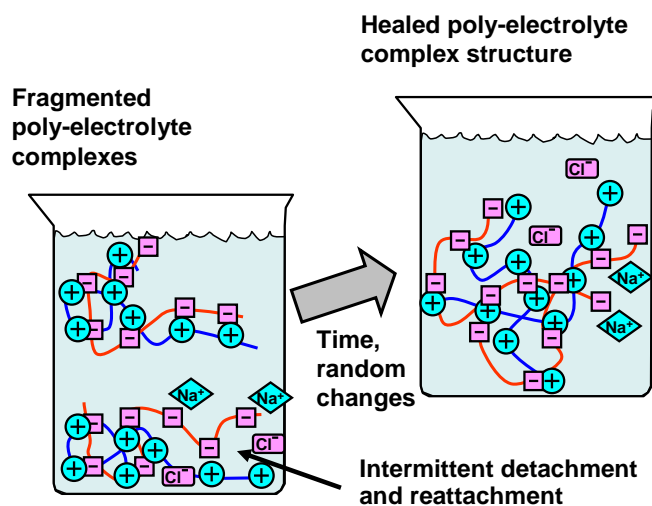


Fig. 24. Schematic illustration of a healing process for a fragmented mixture of polyelectrolyte complex

Using Structural Factors as an Organizing Principle

The physical constraints imposed by limited space, the shapes of boundaries, or the shapes of the entities to be self-assembled all can contribute to self-assembly, even in the absence of interactive forces. Examples of these principles, in their simplest forms, were diagramed in the book by Pelesko (2007). This author stated that templates are one of the key factors that can be used to direct self-assembly, along with energy minimization and nucleation phenomena. This section will go somewhat deeper into such issues, with special attention to issues related to templates and liquid crystals and related features.

Templating

A template can be defined as a physical structure that can determine the locations at which a material assembles. Figure 25 illustrates one of the simplest forms of such a mechanism. As shown, depending on the dimensions of rectangular spaces, the packing of hard spheres in two dimensions is expected to be completely different. In some cases the template goes away and is no longer present after the assembly process. The topic has been discussed in review articles (Suo and Lu 2000; Grzelczak *et al.* 2010; Huang and Gu 2011; Wade and Burdick 2014); Tian and He 2016; Rajasekharan *et al.* 2017). For instance, Wade and Burdick (2014) described how a cellulose template (or “scaffold”) could be used

to organize the self-assembly of biological tissue. Another example is provided in a report by Trovagunta *et al.* (2022), wherein the cellulose nanofibrils (CNFs) were used as a template to align lignin particles using an oriented freezing front method.

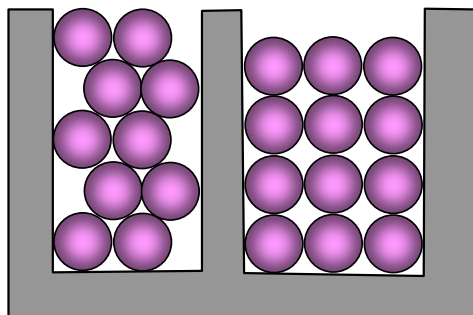


Fig. 25. Schematic illustration of the way in which a template may be expected to direct the self-assembly of a material

Micic *et al.* (2003) used a cellulose template for the deposition of a lignin film. The latter was prepared by enzymatic polymerization of coniferyl alcohol. The formed lignin layer was described as “compact” with a two-dimensional hexagonal close-packed arrangement. The authors proposed that such a result supports a hypothesis that cellulose structures can serve as a template for lignin deposition during biosynthesis in nature. Such an explanation is supported by Mishra and Ekielski (2019a). These authors noted that the location and form of lignin deposition within a growing plant cell is determined by the locations of cellulose and hemicellulose already present, *i.e.*, moments after their own biosynthesis.

Liquid crystals as an organizing aspect

The formation of liquid crystals in suitably concentrated colloiddally stable suspensions of cellulose nanocrystals can give rise to impressive colored patterns due to the rainbow-like interactions of the material with light (Lagerwall *et al.* 2014). Due to a minor twist within such individual crystalline rods of cellulose, the nanostructure will take on a chiral nematic (cholesteric) liquid crystal phase that is arranged as a helix. Figure 26 represents how such a pattern is expected to show periodicity.

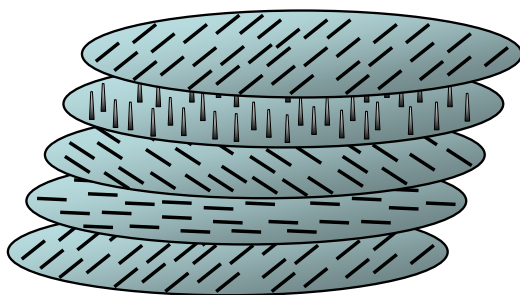


Fig. 26. Schematic illustration of chiral nematic ordering, such that the alignment repeats itself in a periodic manner

The patterns are a manifestation of the net-repulsive colloidal forces between the suspended particles that force the assembly to take on a pattern that avoids close approach (within a few nm) between the nanoparticles at any point. According to Parker *et al.* (2018), such processes have been employed within nature as the basis for forming the vivid patterns displayed by insects or in feathers, *etc.*

Kondo *et al.* (2002) demonstrated epitaxial deposition of bacterial cellulose (cellulose I) at the nano-scale onto oriented templates. Notably, the microfibrils were aligned with the template. It was found necessary to employ a self-assembled nematic liquid crystal template to achieve such results. Such systems are discussed in the review articles by Tian and He (2016) and Rajasekharan *et al.* (2017).

Using Progressive Changes as an Organizing Principle

The progressive changes that accompany freezing, evaporation, and drying can be employed to direct self-assembly, as shown by some examples.

Freezing

The progressive formation of ice crystals, followed by their gradual extension, can be used as the basis for self-assembly (Gutierrez *et al.* 2008; Cheng *et al.* 2017; Lavoine and Bergstrom 2017; Hua *et al.* 2021). Figure 27 illustrates a process that was demonstrated by Albouy *et al.* (2017). As shown, ice was induced to grow in vertical columns, due to an adjacent chilled surface.

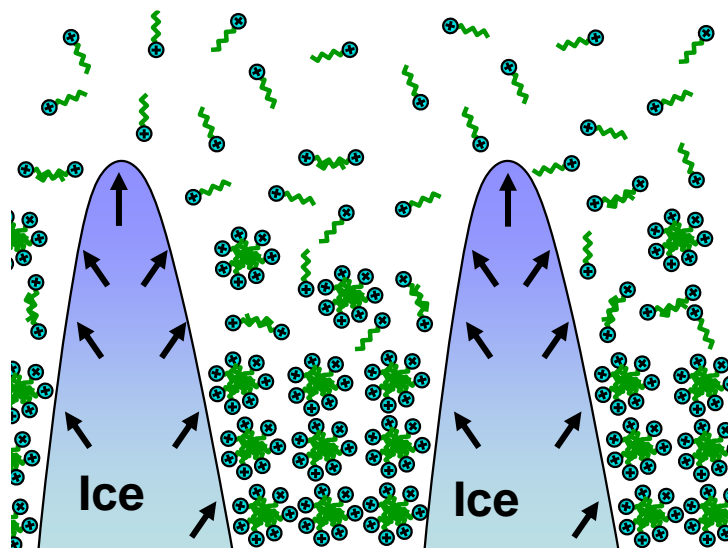


Fig. 27. Schematic illustration of the use of a progressive freezing process as a way to direct the pattern of a self-assembled structure (redrawn based on a concept by Albouy *et al.* 2017)

The progressive confinement of aqueous solution between the ice columns was found to induce a structuring of micelles. Han *et al.* (2013) used freezing, in the course of freeze-drying, as the basis for organization of nanofibrillated cellulose (NFC) particles (or CNF according to ISO terminology). The crystalline ice structures sublimated during the process, leaving behind an organized porous structure. The authors used the term “fibers” to describe the structures formed by the cellulosic materials during the process. Jiang and Hsieh (2014) showed that NFC particles can be organized by cyclic freezing and thawing. The product was described as an aerogel. Yin *et al.* (2019) used a freeze-casting method

to prepare scaffold structures from different forms of cellulosic nanomaterials, together with chitosan. Trovagunta *et al.* (2022) reported the formation of lignin-based foams, having a high degree of directionality, by use of an oriented freezing front method.

Evaporation

Self-assembly can also be influenced by evaporation processes, which can serve as an organizing factor (Brinker *et al.* 2004). As noted by Han and Lin (2012), such systems sometimes can be explained in terms of the progressive confinement of the component particles into restricted volumes, thus forcing the alignment of particles. This can include alignment and subsequent coalescence between adjacent cellulosic surfaces (Pönni *et al.* 2012), which merges into the next topic area of drying. Uetani and Yano (2013) showed that evaporation of droplets could be used as the organizing principle for different kinds of nanocellulose. They found that nanofibrillated cellulose tended to form particles with multiple sharp kinks, whereas cellulose nanocrystals form chiral nematic structures due to confinement within shrinking droplets during evaporation. Liu *et al.* (2018) formed helical cellulose structures from long modified CNC particles with an evaporation method. Tran *et al.* (2018) showed that the liquid crystal patterns exhibited by CNC could be adjusted by varying the parameters associated with evaporation. The details of the resulting structure were affected by the drying rate. Enescu *et al.* (2019) used evaporation as a means of directing the self-assembly of cellulosic nanomaterials in systems that included chitosan and nanoclay. A greater extent of self-organization was observed at lower rates of evaporation. Borrero-Lopez *et al.* (2022) demonstrated the self-assembly of CNC particles within a confined space as a function of gradual evaporation.

Evaporation also has been used as a way to organize lignin particles. Cusola *et al.* (2018) showed that evaporation could be used to organize colloidal lignin at a surface. Beisl *et al.* (2020) brought about the self-assembly of colloidal lignin particles between pairs of glass slides using graduate evaporation. High-strength films were achieved. Evaporation was also shown to be a key step in the preparation of hollow lignin microspheres that were prepared with water and acetone solvent phases (Wang *et al.* 2020).

Drying

The process of drying cellulosic materials can be viewed in terms of a sequence of events. First, as water evaporates, the solids come closer together, until a meniscus is formed at each pair of adjacent surfaces. Capillary forces associated with these films of water exert strong forces of attraction as the water evaporates. And then, after the surfaces have been drawn into molecular contact, hydrogen bonds are formed.

The sequence of events, as just described, appears to have been first proposed by Campbell (1959) as a way to account for the development of highly bonded regions between adjacent cellulosic fibers during papermaking. Calculations by Page (1993), based on a simple model of crossed, smooth cylinders, predicted that such forces could become enormous once the radius of curvature of the meniscus becomes very small. In other words, the simplified equation used by Page implies infinite negative pressure at a zero thickness of the water film. These expectations of very large forces have been confirmed by microscopic evidence, showing the distortion of the shapes of fibers within sheets of paper (Nanko and Ohsawa 1989; Uesaka and Qi 1994). Such a process is illustrated in Fig. 28. At crossing points, where one would have expected the capillary forces to act, the adjacent fibers become mutually stretched and crimped, in the form of skirts, as would be expected only if the surfaces would be held together very strongly

during the drying process. The resulting morphology was shown as a sketch in an earlier review article (Hubbe 2014a). There are some issues concerning the capillary effects that do not appear to have been resolved in the available literature. First, Page's model does not account for the known high elasticity of cellulosic materials, especially when they have been swollen by water and delaminated by refining. Second, there is no explanation of what might prevent the edge of the meniscus area from continually retracting during the evaporation process, thus suggesting the misleading possibility that the resulting bonded areas might be just tiny points of contact rather than involving most of the area at the fiber crossing points (Page *et al.* 1962). It had been proposed that such features as fibrils or deposited colloidal material might impede the retraction of the wetted areas between fibers, thus preventing the potential bonded area from retracting during the evaporative drying of paper (Hubbe 2019).

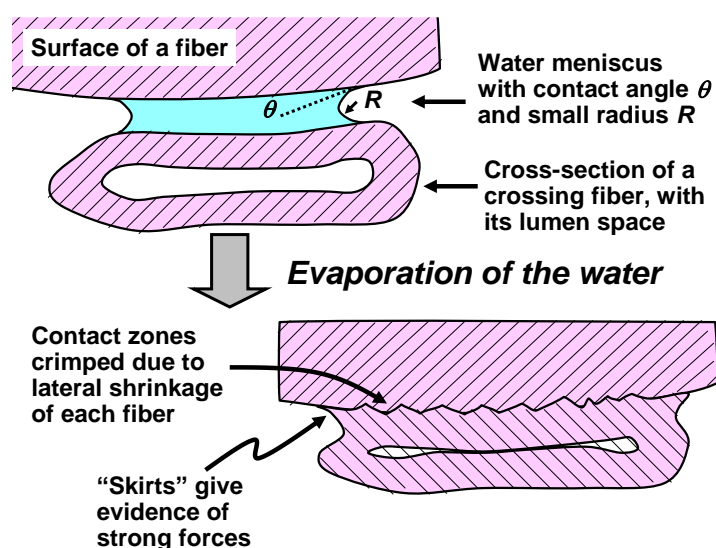


Fig. 28. Schematic illustration of drying as a way to direct self-assembly

As discussed in the review article by Pönni *et al.* (2012), the general mechanism described above appears to have multiple effects and implications during the processing of cellulosic materials, including pulping, refining, papermaking, and the partly irreversible loss of swelling ability when delignified woody material is dried. As reported by Mahoney *et al.* (1997), even the pressing of kraft fibers in the wet state appears to cause an irreversible loss in their ability to swell again with water. The irreversible changes appear to be associated with coalescence among adjacent microfibrils within the fiber structures (Pönni *et al.* (2012)). Thus, the contraction and irreversible bonding effects appear to take place at the nano-scale, within the cell walls of delignified cellulosic fibers. Since this process could be described as a manifestation of self-assembly, it is worth considering whether there may be opportunities to direct the events. As illustrated in Fig. 29, one can anticipate a progressive formation of hydrogen bonds directly between the cellulose surfaces as the water evaporates and forms thin films adjacent to the already-bonded areas. In areas still too far apart for bonds to have formed directly between the surfaces, the $-OH$ groups will still be associated just with water molecules.

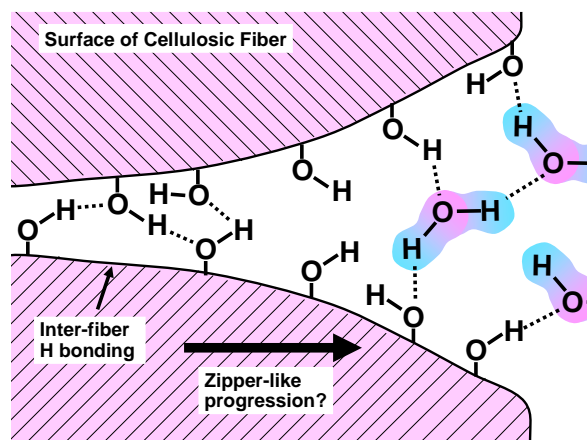


Fig. 29. Schematic illustration of hydrogen bonds forming within the nano-scale spaces where fibers are becoming joined together during evaporation of water, as in the forming of paper

In principle, if two ideal cellulose surfaces were lined up properly, then the formation of hydrogen bonds might be proposed to take place in a zipper-like fashion (Hubbe 2014b). Alternatively, it seems at least equally likely that hydrogen bonds may form in a haphazard, uncoordinated manner, leading to an amorphous bonded area. A research question that might be considered is whether a more orderly self-assembly could be achieved by slowing down the rate of evaporation or other means. In principle, the details of such a self-assembly process might be adjusted through the use of plasticizing agents, co-solvents, or pressurized conditions.

Organization by Means of Applied Fields

Applied fields can influence self-assembly processes in three general ways. First, fields such as gravity, flow, or electrical attraction may cause the entities under consideration to be constrained into limited space, thus requiring them to adopt an arrangement that minimizes their occupation of space (Pelesko 2007; Grzybowski *et al.* 2009). In other words, they align themselves to achieve more efficient packing. Second, if fields or forces act in a dynamic manner, they may provide the chaotic influence that allows the system to overcome minor energy barriers that might otherwise impede a process by which the particles can minimize the free energy of the system (Grzelczak *et al.* 2010). Third, some dynamic perturbations might give rise to a kind of “standing waves” (Trujillo *et al.* 2014; Luo *et al.* 2018). In such instances it is reasonable to consider whether such phenomena can cause the self-assembling entities to arrange themselves according to a regular pattern. For example, such an effect can be induced by a pair of ultrasonic transducers (Greenhall and Raeymaekers 2017).

Flow fields and self-assembly

Figure 30 illustrates a self-assembly principle that tends to favor the deposition of small particles onto cellulosic fibrils attached to a fiber surface rather than onto the broad sides of cellulosic fibers during the formation of paper. This phenomenon was discovered by Haslam and Steele (1936), who used microscopic observations and a flow-through observation cell. They observed that some of the fibrils extending from refined cellulosic fibers became so overloaded with mineral particles that they broke free from the fiber surfaces and were carried away by the flow. The tendency for the fibers to avoid the broad sides of the fibers can be attributed to the main streamlines of flow. As illustrated in part

A of the figure, deterministic calculations of the paths of particles being carried along in a laminar flow field will generally predict that the particles will pass around a much larger, non-moving object in its path (van de Ven 1989). Part B of the figure illustrates how the same fibers would tend to be intercepted by narrow fibrils extending outwards into the flow from the surfaces of well-refined kraft fibers.

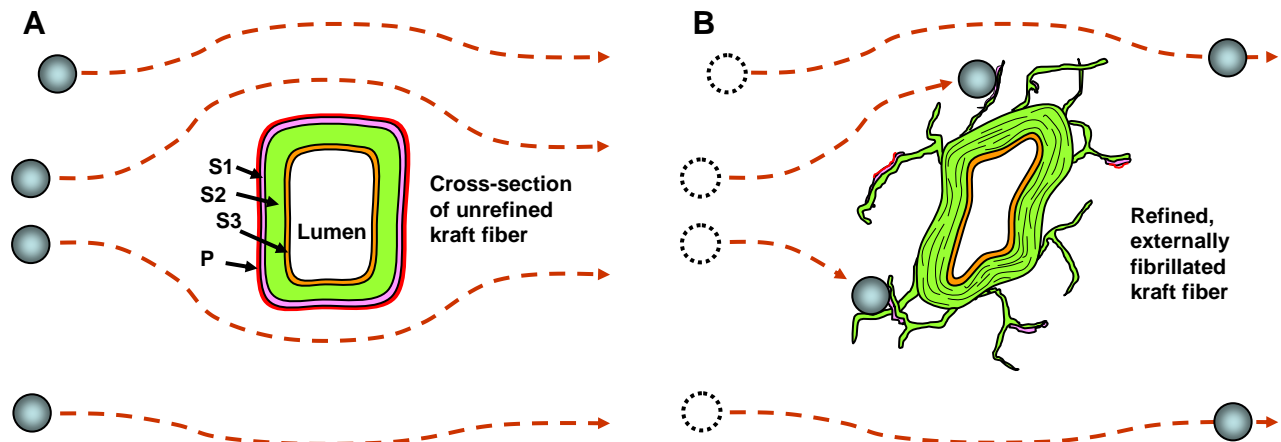


Fig. 30. Schematic illustration of how small mineral (filler) particles are often preferentially retained onto fibrils extending from the surfaces of refined kraft fibers

The mechanism just outlined also can be helpful in accounting for the high effectiveness of very-high-mass acrylamide copolymers, *i.e.* retention aids, in increasing the efficiency of retention of mineral particles and other colloidal particles during the formation of a paper sheet. It had been shown by Walles (1968) that when such a flocculant molecule was added to a stirred suspension of cellulosic fibers, the rate at which fine particles were retained exceeded what could be achieved by lower-mass additives. The difference was attributed to the chains or loops of polymers extending outwards from the surfaces, thus favoring the formation of relatively long polymer bridges as an initial means of attachment.

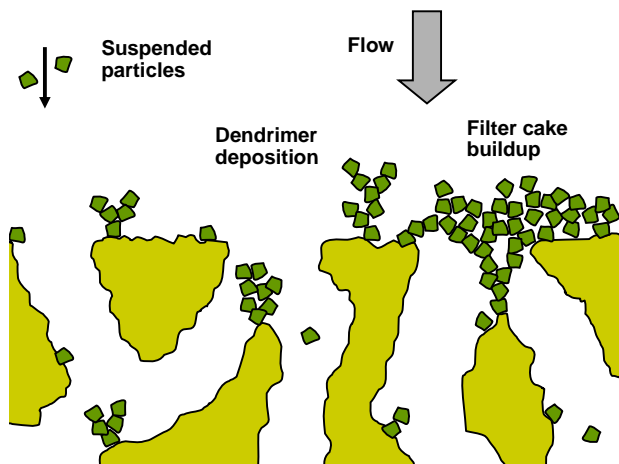


Fig. 31. Schematic illustration of dendrite formation or cake formation due to sticking collisions as a particle suspension encounters a bed of filter media

Another kind of flow-induced self-assembly can take place during media filtration of particles from a suspension, as in the case of sand filtration of fresh water. As illustrated in Fig. 31, in cases where collisions result in relatively permanent sticking, such collection often results in the formation of dendrite structures (Owens and Hubbe 2023). Continuing build-up eventually can bridge over the underlying pore structure of a filter bed or membrane filter, such that a cake of deposited particles covers the surface.

Electrical

Electrical fields have the ability to induce forces on ionically charged entities, such as molecular ions and charged particles. Jung *et al.* (2012) showed that a high electronic field could induce the spreading of materials and the formation of a smooth, two-dimensional layer on a flat electrode surface. The term “corona wind” was used to describe the effect. Bouda (2003) used an electric field to induce self-assembly of carbon particles; the results were interpreted based on the DLVO theory of colloidal interactions, involving electrical double-layer forces and van der Waals attractions. Coll *et al.* (2015) described the self-assembly of nanoparticles by an electrical field in the course of electrospray deposition. However, it appears that very little has been published relative to the use of electrical fields to direct self-assembly processes. Thus, there appears to be an opportunity for focused work in this area.

As illustrated in Fig. 32, one of the most striking applications of electrostatic fields is in the preparation of electrospun filaments (Bhardwaj and Kundu 2010; Adam *et al.* 2020), which are typically collected as semi-random layers. Applications related to cellulose and its derivatives have been reviewed (Ohkawa 2015). Electrospinning also can be used to prepare nano-size lignin filaments, which later can be converted into carbon products (Garcia-Mateos *et al.* 2019). An electrical potential causes a polymer solution of melt, which is being introduced from an electrically charged nozzle, to be accelerated towards a collection plate having the opposite charge. During such stretching, the diameter of the material can be reduced to nano size. A unique aspect of this technology is that electrostatic repulsion is acting between the freshly formed filaments, causing the material to spread out from each other during its passage through the air.

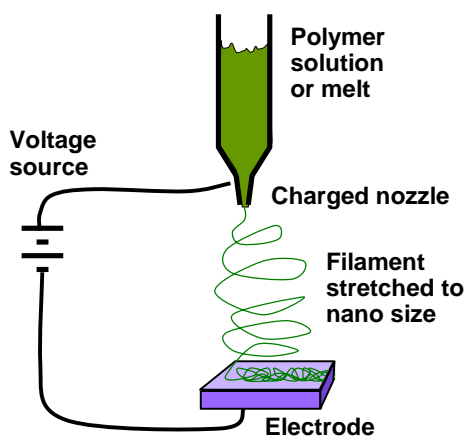


Fig. 32. Schematic illustration of an electrospinning process, in which a melted polymer is forced through an electrically charged nozzle, and the filaments are stretched as they move towards a target having the opposite charge

Magnetic

The forces of magnetism can be used as the basis for self-assembly (Singamaneni *et al.* 2011; Martin and Snezhko 2013). Mashkour *et al.* (2014) reported the magnetic field-induced self-assembly of a cellulose-based hybrid. The cellulose particles became aligned in the field. Zhang *et al.* (2021) used a magnetic field to direct the self-assembly of chemically modified graphene oxide onto cellulose fabrics. The resulting structures were flexible, durable, and showed promise for the preparation of electrically conductive wearable fabrics. In their review article, Ganguly *et al.* (2020) described the use of magnetic fields, among other approaches, to induce the organization of CNC particles.

Ultrasound

Collino *et al.* (2015) showed that the application of an acoustic field could be used to arrange a pattern of microscopic particles. The effects were not dependent on the details of shape or affinities between the particles. The tuning of acoustic waves made it possible to bring about the folding of DNA ribbons, packing particles together, aligning them, or moving them over relatively large distances. Greenhall and Raeymaekers (2017) used ultrasound to direct the final arrangements associated with 3D-printed materials, based on a stereolithographic approach. The nanoscale structures were of the Bouligand type, which is characterized by “uniaxial fiber layers periodically assembled into a helicoidal pattern” (Suksangpanya *et al.* 2017).

Following Nature’s Example, When Practical

Terms such as “bio-inspired” are often associated with self-assembly strategies carried out in laboratories (Bond *et al.* 1995; Sanchez *et al.* 2005; Stone and Korley 2010; Wang *et al.* 2013; Cheng *et al.* 2017; Rajasekharan 2017; Parker *et al.* 2018; Yu *et al.* 2018; Enesco *et al.* 2019; Li *et al.* 2019; Chen *et al.* 2020; Trovagunta *et al.* 2022). While marveling at the structures that can be achieved in living organisms, the modern technologist may be prompted to dream up strategies to achieve such patterns without relying so much on nature, even when the intended materials of construction come from plant materials.

In principle, self-assembly could start at the monomeric, polymeric, or particulate level. Two critical steps in such processes are likely to be not only the organizing into a self-assembled structure, but also the need to keep those structures bound together. Examples already cited show that the formation of hydrogen bonds can provide stable structures in many such cases (Pönni *et al.* 2012; Han *et al.* 2013; Khazraji and Robert 2013; Wang *et al.* 2013; Ratnaweera *et al.* 2015). When bonding is dependent on lignin, the effects are often dominated by non-covalent interactions, along with the use of conditions with enough moisture and heat to plasticize the lignin during a bonding process (Mishra and Ekielski 2019). A further option, in many cases, may be to take advantage of bonding reactions that occur in response to the heating of plant-based materials (Tajuddin *et al.* 2016; Hubbe *et al.* 2018; Nasir *et al.* 2019). Such bonds often can be attributed to the relative thermal instability of hemicelluloses and certain extractive components, leading to intermediates that can participate in cross-linking reactions. Additional options are available *via* various crosslinking reactions, leading to covalent bonds within the assembled structures prepared from plant-based materials (Wang *et al.* 2011; Tayeb and Tajvidi 2019).

Enzymatic processes

Enzymes may provide a kind of intermediate strategy between the complete reliance vs. independence from the use of living organisms to achieve self-assembly. Enzymes can be used essentially as catalysts to bring about either the hydrolysis or the creation of covalent bonds that could be useful in self-assembly. Kim *et al.* (2019) showed that it was even possible, by the means of enzymes, to synthesize cellulose in the absence of other cellular materials, *i.e.*, *in vitro*. In a similar aspect, Micic *et al.* (2003) used an enzyme to promote the polymerization of a monolignol to form a rudimentary lignin-like chain, which was deposited onto a cellulose surface. Kondo *et al.* (2002) used an enzyme-based approach to bring about the oligomerization of cellulose into the form of nano-ribbon. For purposes of bonding cellulose nanofibrils to each other, Varjonen *et al.* (2011) employed the binding domains from cellulolytic enzymes. In addition, the enzyme lipase has been used to catalyze the ester-bond attachment of laurate groups onto cellulose surfaces, rendering them hydrophobic (Yin *et al.* 2020). This approach is diagrammed in Fig. 33.

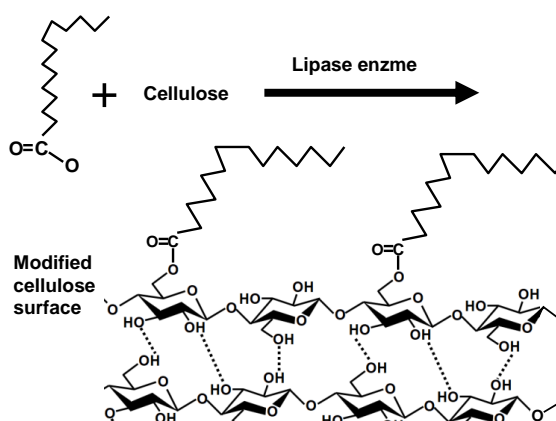


Fig. 33. Use of lipase enzyme to catalyze the esterification of a cellulose surface with palmitate groups

SOME TANGIBLE APPLICATIONS

This final section will deal with some potential applications of self-assembly in the preparation of useful materials. Subjects covered will include 3D printing, barrier films, hydrogels, foams, composites, and paper.

3D Printing

As discussed in the review articles listed in Table 7, there have been numerous research articles published related to three-dimensional printing, which is often called “additive manufacturing.” One of the basic kinds of 3D printing is depicted in Fig. 34, which notes the possibility of placing reinforcing particles into the polymer melt. A few of the articles that deal with the 3D printing of materials intended to represent wood and aspects of self-assembly. Thus, Yu *et al.* (2018) prepared polymeric woods. Their idea was to achieve a relatively high strength-to-mass ratio by replicating the basic structure of wood, especially the hollow spaces within fibers or vessels. In other words, a honeycomb structure was built. Resol phenolic resin was used as a substitute for actual wood material.

Structure was achieved by freezing, followed by curing at 180 °C. However, the present search of the literature did not find any articles that involved actual wood materials, 3D printing, and self-assembly issues.

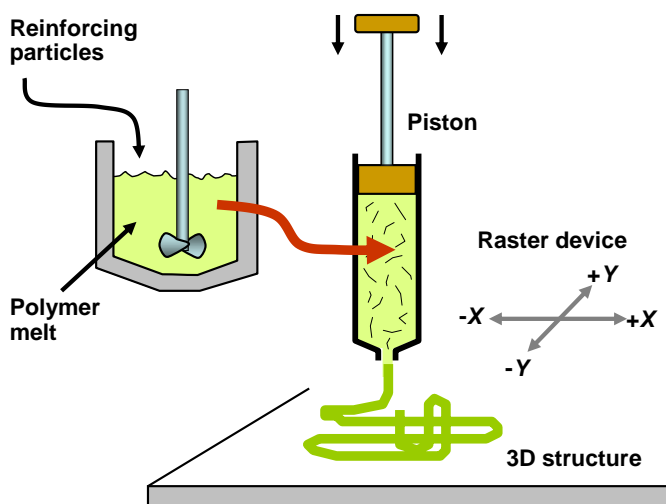


Fig. 34. Schematic illustration of 3D printing, as a modern competitor or potential collaborator for self-assembly processes

There have been many publications dealing with the use of lignocellulosic materials as a component in 3D printing in which there was no reference to self-assembly. Rather than representing self-assembly, *per se*, the effects achieved are most often based on the ability of digital printing to achieve the desired structural and microstructural patterning by direct application. Given the huge amount of research being currently done in this area (see Table 7), one might regard 3D printing as a kind of competitor to various self-assembly approaches. On the other hand, this might be regarded as an opportunity. Many of the self-assembly principles already outlined in this review article could be considered as a supplemental organizing approach in hypothetical future 3D printing processes.

Table 7. Review Articles in Which Cellulose-based Materials Were Used in 3D Printing

Main subject matter	Citation
Cellulose materials in 3D printing	Wang <i>et al.</i> 2018
Biomedical application of wood biopolymers in 3D printing	Xu <i>et al.</i> 2018
Cellulose and its derivatives in 3D printing	Dai <i>et al.</i> 2019
Nature-derived polymers used in 3D printing	Liu <i>et al.</i> 2019
Biomass-derived composites prepared with 3D printing	Ji <i>et al.</i> 2020
Wood and lignocellulosic fillers for 3D printing	Lamm <i>et al.</i> 2020
Cellulose-based polymers in 3D printing	Mohan <i>et al.</i> 2020
Cellulose, hemicellulose, lignin, & derivatives in 3D printing	Yang <i>et al.</i> 2020
PLA composites filled with biomass resources in 3D printing	Bhagia <i>et al.</i> 2021
Wood powder usage in 3D printing	Das <i>et al.</i> 2021
Lignin challenges and roads forward in 3D printing	Ebers <i>et al.</i> 2021
Nanocellulose structure, preparation, applications in 3D printing	Ee & Li 2021
Nanocellulose scaffolds for tissue engineering by 3D printing	Kuhnt <i>et al.</i> 2021
Wood usage as a filler in 3D printing	Tomec & Kariz 2022

Barrier Films

There has been much research progress recently in the area of cellulose-based barrier coatings for such applications as food packaging. For example, Kathuria and Zhang (2022) recently reviewed technology for sustainable and repulpable barrier coatings for food packaging. Kunam *et al.* (2022) reviewed bio-based materials for barrier coatings on packaging in general. Szlek *et al.* (2022) reviewed hydrophobic treatments of barrier layers composed of cellulose and other polysaccharides. It is known that thin films prepared from nanofibrillated cellulose can very effectively block the transport of oxygen gas, but that their barrier performance falls greatly with increasing relative humidity of the air (Aulin *et al.* 2010b).

Some processes that may involve self-assembly during the preparation of a hypothetical barrier layer for a paper product are illustrated in Fig. 35. A hydrophobic agent such as alkenylsuccinic anhydride (ASA) can be prepared by emulsification of the oily compound with a cationic polymer such as cationic starch. Then, when the ASA emulsion is added to the fiber suspension, the ASA particles self-retain on the cellulosic surfaces, which typically have a negative net charge (Ehrhardt and Leckey 2020). As noted in the figure, the spreading and reaction of ASA does not appear to take place until after the bonded areas have been established (Korpela *et al.* 2021). The filtration mechanism, starting with dilute suspensions, provides a means by which the particles of nanofibrillated cellulose will arrange themselves generally into a layered structure that also involves a certain degree of intertwining. Accordingly, when highly platy mineral particles, such as sodium montmorillonite (bentonite) are present, they too can be expected to align themselves preferentially in the plane of the sheet. Such alignment tends to impede diffusion of gases or oils through such a barrier layer due to the more tortuous path that such molecules would have to follow.

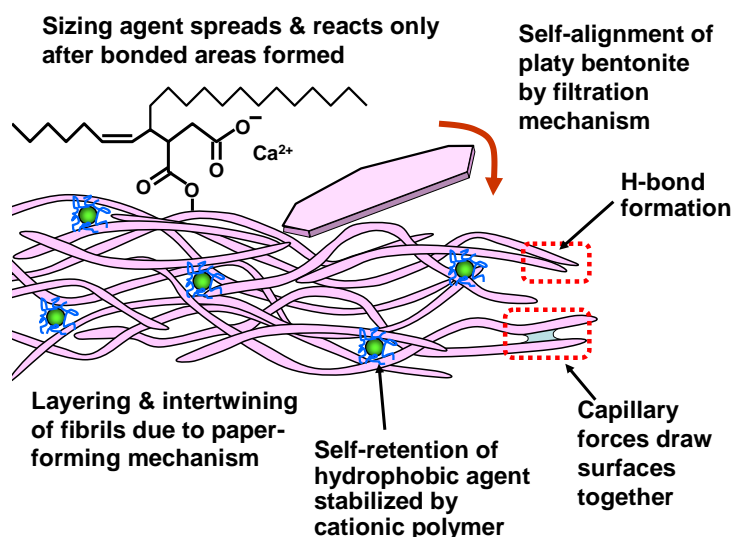


Fig. 35. Schematic illustration of key events during self-assembly of a cellulose-based barrier coating to block the transmission of oxygen, greases, *etc.*

Aspects of self-assembly appear to be involved in many aspects of barrier layer preparation, though their effects can be easy to escape notice. During dewatering, in the formation of the layer of cellulose nanomaterial, it is likely that the individual fibrils move around in a cooperative fashion so as to eliminate spaces between them. The high density

achieved by the cellulosic materials is likely due to a self-optimized development of nearly maximum hydrogen bonding between the adjacent surfaces during the drying process (Pönni *et al.* 2012). The tight contraction of the material, such that hardly any air can pass through the dried sheet (Aulin *et al.* 2010a; Hubbe *et al.* 2017), can be attributed to the capillary forces and hydrogen bonding mechanism already discussed. Tayeb *et al.* (2018) made the case that cellulose nanomaterials self-assemble during the formation of multiphase polymer structures. Self-assembly also appears to play a major role in the optimized usage of polyelectrolyte complexes, which can include carboxymethyl cellulose and chitosan, in barrier coatings that may also contain nanocellulose (Hubbe 2021).

Hydrogels

Several review articles have noted that self-assembly phenomena are likely involved in technology related to hydrogels, many of which are prepared with carboxymethyl cellulose as one of their components (Hubbe *et al.* 2013). In particular, Ghorbani *et al.* (2018) reviewed research publications related to hydrogels based on cellulose and its derivatives. These authors asserted that self-assembly processes are responsible for the formation of physical gels, which are held together by ionic or hydrogen bonds. Collino *et al.* (2015) described the use of acoustic fields to direct the self-assembly of hydrogel matrices during photopolymerization. Mendes *et al.* (2013) described the involvement of self-assembly during the preparation of hydrogels for cell culture.

Composites

The field of composites is a broad area, and therefore one can expect that a diverse range of findings would have been reported related to self-assembly. Table 8 lists some studies that dealt with self-assembly issues in cases where the resulting composites contained cellulosic materials.

Table 8. Studies Involving Self-assembly Issues with Preparation of Composites Containing Cellulose-based Materials

Main subject matter	Citation
Biological structural materials' self-assembly aspects	Bond <i>et al.</i> 1995
Pullulan abietate as model for lignin-carbohydrate complex	Gradwell <i>et al.</i> 2004
Cellulose-based nanocomposites	Hubbe <i>et al.</i> 2008
Nature's examples of high-performing composites	Stone and Korley 2010
Plant cell wall components self-assembly, review	Murugesan <i>et al.</i> 2015
Cellulose serving as a scaffold for self-assembly with nanoparticles	Tian & He 2016
Ultrasound waves used together with stereolithography	Greenhall & R. 2017
Bio-based and ceramic self-assembled composites	Rajasekharan <i>et al.</i> 2017
Colloidal lignin self-assembly by precipitation from THF solution	Ashok <i>et al.</i> 2018
Cellulose-based multiphase self-assembled structures	Tayeb <i>et al.</i> 2018
All-cellulose composites with nanocellulose & regenerated cellulose	Cheng <i>et al.</i> 2019

Foams

Porous structures such as solid foams or aerogels can be prepared by specialized drying of wet foams that contain solid materials. Such foams, when containing cellulosic materials, have attracted strong attention for such purposes as cushioning and sound insulation (Lavoine and Bergstrom 2017; Yu *et al.* 2018; Zhao *et al.* 2018; Mimini *et al.* 2019; Nechita and Nastac 2022). The arrangements of bubbles within a fluid foam follow well-known self-assembly rules (Pelesko 2007; Fameau and Salonen 2014). Ashok *et al.*

(2018) used the word self-assembly when describing the preparation of a solid lignin-based foam structure that appeared promising as a cushioning material for packaging. Han *et al.* (2013) used freeze-drying as a means to convert a foamy mixture containing CNC and NFC into solid foams having aligned layers. The alignment within the structures was attributed to ice structures, which became sublimated in the process.

Papermaking

Self-assembly phenomena are involved with papermaking processes in multiple ways. Ultimately, the papermaker needs to depend on the self-arrangement of different entities in the structure at various times. This will include the adsorption of additives onto fiber surfaces, alignment of fibers in flow, flocculation of fibers with each other as a result of flow, and flow-induced collisions resulting in the retention of fibers. Then, as mentioned in previous sections, a sequence of capillary force action and formation of hydrogen bonding takes place during evaporative drying of the paper sheet (Hubbe 2014a). Throughout all of this, the components of paper act as if they know what needs to happen, since there is no way that anyone could purposefully direct the huge number of individual events that have to happen at high speed during the manufacturing process.

The term “healing,” which already was discussed, especially in relationship to polyelectrolyte complexation, also has significance for the process of papermaking (Hubbe 2007). Figure 34 illustrates the basic mechanism (Hubbe *et al.* 2020b). The illustration represents what can be expected when the wet web of paper, resting upon a fabric screen, passes over a slot where vacuum is being applied. As shown, the flow of water out from the paper web tends to draw fibers toward those places in the paper that have the least coverage. Such locations will have the least resistance to flow. The middle frame of the figure represents an observed back-flow of drainage water. It has been proposed that such back-flow can partially redistribute materials within the wet paper web (Hubbe *et al.* 2020b). Thus, each cycle of suction and rewetting can provide an additional chance for evening out of any non-uniform distribution of the fibers in a sheet.

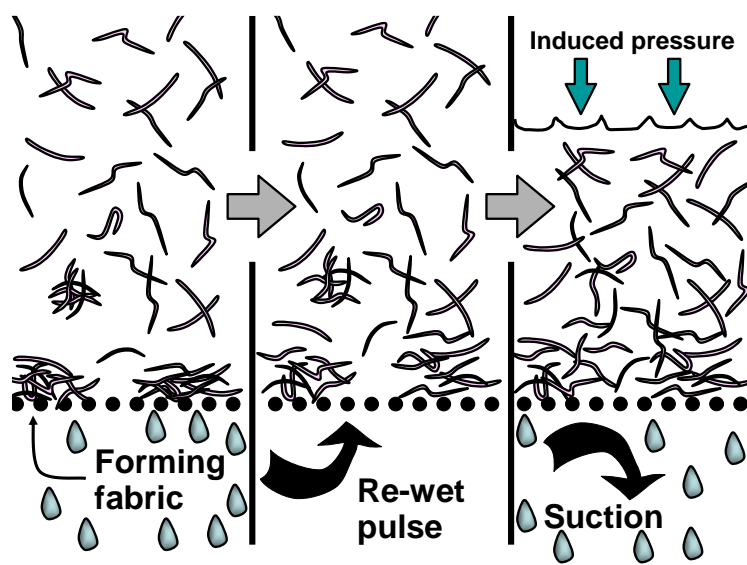


Fig. 36. Schematic illustration of key steps in the papermaking process that appear to involve aspects of self-assembly

Papermakers have opportunities to influence the direction of self-assembly through such strategies as optimizing the orders of addition and the dosages of oppositely charged additives to the process (Hubbe 2014c). Taking advantage of the fact that untreated cellulosic fibers generally have a negative charge, it is common that the first additives to the process are cationic (Marton and Marton 1976; Howard and Jowsey 1989; Hubbe 2006). Subsequently, papermakers sometimes apply a negatively charged additive, *e.g.*, an anionic copolymer of acrylamide (a retention aid), taking advantage of the fact that cationic (initial) additive can provide anchoring sites for the second additive (Wågberg and Lindström 1987; Hubbe *et al.* 2009). It is even possible, at least in theory, to build up precise multilayers of cationic and anionic polyelectrolytes, a strategy that is predicted to greatly increase the strength of the resulting paper (Wågberg *et al.* 2002). A much quicker approach can be employed based on the *in-situ* self-assembly of polyelectrolyte complexes in the presence of cellulosic fibers, such that they immediately adsorb onto those surfaces. Such strategies, though they are prone to deposition of sticky materials onto papermaking equipment, can achieve very high levels of paper dry-strength (Hubbe 2005; Heermann *et al.* 2006). Self-assembly phenomena also appear to play a role in various other aspects of papermaking, such as the flocculation and simultaneous redispersion of fibers when present in agitated suspension (Kerekes and Schell 1992; Hubbe 2007). The flow of water out from the formed paper sheet, in addition to the healing effects emphasized in Fig. 36, also tends to densify the sheet. As paper made from kraft fibers is being dried under tension, the crimping action caused by lateral shrinkage of each of the fibers, while being tightly held together by hydrogen bonds (Page and Tydeman 1962), causes each fiber to straighten, thus contributing to the strength and dimensional stability of the product.

CONCLUDING STATEMENTS

It has been stated that self-assembly is the ultimate dream of a lazy technologist (Grzybowski *et al.* 2009). Rather than having to do all the work of organizing the materials, the materials just organize themselves on their own. Though the articles cited in this review show that the real situation often is a lot more complicated than that, the weight of evidence suggests that the general thrust of the statement is right: By designing systems that can take advantage of innate propensities to self-assemble in advantageous structures, the developmental technologist can work toward such goals as sustainability, emulating what can be achieved by nature (bio-inspiration). In addition, there can be opportunities to make use of cellulose, hemicellulose, lignin, and wood extractives, either individually or in combinations.

Sustainability

Sustainability can be understood as the establishment of processes that can be carried out over long periods of time in a way that minimizes any adverse effects on the environment. The usage of photosynthetically renewable raw materials can be an important contribution to sustainability. Another contribution can be the efficient usage of residues and byproducts. Because the residues and byproducts of cellulosic materials are often rather small, especially in comparison to the trunks of mature trees, the assembly of those small parts into larger structures can be expected to constitute a major ongoing need in the coming years. As has been illustrated by examples discussed in this article, such self-assembly can be promoted by natural propensities of the biomaterials themselves,

taking advantage of their hydrogen bonding ability, charge interactions, polar or nonpolar affinities, and also some covalent reactions.

One of the big challenges in the upcoming years will be to transform some aspects of what has been learned in the laboratory or through simulations into high-volume, everyday technologies. An important step in that direction can be provided by techno-economic analyses (Wenger *et al.* 2020). For example, Ashok *et al.* (2018) used a simulation approach, along with the input of suitable data, to predict the economic viability of a self-assembly process for making products from lignin. Ding *et al.* (2022) considered the techno-economic tools that can be used to evaluate the viability of engineered wood products. Poveda-Giraldo *et al.* (2021) presented a preliminary techno-economic assessment involving the transformation of a conventional pulp mill into a biorefinery. Such studies provide entrepreneurs, even if they question some of the details, with a starting estimate of the costs and potential profits that might be achieved through technological ventures that involve self-assembly aspects.

A Need to Consider Applications Focusing on Biomass Components

A further challenge will involve focusing on each of the main building blocks of lignocellulosic materials, as well as some of the minor ones, in seeking some of the most valuable potential applications of each. The operative word is valorization. As an example of this, Zanoni *et al.* (2020) used glycerol and carbon dioxide to prepare biodegradable polymers that can be self-assembled to make potentially valuable nanoparticles. Song *et al.* (2022) considered the valorization of lignin by self-assembly to form spherical particles in the microscopic range. There is a need for more studies of that type.

Lignin

Recent publications dealing with lignin moieties have revealed that the manipulation of solubility has been the most important tool being used to bring about self-association (Qian *et al.* 2014; Ratnaweera *et al.* 2015; Li *et al.* 2016; Salentinig and Schubert 2017; Xiong *et al.* 2017a,b; Ashok *et al.* 2018; Mattinen *et al.* 2018; Hubbe *et al.* 2019; Mishra and Ekielski 2019a; Trovagunta *et al.* 2022). The formation of small lignin particles has been a primary focus of such work. The manipulation of surface charges by the addition of cationic polymer has provided a section route to lignin self-assembly, providing a way to get it to form a film onto cellulose surfaces (Maximova *et al.* 2001). A third avenue that merits future attention would be to make use of vestiges of lignin-polysaccharide complexes (Bjorkman 1957; Meshitsuka *et al.* 1982) as a route toward directed self-assembly of lignocellulosic materials. Other aspects, including condensation reactions (Kim and Kim 2018) and curing reactions involving phenolic groups (Yu *et al.* 2018), might be considered in future research involving the self-assembly of lignin fragments.

Cellulose

Though terms related to self-assembly have been utilized much less often in publications dealing with the interactions of cellulose and its byproducts, one can expect there to be a lot of progress in the coming years with such surfaces. A primary tool for the organization of cellulose has been the alignment of CNC into liquid crystal structures (Kondo *et al.* 2002; Lagerwall *et al.* 2014; Tian and He 2016; Rajasekharan *et al.* 2017). There are prospects of using such tendencies as the basis for preparing innovative types of products, such as barrier films and binders (Tayeb *et al.* 2018). It seems that not enough

attention has been placed on issues such as whether or not the hydrogen bonding interactions between adjacent cellulose surfaces can be directed to follow the alignment directions of the individual macromolecules. In particular, can cellulose fibrils be manipulated to self-assemble in a zipper-like manner? For example, such alignment could be facilitated by an ice-templating process (Trovagunta *et al.* 2021a). Another relevant question is whether cellulose self-assembly, starting with various dissolved forms of cellulose, can be directed in such a way as to minimize the crystalline character.

Hemicelluloses and soluble polysaccharides

The self-assembly of hemicelluloses and related polymers may be expected to provide important opportunities in coming years. Many questions remain concerning an observed tendency of such macromolecules to form agglomerates in aqueous systems (Blake and Richards 1971; Saake *et al.* 2001; Linder *et al.* 2003). The fact that such associations form, despite the amorphous nature of hemicelluloses and their high affinity for water, can be viewed as evidence of a strong tendency for assembly based on high densities of hydrogen bonding. Again, it will be important to find out the extent to which such association involves zipper-like progressions of hydrogen bond formation, or whether somewhat haphazard bonding is the rule. Also, it is of interest to know whether such associations tend to form the structures into kinetically locked non-equilibrium trapped structures (Bishop *et al.* 2009) or whether healing mechanisms are subsequently able to repair damage and allow such systems to achieve more ideal films or other structures with the passage of time in the wet condition (Mitchell *et al.* 2018). The fact that isolated specimens of xylans often contain some aromatic content (Linder *et al.* 2003) suggests that byproducts related to lignin-polysaccharide complexes may play a role in some such systems. Because xylans and related hemicellulose products often can be pre-extracted before a pulping operation (Ebringerova and Heinze 2000; Hamaguchi *et al.* 2013), there is potential to have very large amounts of such materials available in the future. For instance, such materials could be key components in barrier films for food packaging (Mikkonen and Tenkanen 2012; Farhat *et al.* 2017; Qaseem *et al.* 2021).

Wood extractives

Due to their hydrophobic, or often surface-active nature, as well as their disparate characteristics, the extractives from wood and woody materials can be expected to undergo self-association when present in aqueous systems. Examples of such interactions were considered in an earlier review article focusing on the fatty acids and related components of woody materials (Hubbe *et al.* 2020a). Due to the large scale of the pulping industry, such extractives are widely available on the market and are currently used in many product formulations (Chang *et al.* 2010). From the perspective of opportunities for implementation of self-assembly in industrial processing, it has been found that some extractives can serve as effective bonding agents within plant-based materials (Roffael 2016). In particular, tannins can be very effective as bonding agents for such applications as the so-called “binder-free” engineered wood products (Pizzi 2008; Alvarez *et al.* 2015; Ghahri and Pizzi 2018; Hubbe *et al.* 2018; Dunky 2020). Binders also can be formulated with tall oil fatty acid components (Uschanov *et al.* 2008).

Putting it all together

Based on the published work, it can be stated in general that research related to self-assembly of lignocellulosic materials, from a product development standpoint, is still

generally at an early stage of development. Such applications seem likely to be highly complex, involving the specificity of interactions among many different kinds of surfaces with different chemistries, morphologies, and responses to aqueous or thermal conditions. Future researchers can be expected to continue to have difficulties in judging whether or not specific interactions can be classed as involving self-assembly or not. Whatever is decided, the examples of self-assembly that come from the natural world will continue to inspire modern developmental technologists to build more sustainable products for coming generations of consumers.

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