Fabrication technology of biofiber based biocomposites

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23.1 Introduction

The matrimony of "materials" and "creativity" is experiencing a steep discovery path accelerated by the recurring theme of "re-design" and "innovation" chaperoned by nature. The intensity shift is currently propelling the pace of technological innovation. Nature uses assembly processes in tune with its environment—A leading and global ambition of the 21st century to bring forward the next generation of low cost "breakthrough" materials of exceptional performance (Council of Europe, 2017) while fitting in harmoniously with the natural world.

In this era of advanced materials development, the discovery of functional materials has become an important research focus offering considerable interdisciplinary value (Arroyave et al., 2018) across a broad range of technological pursuits. Perhaps, the most pursued sector in materials research is the field of biocomposites and their associated applications, renewing the importance of fabrication methods in the design of diverse material assemblies that may be of synthetic or biological origin. The growing awareness of the potential environmental impact of toxic waste accumulation from synthetic material production posing considerable technological barriers to their safe and harmless disposal has paved the way for sustainable ecofriendly polymer compositions as replacements for non-degradable materials. The tightening of regulatory controls over the decades has been a catalyst for directing the use of "greener" or "renewable" alternative sources for the design of polymers more aptly aligned with materials found in nature and are compositionally biodegradable. However, incorporating the principles of green chemistry has been challenging in engineering more innovative synthetic polymers with feasible solutions for their safe environmental clearance. This primary concern has unlocked the search for biocompatible and biodegradable materials with novel properties for diverse engineering and biomedical applications. Nature teaches us that the intrinsic characteristics of bio-driven assemblies are determined by the principles of design from which they originate at the nanoscale and may lead to smarter material properties (e.g., stimuli response properties). However, primary material operations intrinsic to mechanical behavior, modulus, elasticity, stress-strain factors, stiffness and anisotropic behavior among others are the basic descriptors of functionality and performance of materials required to support

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and sustain life. These important concerns that must be addressed concurrently with the search for renewable materials makes the task considerably more complex and challenging. Promising materials however that lack in part some or all of the desired characteristics as functional biomaterials may potentially be re-engineered with existing fabricating technologies. The synthetic growth of materials unlike those found in nature conform to homogenous states of matter limiting their potential in applications which are more often than not broadly allied to heterogenous states. It is desirable to have materials that exhibit a good degree of variability in their intrinsic mechanical properties at multi-levels as a single constituent material. Equally important in the current era of materials development is the structural and compositional harmonization of materials with nature through core requirements that permit sustainability, recyclability, and biodegradability.

Nature supplies a range of abundant materials. A leading question centers around material diversity and its correlation with structure and properties, which surprisingly are equally diverse unlike the biomaterials that are used to build them. The perplexity from a materials engineering perspective relates also to the depth of functional diversity from building blocks that originate from a small number of naturally occurring material types for example, cellulose, cellulose fibers, hemicellulose, calcium carbonate, keratin, minerals, lignin, hydroxyapaptite, elastin, chitin and collagen. The functional homogeneity of biomaterials aligned to task specific biological functions such as providing mechanical strength, ductility, fracture, stress and strain events, elasticity, deformation and its effect on shape and size recovery demonstrate considerable versatility of materials and utility range in different biological contexts. For example, biomaterials can impart selective behavioral properties in biological events spanning adhesion at soft and hard interfaces, dynamics of signaling that rely on surface texture, shape-to-shape interactions, mobility and growth, division where length and scale are the determining factors of the magnitude of biomechanical force (Li, Eyckmans, & Chen, 2017) exerted during intra- and extracellular signaling.

Bio-driven materials in our environment have evolved to adapt surface properties to suit their surroundings tailored for specific functions and thus enabling living organisms to perform tasks on different scales. Different types of forces are prevalent in nature, and the mechanical characteristics of materials are largely defined by the magnitude and the nature of influences that cause a change in material behavior. The interaction between surfaces in mechanobiology generate forces arising from compressive stresses for load bearing tasks to mechanics that involve contraction, stretching, adhesion and varying degrees of stiffness. For example, how do biomaterials resist external forces through *tensile* or *compressive* stress and not rupture or fracture (*strength*), retain their original shape in the absence of the applied force (*elasticity*) and resist deformation (*stiffness*) or to be permanently deformed (*plasticity*). If materials are hard, resistance to fracture defined by their *toughness* and *hardness*, resilience to absorb energy without causing material damage and resistance to *fatigue* through repeated processes that may eventually result in property failure. Other properties such as surface curvature, material reinforcement through matrix formation and associated tension-traction stresses, shape and dimensions related to mechanical factors, pressure due to confinement and externally generated forces such as magnetic fields are examples of different ways materials provide insight in orchestrating forces in biological systems. In view of this, a leading question in materials engineering centers on how surface properties relate to mechanical information and how surfaces can be adaptively tuned artificially to respond and behave to the specific requirements of mechanical behavior? Can materials be intrinsically designed to exhibit structural architectures that are sensitive to mechanical signals generated by surface−surface interactions? The answer lies in natural materials which exploit multi-material properties to enhance resistance to the multitude of forces in local environments to prevent or minimize localized damage in the form of composites. Hence, material responses are important to their structural integrity to the demands of their functional role in living species at the macro- to nanoscale. A cornerstone to predicting material reliability and the successful development of artificial materials lies in understanding the nature of the forces and their relationship to the material compositions found in the natural the world. Fig. 23.1 compares a broad selection of engineered materials with natural materials charting tensile strength σ_{ts} against Youngs's modulus, E (Ashby, 2007). The computer based visual demonstrates that the tools of nature are remarkably suited to using building blocks for the assembly of materials that cover the broad spectrum of tensile properties reflecting their diverse functional importance of biomechanics in the environment. From nature's perspective, this means that making new constructs

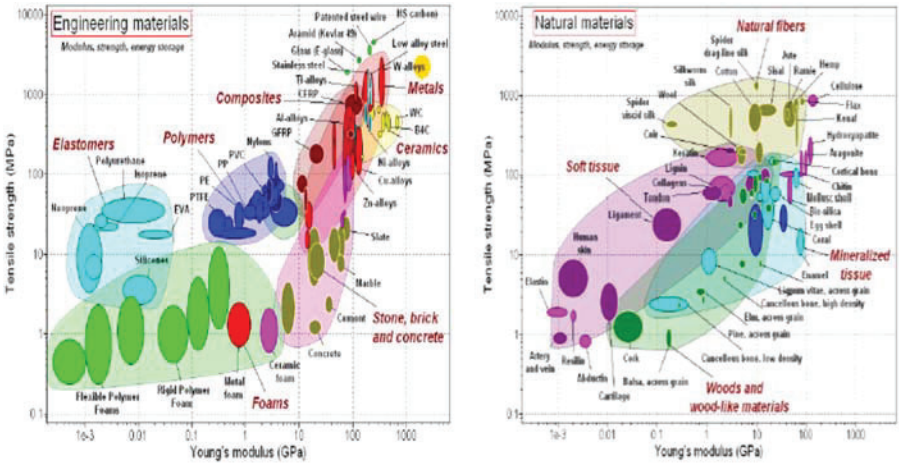


Figure 23.1 Ashby plot. A modulus-strength ($E - \sigma_{ts}$) chart database comparing engineered materials (left) with natural materials (right). Bubble areas represent the $E - \sigma_{ts}$ range of selected materials.

Source: Reproduced with permission from Ashby, M. F. (2007). *The CES EduPack database of natural and man-made materials*. Cambridge: Cambridge University and Granta Design; Liu, Z., Zhu, Y., Jiao, D., Weng, Z., Zhang, Z., & Ritchie, R. O. (2016). Enhanced protective role in materials with gradient structural orientations: Lessons from Nature. *Acta Biomaterialia, 44*, 31−40.

becomes a question of optimizing the way materials are constructed and its convergence toward a structural framework that closely matches both purpose and performance.

In the design of newly engineered materials toward a useful functional end, it is therefore imperative to identify a design criterion based on structural principles that is well understood. This may best be appreciated from composite materials whose constituents comprise nanosized materials. While biomimetic materials are on an important trajectory to solving challenging issues in response to a changing environment and human needs, the intricacy of complex hierarchical arrangements of natural materials and their multifunctional nature across all length scales, remains overwhelmingly attractive. The process of mimicking nature to construct new materials essentially employs the principles of biomimicry but this "nature" inspired concept does not use the elements of nature itself. The difficulty here is that the essential design principles used in biology are largely unknown and therefore cannot be replicated easily, however their utilization is a necessary outcome for performance-related durability and robustness and dynamics of mechanical work. Deciphering complex natural phenomena that govern structure-function relationships and their adaptation in an evolving environment is enormously challenging. For this reason, engineering of complex biological architectures into applicable design criteria particularly into well-orientated graded surfaces of living systems with intricately driven mechanical features (Liu et al., 2016) has been demanding.

Since the discussion here is mainly concerned about generating materials with a desired mechanical function, mechanisms that underline the attributes of material character such as strength, stiffness and stress properties resides in the molecular interactions. A unifying feature here are the nature of forces that bind components together potentially forming new materials. Knowledge of these molecular interactions between biological and artificial materials at interfacial boundaries that form favorable molecular associations between host-guest structures has become an important directive in tuning intermolecular forces for introducing desirable mechanical properties. Configuring the physical, chemical and mechanical properties between two or more material compositions (one being of biological origin) to alter and enhance their properties and biodegradability of the resulting material constitutes a biocomposite. The level of complexity of the molecular arrangement is multi-organizational in plants connecting (1) nanostructured chemical cell wall compositions molded by (2) shape and size driven patterning of structural constituents which (3) align hierarchically into an overall composite defining a structure orientated path to assembly. This basic framework allows the reinforcement of the core matrix—a cross-linked network that has formed the basis of a bio-inspired architectural feat for material engineers and polymer chemists.

A more viable alternative (with reference to Fig. 23.1) is the modification of surface characteristics of materials of choice on the property map (Teeri, Brumer, Daniel, & Gatenholm, 2007) to improve performance ratios using instead natural components provided by nature itself. A common approach to engineering material properties rests on the principle that measurable performance is often achieved through carefully designed material blends and their combination out performs their mechanical function when operating unassisted or individually. One such high performance material is cellulose derived from plants (Asrofi et al., 2018) and bacteria.

The abundance of cellulose as a naturally occurring renewable polymer and its non-toxic biodegradable characteristics with attractive mechanical properties renders it as one of the most sought after and effective biomaterials for technological development. The structural versatility of the material allows cellulose to exist in different morphological forms as diverse as nanofibrils, whiskers and nano to microcrystalline cellulose. The functional significance of different structural morphologies of cellulose encountered in nature implies that the material exhibits variable surface chemistries with differing degrees of crystallinity. The economical value as a material commodity is immense as a multifunctional material since its structural versatility caters for a range of exploitable mechanical properties.

As we move toward a more comprehensive understanding of microstructures and structure-property relationships, in this chapter we discuss how progress in fabrication techniques has aided our understanding of adhesion behavior and interfacial properties of nanocellulose based biocomposites and their integration with emerging technological platforms. With a view to replacing less desirable materials with renewable forms, the most abundant being nanocellulose material types, we discuss the importance of scale in understanding hierarchical behavior, bonding and technical aspects aiding our understanding of the nanocellulose architecture and explore key strategies for biocomposite fabrication currently used (Murawski, Diaz, Inglesby, Delabar, & Quirino, 2019) for advancing biomimetic design.

23.2 Scale in the hierarchical path to behavior and function in nanocellulose

Nature teaches us as that the physicality of scale is inherently linked to behavior and bio-material function. The molecular arrangement and packing of molecules, building blocks and their associated assembly processes are essential to the design of hierarchical structures. However, a greater appreciation of design characteristics and their evolution at the marcoscale is more insightful at the nano-dimensions since the origin of growth at the nanoscale determines the pattern of growth at larger scales. It follows that the mechanisms underlying the physical and chemical properties of structures in accordance with the rules of design at the smallest scale can be traced as an influencing factor of function and behavior for both bio- and synthetic materials. Hence, the ability to configure structure-function and behavioral relationships knowledgably lies in understanding how materials form at the nanoscale. Understanding the effects of scale and the correlation of influencing parameters that operate across scales has mechanistic significance in tailoring material properties.

Fig. 23.2 show the hierarchical growth of cellulose-based materials and the position of scaled growth to structure-property relationships and multiscale modeling in the pursuit of bottom#up design strategies. The scalar growth of cellulose nanocrystals to micro- and macrofibrils forming mature fibers is a complex growth process of self-assembly events. It is important to emphasize that the instructional blue-print defining the mode of self-assembly of cellulose achieved through layered growth is predominately dictated by the

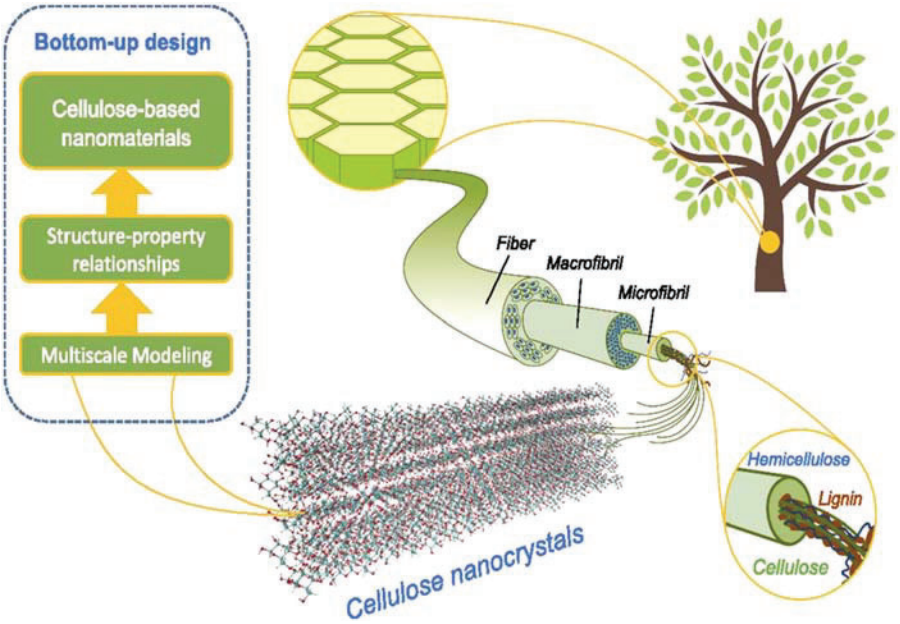


Figure 23.2 Bottom-up design. The Schematic depicts the nanoscale core as the origin of hierarchical outgrowth and its importance in “bottom-up-design” strategies. Structure, behavioral and functional relationships have a common significance at the nanoscale. *Source*: Reproduced with permission from Martin-Martinez, F. J. (2018). Designing nanocellulose materials from the molecular scale. *Proceedings of the National Academy of Sciences*, *115*(28), 7174−7175.

organization at the level of building blocks at the complex hemicellulose and lignin interface. Hence the bonding networks, growth orientations and assembly patterns and molecular dynamic interactions of supramolecular structures are the result of chemically and physically generated forces intrinsic to the growth environment. Hence, the dynamics of atomic-scale patterns have a principle role in shaping the mechanics and ultimate material characteristics. There is much deliberation in deciphering the hidden rules of assembly in our quest to fabricate materials from the molecular scale with precision structure and performance (Martin-Martinez, 2018). However, the mechanics of response to the environment guided by the principles of design are deeply implanted at the core at the epicenter of the nanoscale outgrowth.

23.3 The basics: cellulose architecture and underlying stability

Before we can identify the potential barriers in the use of nanocellulose in applications and to and address these challenges in the pursuit of technological advancement, it is worth re-visiting the basic architecture of nanocellulose and the physicochemical characteristics that define its integral nature and primary properties governing its interfacial behavior. Cellulosic materials that exhibit nano-dimensional morphologies are distinctly separated into cellulose nanofibrils (CNFs) and nanocrystals (CNCs) and bacterial nanocellulose (BNCs). Some key properties are summarized in Table 23.1. The topological aspect of cellulose that enable resistance to continuous deformation from bending, twisting and stretching under geometrical stress and strain across the length of the structure preventing disintegration of chains is through a "flexible" chemical coupling ring-like arrangement of glucopyranose units formed via glyosidic bond linkages. Cellulose is inherently linear conforming to the elementary structure $(C_6H_{19}O_5)_n$ with a chain configuration of repeating ring units. The geometric arrangement allows adjacent rings to align and stack using both intra- and molecular inter-hydrogen bonding (Fig. 23.3A and B). Cohesive binding enabled by short bond interactions enforces a compression of 3 GPa across the fibers

Table 23.1 A summary comparison of key some features of the generally categorized nanocelluloses.

Side-by-side comparison of bacterial nanocellulose (BNC), cellulose fibrils (CNF), and cellulose nanocrystals (CNC) morphology and physical properties

Nanocellulose	**Length**	**Cross section**	**Degree of polymerization**	**Crystallinity/ Crystal structure**
Bacterial nanocellulose	Different types of nanofiber networks	20–100 nm	4000–10,000	1α (shell) and 1β (core)—highest degree of crystallinity
Cellulose fibrils	0.1–2 μm	5–60 nm	≥ 500	Primarily 1β—lowest degree of crystallinity
Cellulose nanocrystals	100–250 nm (from plant celluloses); 100 nm to several micrometers (from celluloses of tunicates, algae, bacteria)	5–70 nm	500–15,000	Primarily 1β—sometimes 1α medium degree of crystallinity

Source: Reproduced with permission from Tayeb, A. H., Amini, E., Ghasemi, S., & Tajvidi M. (2018). Cellulose nanomaterials—Binding properties and applications: A review. *Molecules (Basel, Switzerland)*, *23*, 2684.

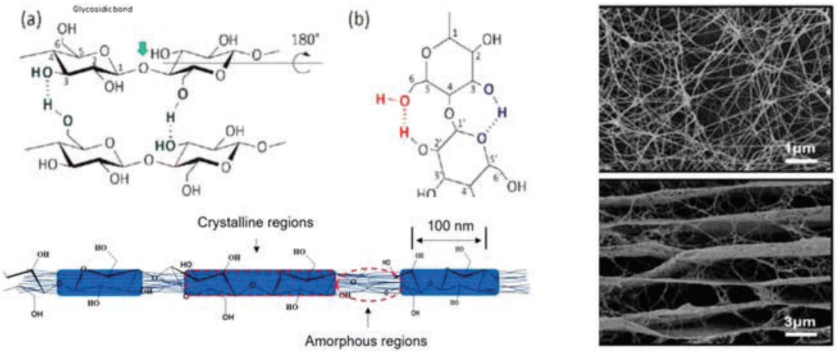
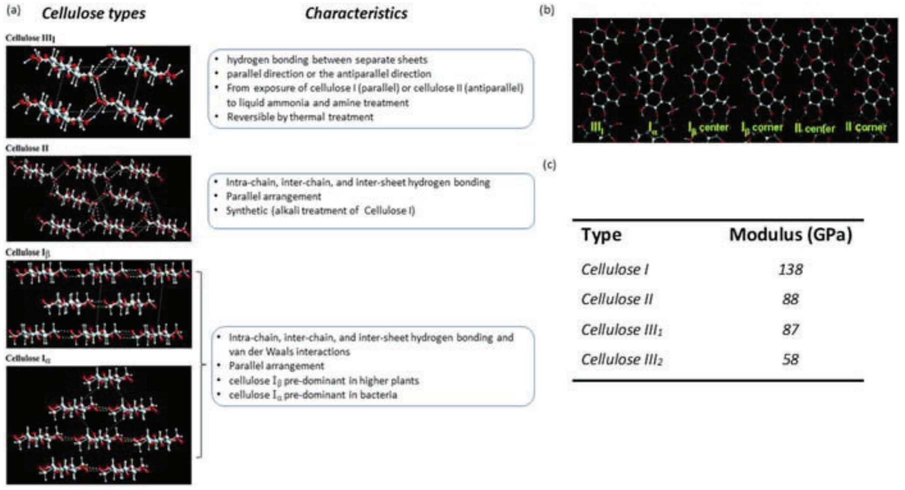


Figure 23.3 Cellulose forms molecular (A) inter- and (B) intra-hydrogen bonds among adjacent cellulose units forming chain assemblies with varying aspect ratios across scales. *Source*: Reproduced with permission from Nascimento, D. M., Nunes, Y. L., Figueirêdo, M. C. B., de Azeredo, H. M. C., Aouada, F. A., Feitosa, J. P. A., et al. (2018). Nanocellulose nanocomposite hydrogels: technological and environmental issues. *Green Chemistry*, *20*(11), 2428−2448. Bottom panel shows nanofibrils composed of crystalline and amorphous regions. Adapted with permission from Tayeb, A. H., Amini, E., Ghasemi, S., & Tajvidi, M. (2018). Cellulose nanomaterials—Binding properties and applications: A review. *Molecules (Basel, Switzerland)*, *23*, 2684. FE-SEM images of bacterial cellulose fibers showing (A) surface and (B) cross section of freeze dried components. Reproduced with permission from Park, M., Lee, D., Shin, S., Kim, H.-J., & Hyun, J. (2016). Flexible conductive nanocellulose combined with silicon nanoparticles and polyaniline. *Carbohydrate Polymers*, *140*, 43−50.

and the magnitude of mechanical strength is directed by the topological arrangements and may be altered to facilitate deformation events to preserve the structure across the scale range. The bond strength variability of inter and intra-hydrogen bonds depend on the nature of the bonding and their localization in the primary fibril structures of nm width (2 ~ 60 nm) to micron-scale aggregated assemblies comprising multiples of *n* fibril units (Fig. 23.3, bottom panel). A "stacked" architecture formed via the inter-network of bridges across the fibril structure is a remarkable engineering accomplishment designed by nature and forms the basis of much technological interest in its utilization as a "reinforcing" structure for materials lacking rigidity, stiffness, deformity, tensile strength, hardness and elasticity—some of the key attributes of mechanical superiority manufactured by nature. Exploitation of cellulose lies in understanding its chemical nature as the "bench mark" to achieving a workable appreciation of surface chemistry on a level that nature aspires to and implements with exquisite ease with limited and "renewable" resources. The question arises whether the mechanical properties in cellulose are attributed to bonding interactions of a dominant single type such as hydrogen bonds or does the bonding signature entail the topology of the system that allows a multitude of bond types contribute synergistically (Satarifard et al., 2017) during adhesion. The effects of bond synergy has may be challenging to decipher in cellulose (Kummala, Xu, Xu, & Toivakka, 2018).

The hydroxyl-hydrogen band energy interaction is cooperativity redshifted to lower vibrational energy states signifying increased stability and are accompanied by electrostatic interactions, van der Waals forces, hydrophobic / hydrophilic and London dispersion interactions increasing accessibility to inter and intra bond formation. The consensus view on stiffness and sheet-like morphology structure of cellulose is seeded in intramolecular and intermolecular bonding mechanics () and 3-dimensional folds. The perceived idea that inter- and intra-hydrogen bonding dominate surface interactions, solubility, chain separation, swelling (Wang, Wang, Wu, Fan, & Li, 2020) and cellulosic mechanics has been broadly encouraged in the literature bolstered by the lack of quantitative measurements of other influential forces that may play an important role. For example, chain conformation and band shifts from X-ray diffraction and FTIR data evidence a zig-zag conformation in which chain stretching is geometrically constrained by the $O_3'{-}H\cdots O_5$ hydrogen bond position enhancing mechanical stiffness in the vicinity of the glycosidic bond (Altaner et al., 2014). While the $O_6\ldots H{-}O_2'$ bond length remains unaltered, disengagement of the $O_3'H\cdots O_5$ hydrogen bond from the deformation the glycosidic bond supports a mechanism. The modeled structures in Fig. 23.4 (A and B) show the hydrogen bonded crystalline order of synthetically modified cellulose (type II and III) compared to native cellulose (type I) and the associated changes in the



- hydrogen bonding between separate sheets
- parallel direction or the antiparallel direction
- From exposure of cellulose I (parallel) or cellulose II (antiparallel) to liquid ammonia and amine treatment
- Reversible by thermal treatment

- Intra-chain, inter-chain, and inter-sheet hydrogen bonding
- Parallel arrangement
- Synthetic (alkali treatment of Cellulose I)

- Intra-chain, inter-chain, and inter-sheet hydrogen bonding and van der Waals interactions
- Parallel arrangement
- cellulose I$_\beta$ pre-dominant in higher plants
- cellulose I$_\alpha$ pre-dominant in bacteria

Type	Modulus (GPa)
Cellulose I	*138*
Cellulose II	*88*
Cellulose III$_1$	*87*
Cellulose III$_2$	*58*

Figure 23.4 (A) Cellulose types and characteristics (B) Models showing intra-chain hydrogen bonding in cellulose III, cellulose Iα, cellulose Iβ, and cellulose [C, O, and H atoms are shown in gray, red, and white balls, respectively] and (C) modulus performance (Nishino, Takano, & Nakamae, 1995).
Source: Adapted with permission from Wada, M., Chanzy, H., Nishiyama, Y., & Langan, P. (2004). Cellulose IIII crystal structure and hydrogen bonding by synchrotron X-ray and neutron fiber diffraction. *Macromolecules*, *37*(23), 8548−8555. Characteristic data was compiled from Hickey, R. J., & Pelling, A. E. (2019). Cellulose biomaterials for tissue engineering. *Frontiers in Bioengineering and Biotechnology*, *7*, 45.

hydrogen bond arrangement after modification. Nishiyama, Langan, and Chanzy (2002) elucidated the crystal structure of cellulose—cellulose I_β differing from cellulose I_α comprising uniquely structured chain with distinctive hydrogen-bonding arrangements that are cooperatively networked to other parts of the structure. The underlying complexity of the structural networks and how they facilitate better understanding of the cellulose mechanics and dynamics is opening up new avenues for discovery. The high modulus of cellulose (Fig. 23.4C) suggests that the hydroskeleton network intrinsic to type I is mechanically important to its stability and the decreased modulus (Fig. 23.4C) can be mapped to the re-orientation of the hydrogen bonding. In addition to the $O_3{-}H\cdots O_5/O_6$ intra-chain hydrogen bond in cellulose III, cellulose I also adopts a *tg* conformation of the hydroxymethyl group through "chain restriction" and the presence of a second intra-chain bond located between O_6 and O_2' might be attributable to a pattern of disorder disrupted by the donor-acceptor role (Wada, Chanzy, Nishiyama, & Langan, 2004). This arrangement contradicts the chain flexibility observed in type III and its ability to engage in hydrogen bonding without disturbing the hydroxymethyl bond arrangement in adjacent molecules. An important interpretation of these investigations provides information on the compact nature of type I compared to type III in terms of the packing of layered sheets and the ease of detachment. The nature of the stronger $O{-}H\cdots O$ bonds relative to weaker electrostatic and van der Waals $C{-}H\cdots O$ renders the chains in type III more easily accessible to surrounding molecules during functionalised attachment. In fact, the network topology formed in type III permits the gain in guest-host binding energies to temporarily occupy "pseudo" minimum energy states for self-stabilization while retaining the ability to revert back to the type I *tg* from *gt* conformations after (1) removal of guests molecules or (2) hydrothermal treatments to re-establish the native-like rotational H-bond barriers (Wada et al., 2004). A thermal response analysis investigation of cellulose using mechanical models shows the intra-chain H-bond O_3H_3 to be particularly prominent over a range of temperatures (Shen & Gnanakaran, 2009) and also reports an interesting role "exchange" between hydroxyl groups O_6H_6 and O_2H_2 favoring a change in bond dynamics of the H-bond in $O_2H_2\cdots O_6$ from an intramolecular to intermolecular state.

The complex dynamic nature of cellulose however has led others to suggest that some behavioral aspects of cellulose mentioned here and elsewhere cannot be sufficiently explained by hydrogen bonding interactions but require deeper contributions from other experimental areas (Kummala et al., 2018). Low aqueous solubility of cellulose for example has been rationalized to the relatively strong intermolecular hydrogen bonds within the biopolymer that limit solubility in solution because of the number available bonds. This has been considered in the analysis but deemed inadequate to explain solubility limitations. Evidence however suggests that improvements to solubility may lie in better understanding contributions from hydrophobicity (Medronho, Romano, Miguel, Stigsson, & Lindman, 2012) which remains to properly elucidated. An understanding of unresolved adhesive forces associated with cellulose surface chemistry and nanocellulose may be important in allowing the manipulation of bonds to more desirably re-assign and re-shape

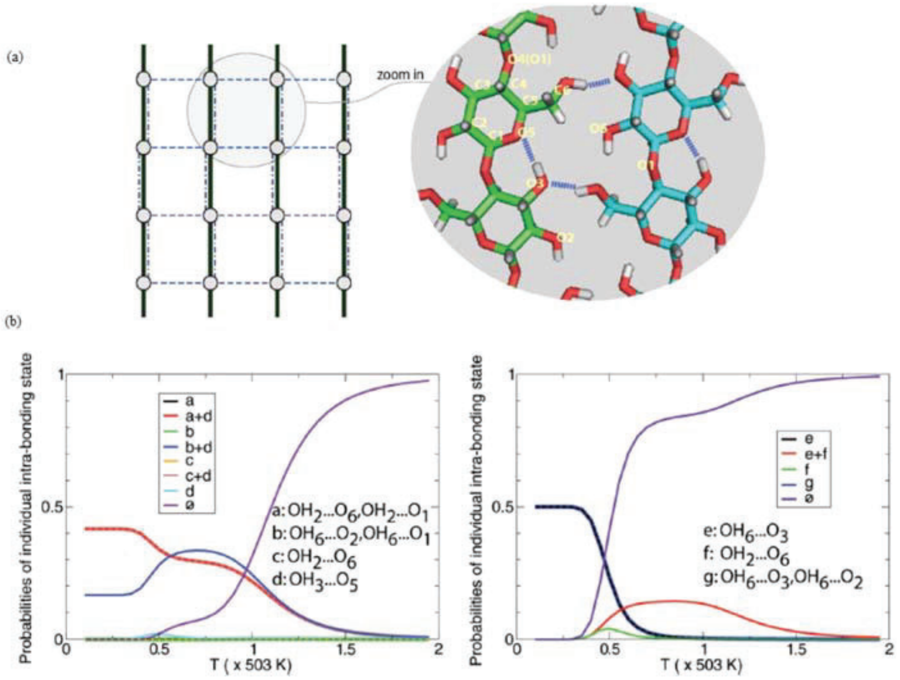


Figure 23.5 (A) A schematic representation of the cellulose type I sheet structure. Cellulose chains (solid black lines) composed of monomers (filled circles) are linked by hydrogen bonded intrachains (dashed lines) (B) intra-chain H-bonding combinations (colored line symbols) showing the probability of engagement across a temperature range.
Source: Reproduced with permission from Shen, T., & Gnanakaran, S. (2009). *Los Alamos National Laboratory*, Retrieved from: https://www.lanl.gov/errors/service-unavailable.php, https://www.lanl.gov/orgs/adtsc/publications/science_highlights_2009/2shen.pdf.

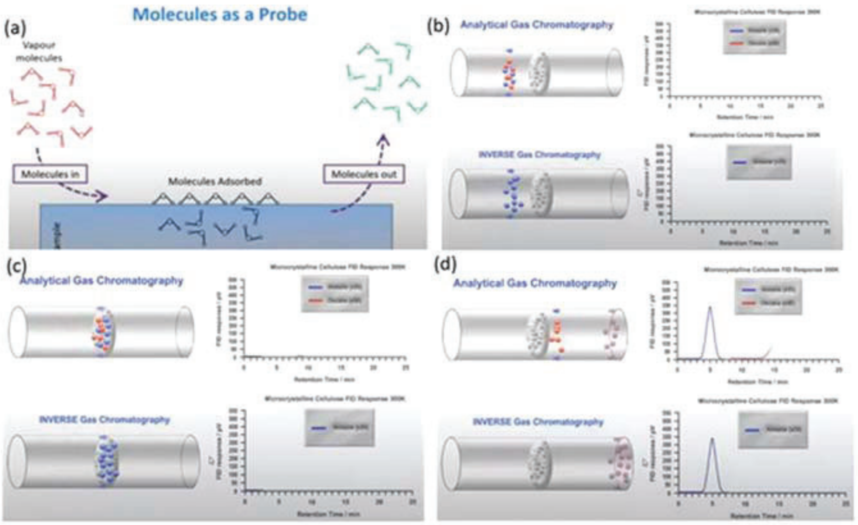
structures for fabricating new material hybrids are avenues to pursue. Fig. 23.5 describes the probable hydrogen bonding combinations of intra- and interchain bonding in nanocellulose and their relationship across a temperature range. Our understanding at the molecular level could help dispel the challenges associated with aggregation and the search for better strategies for chain dispersion.

23.4 Intrinsic behavior of biomaterials: a path to understanding material topological properties in biocomposites

In biology, as a primary function, material growth is shaped by local mechanical forces and adopts a topology network to adapt within its environment. A common denominator that applies across the network of growth of a material is the importance of stress-driven or strain-driven growth. This has important implications for materials for their biomechanical role both within and outside biological environments. Understanding biomechanics of materials provides new possibilities to modulate structure-function relationships and steer material behavior more desirably. The biomechanics of materials (e.g., stress/strain, stiffness, elasticity, etc.) is inherently linked to diverse biological functions such as pathway signaling and activation (Zhang, Ying, Wu, Hiberty, & Shaik, 2009), while the technological concern here is exploiting the mechanical properties for improving material geometry and mechanical related performance. The topology and mechanical growth pattern inherent to their biological role may be in an important consideration for use in surface fabrication distinguishable by stress and strain-driven growth dynamics in series or perpendicular to cell growth respectively (Zhang et al., 2009). Recently, Satarifard et al. (Nishiyama, 2018) modeled the intrinsic nature of intra-chain pairing of polymer chains forming a “series” or “parallel” arrangement under spatial confinement. The topological study shows relevance to chain growth under the confinement of intracellular or extracellular environments such as packing of fibers in plants and bacterial organisms. The topological outcome of confined growth defined by the ratio of persistence length to radius (l_p/R_c) revealed a simple growth pattern that favored non-cooperativity in a series type arrangement far from the expectations of complex interactions among chains. The findings imply that the kinetics of growth alone may not correlate well with contact order results under a broader range of (l_p/R_c) representing different topological states.

23.5 Methods for probing bond-type contributions in adhesion and their correlation to key states of matter in surface energetics

A wide range of tools that function as probes have been explored to gain greater insight to expose the hidden dynamics of cellulose and nanocellulose based materials to enhance their utilization with particular emphasis on surface chemistry and behavioral properties by investigating surface energetics, effects of surface modification and wetting as key areas of focus. Physical probes can be energy in the form of light and x-rays for deciphering information concerning structural complexity and organization and the application of calorimetry to obtain thermodynamic information. This aids our understanding of how surfaces are designed for using energy and adapting chemically by measuring differences in input and output through gain, loss or transfer modes from the energy source and advancing modeling tools using input parameters from experimentally fed parameters. Of particular interest is surface free energy measurements that describe the natural spontaneity of materials to adopt energy stable conformations along pathway trajectories. Chemical probes in the form of charged molecules of varying size and charge with distinct molecular characteristics are a favorable option for providing information about heterogeneity of surfaces via sorption or adsorption/desorption techniques under two phases, for example, solid-vapor phase. Fig. 23.4A describes the principle of probe analysis and vapor-solid techniques exemplified by inverse gas chromatography (IGC) Fig. 23.4 (B–D). The chemistry of structure types that co-exist offer an analytical approach to identity active groups and their functional role. A prominent example here is the property of adhesion. Its knowledge is central to understanding the challenges of cellulose as a material and the underlying relationship with surface energy of the solid, γ_s. The property is fundamentally embedded in the thermodynamic of adhesion of materials and separated into acidic, basic and dispersive components. Further, Fig. 23.5 shows key components that affect surface energy. The first is wettability of a surface and the contact angle between the liquid and solid surface. This quantity (Chattoraj and Birdi, 1984) has relevance to the biological and physical response of biomaterials (Agrawal et al., 2017). The second phenomena relates to cohesive properties, which increases with surface energy as does wettability. Molecules of the same tend toward cohesive behavior with increased $\gamma_{s.}$ Mechanical or thermal stress during fabrication processes can generate disorder in materials that may result in an increase in defects sites or the disruption of crystal states to amorphous states disturbing native shapes and patterns at the surface. The increased disorder amplifies the surface energy (Fig. 23.6) of components of materials that deviate from their stable orientation accompanied by a shift in the relative positions to other molecules. The concept of adhesion arises when “unlike” molecules overcome cohesive forces of “like” molecules to interact through surface energy such that new forces (e.g., electrostatic) can generate new bonding associations with other molecules. Here, understandably chemical modification processes are critical creating new formulations between different surfaces for low surface energy materials. This invites the idea of using probes specific for bond-type character to quantify surface free energies during interfacial interaction. In the recent past, Watts (2011) has considered the importance of mapping surface free energy by measuring contact angles and probing bond-specific interactions through the application of IGC. For example, to assess the contributory role of polar interactions in adhesion between acid-bases, polar probes were rationalized to specifically disrupt the interaction. As reported, the magnitude of deviation was detectable by IGC by quantifying the retention time between the stationary phase and in the presence of the five polar probes introduced simultaneously (Fig. 23.7). The retention time was used to characteristically and quantitatively map the specific nature of the bonding interaction. This technique was successful in establishing the presence of both basic and acidic sites at the surface and quantifying the acidic and basic polar regions and their relative contributions. In relation to polymers, IGC has been adapted for polymer investigations for the determination of thermodynamic parameters, solubility, permeability, crystallinity and diffusion constants can be determined (Guillet and Al-Saigh, 2006). For surface-to-surface studies, the shape contour of adsorption isotherm profiles have been used to assess interacting adsorbate–adsorbant polymers interfaces in the absence of a linear isotherm in which curvature often represents heterogeneity and saturation. The principles of IGC have been informative in yielding adhesion behavior between synthetic polymers and cellulose fiber-matrix surfaces signifying the role of acid-base interactions in adhesion



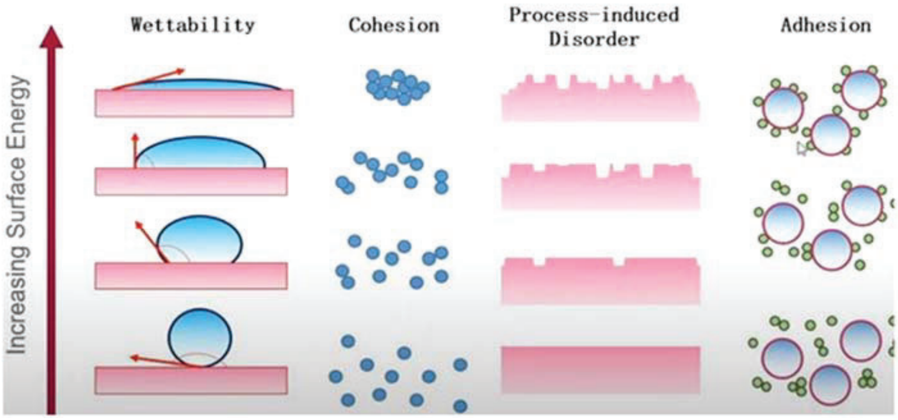


Figure 23.6 (A) Use of molecules as probes at solid-vapor interfaces. The effects of vapor molecules adsorbed onto a solid polymer is monitored in terms input and out chemistry to gain structural information of polymers. (B–D) Gas chromatography as method to identify structural and functional information at interfaces by monitoring retention time at the interface for surface information, for example, surface energy.
Source: Reproduced with permission from Dr. Burnett, Vice President for Surface Measurement Systems [Burnett, D. D. (2020). *Surface Measurement Systems*. Retrieved from: https://www.surfacemeasurementsystems.com/webinar-cellulose-natural-fibers/].

processes. This is inferred from adsorption enthalpy curves by pairing acid-base associations of each component respectively (Tze, Wålinder, & Gardner, 2006). The technique has also been useful in providing further insight into acid-base interactions and

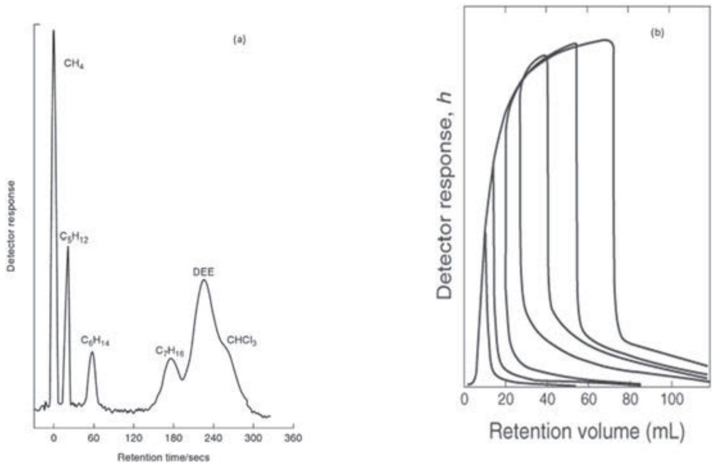


Figure 23.7 (A) Application of inverse gas chromatography (IGC) for probing bond-specific interactions at interfaces. (B) The shape feature of the retention volume—response chromatographic peak of interacting polymer interfaces can be used to provide information related to adhesion properties.
Source: Reproduced with permission from Guillet, J., & Al-Saigh, Z. Y. (2006). Inverse gas chromatography in analysis of polymers. In R. A. Meyers, & T. Provder (Eds). *Encyclopedia of analytical chemistry*. Wiley, Encyclopedia of Analytical Chemistry; da Silva, L. F. M., Öchsner, A., & Adams, R. D. (Eds) (2011). *Handbook of adhesion technology*. Berlin, Heidelberg: Springer-Verlag.

nanomorphological differences among variants of cellulose, highlighting surface sensitivity of the matrix to humidity (Papirer, Brendle, Balard, & Vergelati, 2000), surface temperature changes (Hamieh, 2018) and disperse surface energy correlations with fiber compositions (Mills, Gardner, & Wimmer, 2008).

Another important aspect in relation to adhesion and surface topography in refining our current understanding of structure-function relationships of nanocelluose are the role of interfacial forces in surface creation and how such forces govern mechanical performance along two different material surfaces. Since adhesion is entrusted in the establishment of intermolecular forces, their measurement becomes an important part of material criteria for not only allowing sound judgement of material compatibility and suitability for applications but also for understanding self-assembly of cellulose-cellulose interactions. Certainly from a fundamental point-of-view, a primary area of concern has been the lack of insight of the integral molecular factors controlling cellulose assembly. It has been suggested that this may be partly due to the use of models that do not correlate well with rough contour surfaces in cellulose but instead are replaced by smooth contacts limiting a realistic measure of adhesion forces that better adhere to complex interfacial behavior (Johnson et al., 1971). The tip-to-surface contact employed in atomic force microscopy can provide an image of the surface tomography mapped by force curves which can characteristically probe mechanical measurements of low-spring deflection sensitivity. Using a method to more precisely measure surface roughness to better account for adhesion forces at the cellulose-tip interface, Lai, Zhang, Sugano, Xie, and Kallio (2019) used a colloidal probe composed of spherical cellulose microspheres to obtain force data. The technique was able to correlate force data with surface morphology with considerable resolution. Fig. 23.8(B and C) shows the topography data using the colloidal probe compared to the normal ATM tip Fig. 23.8(A). The same authors reveal that the use of aqueous cellulose or surface modified cellulose preparations in previous studies failed to yield a correlation between adhesion and surface morphology with the exception of one study (see Table 23.2). The success was attributed to minute uneven contours at the colloid-tip surface.

The importance of defects and their introduction at the cellulose surface through controlled manipulation has provided investigators an in-depth look at into molecular features which have eluded examining fundamental relationships between fibril design and mechanical structure. More recently, atomic force microscopy (AFM) has provided revealing structural insights by probing mechanical deformation of cellulose at the nanoscale (Ciesielski et al., 2019). The technique has enabled a visual insight of the mechanics of cellulose at the level of single nanofibrils. The study reports a series of trajectory manipulations using the AFM tip in configurations that have not previously been visible and quantifiable by a direct nanomanipulation approach. The strategy used here is of significance in seizing some of the technical challenges in the direct manipulation of chains under conditions of stress and strain. Fig. 23.9 shows the probing of the mechanically induced "kinks" in singular nanobrils. Notably, low adhesion at the fibril-substrate interface at the

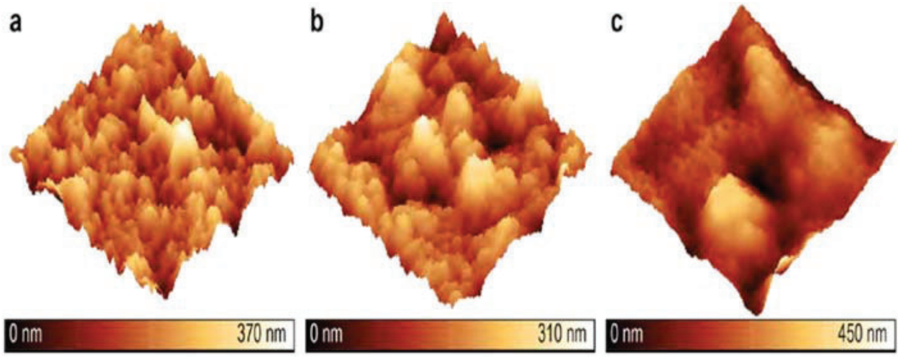


Figure 23.8 Topography of the cellulose membrane by atomic force microscopy (AFM) showing images using (A) a normal AFM probe (B) colloidal probe composed of spherical cellulose microspheres, 2.5 μm (C) colloidal probe composed of borosilicate microspheres, 2.5 μm.
Source: Reproduced with permission from Lai, Y., Zhang, H., Sugano, Y., Xie, H., & Kallio, P. (2019). Correlation of surface morphology and interfacial adhesive behavior between cellulose surfaces: Quantitative measurements in peak-force mode with the colloidal probe technique. *Langmuir: the ACS Journal of Surfaces and Colloids*, *35*(22), 7312–7321.

Table 23.2 AFM (atomic force microscopy) studies on surface treated cellulose.

Material[a]	Contact mode	Measured force	Technique	Surface treatment	Environment	Adhesion/surface Morphology Correlation
c—c	s — p	Interaction	Scanning probe	Yes	Aqueous	No
c—c	s—p	Friction		Yes	Aqueous	No
c—o	s—p	Interaction	Pull-off	No	Aqueous	No
c—c	s—p	Interaction	Pull-off	Yes	Aqueous	No
c—c	s—s	Interaction	Scanning probe	No	Air and aqueous	No
c—c	s—s	Interaction	Pull-off	No	Air	No
c—c	s—p	Friction		No	Aqueous	No
c—c	s—s	Friction		No	Air	No
c—o	s—p	Interaction	Pull-off	No	Air	No
c—c	s—p	Interaction (adhesion)	Peak force	No	Air	Yes

[a] c—c, cellulose-cellulose; c—o, cellulose-other material; s-s, sphere-sphere; s-p, sphere-sphere.

Source: Reproduced with permission from Lai, Y., Zhang, H., Sugano, Y., Xie, H., & Kallio, P. (2019). Correlation of surface morphology and interfacial adhesive behavior between cellulose surfaces: Quantitative measurements in peak-force mode with the colloidal probe technique. *Langmuir: the ACS Journal of Surfaces and Colloids*, *35*(22), 7312−7321.

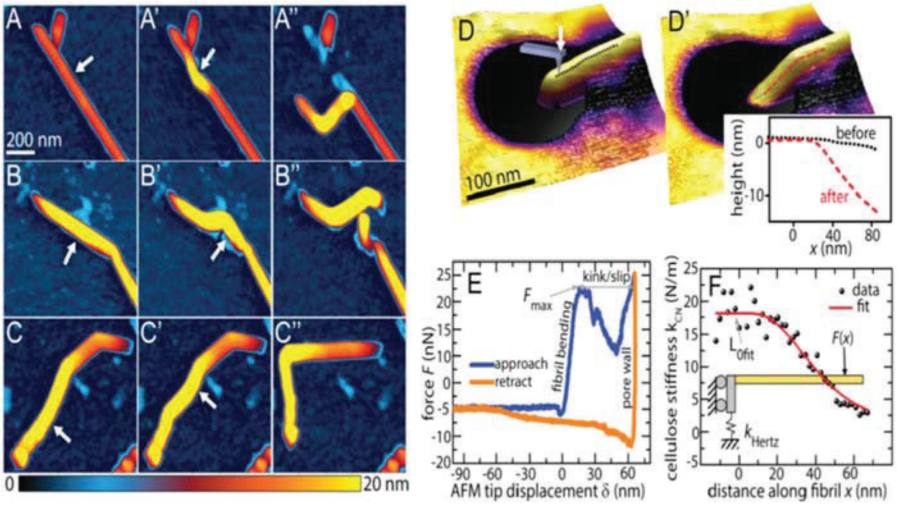


Figure 23.9 Nanoscale manipulation of cellulose chains using AFM. (A-A'' − C-C'') AFM images of nanofibrils demonstrating responses to mechanical deformation by inducing kink formation and chain reformation. (D) Nanofibril localized across a 200 nm pore in trek etched polycarbonate and (D'') the induction of a kink defect produced by a 48 nN load. (E) "Approach and retract" directed indentation curves at the nanofibril surface facilitating entry of tip into the pore well. (F) Bending measurements conducted across the length of the fibril allowing deformation calculations fitted to a model beam (*AFM*, Atomic force microscopy). *Source*: Reproduced with permission from Ciesielski, P. N., Wagner, R., Bharadwaj, V. S., Killgore, J., Mittal, A., Beckham, G. T., et al. (2019). Nanomechanics of cellulose deformation reveal molecular defects that facilitate natural deconstruction. *Proceedings of the National Academy of Sciences*, *116*(20), 9825−9830.

unconstrained end permitted the placement of kinks adjacent to contact points at sub-surface levels and thus ensuring sufficient connectivity remained in fibrils at "hinge" points through a "approach" and "retract" method. Reported deformation stress values of (4.0 ± 1.4) and (3.2 ± 1.1) GPa signify magnitudes similar to covalent bond breakage initiating kink formation as a result of bending stresses. The creation of kinks from strain-induced glyosidic bond breakages and their manipulation provides opportunities for new technological breakthroughs for advancing new material design.

With the availability of better tools for probing structure at the molecular scale, the field of biocomposites has naturally expanded to include behavioral−structure correlations mapped to a growing number of cellulosoic materials. Although the basic structure and behavior of cellulose is of interest, from an applications perspective, the vast majority of this interest is directed toward investigating the interfacial hybridization of cellulosic material with other surface chemistries. A rationalized field of study is now unfolding with emerging research focused on particle−particle interactions and behavior at interfaces for tailoring material properties. A prominent feature is the hydrophilicity of cellulose fibers. Reputably, the multi-faceted nature of the structure has raised more questions than answers and has become one of the most widely pursued structural problems in the biopolymer field. Perhaps this stems from intrinsic native complex state determining its contractile properties, lateral interactions and orientation of microfibrils entrapped in the polysaccharide matrix at high concentrations, mesoporosity and deformations at the boundary layers directing site specific inter- and intra-molecular interactions (Mikshina, Chernova, Chemikosova, Mokshina, & Gorshkova, 2013). Understanding the native state dynamics seems critical to its use in diverse applications. The lack of surface-to-surface equivalency and homogeneity adds to the ability of cellulose to diversify surface interactions using hydrophobic crystal planes which are more resistant to modification. Because such interactions result in covalent or non-covalent binding through different binding patterns, the nature of the bonding has a strong influence on the final properties of materials coupled through structure, shape and size.

A primary area of concern in biocomposites fabrication is the condition of dispersibility. It has been mentioned earlier that the success of surface modification approaches rely on maximum exposure of the space around individual fibers to access chemical bonds and enable nanoscale particle—particle interactions. Here, it becomes relevant to gain an appreciable understanding of key interactive forces and the synergy associated with self-assembly. The relative magnitude of these forces differ by the type of interaction which constitute physisorption (weak forces, e.g., van der Waals forces) and chemisorption (e.g., covalent bonds) liberating low and high Gibbs free (ΔG) enthalpies of adsorption respectively. Most interactions are enthalpically (ΔH) and entropically (ΔS) driven and disturbance of the hydrogen bonding associations if thermodynamically feasible, result is bond scission and replacement of existing bonds with surrounding solvated ions. Negative ΔH values imply spontaneous bond exchange with its surrounding ion constituents whereas oppositely charged or electrostatic interactions at the surface in nanocellulose are entropic in nature increasing molecular disorder by liberating water molecules increasing the free energy of adsorption. To understand the thermodynamic implications of adsorption processes for a wide range of bio-macromolecules separately adsorbed on the surface of nanocellulose using different bond associations, Lombardo and Thielemans (2019) report opposing contributions to Gibbs free energy for ΔH and ΔS favoured by the entropic release of water shown in Fig. 23.10. Thermodynamic explorations could yield valuable and insightful information in improving binding efficiencies at interfaces against parameters such as shape, size, composition, charge and dispersibility of resulting biocomposites.

However, forces acting at the water-cellulose interface has not been explored. For example, does swelling of CNC films in aqueous environments occur by increasing the size of cellulose particles or the inter-space area surrounding the particles? There has been little work in understanding the cohesive particle behavior of CNCs at the nanoscale. Reid, Villalobos, and Cranston (2016) has recently addressed the hydrophilic nature of CNC and the associated swelling effect of solvent environments. This has been of interest since long but quantification of dimensional changes and existing structural relationships is being addressed using multi-wave length surface plasmon resonance (SPR) (Granqvist et al., 2013). In the case

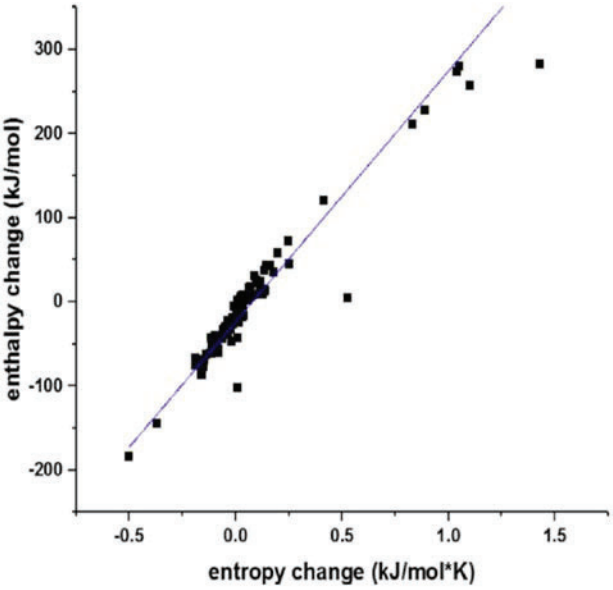


Figure 23.10 Enthalpy-entropy correlation plot revealing a linear relationship between (ΔG) and (ΔS) for the adsorption of bio-macromolecules on the surface of cellulose. The slope signifies the Gibbs free energy of adsorption of −23 KJ/mol.
Source: Reproduced with permission from Lombardo, S., & Thielemans, W. (2019). Thermodynamics of adsorption on nanocellulose surfaces. *Cellulose*, *26*(1), 249−279.

of CNC films, particle−particle interspacing of 1.6 nm was detectable that lies outside the hydrogen bonding range but within in the range of van der Waals attraction forces and repulsion forces from the double layer of counter ions in the DLVO theory (Fig. 23.11A). The need for dispersion forces that rely on kinetic energy input (e.g., sonication) to overcome the forces of attraction and reduced particle mobility enforced by van der Waals interparticle interaction might quantifiably answer undisputed issues of surface separation inherent to cellulose (Fig. 23.11B). A step toward understanding the molecular disruption of the hydrogen bonded CNC−CNC network and increasing dispersibility of the cellulose polymer is shown in (Fig. 23.11C). A clear distinction is established between different solvents and their ability to weaken cohesive particle−particle interactions encountered in CNC−CNC layers. Multi-wave length SPR investigations as a technique has provided better insight in identifying solvent systems to reduce the cohesive behavior of nanocellulose. It is vital that experimental approaches not only help to build a molecular understanding of cohesive and adhesion properties but to provide opportunities to increase or diminish intermolecular bonding strengths between particles in biocomposites. In hindsight, the layering of solvent molecules around the periphery of cellulose structures can provide opportunities for the displacement of native bonds through increased interlayer spacing in a tunable fashion. Interestingly, solvents that are chemically incapable of disengaging

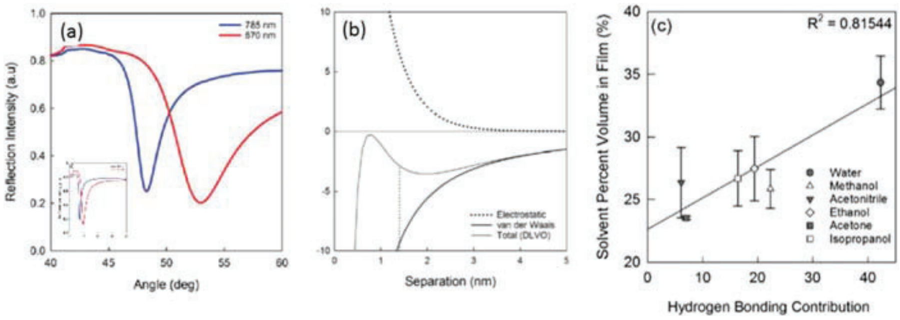


Figure 23.11 (A) A typical SPR response profile for a CNC functionalised senor surface. The increased depth of the signal represents the increased roughness interface after deposition on the chip surface compared to the unfunctionlised chip surface shown in the inset. (B) A separation-interaction energy plot simulation showing van der Waals attraction, electrostatic double layer repulsion and the combined contribution Derjaguin-Landau-Verwey-Overbeek. (C) Hydrogen bonding contributions as a function of solvent percent volume (volume fraction). The analysis reveals a general trend that relates swelling effects with increased hydrogen bonding. In aqueous environments with different solvents, the plot reflects the ease of replacement of CNC−CNC hydrogen bonds with CNC-solvent hydrogen bonds (*SPR*, Surface plasmon resonance; *CNC*, cellulose nanocrystals).

Source: Reproduced with permission from Reid, M. S., Villalobos, M., & Cranston, E. D. (2016). Cellulose nanocrystal interactions probed by thin film swelling to predict dispersibility. *Nanoscale*, *8*(24), 12247−12257.

native hydrogen bonds in CNCs by participating in the formation of alternative bonding mechanisms as the study suggests, may be equally affective in interrupting driving desired surface bond interactions.

Donor-acceptor interactions at interfaces provide important information about free energy at interfaces (Fowkes, 1972) and are strongly coupled to adhesion and surface properties with cellulose (Gardner et al., 2008). Modulating the surface energy of cellulose becomes an important prerequisite to tuning interfacial properties in nanocomposites (Hosseinmardi et al., 2018). An equally important facet of polymer-filler synergy is the role of dispersion and its dependence on surface energy and the degree to which nanocomposite infusion is achievable in the final blend. The dynamics that exist between filler-filler and polymer-filler cooperation is often determined by surface modification (Mozetič, 2019) to re-tune chemical associations coupled to their thermodynamic stability and bond feasibility affecting adhesion properties. Surface energy investigations have considerable utility as a technique and may lead to insightful cues for improving fabrication processes for better performing materials. The method however has not been widely applied to establish a pattern of difference in surface energy and interfacial tension among differently fabricated biocomposites. Fig. 23.12 shows a pendant drop setup used to differentiate interfacial parameters between interfaces at phase boundaries. The shape of a drop is dependent on the surface tension and gravity acts to pull the drop downwards on the drop resulting in an elongated configuration and the geometrics

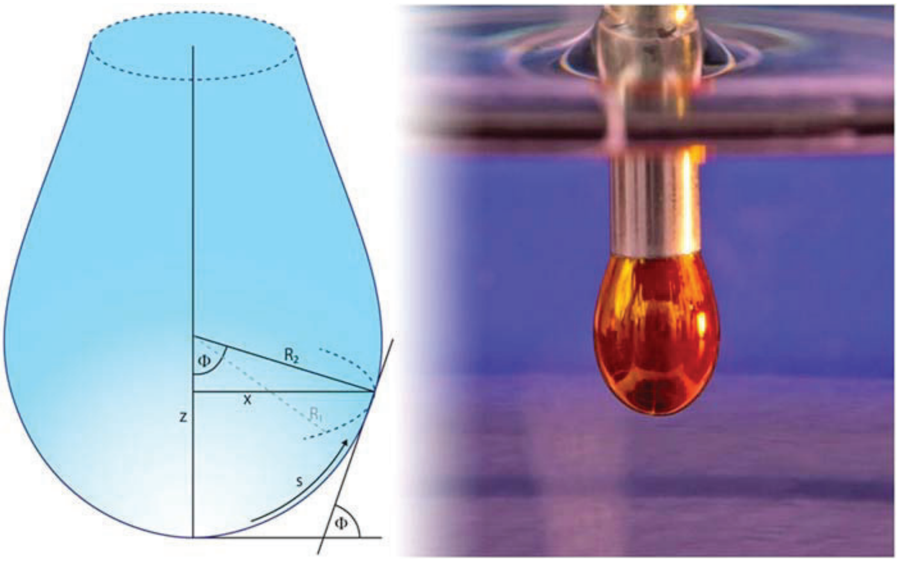


Figure 23.12 (A) Interfacial tension measurement by pendant drop method.
Source: Reproduced with permission from Dataphysics Instruments, GmBH.

of the shape define the interfacial tension of the interface of interacting materials. With respect to polymer-filler interactions in biocomposite fabrication, differences in the thermal coefficient of surface energy measurements can provide considerable insight into polymer-filler associations using melt contact angle measurements between the polymer and nanocellulose. This is particularly true for particle-polymer systems. Central to the application of nanocellulose biocomposites is the property of adhesion. Contact angle and pendant drop techniques have been critical to understanding and uncovering the effects of nanoparticle dispersion on adhesion at interfaces from changes in surface energies resulting from surface modification. In the context of filler-matrix associations, it becomes useful to quantify the energy of adhesion released when interacting surfaces combine. This suggests that work must be done to replace an existing interface such as liquid— or solid—air with new interfacial forces driven by surface tension. For adhesion to occur favorably, a large energy difference between the surface free energy and interfacial free energy at the phase boundary would ensure a strong level of adhesion and increasing mechanical strength. In a study by Khoshkava and Kamal, 2013, surface adhesion between nanocrystalline cellulose and the polypropylene monomer is enhanced by reduction of the surface tension after modification. The work establishes that polymer polarity is a strongly defining parameter governing the cohesive-to-adhesive shift by mechanical forces such as shear, stress and strain. The effectiveness of surface modification in yielding size-dependent dispersion for other systems studied however, might affect the ability of particles to depart effectively from cohesive behavior favoring adhesive bond formation and improving mechanical strength.

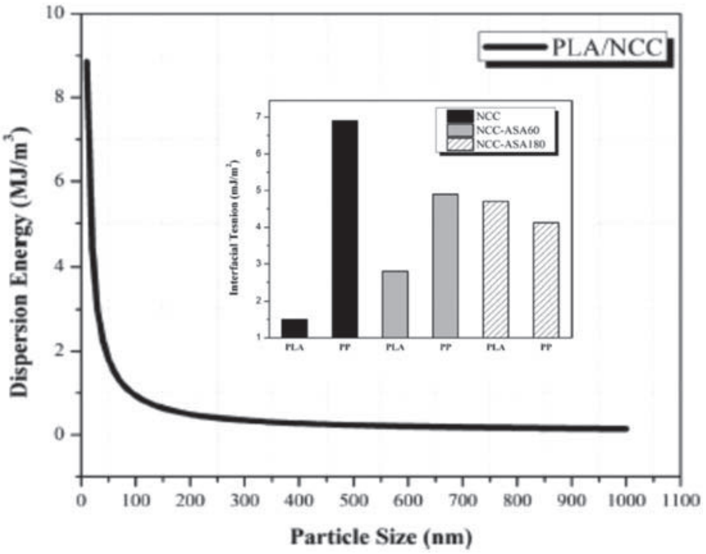


Figure 23.13 Particle size vs dispersion profile for crystalline cellulose calculated form surface energy data. The inset documents the interfacial tension with different polymer compositions.
Source: Reproduced with permission from Khoshkava, V., & Kamal, M. R. (2013). Effect of surface energy on dispersion and mechanical properties of polymer/nanocrystalline cellulose nanocomposites. *Biomacromolecules*, *14*(9), 3155−3163.

Fig. 23.13 generated from surface energy data from the interaction of nanocrystalline cellulose with polylactic acid reveals a particle size-led dispersion dependency controlled primarily by increase in interfacial surface area. An exponential decrease in nanoparticle dispersion favoring agglomeration can considerably reduce interfacial re-distribution of nanocelluloses during nanocomposite fabrication.

23.5.1 Surface engineering: challenges in multiscale control

The engineering challenge is somewhat eased when materials from nature itself are used but the rules of engagement remain crucially important when introducing potential surface modifiers to incorporate new mechanical functions without disrupting useful characteristics associated with multiscale patterns. Indeed, the introduction of unwanted defects at the nanoscale can drastically disturb the network alignment and order of structural components hindering mechanical performance. Blended material components often result in properties that are different to the separated components suggesting perhaps new routes to acquire characteristics that do not exist in nature. However, the strong adhesion and compressed packing of cellulose fibers poses an inherent problem of separation which is an important prerequisite for biocomposite fabrication to be optimally successful. Secondly, aggregation (Capron et al., 2017) further limits homogeneity of preparations at the industrial scale of CNCs and CNFs. A strong tendency to aggregate via hydrogen bonding networks is enhanced in non-aqueous states and under these conditions polymer stability is reliant on compact packing of fibers. Further, the choice of aqueous environments for dispersion become important in suppressing fiber aggregation e.g., replacement of water with solvents such as butanol. Aggregation is problematic and a hindrance in "grafting" processes where the availability of functional hydroxyl groups is essential for functionalisation with externally applied chemical groups. Aggregation however, reduces the availability of surface groups as a result of cellulose-cellulose interactions through the occupation of bonds via inter- and intra-hydrogen bonding and reduces grafting densities. The issue back-circles to advancing processability methods and achieving controlled dispersion. In the interest of sustainability, modification methods used for biocomposite fabrication must ensure that renewability is made feasible by safeguarding against non-sustainable approaches. This is guided by the concept of 12 principles of green chemistry that demands processes are aligned with natures environmentally friendly use of non-toxic materials and avoidance of harmful chemical processes (Onwukamike, Grelier, Grau, Cramail, & Meier, 2019).

23.5.2 The case of nanocellulose

Nanocellulose is a reputable renewable material and a key target for engineering new properties within its existing architecture using largely modification techniques to tune its mechanical associated properties. The materials ability to self-associate into multi-fibers has predominantly sparked interest in its adhesive behavior with other materials of choice. This choice is dictated by morphological and structural concerns across the various forms of nanocellulose and its surface behavior. In view of these observations, surface adhesion and behavioral properties of nanocellulose has provoked much interest at the boundary phase of interacting materials of technological importance. Of central importance to the dynamics influencing attachment and dispersion of particle components at interfaces are adhesion forces acting across length scales of the polymer. The ease of attachment of nanocellulose has aroused investigators to pursue more ambitious aims in innovating material design but not without its challenges. These challenges are rooted in the bonding phenomena entwined by physical and chemical forces interlocked within a mechanical arrangement of chains that are further mapped by shape and size cooperativity. The network of cooperation at the structural level has become increasingly important to elucidate and understand how shape, size and morphology molecularly embrace and influence the pattern of adhesion on different surfaces. Cellulose forms microfibril polymers of biogenic origin through chain assembly of polysaccharide units that typify bond attachment formed via glycosidic-linkages in a broad range of biomaterials. Nanocelluosic materials are not intrinsically surface-active but are found to broadly localize and align across material interfaces upon exposure to other materials. Adhesion is determined by the physico-chemical anchoring of the fiber network through penetrable pores of the matrix surface and the degree of mechanical interlock is attributed to varying molecular forces. The magnitude of forces often depend on materials such as charge differences, hydrogen bonding at the surface interface or more weakly generated forces that reside at localized sites due to van der Waals forces and bulk phase transitions resulting from hydrophobic-hydrophilic surface adsorption and wetting.

23.6 Fabrication of biocomposites—surface considerations

The current materials perspective is on exploring the assembly of different material types and the phase arrangements that enable building blocks to form in a controlled hierarchical fashion as a single and distinct material across multi-scales (Mitragotri & Lahann, 2009). In the case of synthetic materials, this provides a feasible route for heterogenous associations that often lead to superior mechanical (Mirzaali et al., 2018) or tunable properties. Advancing material feasibility in this area of research requires better precision engineering of micro-nano environments of materials to map structure with behavior. The design criteria employed by templates and bio-machineries in nature in constructing elegant and diverse structures with micro- or nano-precision has been hard to replicate using the current techniques. Since it is now critically important to meet controlled requirements for product manufacturing, naturally occurring polymers and their utilization as composites from polymeric blends are an increasingly attractive route over artificial ones to achieve more desirable products. With limited availability of non-biological eco-friendly materials, the fabrication of multiscale hierarchical structures with heterogeneous interfaces composed of complex ordered patterns observed in nature continues to inspire researchers. Indeed, the surface properties of biopolymers are critically related to the assembly process of building blocks and determine their precise functionality in native biological environments. Imitating such environments that direct the self-assembly of components with specific hierarchical and functional outcomes requires deeper insight of the underlying mechanisms (Wu & Zhu, 2017) to enable desired structural patterns.

Nanocelluloses have found considerable utility as reinforcing agents attributable to their fibrous morphology. The dominating features of nano-dimensional cellulose crystals and the extent to the which interfacial regions of the biogenic polymer can engage in surface-to-surface interactions resides at the level of surface reactivity and is predominately determined by the availability of functional group interaction and surface area accessibility. This is rapidly advancing as an attractive route to accessing new materials. Although this not a new trend in materials research, the search for innovative fabrication processes and techniques to alter and compatibilize surface chemistries by exploring new adhesion properties is continuously being pursued and progressively renewed to re-shape physico-chemical behaviors. Traditional and modern-day approaches to designing polymers and fibrous structures have often adopted ways to imitate the structural features occurring in nature as a means to inherit the functional properties associated by design. However, the complexities of nature are often difficult to imitate with existing fabrication methods at the bulk scale and are increasingly difficult at dimensions close to or at the nano or sub-nano scale.

Technological development is underpinned by the relationship between material composition and scale to evolving structures and finally their perceived function in driving innovation. While performance is often viewed as a guiding principle in tuning the behavioral properties of emerging materials to atomic configurations or surface adaptations that render them potentially useful, the science of materials is a complex affair raising more questions than solutions. This originates from the disciplinary nature of materials and like events in nature, both synthetic and naturally occurring materials assemble through patterns of self-assembly which have not thus far been properly correlated with structure and behavior. A dominating area in material science in which the relationship between structure-function correlations and scale and shape predominates is the field of polymers.

23.7 Approaches to fabrication of biocomposites

A widely adopted route to controlling the chemical and physical characteristics of natural polymer surfaces is by blending bio-based materials with a broad range of material to fabricate biocomposites with the effect of reinforcing the primary material properties. Typically, composites are structurally complimentary where reinforcement of one material type is achieved by the other acting as a filler. Knowledge of surface chemical structure, compositional nature and functional group chemistry of biomaterials play a strategical role in understanding structural-functional connections and barriers to achieving desired properties. Molecular information can reduce material incompatibles between biofibers and polymer scaffolds introducing new levels of mechanical support via cooperative interactions. The “material performance” path is a complex transition of challenges and unknowns even for the more well-studied materials. However, an on-going challenge is to inform more systematically the polymer-filler scenario of interactions that are known to exist and those that can be predicted.

The nature of interactions at the phase boundary in cellulose with the interacting material can usually be described as physisorption or chemical adsorption. Surface attachment by physisorption is non-specific forming reversible multilayers via weak forces (e.g., van der Waals) which is not activation energy dependent and is accompanied by low energy release (Fig. 23.14). In contrast, chemical adsorption is highly bond-specific and occurs irreversibly over a large surface area. The barrier to activation (depending on bond-type) ensures that strong bond activation through covalent or ionic interaction is associated with energy release orders higher than physisorption processes. Earlier investigations proposed the chemical surface modification of nanaocellulose to diminish the hydrophilicity and interfacial stress between each constituent of the nanocomposite. Charge density and mechanical properties of fibrils is affected by the swelling nature of closely packed chains and

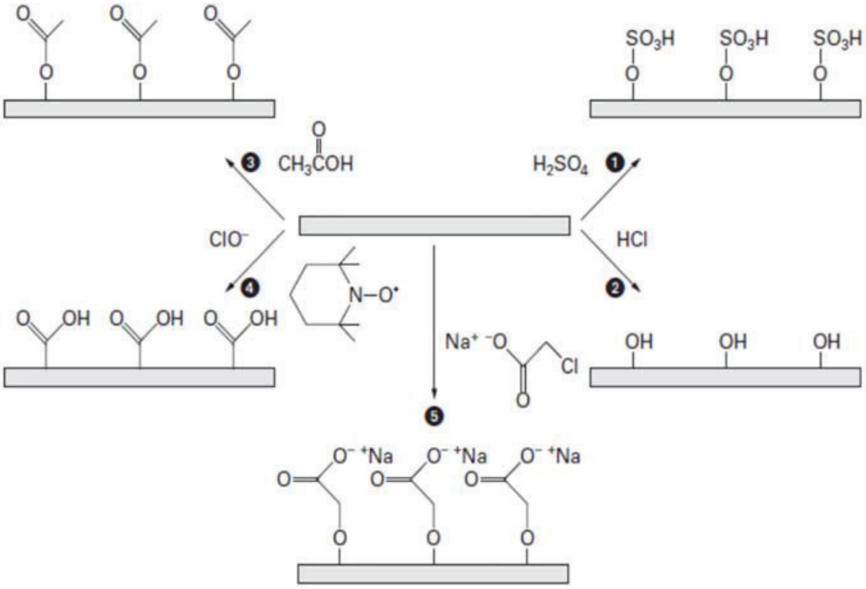


Figure 23.14 (A) Scheme showing surface modification of nanocellulose induced by chemically applied processes. The routes describe different ways to chemically engineer nanocelluloses by introducing (1) sulfate ester groups via sulfur hydrolysis (2) hydroxyl groups via hydrochloric acid hydrolysis (3) acetylation via acetic acid hydrolysis route (4) the effect of TEMPO driven hypochlorite medium and (5) carboxymethylation of surfaces. *Source*: Reproduced with permission from Anon. (2012). 5 – Chemical modification of nanocellulose, In *Nanocellulose* (pp. 147–192). Berlin, Boston: De Gruyter.

typically 5 nm fibril width is consistent with 40 chains and 52 nm comprises around 4000 chains (Siqueira, Bras, & Dufresne, 2010). Accessibility to hydroxyl groups for modification is considerably reduced due close packing (2%) in culture media (Kummala et al., 2018) and the swelling affect observed in water as discussed previously. The swelling here refers to both intra-particle and interparticle distancing to overcome the constraints of forced compression imposed by tightly packed morphologies. The packing forces of these barriers, the disruption of fibrillar aggregates and better exposure of internally orientated chains by diminishing forces associated with hydrogen-bonding have involved the use of ionic, polar and non-polar reagents such as solvents over the last decade or so (Roy, Semsarilar, Guthrie, & Perrier, 2009) in efforts to change the surface chemistry of cellulose. Counter ions drastically effect swelling ability of nanocrystalline cellulose (Maloney, 2015). These chemically driven advances while regulating swelling effects and group functionalities to control the underlying chemistry and dispersibility of isolated nanocelluloses have also encountered losses in reactivity and surface accessibility during solvent exchange. This was identified to mainly occur by air contamination during drying cycles. However, more recently to circumvent these challenges, interest in "end-wise" modification of cellulose which allows the modification of cellulose while maintaining the natural structure in the native form is being pursued and rationalized as unexplored routes to gain new material types (Heise et al.). The concept uses the phenomenon of "mutarotation" (Lowry, 1903) which in the context of cellulose, a structural equilibrium exits between its native glucose structure and its open conformational hemiacetal form or its open-chain aldehyde form. Acid hydrolysis as a preparatory method for nanocellulose assemblies does not only effect reproducibility and hinders reactive sites through introduction of sulfated half ester groups but also its isolation by H_2SO_4 hydrolysis is not deemed to be orientated to site specific locations on the chains as reported for H_3PO_4 (Lemke, Dong, Michal, & Hamad, 2012). This might suggest that the balance between achieving a near-native biocomposite structure of cellulose by preserving the hierarchical multiscale patterns in a synthetically reinforced environment through surface modification is delicate and can easily be disrupted by a change in its peripheral chemical framework.

The disruption in the ordered networks can disfavor adhesion properties through the introduction of defects resulting in misaligned configurations along the chain in the positioning of unit building blocks, chain orientation, intra- and intermolecular bonding arrangements and chemical functionalities during preparatory procedures. Since nanoscale geometry underpins microscale and macroscale order, nanoscale imperfections can form the basis of poor adhesion and mechanical performance. An example is the application of sonication for the fragmentation of cellulose nanofibrils using 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) as an oxidative catalyst as a promising method for tailoring their separation into individual particles. While ultrasonic waves can assist in the dispersion of nanofibrils, frequencies exceeding the mechanical tolerance of these structures may introduce defects and structural interruptions within the architectures such as comprising mechanical strength (Kurokawa et al., 2016; Saito, Kuramae, Wohlert, Berglund, & Isogai, 2013).

The importance of "free" bond rotation, diffusion, mobility and chain directed orientation—some parameters intrinsic to the behavior of multiscale self-organization during fibril-fibril assembly during chain alignment was recently investigated in a pioneering study to minimize the effects of stress transfer. Using a process termed "flow-assisted" assembly, Mittal et al. proposed to maximize optimal binding contacts between interacting fibrils permitting flexible responses to Brownian motion, attractive forces and electrostatic repulsions during microfribillation by reducing stress transfer under conditions of flow. Fig. 23.15(A) shows the schematic arrangement of a flow-focusing channel comprising CNCs. At position 1, fibrils are seen to self-adhere poorly under conditions dominated by Brownian motion and repulsive forces attributed to −COOH bond dissociations. Position 2 shows the effect of hydrodynamic forces that dominate fluid motion relative to the fiber flow causing unidirectional re-orientation in the direction of fluid flow. Accelerated flow is further observed to align fibers (Position 3) with the addition of acid solution (Position 4). While there is universal agreement that particle dispersion is necessary to make optimum use of their functions for industrial applications (Higashitani et al., 2000), flow related mechanisms provide opportunities for the re-orientation of particles of diverse shapes spontaneously and more freely without

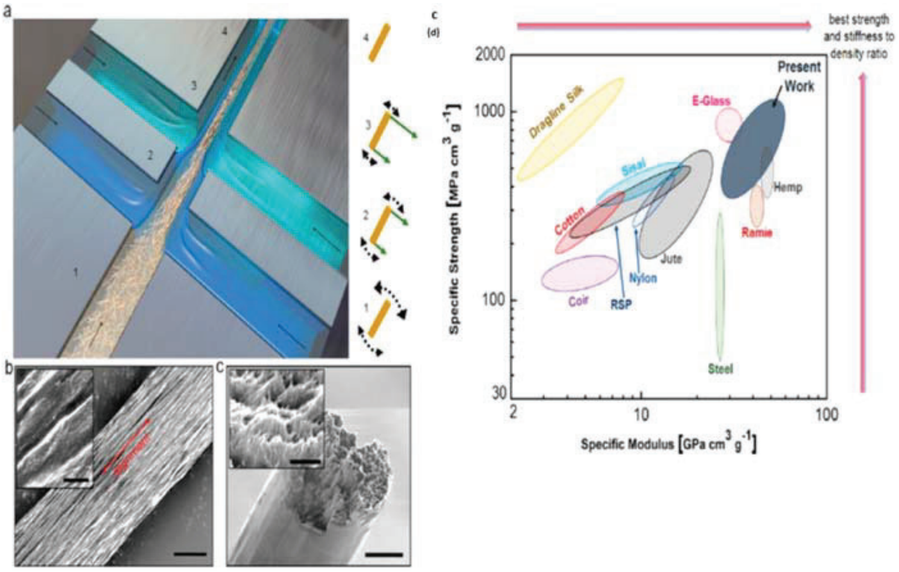


Figure 23.15 (A) Flow-assisted alignment of cellulose nanofibers (A) A schematic representation of fabricated channels to assist the alignment of nanocellulose chains during flow. Fibers are introduced in the main channel entry (labeled 1) and the direction of flow is shown by the arrows. The liquid shown in blue represents water and the light green color is low pH acid. The panel to the right depict the direction of hydrodynamic and electrostatic forces as shown by the arrows. At position 1, the random orientation of particles signify poor alignment of fibers attributed mainly by charge-charge surface repulsion caused by the of loss of −COOH from the surface. Position 2, shows fiber alignment in which the relative hydrodynamic forces the motion of fibers to re-orientate uni-directionally during increased acceleration at position 3 and subsequent alignment via introduction of acid at position 4. (B) surface of the fibers captured by scanning electron microscopy (C) fiber cross-section image by SEM. (D) A comparison of the mechanical properties of documented biomaterials comparable to cross-linked cellulose nanofibers using "flow-assisted" methodology.
Source: Reproduced with permission from Mittal, N., Ansari, F., Gowda, V. K., Brouzet, C., Chen, P., Larsson, P. T., et al. (2018). Multiscale control of nanocellulose assembly: Transferring remarkable nanoscale fibril mechanics to macroscale fibers. *ACS Nano*, *12*(7), 6378−6388.

restrictions under conditions of shear-induced assembly. This phenomena describes a degree of self-organization between attractive particles that utilize intramolecular bonding such as forces of attraction between biological molecules that respond to shear stress (Takayama & Kato, 2018) under directional flow within confined geometries where hydrodynamic interactions are dominant (Varga et al., 2019). Since hydrodynamic forces originate from the velocity of particles and fluid-driven acceleration, hydrodynamic parameters that govern particle dynamics, orientation and alignment with respect to motion fluid acceleration can be used to diminish the effects of non-hydrodynamic parameters such as Brownian forces and diffusion and even chemically driven associations impairing the influence of shape, size and chemical composition. Hence, random adhesion between particles becomes uniformly regulated due to hydrodynamic compression between particles which reorientates the alignment of nanoclellulose chains. The systematic fluidization of nanocellulose from water to an acidic environment from loosely arranged fibers to tightly packed cross-linked fiber networked permitted stress transfer effectively from macro-to nanoscale order. The study reported an exceptionally strong Young's modulus of 86 GPa with a corresponding tensile strength of 1.57 out-performing previously reported values for bio-polymeric materials. Biomimetic alignment of nanocelluose embedded into microelectromechanical actuating devices using MEMS fabrication tools achieved through a fluid-based medium produced moduli and fracture strengths of 51 and 1.1 GPa (Saha, Ansari, Kitchens, Ashurst, & Davis, 2018). Mechanically induced properties using CNC MEMS processing on a 4 μm device thickness were better achieved using a parallel arrangement to a perpendicular alignment which resulted in diminished mechanical performance.

Another interesting approach for the alignment of nanocellulose fibers has been recently focused on "shear stress" which occurs when two surfaces exert a sliding motion across the interface and is often accompanied by change in the shape of the interacting materials. Shear stress and strain has importance in 3D extrusion processes and efforts have been devoted to understanding how materials driven by extrusion processes can be desirably orientated anisotropically and this has much relevance to biocomposite design and fabrication in 3D-printed processes. Digitally driven alignment of nanocellulose has been a recently new exploration to enable "programmed particle orientations" via extensional flow during the extrusion process facilitated by a nozzle. Unlike other alignment approaches, the "additive technological" processes can be programmed to design complex structures and shapes from printable materials blended with biologically derived materials to mimic natures geometrical architectures with better precision. The group of André R. Studart (Siqueira et al., 2017) has pioneered the use of direct ink writing (DIW) making use of nanocellulose crystals as reinforcing agents in inks composed of polymer matrices designated as HEMA (2-hydroxyethyl methacrylate) and PUA (polyether urethane acrylate) oligomers either as water based suspensions or as organic solvents mixed into the ink medium. To improve dispersibility of nanocellulose crystals and bond associations at interfaces, surface modification of CNC was performed with methacryclic anhydride. The acetylation of surface OH groups on nanocellulose to vinyl moieties is one example of a host of chemical functionalities (Fig. 23.16) that in this instance enables its participation of cellulose chains in bond covalency via polymerization of vinyl monomers through -OH group modification. The composition of CNC ink combinations with varying oligomer ratios either with modified or unmodified CNC surfaces provided crucial rheological control of the ink blends defining both material geometry and pressure at the nozzle exit. The methodology permitted the "shear-induced" alignment of CNCs intercalated between the material interface of the blend and precise positioning while localized in the printing direction was possible using polarized light microscopy and AFM. Surface chemistry and orientation of CNCs were important to its adhesion properties accompanied by

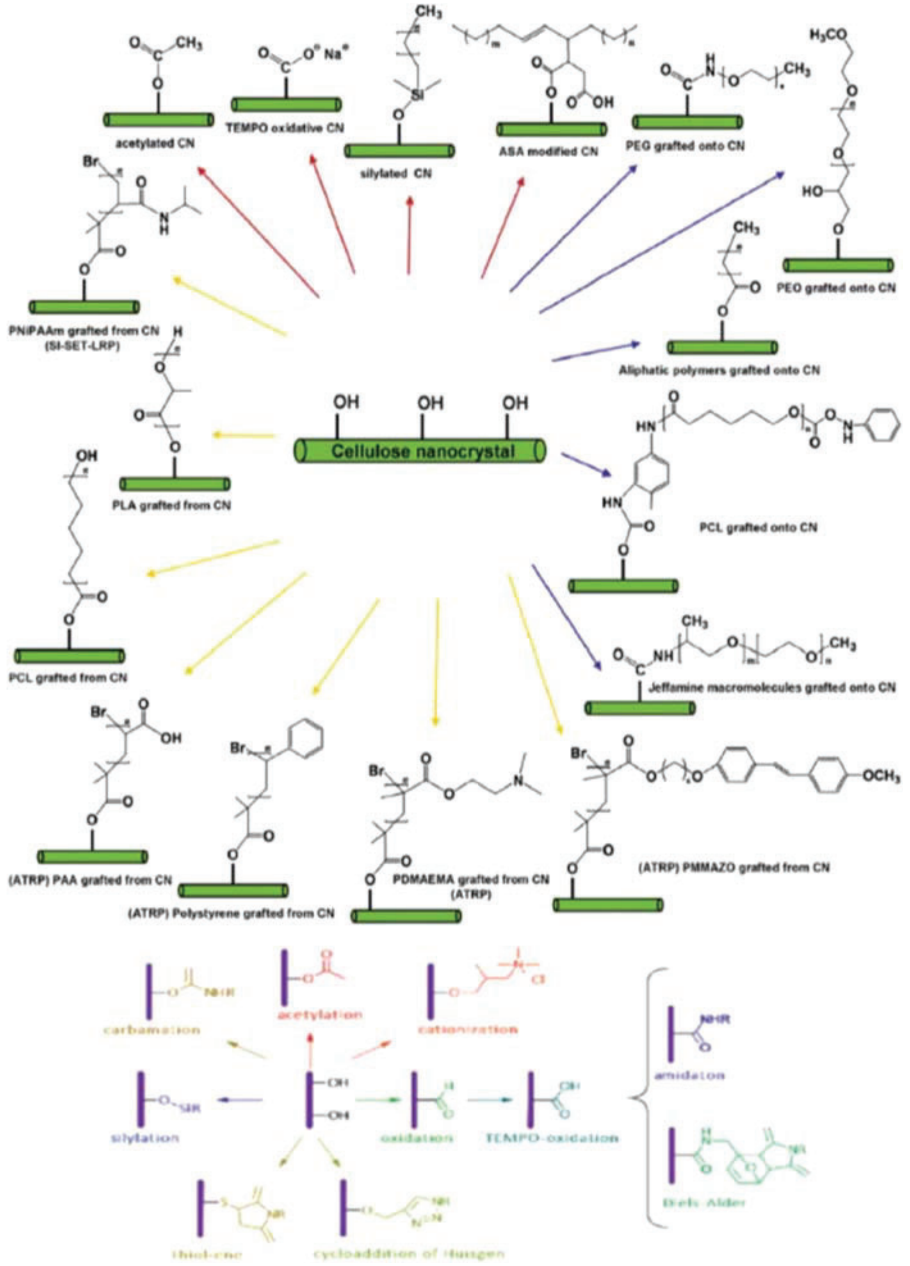


Figure 23.16 Chemical group modification of nanocellulose via −OH group modification. *Source*: Reproduced with permission from Klemm, D., Cranston, E. D., Fischer, D., Gama, M., Kedzior, S. A., Kralisch, D., et al. (2018). Nanocellulose as a natural source for groundbreaking applications in materials science: Today’s state. *Materials Today*, *21*(7), 720−748. (top panel) and Nascimento, D. M., Nunes, Y. L., Figueirêdo, M. C. B., de Azeredo, H. M. C., Aouada, F. A., Feitosa, J. P. A., et al. (2018). Nanocellulose nanocomposite hydrogels: Technological and environmental issues. *Green Chemistry*, *20*(11), 2428−2448. (bottom panel).

increases in elastic modulus of the matrix by 80% when supplemented with 20% modified CNC with no change in the fracture strength. Further analysis by the same group in applying the concept of DIW by incorporating strategically aligned CNCs for the fabrication of mechanically superior ink compositions revealed an inverse stoichiometry between particle alignment and shear rate but a direct relationship with particle concentration (Hausmann et al., 2018). Here, the method can be adapted to align particles as a function of composition influencing the rheology of materials and further controlled by the extrusion flow governing the interfacial properties from simple to complex architectural design features. Basic shear flow or modulation of the alignment strength depends on the introduction of extensional flow conditions controlled by the nozzle geometrical design providing unprecedented versatility for the creation of biomimetic structures. Fig. 23.17 describes the design features that enable the evolution of future 3D printing platforms needed for biocomposites design. Li, Zhu, et al. (2017) recently used the process of "extrusion" for the preparation of conductive 3D-printed aligned microfibers in the form of carbon nanotube/nanofribillated nanocellulose composites improving tensile strength with a reported value of 247 ± 5 MPa. Effective use of the carboxyl functionality induced by partial acid treatment enabled sufficient dispersion by an extrusion generated "shear" force. This is discussed further (Fig. 23.18).

The polymerized form of aniline has been particularly attractive as a conducting polymer with the ease of modulating the surface properties and the ability to assemble supramolecular polyaniline structures (Lee, Chung, Kwon, Kim, & Tze, 2012; Sapurina & Stejskal, 2008). Bacterial cellulose has been used as a growth template facilitating the assembly of polyaniline chains by a multi-step chemically induced mechanism that is not completely understood. However, the commercial interest centers on the morphological variability formed through different reaction products mediated via their protonated states. For example, ammonium persulfate (APS) and p-Toluenesolfonic acid (p-TSA) were used for the chemical oxidative polymerization of

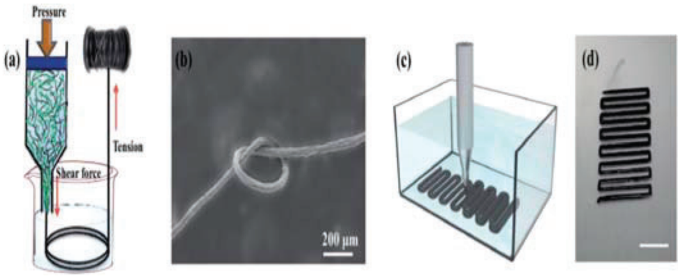


Figure 23.17 (A) Extrusion assisted pre-alignment of carbon nanotube/nanocellulose microfiber particles showing (B) knot-type flexible morphologies generated from (c and d) 3D-printed conductive ink prototypes as schematically shown.
Source: Reproduced with permission from Li, Y., Zhu, H., Wang, Y., Ray, U., Zhu, S., Dai, J., et al. (2017). Cellulose-nanofiber-enabled 3d printing of a carbon-nanotube microfiber network. *Small Methods*, *1*(10), 1700222.

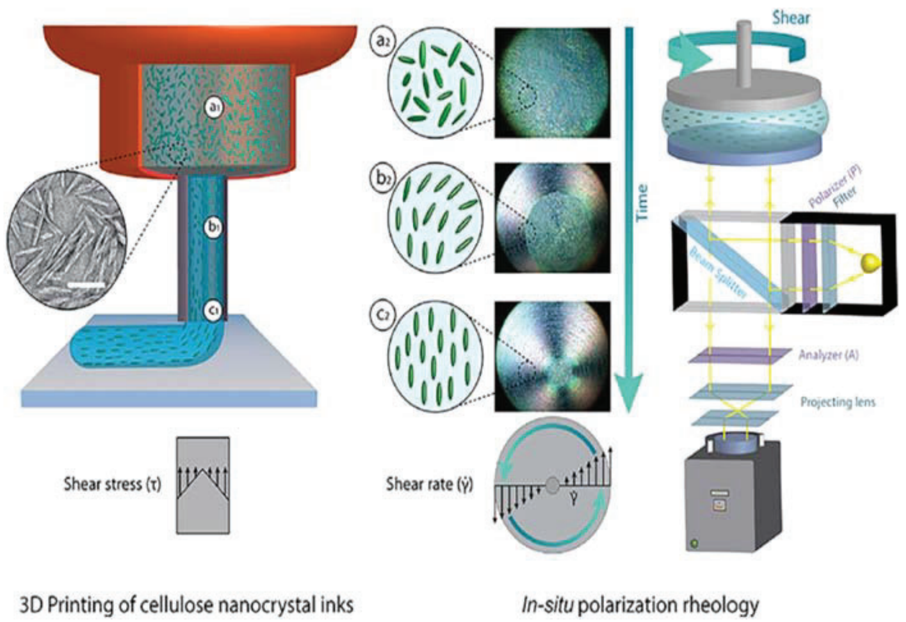


Figure 23.18 (A) The alignment of nanocellulose crystals generated in "ink" during the 3D printing process. (L.H.S) Setup depicting the process of 3D printing during which (A1) randomly arranged nanocellulose crystals are introduced in the holder (B1) exposure of nanocellulose crystals to shear-stress conditions favoring the extrusion-driven alignment of crystals into the nozzle (C1) second and final thrust causing a "velocity" orientated flow under shear-stress. (R.H.S) A schematic of polarized light imaging system enabling the shear-extrusion process to be observed using a parallel plate geometry. The setup shown (A2, B2, and C2) allows the assessment of shear rate and time on and its relationship with the orientation process.
Source: Reproduced with permission from Hausmann, M. K., Rühs, P. A., Siqueira, G., Läuger, J., Libanori, R., Zimmermann, T., et al. (2018). Dynamics of cellulose nanocrystal alignment during 3D printing. *ACS Nano*, *12*(7), 6926–6937.

aniline on bacterial cellulose aided by the protonated state of the nitrogen group revealed by X-ray photoelectron spectroscopy (XPS) imparting electrochemical properties at the polyaniline-cellulose interface (Lee et al., 2012). Deconvolution of XPS peaks corresponded to the protonation of nitrogen species of the monomers that differed not only by the extent of protonation but also by the chemical routes driving protonation. In this study, polyaniline was observed to form spheres encapsulating nanocellulose in the size range of 100–200 nm while others have reported a controlled interfacial polymerization process involving the polymerization of polyaniline aligned along a single side of cellulose resulting in a conductive and non-conductive (high resistive) nanocomposite under conditions of low and high oxide concentration respectively (Lin, Guan, & Huang, 2013). Curing by self-assembly in the presence of a catalyst as described above is the most simplest method but may not be the most efficient for ensuring the removal of trapped air or water and other liquids. The importance of surface chemistry in cellulose polyaniline blends in improving conductivity in this case is underlined by the pre-treatment of bacterial cellulose when subjected to different processing methods such as draining, freeze drying and regenerated membranes. Here, the emerging physical properties of the matrix can induce in situ polymerization of aniline monomers inside of the membranes under oxidation (Alonso et al., 2018). A key consideration is the surface energy compatibility between nanocellulose and the solvent environment permitting optimal coverage and dispersion by curing the blend constituents and their correlation with mechanical strength (Ferguson et al., 2016; Yudianti et al., 2016). The degree of compatibility is consolidated with physical processes that involve temperature, pH change, pressure/compression or interacting radiative waves (UV, photons, electron beams, microwaves, X-rays, ionized particles) initiating bond breakage and formation or in the absence of air during multi-curing stages.

With applications at the forefront in biocomposite design, methodologies originate from the need to fulfill or meet design criteria particularly at larger manufacturing scales but these challenges largely exist to assist fabrication design between interacting materials and how well a biocomposite fits with its end application. While surface treatment with chemicals is still necessary to replace the hydrophobic character to the hydrophilic one which is much less problematic in terms of interfacial adhesion, methods such extrusion has been employed to preserve structure during nano-reinforcement with the polymer matrix of choice acting as a filler in fibers. The extrusion process is highly applicable to nanocellulose- polymer loading and polymer melts that can form a homogenous blend with cellulose fibers undeterred by the polymer hydrophobicity at a temperature suited to the polymer melt and plasticity. The method has the advantage of selecting the extrusion screw design around which the polymer winds and takes a thread like shape which can readily form a continuous uniform blend around nanocellulose (Cardon et al., 2017).

Premixing of polymer nanocellulose materials before extrusion processes are applied have important implications for reinforcing the composite matrix and their associated mechanical properties (Ranjeth Kumar Reddy & Kim, 2019) at multi-material interfaces of varying compositional mix (Sukyai, Sriroth, Lee, & Kim, 2011; Tran et al., 2011). In the relevant study cited, a premixing and extrusion process required only a small amount of nanocellulose with kenaf and polylactic acid to improve mechanical properties. This supports the opinion that premixing imparts better dispersion properties with uniformity prior to extruding. This is important to counteracting the effects of segregation during extrusion when mixtures are exposed to sliding between interfaces during shearing. Hence, design features of the extruder are implicit to the final physical and chemical nature of the microfibers defining its compositional behavioral. This relates to how the screw enables or restricts orientations and composite geometry as a function of the shear force distribution generated from the extrusion forces based on the characteristics of the screw design. Design parameters can influence the flow between the polymer and fibers, interactions from the vibrational energy of the enviroment and impact the shape, size and roughness among other factors. Fig. 23.19 illustrates the effects of segregation in polymer-additive mixtures that materialize from interfacial interactions aiding particle−particle separation during the mixing phase.

Another process of increasing applicability in the re-orientation and alignment of fibers is the carding process ("spinning will") and is slowly gaining recognition as an importance technique for alternative renewable reinforcement of biocomposites materials (Adekunle and Skrifvars, 2015). Rotating cylinders take the form of the carding apparatus that can operate under variable speeds encompassing functions that execute three processes namely; carding, peeling and lifting. The combination of these processes enable the detachment of fibers entanglement enforcing their alignment. The carding processes has high utility in the organization of fibers that are inherently disorganized individually separating and aligning them in a parallel arrangement. Fig. 23.20 illustrates the schematics of the carding process and describes the rolling action of two cylinders untangling fiber lengths. The orientation of fibers have been recently applied to drawn silvers by making use of polyester staple in fiber processes (Das et al., 2011). The study shows that increasing cylinder speed and decreasing doffer speed provides control over anisotropy in a directional way. The physical attributes of the carding process have been useful for fabricating "long-and-discontinuous" natural fibers and for formulating biocomposite blends as done with propylene. The outcome suggests that the process was successful in assisting fiber-matrix bonding effectively aligned along their natural growth path. By improving the utility of the carding process and tailoring

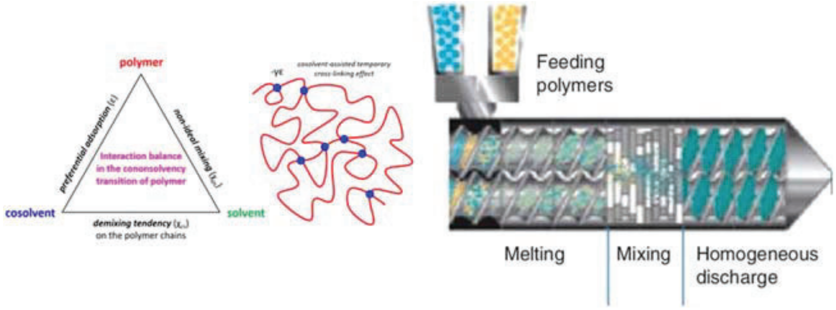


Figure 23.19 (A) Importance of co-solvency effects in polymer premixing at the polymer-solvent co-solvent interface resulting in ideal or non-ideal phases during polymer crosslinking. (B) A schematic showing the random distribution of particles in polymer-additive mix and the potential to induce polymer-additive homogeneity from the melt and mixing phase.
Source: Adapted with permission from Gajda, M., Nartowski, K. P., Pluta, J., & Karolewicz, B. (2018). The role of the polymer matrix in solvent-free hot melt extrusion continuous process for mechanochemical synthesis of pharmaceutical cocrystal. *European Journal of Pharmaceutics and Biopharmaceutics*, *131*, 48−59; Yong, H., Merlitz, H., Fery, A., & Sommer, J.-U. (2020). Polymer brushes and gels in competing solvents: The role of different interactions and quantitative predictions for poly(N-isopropylacrylamide) in alcohol−water mixtures. *Macromolecules*, *53*(7), 2323−2335.

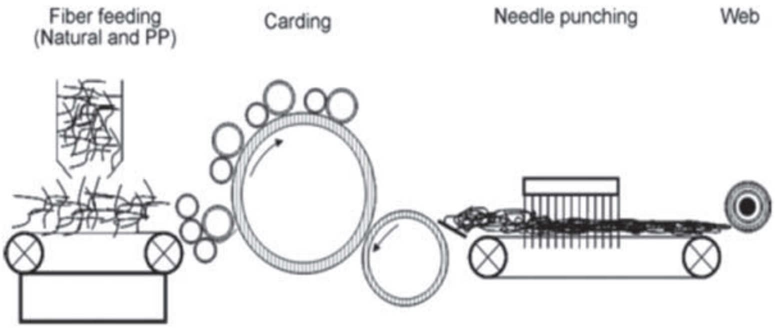


Figure 23.20 The setup and dynamics of the carding process.
Source: Reproduced with permission from Lee, B.-H., Kim, H.-J., & Yu, W.-R. (2009). Fabrication of long and discontinuous natural fiber reinforced polypropylene biocomposites and their mechanical properties. *Fibers and Polymers*, *10*(1), 83−90.

methodologies to generate mechanically reinforced and well aligned cellulosic fibers, mechanical properties may be better guided by natural shape adaptation of diverse compositions. This inevitably involves parameter optimization of directional rotating speeds, mechanics of contact to significantly improve the quality of aligned fibers.

23.8 Concluding comments

The development of cellulose-based nanocomposite materials has significantly advanced in recent years marking their positional importance for the next generation of renewable polymers. An important directive in their behavioral evolution has been geared toward understanding their mechanical properties. A particular aspect critical to its broader applicability for technological innovation has been an exceptionally challenging pursuit and one that is closely allied to its intrinsic nature. The scale-driven alignment of fiber monomers has been central to addressing this need and routes to adopt more stringent biomimetic pathways for enhancing performance-related, morphological, and mechanical behavioral properties.

Probing the intricacies of fiber-to-fiber interactions at the molecular level and directional multi-fiber packing has been dependent on developing key methodologies to determine the nature of interacting bonds and the forces associated with them. Much effort has been directed in understanding fiber dispersion and the effects of surface chemical modification in driving micrometer to nano morphological control. Mapping chemical changes to morphological and mechanical behavior has been considerably insightful paving the way to innovative fabrication techniques for the directional alignment of fibers and their dynamic control. Nanoscale advancement and progress in the manipulation of well aligned fibers has been encouraged by new heights in mechanical nanocomposite design.

We are now entering an exciting new era in cellulose nanocomposite fabrication at the smallest convergent scales achieved so far. Improving biomimetic conditioning enabling self-directed assembly (e.g., chemical environments) and the physical dynamics (e.g., directional flow) of interactive binding that is both flexible and environmentally responsive in semi-synthetic blends promises much for innovating new technologies. Consolidated efforts at disciplinary boundaries demanding a better understanding of nanocellulose biology, surface nanochemistry, and the application of nanoengineering tools are needed to facilitate biomimetic approaches to ameliorate natures design criteria.

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