Packaging Applications of Biodegradable Nanocellulose Composites

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Packaging Applications of Biodegradable Nanocellulose Composites

Sanjiv Sonkaria, Kwang-Hyun Ryu, Varsha Khare, and
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Abstract

Ensuring the safe disposal of waste materials to prevent irreversible environmental damage is a major priority concern of the current century. The alarming rate of consumption of plastic-based packaging materials has steadily increased and plastic accumulation now seemingly contributes to the global carbon footprint substantially adding to greenhouse gas emissions. While it is difficult to reduce the global dependency on plastics as a cheap and easily polymerizable material source, nature provides a sustainable alternative to process waste into eco-friendly breakdown products that are recycled back as nutrients by microorganisms and are not harmful by-products. Packaging in the form of naturally occurring biodegradable matter is becoming an increasingly attractive alternative to replace common nonbiodegradable plastic. Biopolymers assembled in nature are by their intrinsic nature biodegradable but retain some ability to exhibit plastic-like properties. Hence in this review, the knowledge gap that currently

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prevents the use of readily available natural biopolymers namely nanocellulose that have the potential to be engineered into biodegradable plasticized products is highlighted. This review aims to focus on discussion points that are underrepresented with regard to aspects on nanocellulose. Here, bond fragility of nanocellulose is one concern limiting its use as a viable biodegradable bioplastic. Material failure has its origins in chemical bond breakage and while much progress has been directed toward experimental investigations of nanocomposites formed form nanocellulose, the connection between an intrinsic understanding of chemical bonds with structural-functional nature of nanocellulose is lacking. Here, we explore these in more detail in our efforts to build a greater appreciation to broader areas covered elsewhere.

Keywords

Biodegradbility · Nanocellulose · Bioploymers · Recyclability · Renewability · Microplastics

Introduction

Importance of Biodegradable Packaging

Cheap packaging has been synonymous with the birth of plastics since the turn of the twentieth century and has since symbolized the face of durability, strength, and tough polymer chemistry. The oversupply of the “make, consume, and dispose” business model is symbolic of a huge disposal waste problem for an industry worth $450 billion dollars. Now decades into the new millennium, the future is firmly embedded by a plastic-dependent existence with overwhelming consequences to the environment and human and animal life by diminishing the eco-benefits of a plastic-free world. Plastic production and its disposal are major climate change issues and the worlds’ dependence on plastics promises to be a significant growth driver by industries. While plastic has favored an economic advantage to the consumers and industries alike particularly in terms of packaging of products, recyclability has not featured heavily in the “plastic” business model largely due to the cost burden. Insight into the sense of scale of plastic consumption is appreciable from an expected drop of 100,000 tonnes if its utilization was met by a 50% reduction. In reality, less than 10% (Rahimi and Garciá 2017) of plastics are recycled with little prospect of depolymerizing the most toxic plastics that contain liquids and food products. Figure 1 shows that the plastic industry is predominately driven by the packaging industry and this dominance is set to increase and plastic utilization (Fig. 1; green bubble) is not expected to slow down. The most popular plastics are related polyethylene low density (PE LD), polyethylene high density (PE HD), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET).

More than nine billion metric tons of plastic have been manufactured since the 1950s of which 40% represents single-use plastics. Such industry-led challenges

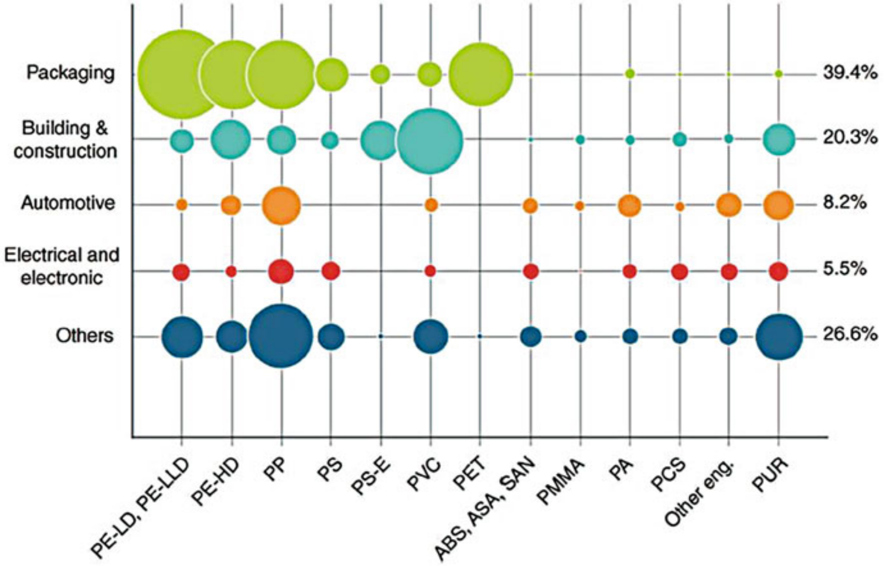

Fig. 1 The dominance of the packaging sector among other industries as a leading consumer of synthetic plastics. (Reproduced with permission from Lackner 2015)

pose a prime environmental concern of growing catastrophic proportions originating from technological gaps in the disposal of nondegradable plastic packaging. The accumulation of plastics in landfills impacts both land-based and marine animals as water-dissolved plastic waste is carried by rain water deeper into soils groundwater that connect streams, rivers, and oceans. This permits the systematic poisoning of all with types of ecosystems it encounters into a collective patch of plastic debris that accumulate into the Great Pacific Garbage Patch (GPGP), a vortex of marine debris which was surveyed to be the size equivalent to 1.6 million km^2 in 2018 (Lebreton et al. 2018). Plastics of varying size including millimeter-sized plastics find their way within marine animals and into the human food chain. Microplastics have been identified in table salt, tap water through water contamination, and synthetics like nylon and polyester can release thousands of microparticles into our laundry. It was also found that plastic feeding water bottles and injectors released as much as 393 particles/mL just from repeated opening and closing cycles (Song et al. 2021). Figure 1 shows that common cutting processes like scissoring, tearing, and cutting of packaging results in the release of microplastics demonstrated by the mass change (Sobhani et al. 2020). Further, microfragments originating from other everyday plastics like tearing of bag of chocolates, sealing tape, and bottle caps were visualized under SEM and the morphologies were correlated to FTIR and QCM analysis of freed microparticles by the tear (Fig. 2). More recently, examination of human feces for the existence of ingested microplastics in the guts of humans from a group of a small group of disease-free study subjects aged 33–65 years led to the identification of ten types of microplastics. Polypropylene and polyethylene terephthalate were

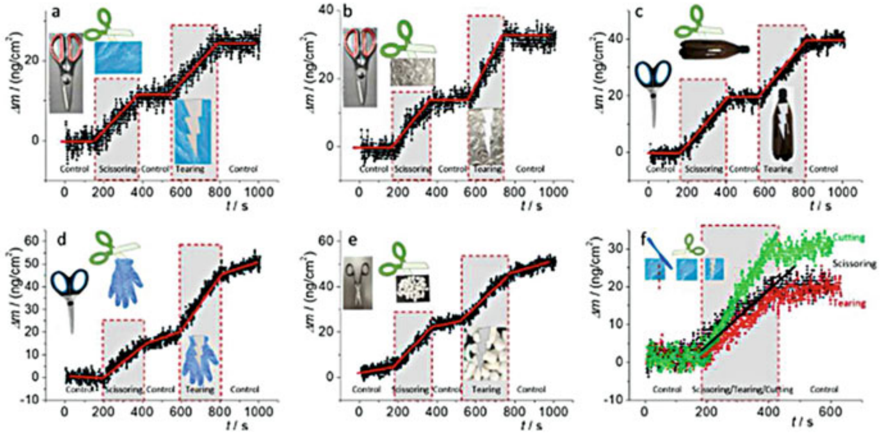

Fig. 2 Microplastics generated from scissoring, tearing, and cutting of plastic packaging. Increase in mass associated with microplastics was measured by quartz crystal microbalance. (Reproduced with permission from (Sobhani et al. 2020). This work is licensed under a Creative Commons Attribution 4.0 International (CC BY 4.0))

correlated to nine of the study subjects as the most commonly occurring type and eight samples revealed microplastics ranging from 50–500 μm in size (Schwabl et al. 2019). Microplastics have been shown to exert their effects which are cell dependent (Caldwell et al. 2021) and new methodologies have evolved to follow the biological effects of nanoplastics as small as 50 nm. Particle imaging by stimulated emission depletion (STED) (Fig. 3 RHS b, d, f and h) shows the shapes adopted by common in the form of nanoplastics which could not be resolved by confocal microscopy (Fig. 3 LHS a, c, e, and g) (Nguyen and Tufenkji 2021). With specifics to a model study using the commonly used packaging material polypropylene (PP), the biological fate of fluorescently tagged PP was followed in zebra fish embryos and was shown to be localized in the gut (Lee et al. 2022). This brings into awareness the existence of submicroscopic particles where the short-term and long biological effects on potential disease development and progression are completely unknown. The persistent nature of plastic packaging is a complex problem of global proportions. Implementing safeguarding strategies against accumulating plastics is energy demanding and current approaches may not be applicable in handling highly toxic plastics like polyvinylchloride (PVC).

The petroleum and fossil fuel origin of the most durable plastics and their future sustainability is a global concern. While plastics are indispensable for the important purpose they serve in packaging of a diverse range of products, the physical, chemical, and mechanical properties do not allow their recyclability at the end of their life cycle. The recyclability and renewability of synthetics are inefficiently low resulting only in partial degradation, the energy demands for breaking down the polymer structures is very high. For example, thermolytic processes that drive polymer breakdown require a high-energy input and control over product

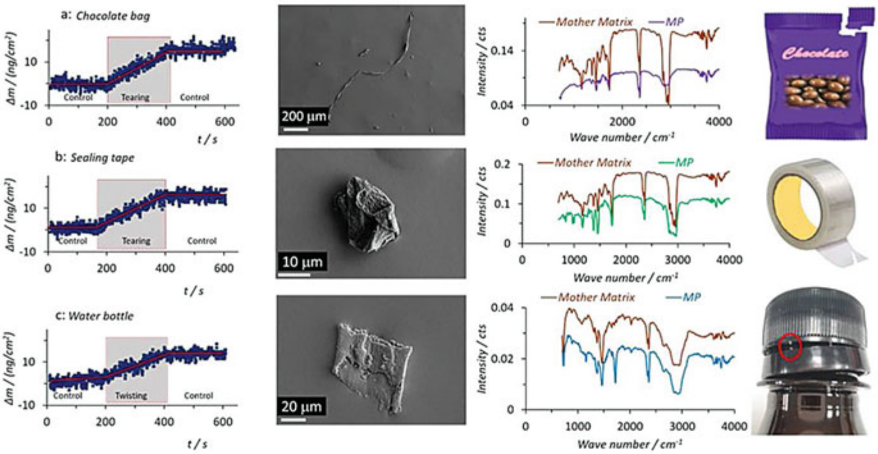

Fig. 3 Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) correlate to microfragments of plastics measured by quartz crystal microbalance (QCM) from tearing of plastic packaging of (**a**) chocolates, (**b**) tape, and (**c**) bottle cap. (Reproduced with permission from (Sobhani et al. 2020). This work is licensed under a Creative Commons Attribution 4.0 International [CC BY 4.0])

degradation is variable depending on the nature of the polymer due to strong bonding. However, thermoset polymers used in the rubber industry were recently engineered using polydicyclopentadiene as model for inserting cleavable cross-linked bonds to render the polymer degradable without affecting its mechanical properties (Shieh et al. 2020) which is a promising alternative to recycling of polymers (Hamad et al. 2013) which require areas of technological advancement to address the chemically diverse and different toxicities often associated with nonbiodegradable plastics and their degraded products. Work toward the design of building blocks that may function at the unit level of monomers and cross-linkers as reactive networks in polymers (Winne et al. 2019) could potentially in the future be used to take advantage of mechanical and physicochemical properties that facilitate depolymerization (Rahimi and Garciá 2017). Currently synthetic polymers are not naturally cleavable in nature but instead were designed to durable and tough.

There is great demand for sustainable packaging which is both cost-effective and eco-friendly. At the leading edge of this endeavor is biodegradable packaging. For any plastic to be biodegradable, the material composition must be chemically and physically accessible to living entities such as microorganisms which can actively recognize chemical groups and release enzymes that specifically digest bonds into monomers and oligomers. The process is sustainable by virtue of the nature of the degradation products since they are a source of nutritional value and energy for the diverse ecosystem of living microspecies that inhabit our planet. Many of the synthetic plastics can potentially serve this purpose as a rich source of hydrocarbons as a feedstock for organisms that hugely outnumber the small number of core synthetic materials in circulation today. Such materials of high molecular weight include polyethylene (PE), polypropylene (PP), polyvinyl chloride, (PVC), polystyrene (PS), polyethylene tetraphthalate (PET), and polyurethane (PUR). While findings suggest that some bacteria and fungi can adapt their biological machineries to degrade synthetic polymers, biodegradation rates are poorly inefficient against the rising accumulation of plastics. However, factors such as structure, molecular weight, surface morphology, mechanical strength, and varying degrees of crystallinity/amorphicity effect degradation which reflect the overall bioavailability of the polymer. Natural or formulated semisynthetic biopolymers are currently of value. Biodegradable and semibiodegrable polymers are attractive targets for the replacement of plastics but lack durability and toughness of plastics. Examples include polycaprolactone (PCL), poly(lactic acid (PLA), polyethylene succinate (PES), polyhydroxyl butyrate (PHB), butylenes succinate (PBS), polyhydroxy alkanoate (PHA), and poly(butylenesuccinate-co-adipate) (PBSA), among others. Another distinguishing factor between synthetics and biodegradable materials is the occurrence of functional group sets that likely influence the broader reason for differences in their bioavailability.

With a greater focus on biodegradable materials, naturally produced environmentally compatible materials are in demand as packaging materials. Rising population and consumer demand is proposing a new technological vision for packaging being actively responsive to its environment particularly to microbes and such intelligent packaging may evolve into sophisticated sensing technologies equipped with indicators interacting with the surrounding atmosphere. Therefore, a strong mandate for “next-generation” materials are alternatives that are easily adaptable to different environments with the ability to be efficiently degraded or converted back into some form of usable packaging. Material availability, renewability, processability and ease of modification for improvement, disposability through efficient recycling, and eco-friendliness and biocompatibility are characteristics that are highly attributable to a class of biodegradable materials termed biopolymers found in nature. Their alignment with diverse microbial communities has evolved mechanisms to break down biodegradable polymers into digestible constituents and satisfy many of the abovementioned requirements.

“Sustainability” and “renewability” are umbrella terms synonymous with natural and biodegradable materials. While renewable materials impose a cost factor from natural sources such as sugar and ethanol, the abundance of natural biopolymers could potentially bring advantages to reduce cost barriers. However, the scale to which biopolymers will eventually need to be manufactured to meet the current and future consumer demands is challenging. The difference among biodegradable materials is the rate at which they degrade. The ideal targets are weak molecular structures that undergo disintegration. Nanocellulose is one such biopolymer. With consideration to renewability, nanocellulose as a bioplastic has numerous physical and chemical exploitative properties and can provide opportunities to introduce new and improved functionalities. However, much of the enthusiasm has been hindered by the cost of mass processing but expectations continue to be high (Lindström and Aulin 2014).

This chapter examines the broader potential of nanocelluloses as a feasible option for replacing petroleum-based plastic packaging and discusses these advancements in reaching the longer-term goals of bringing nanocellulosic materials closer to marketable quality. As plastic has been seen to revolutionize polymer chemistry, by the same token the future packaging materials will be looking to bring newer innovations and packaging will have a multifunctional purpose attached to it. To advance this, a thorough grounding of the fundamental properties of nanocellulose is essential to allow its modification to become a true innovative material for decades to come.

Nanocellulose

Potential Use of Nanocellulose in Packaging

Nanocellulose is probably one of the most interesting plant biodegradable biopolymers that exist. It is abundantly available from wood biomass, plants, and other inexpensive vegetation sources. The market value of nanocellulosic a raw material is expected to reach USD 963 million by 2026 (Markets and markets, 2022) and marks the increasing trajectory of global interest toward biobased renewables. An important requirement for material renewability is its degradable value for energy or food for organisms that rely on it. Because of the increasing demand for packaging as the global population expands, from the perspective of renewability it is also important to consider materials that can be degraded at rates higher than disposal rates to maintain a feasible cycle of replenished packaging material. This aspect directs to material performance and may well be an engineering challenge for biopolymer-synthetic material optimization. Material competency may have a direct or indirect relationship among parameters of surface modifiability, processability, and by-product degradation with overall efficiency and utility in packaging applications. For example, surface modification to provide rigidity to the nanocellulose framework for utility as a plastic may have implications at the biosynthetic interface in biosynthetic polymer blends. Structural and chemical synergy of nanocellulose as part of a blend can result in stiffness, strength, ductility, and toughness (Mautner et al. 2018) and depolymerization is a trade-off between mechanically strong plastics and biosynthetics resisting biodriven degradation. Figure 4 shows nanocellulose composed of unit size structural elements which form covalent bonds and extend into nanodimensional fibers. The large molecular weight can hinder the control of the biopolymer which is largely influenced by viscosity, hydrophobicity, and aggregation. The utility from a commercial point of view is very limited particularly if biopolymers suffer from fragility and brittleness and poor mechanical properties. Enhancement in the surface area facilitated by nanoscale dimensions provides heightened exposure and opens considerable opportunities for interaction with the surroundings. The intrinsic properties of the biopolymer strands can thereby be tailored to desired outcomes with a host of different materials and their blends.

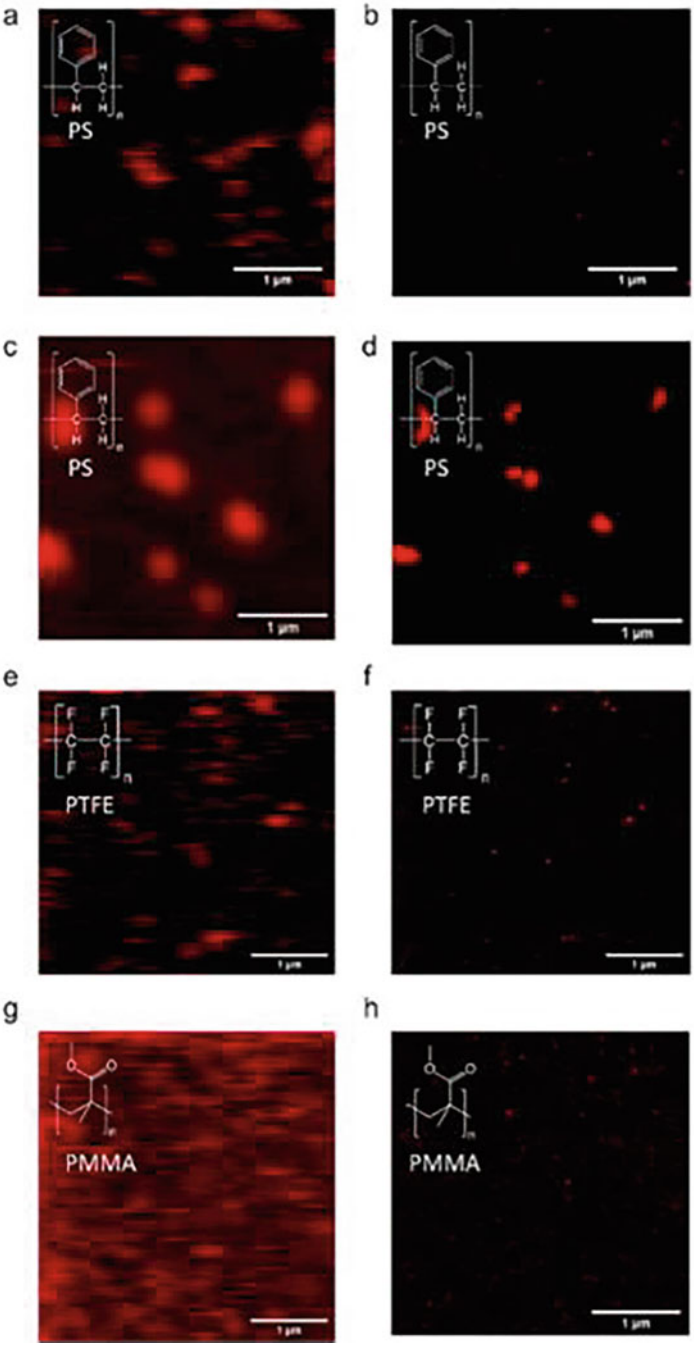

Fig. 4 Fluorescently labeled of differently categorized nanoplastics using confocal (LHS)-stimulated emission depletion (STED) microscopy. (Reproduced with permission from (Nguyen and Tufenkji 2021). This work is licensed under a Creative Commons Attribution 4.0 International [CC BY 4.0])

A Brief Look at Degradation from a Biopolymer Bonding Perspective

Since nanocellulose is a biopolymer, its origins like all polymers such as polypeptides (proteins) and polynucleotides (RNA and DNA) are embedded in biological chemistry as it exists as a polysaccharide (chained sugars) linked by β-1,4-linked d-glucose units. This suggests that such polymers are intrinsically adapted to fold and minimise degradation unlike linear native conformations that more readily degrade in aqueous environments (Runnels et al. 2018). Interestingly Runners et al., describe the resistance to degradation of biopolymers as a possible mechanism operated through "kinetic trapping" of nonequilibrium states favored by folded assemblies. From the perspective of employing nanocellulose for biodegradable packaging, it would therefore be strategically essential to ensure folding states of biopolymers of this type are still accessible to degradation by microbial communities by preventing misfolding under aqueous conditions and that properly formed "transition states" are recognized by enzymes for degradation to occur through accelerated hydrolysis. It should therefore be a primary goal to develop new technologies that reduce the persistence of nondegradable states during processability of the bioplastic. Hence, the linkage stereochemistry and fiber elongation signified by the β- versus α-anomer states of biopolymerization is essential to its biocongruence bearing structural complementarity to enzyme active sites also engaged in reversing polymerization. Figure 5 describes the self-complimentary behavior that extends to all biopolymers (but illustrated by cellulose). Here, the network of hydrogen bond donors and acceptors ascribe to an important role that does not only result in precise alignment of the multilayer structures but also the chemical space generated within polysaccharides through linkage chemistry. Occupation of the chemical space by plasticizers and compatibilizers often have profound effects on both physical and chemical properties affecting the entire structure in the blend. Biopolymer properties

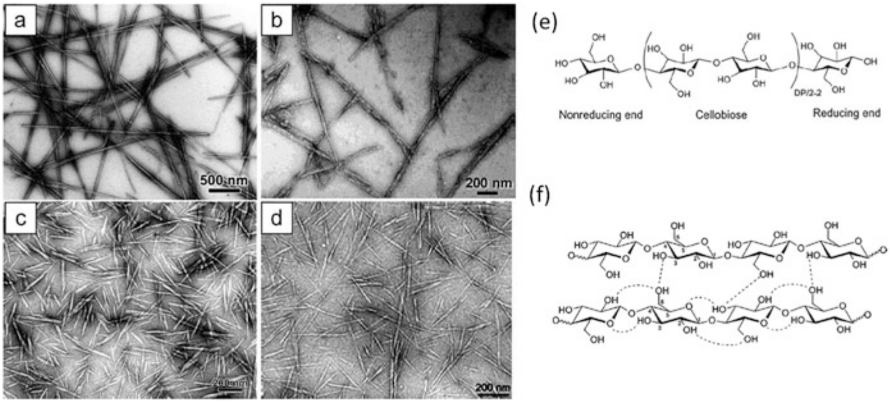

Fig. 5 A TEM representation of images of nanocellulose nanocrystals obtained from (**a**) tunicate, (**b**) bacterial, (**c**) ramie, and (**d**) sisal. (**e**) Molecular assembly of cellulose chains. (**f**) Hydrogen bonding in nanocellulose with water molecules. (**a**–**e**) Reproduced with permission from (Qiu and Hu 2013) (**f**) Reproduced with permission from (Pinkert et al. 2009)

of cellulose at the submicroscale has been the focus of attention in numerous works and more relevance to the macroscale properties in correlation to chain dynamics of monomers has been lacking. Local flexibility, for example, is fundamental to identifying how unit scale behavior drives collective behavior at the macroscale where ultimately their utilization in applications will rely on a globalized structure. Structure-property relationships, however, are useful for predicting outcomes and can guide polymer engineers to more precisely tune materials in mapping three dimensions with biopolymer function. Scanning tunneling microscopy and electrospray ion-beam deposition have been particularly useful in this regard in correlating levels of hierarchical structure in terms of sequence and chain confirmation of the biopolymer chain of cellulose with local flexibility. In a recent study using cellulose as a model (Anggara et al. 2021), changes to the primary structure through substitutions that affect intermolecular hydrogen bonding provided a series of architypes to investigate chain flexibility, molecular conformation, and local secondary structure. The changes to the unmodified cellohexaose represented by [AAAAAA] as the native structure constituted substitutions defined by [ABAABA], [ACAACA], [ADAADA], and [AFAAFA] where A is Glc, B is Glc methylated at OH(3), C is Glc methylated at OH(3) and OH(6), D is Glc carboxymethylated at OH(3), and F is Glc deoxyfluorinated at C(3). Figure 6 demonstrates that the sugar chains for the

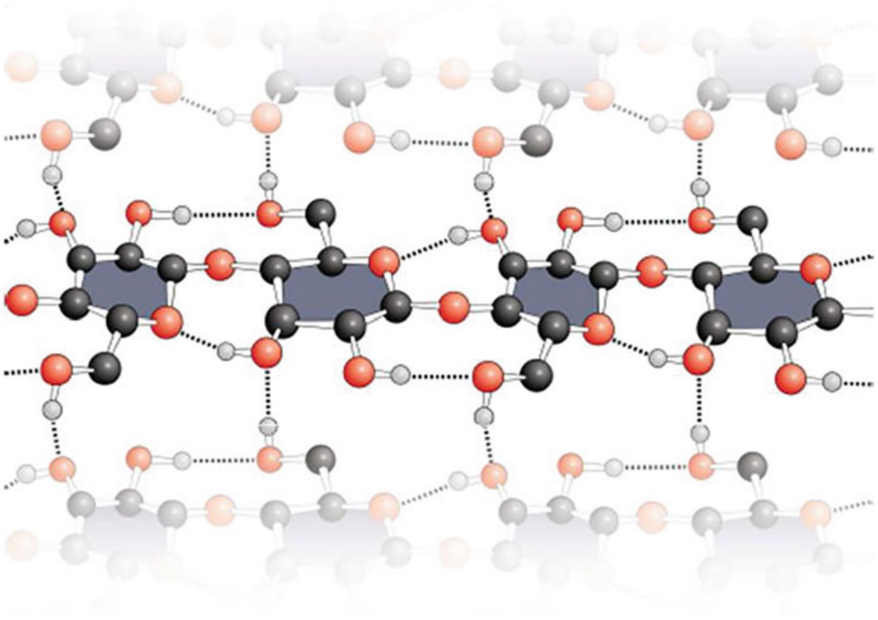

Fig. 6 A schematic illustrating the stability of cellulose by the hydrogen bond donor-acceptor network of complementary units which polymerize along theβ (1–4) directional folding path. (Reproduced with permission from (Runnels et al. 2018). This work is licensed under a Creative Commons Attribution 4.0 International (CC BY 4.0))

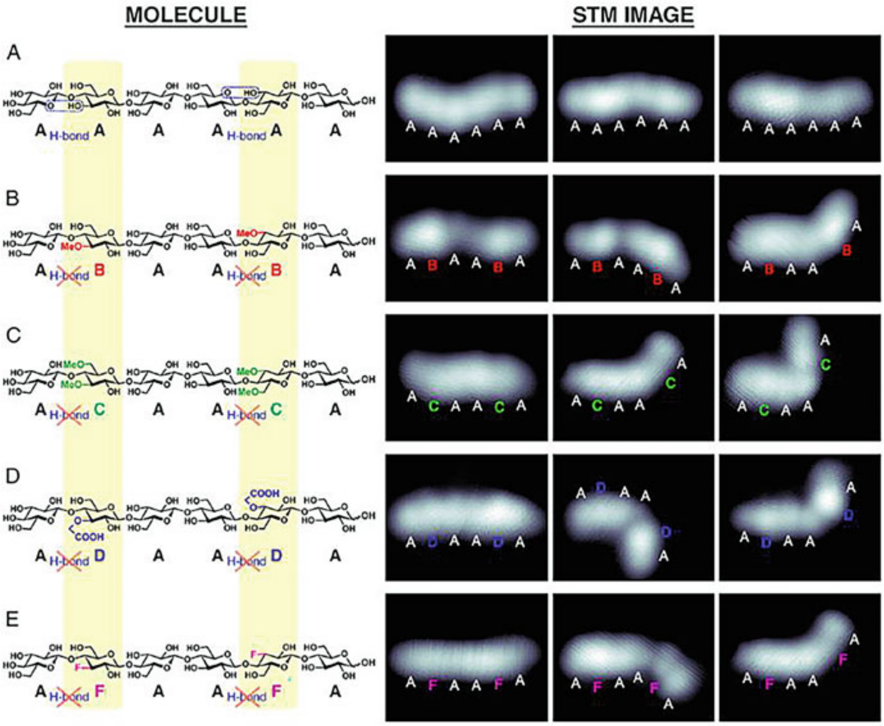

Fig. 7 Native and modified cellohexaose imaged by scanning tunneling microscopy (STM) showing the effect of substitutions on chain flexibility conforming to structures A, B, C, D, E, and F. Taken from (Anggara et al. 2021). This work is licensed under a Creative Commons Attribution 4.0 International License

native structure is linear and the modified chains are more flexible as they can adopt both straight and bent geometries. The conformation of the chain is defined by structural association between adjacent sugars with respective to their relative geometries. Figure 7 shows twisted and untwisted chains and its importance to the degree of chain flexibility. The corresponding angle measurements (Fig. 7, B, C and D) differentiate between H and V states of the Glc sugar separated by height of the ring either in a parallel or perpendicular orientation to the surface with respective H and V. The twisted linkages were determined to exhibit greater chain flexibility compared to untwisted chains. Twisting directly diminishes the interaction between adjacent Glc units and increases flexibility. The freedom to bend results from the exclusion of intermolecular hydrogen bonds and stresses the importance of extrinsic chemical factors that have the potential to alter the folding patterns of biopolymers affecting their ability to resist or enhance aggregation and interaction with key molecules like water. The study also revealed that mechanical parameters like stiffness is likely a consequence of modifications to intramolecular interactions and less influenced by surface-to-surface interactions.

Functional Group Similarity and Dissimilarity Between Synthetics and Biodegradable Polymers

The highly abundant hydroxyl moiety [OH-C-] pronounced within the group chemistry of nanocelluloses positions this material as one of the most natural and easily biologically accessible functional group structures on the planet. It is not surprising that this single structural feature that is an integral part of the unique assembly of nanocelluloses appears to be commonly shared among natural product functional group repertoire displayed in Fig. 10. The overall polymer reactivity is connected to surface hydroxyl groups and their relative positions largely determine the biopolymer characteristics.

Since functional group in polymers renders them degradable or nondegradable and is the chemical epicenter of the polymer, it may be meaningful to correlate the occurrence of functional groups characteristic of its nature. It may be important to understand the chemical properties of semisynthetic polymer as a result of a blend with unknown behavioral properties. Dominant functional groups become important to the identity of a complex blend and so much can be inferred about the overall chemical nature of the material and behavior. Identifying patterns of behavior through molecular structure analysis using analytical approaches can also be supported by cheminformatics (Ertl 2017) and machine learning (Nalla et al. 2018) routes. Cheminformatics has been insightful in highlighting differences in the distribution function groups in natural systems in comparison to synthetic ones. In a recent computational study designed to identify differences in functional group occurrence, alcohol hydroxy group (61.1%), alkenes (39.9%), ethers (35.2%), esters (28.7%), and phenolic hydroxy group (28.4%) feature most commonly (given by the frequency percentage in the parenthesis) and the corresponding structures are shown in Fig. 8 (Ertl and Schuhmann 2019). It is not surprising that oxygen is the dominant atom that forms a part of the hydrocarbon structural backbone and is well aligned to

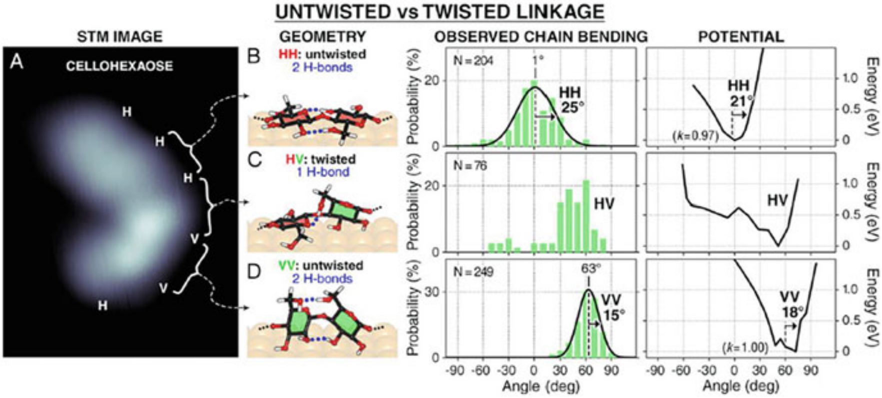

Fig. 8 (A) Cellohexaose showing two types of AA linkages, untwisted (HH and VV) and twisted (HV and VH). Corresponding bending angles and the computed potential curve are shown in B for HH, C for HV, and D for VV. Taken from (Anggara et al. 2021). This work is licensed under a Creative Commons Attribution 4.0 International License

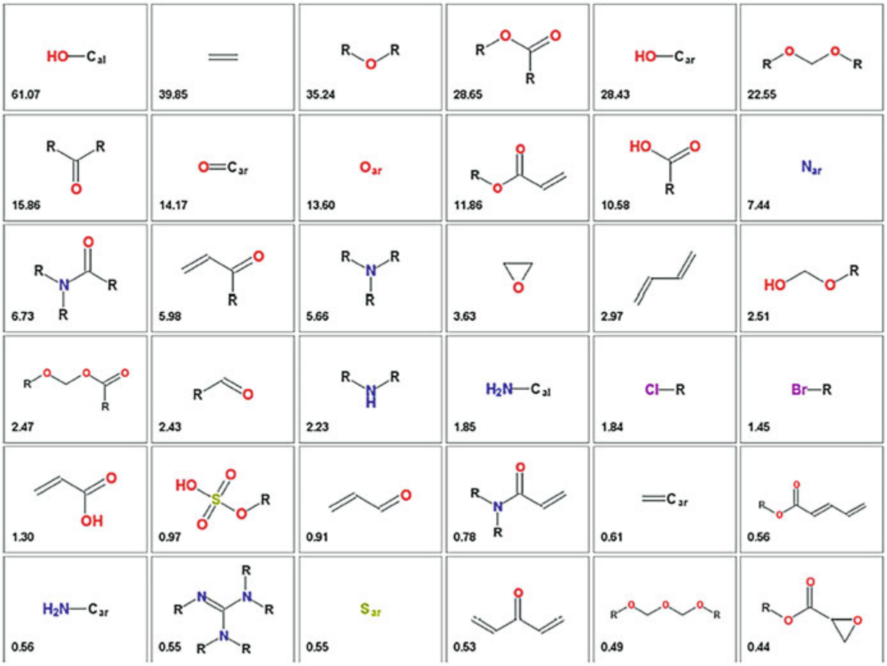

Fig. 9 The most prevalent functional groups found in nature. (Reprinted with permission from [Ertl and Schuhmann 2019]. Copyright [2019] American Chemical Society)

enzyme active sites of biodegrading enzymes. This signifies that preoxidation of synthetic plastics is a necessary perquisite to their biological degradation and the inclusion of oxygen likely reduces the energetic barrier relative to nitrogen bonds. Of greater relevance to assess the extent of the dissimilarity between natural and synthetic functional plastics is presented by Fig. 9 which highlights the distribution of the most frequently identified chemical functional groups. The plot reflects the diverse distribution of biodegradable functional materials that are of value in the microorganism food chain as natural substrate polymers while others are allied to the synthetic type. It can be reasoned that microbes show preference for biodegradable polymers which fall in the region of functional groups circled in Fig. 5. Polyethylene and polypropylene, for example, show a strong carbon-hydrogen backbone and are not readily degradable due to major differences in the functional groups that define characteristics and behavior. Polyethylene terephthalate, for example, also show different competency to biodegradability that reflects the variation in the functional groups and enzyme accessibility to the structure is made possible through exposure to UV light by photooxidation or hydrolysis. For synthetic polymers, functional group accessibility is followed by depolymerization. Table 1 summarizes the mode of trigger applied to different PEs and the functional groups isolated were identified. In the microbial environment, increased carbonyl index was observed during the biodegradation of LDPE over a

Table 1 Summary of functional group types after triggered degradation

Degradation trigger	Functional group	Category of polyethylene
UV	Aldehydes, Ester	HDPE, LDPE, and LLDPE
	Ketones	
Xenon	Carbonyl	LLDPE
	Acid	
Electron beam and gamma	Ester, ketone	HDPE
Photooxidation Thermo-oxidation	Esters and lactones Ketones and acids	PE with vinyl and t-vinylene groups
Accelerated environmental conditions	Aldehydes, ketones	LDPE and LLDPE
Environment	Esters	Environmentally beached PE pellets
	Ketones	
Natural	Ketones and acids Carbonyl	HDPE

Adapted from (Fotopoulou and Karapanagioti 2017)

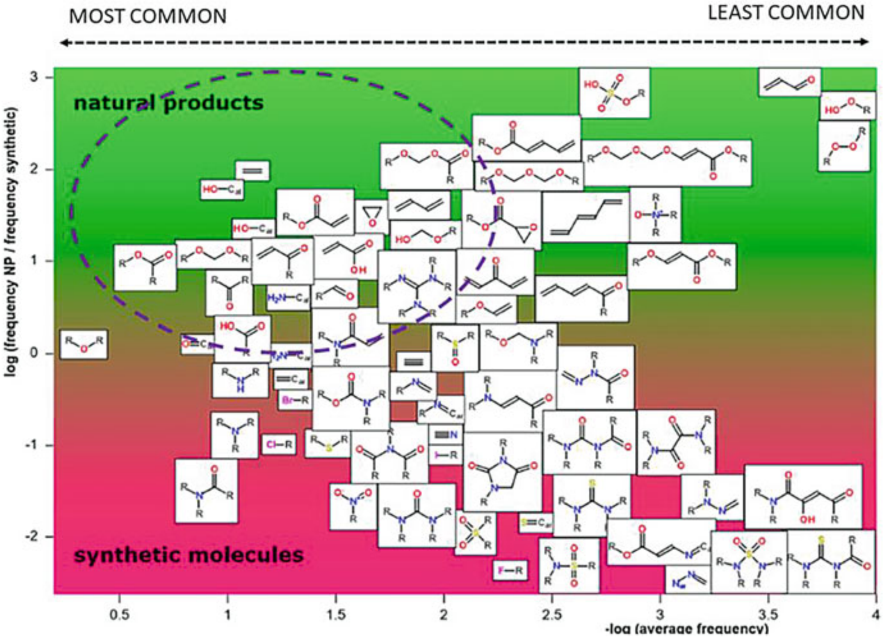

Fig. 10 Distribution of functional groups in relation to frequency of occurrence and their propensity toward natural (green) or synthetic (red). (Reprinted with permission from (Ertl and Schuhmann 2019). Copyright (2019) American Chemical Society)

period of years with weight loss. Under accelerated growth, carbonyl products are also formed resulting from increased surface cracks and increased fragility during the timescale of the exposure period (Fotopoulou and Karapanagioti 2017) (Fig. 10).

Formulating Bioplastics: Considering Pre/Post-Extraction Phase of Nanocellulose

The purpose of bioplastics is one that drives an environmental goal but also attains to an economic one which while satisfying the greener concepts of sustainability, renewability, and biodegradability of eco-bioplastics can replace synthetic plastics without incurring a cost burden against the cheaper alternative to conventional plastics. International standards for biodegradation for environmentally degradable plastics and biobased products sets performance standards which must be met to categorize bioplastics as environmentally acceptable (ASTM D6954 2013). While CO_2 and evolution methane (CH4) are the important measurement criteria from biodegradation, oxygen consumption has also been suggested to be important for aerobic biodegradation (De Wilde 2012). Currently, bioplastics are in the infancy of development despite the considerable research-based publications which point to considerable potential to formularize a truly biodegradable bioplastic of wide applicability. In this direction, nanocellulose is a popular target and example of the scope of blended products as semisynthetics. The prospects of using a naturally occurring biopolymer as a base material for sustainability while introducing strategically informed modifications to improve performance plastic replacements in an economic way are already underway. Currently, semisynthetics resembling bioplastics for packaging (Ibrahim et al. 2021) have their origins in biopolymers which are subjected to modification by chemical processes via abiotic routes (Ganie et al. 2021). Figure 11 emphasizes some of the performance outcomes the future envisages from technologically engineered bioplastics.

Nanoscale cellulose exists as cellulosic nanofibrils (CNFs) and cellulosic nanocrystals (CNCs) and these forms typify nanocellulose and are extractable by a combination of physical (e.g., mechanical homogenization) and chemical treatments (e.g., acid hydrolysis) (Phanthong et al. 2018). Acid hydrolysis can affect the hydrogen bond network and has been inferred to cleave on intramolecular hydrogen bonds at the macromolecular level on the O(3)H···O(5) bonds (Li et al. 2021). Morphological analysis also reveals bond breaking and bond reordering was

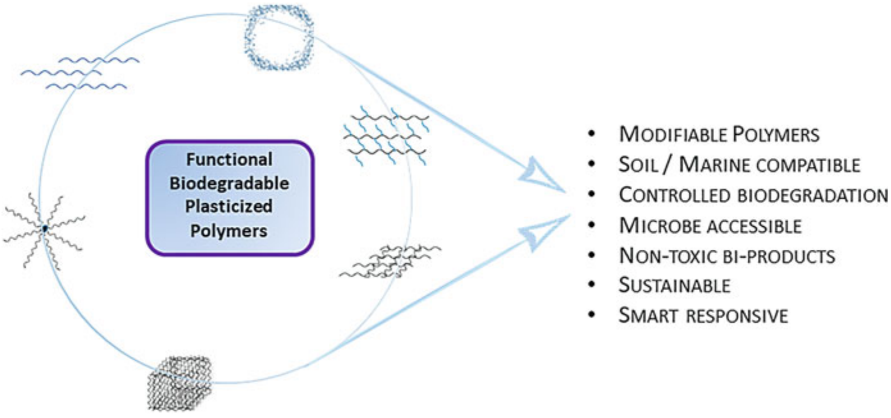

Fig. 11 A schematic summary relating different biodegradable polymers

Table 2 Relationship between nanocellulose type and dimensional size

Natural fibers/Plants	Type of nanocellulose	Dimensions of extracted nanocellulose	
		Length	Diameter
Eucalyptus pulp	CNC	150 nm	10–50
Pinecone	CNF	–	5–20
Soybean straw	CNF, CNC	>1 μm	10
Hyacinth fiber (*Eichhornia crassipes*)	CNC	147.4 nm	15.6
Pineapple leaf fiber	NC	<(88–1100) nm	68
Rice hull	CNF	–	<100
Banana rachis, kapok, pineapple leaf, and coir	CNF	–	10–25
Oil palm trunk	CNF	170–800 nm	4–10
Bamboo	CNC	–	50–100
Waste paper	CNC	100–300 nm	3–10
Banana peels	CNF	455 nm	10.9
Palm residue	Coir NC	–	108
	Fronds NC	–	90
Coir fiber	CNF	–	37.8
Jute fiber	CNF	–	50
Beer industrial residues	NC	–	73–145
Coconut residues	CNF	–	70–120
Silkworm silk fiber	CNF	–	0.1–0.4
Flax	CNC	57 nm	6
Cotton	CNC	68 nm	8

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accompanied by reduction in size. This change relates to the opening of the glyosidic bond which provides opportunities for reordering. Ultrastructural differences among nanocelluloses can indeed affect susceptibility by acids (Palme et al. 2016). A high variability in structural dimensions and shape and size can result from the source of the biopolymer and pretreatment methods used for extraction which affect yield, crystallinity, and can potentially tailor desired morphological, surface chemistry, and numerous physicochemical outcomes governed by methodology employed. Table 2 shows that the dimensional size of extracted nanocelluloses is largely source dependent (Khalid et al. 2021). Hence, chemical and mechanical processes can introduce profound changes to the structural properties of the biopolymer through pre- and posttreatment regimes which at the molecular level interfere with the inter- and intramolecular bonding (Fig. 12). It is necessary to understand the implications and consequences of these alterations before using nanocelluloses from different sources due to the broad variability in properties. For example, the crystal packing and the degree of crystallinity or amorphicity can comprise the integrity of the nanocellulose structure if penetrating water molecules can enter the chemical spacing between adjacent units and compete for bonds and thus reducing mechanical properties.

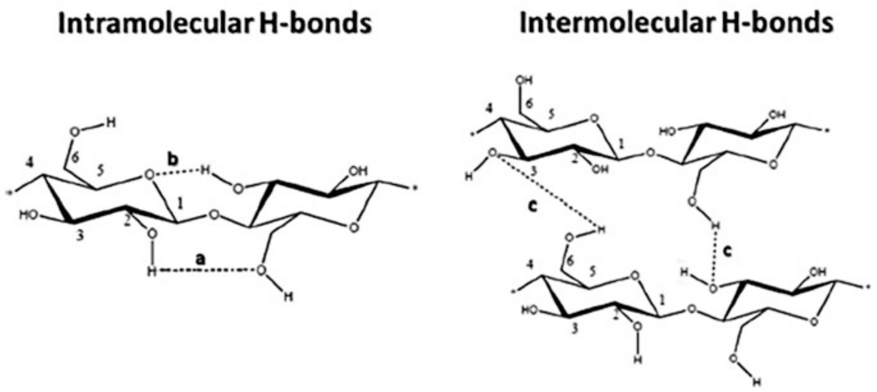
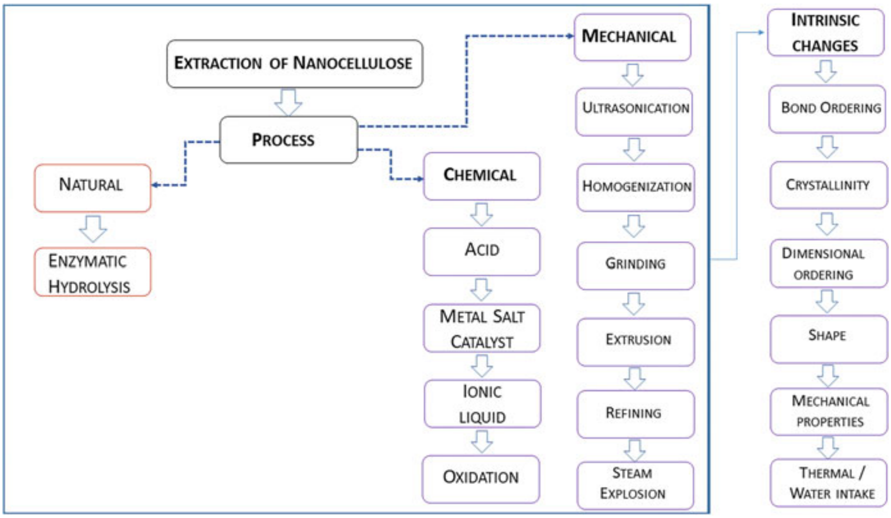


Fig. 12 Structural arrangement of intra- and intermolecular bonding in cellulose. Reproduced from the thesis entitled "Interfacial Forces in Nanocellulose-Based Composite Materials" (Olszewska 2013)

However, in well-dispersed reinforced polymer nanocomposites, cohesive interaction between nanocellulose crystals offer less resistance to degradation by solvents and thus highlights the understanding of cohesive particle–particle interactions (Reid et al. 2016) and meets the design for bioplastic packaging. Blending with other materials may affect the nature and magnitude of forces such as van der Waals, hydrophobic, hydrodynamic, electrostatic (between layers), repulsive, and steric forces. The current challenge is to find a structural and functional balance of material combinations that are mutually synergistic with each other (Scheme 1).



Scheme 1 Extraction processes for nanocellulose and the effect of intrinsic changes induced by external processes. (Adapted with permission from [Khalid et al. 2021]. This work is licensed under a Creative Commons Attribution 4.0 International [CC BY 4.0].)

Considerations of Nanocellulose from Natures Perspective: Future Implications for the "Brittleness" Problem for Biodegradable Bioplastics

Much of the research for nanocellulosic materials has been devoted to engineer strategies for modification of the biopolymer surface with synthetic materials as blends. Such studies for packaging applications (Abdul Khalil et al. 2016) have centered on reinforcement for enhancing compatibility (Wang et al. 2021), dispersion (Chu et al. 2020), interfacial adhesion (Wolf et al. 2013), processability (Souza et al. 2020), stability (Santmartí and Lee 2018), moisture resistance (Cherpinski et al. 2018), and tensile strength to improve mechanical properties (Talebi et al. 2022). Some studies have escalated to provide active and intelligent functionality and smarter nanocellulose materials (Heise et al. 2021) including sensing (Fuertes et al. 2016) toward more innovative packaging. However, there has been little discussion focusing on using nanocellulose for biomimetic composites. Much of the emphasis has been to find reinforcements for nanocellulose as a biosynthetic composite to solve issues of fragility particularly in its interaction with water.

In nature, nanocellulose relies on its hierarchical existence to achieve many of the above properties that would readily endorse its use as a packaging material. This suggests that clues to mechanical optimization lie within the hierarchical makeup of the biopolymer. A very small body of knowledge has emerged that is pointing to improve our knowledge of structure and function which nature has inherently designed to be more adaptive than rigid. This could be taken to support the notion that natural materials may succumb to stress imposed upon them by the environment, but such stresses seldom destroy the material in its entirety or irreversibly. In contrary, mechanical and chemical processes can impose considerable stresses through deformation or fracture which primarily leads to bond loss.

Only under extreme deformation, irreversible disintegration can occur. Hierarchical cooperation from the nano- to macroscale exists and require further appreciation. It is plausible to say that an understanding of material hierarchy is not understood such that the mechanical deformation at one scale due to hidden interconnections can affect the properties at other scales in the same material. Under bearable loads, biopolymers are capable of adjusting material responses that allow multimechanisms to operate which defines the robustness of a material. In this respect, studies that relate chemical bonding networks of natural structures and mechanical properties offer greater potential for new technological outcomes.

Bioinspired Biopolymer Synergy

Reduced toughness is a potential technological flaw in applying nanocelluloses for long-term applications in packaging for durability. This weakness is characteristically attributed to the lack of deformation – the mechanisms of which are still largely unaccounted for at the molecular level. Needless to say, attention has been given to improving the mechanics of the biopolymer in the form of composites with numerous synthetic molecules that bear many of the desirable mechanical properties biopolymer fall short on. The delicate balance between toughness and biodegradability is viewed as a critical setback of structure-function relationships. Lessens in sustainability of biopolymers rest in understanding how mechanisms unfold under normal environmental conditions through the use of structure-sensitive tools which could better inform researchers of the behavioral aspects of nanocelluloses.

Surface cross-linking of nanocellulose takes advantage of the abundant hydroxyl group moieties inherent to its structure. The prevalence of hydroxyl groups in nature demonstrated by the functional propensity and frequency plot of Fig. 10 predicts that the probable deviation from its assigned role in nature might drastically reduce nature's ability to degrade the biosynthetic blend. This is particularly true if nitrogen-containing synthetics are blended within the nanocellulose structure as judged by the functional group content of plot 10. Consideration between physical- and chemical-based cross-linking of hydroxyl groups also give rise to concerns over "stronger" versus "weaker" arguments and implications of bond strength in resulting blends. In recent times, it has been righty recognized that the surface interactions of nanocelluloses are far from trivial. This is certainly true of water vapor adsorption at the amorphous/crystalline interface that exists as a 1 nm layer (Niinivaara et al. 2015) and the availability of hydroxyl groups can affect its ability to swell to control permeability which may affect its use technologically (Capron et al. 2017).

Poor moisture resistance of nanocellulose is perceived to be major barrier to technologically advancing in the area of packaging and related areas (Cherpinski et al. 2018) and the sensitivity to humidity is professed to an unresolved issue. The persistence of humidity in the environment has a tendency to drive deformation and induce a loss of mechanical stability. Often, the material complexity of nanocellulose blended materials circumvent a better understanding of the accurate nature of the interaction of water vapor in the surroundings with the molecular intricacies residing in the biopolymer structure itself. In hindsight, the mediated effects of moisture are elusive in the midst of reported observations that support the role of water as a plasticizer (Mittal et al. 2018). The computational study revealed that while the presence of intercalated water molecules could be unfavorable universally for the global performance, a considerable change in shear modulus fits in with its bio-inherent ability of hierarchical fiber networks to respond to changes in the vapor content of the environment in the same way as a fabricated sensor might. In Fig. 13, simulation trajectories predict the molecular importance of water molecules (Chami Khazraji and Robert 2013) by forming associations termed "capillary bridges" at the nanocellulose interface and serve to increase the fracture energy by

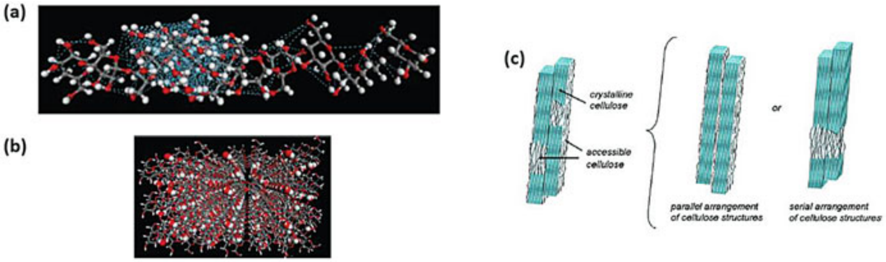


Fig. 13 (**a**, **b**) Simulation of water molecules at the cellulose nanocrystal interface showing preferential contact between water molecules. (**a**, **b**) Taken from (Chami Khazraji and Robert 2013) (**c**) (Salmén and Bergström 2009).

acting to increase the interface prior to failure. Further, strain force has grater toleration under moist conditions compared to dry ones and a parallel-type arrangement of water molecules could be conducive to load-bearing operations (Salmén and Bergström 2009). This suggests water has a bigger role to play.

Greater relevance might come from deciphering the hydrogen bond network with interconnections to water molecules with the aim of predicting more precisely the role of water molecules under differing atomical arrangements. This scenario should reflect the completion for CNC binding sites that likely occur between CNC and water molecules. To this effect, with increased accessibility of water molecules, the study considers that under conditions of humidity, CNC−CNC bonds are intercepted by water molecules and rearrange to a water intercalated arrangement, CNC−water−CNC. A combination of multiscale simulations and experiments were applied to investigate differences between hydrogen (HBs), CNC−CNC (nanocellulose), and CNC−water−CNC bonding arrangements under variably defined conditions for humidity at the interfaces. The study is insightful in that it provides a relative percentage of humidity which is correlated to monitor changes in the mechanical properties mapped for all three bonding arrangements. The main findings of the study signify the formation of a denser hydrogen-bonded network for CNC−water−CNC and MD simulations and surprisingly strain-stress profiles comply with strain reinforcement applying to both tensile stress and the strain at break. Relative humidity (RH) falling in the range $30\% \leq \text{RH} \geq 50\%$ reveals the relative condition for the strain hardening phase which is lost to a weaker modulus and interfacial strength when $\text{RH} \geq 60\%$ resulting from a higher accumulation of water (Hou et al. 2021). Hence, depending on the conditions, the water-intercalated nanocellulose interface can switch between a mechanically strong and weak interface by adjusting to the environmental conditions in sensory fashion. Figure 14 shows the tensile stress curves and number of bonds as a function of water, and Fig. 15 shows tensile stress curves, tensile stress as a function of relative humidity profiles, and SEM images of fracture morphologies under variable conditions of humidity. Hence, self-modulation of mechanical properties in response to conditions of stress and strain hierarchy in nanocellulose has a multifunctional role that reaches far beyond the confines of structure.

Stress transfer between two different interacting components can serve a useful purpose for enhancing mechanical strength. Almost universally, strength increase is achieved at the cost of strain and toughness which is true for most nanocomposites. However, this mutually exclusive relationship is contradicted by increases in strength, elongation, and toughness. With brittleness as a primary problem of nanocelluloses, bioinspired strategies have proven to generate remarkable results for high-performance nanocellulose-based materials. In one study, a combination of two biopolymers comprising bacterial cellulose nanofibers (BC) and alginate were combined into a bioinspired hierarchical helical shape. The hydroxyl moieties of BC were readily accessible to the anionic polysaccharide carboxylate groups of alginates via a single capillary wet extrusion process in the presence of an aqueous $CaCl_2$ bath under a shear force and combined together under a wet twisted motion. The simultaneous accompaniment of all the three mechanical parameters of strength,

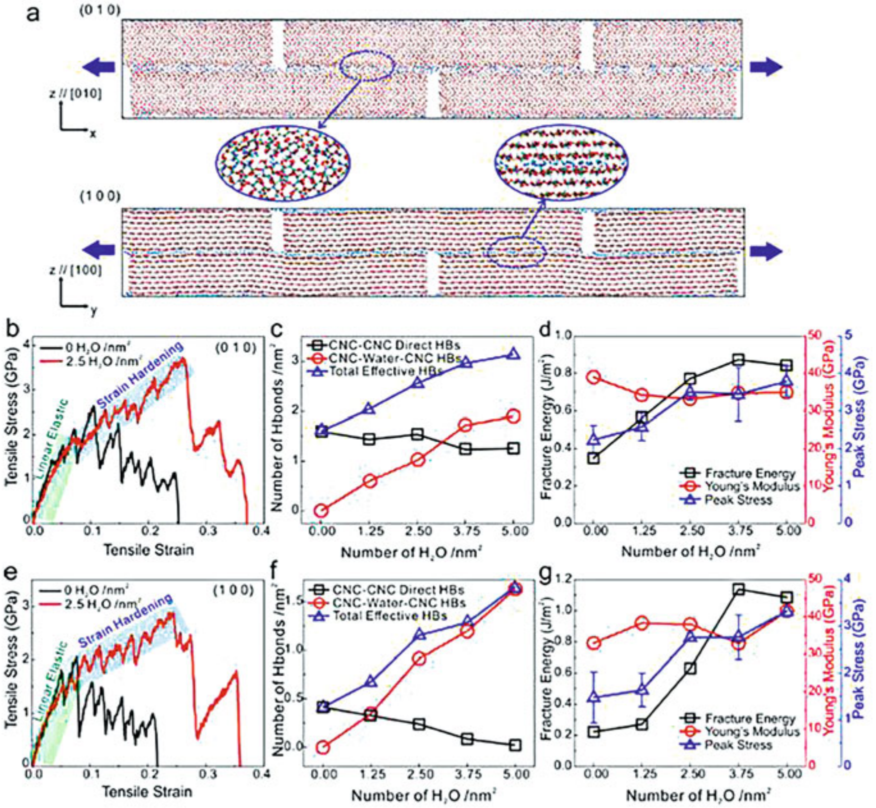


Fig. 14 (**a**) Humidity-mediated interface mechanical models, (**b**–**d**) tensile stress curves, number density of hydrogen bonds (**e**–**g**) profiles using the nanocellulose as a model. Blue/Green areas denote elastic stage and hardening stages during tensile process. (Reprinted with permission from (Hou et al. 2021). Copyright (2021) American Chemical Society)

elongation, and toughness were also achieved with increase of 50 and 100% under variable conditions of relative humidity resulting from the twisted synergy of fibers. In contrast, untwisted nanocomposites in their dry states with considerable loss of water experienced inferior mechanical properties compared to the wet gel filaments (Gao et al. 2020). Figure 16 summarizes the fabrication of twisted morphologies of BC-Alg accompanied (a) by TEM and AFM images with height profiling (b-d) and the extrusion of hierarchical structures. Figure 17 summarizes the mechanical properties of BC-Alg morphologies in terms of their stress-strain, tensile strength, and toughness.

Concluding Comments

There is a slow but steady rise toward the development of biodegradable materials while researchers and technologists aim to re-formularize the way we create, utilize, and dispose of plastics. Hence, investment growth in new technologies and

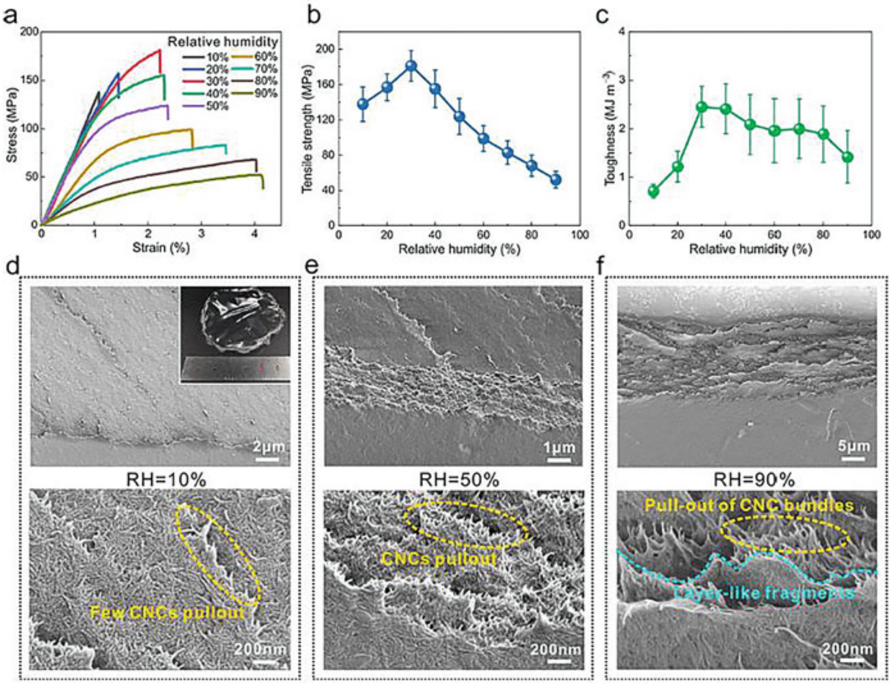


Fig. 15 (**a**) Tensile stress curve of CNC with 10–90% RH range. (**b**) Tensile strength measured as a function of RH, (**c**) toughness as a function of RH, and (**d**–**f**) SEM images showing morphology of fractures experimentally obtained under 10%, 59%, and 90% RH, and (**d**) prepared CNC film. (Reproduced with permission from (Hou et al. 2021). Copyright (2021) American Chemical Society.)

innovative tools is elemental to material renewability and sustainability to visualize a new industry *in* bioplastics. However, till the present day, the situation still remains largely unchanged in implementing safeguarding strategies against accumulating plastics which are energy demanding and may not be applicable in handling highly toxic plastics like polyvinylchloride (PVC). Thus, rethinking the approach to plastic packaging has become a conceptual challenge from design to recyclability of by-products to reduce the carbon print. To strive for a carbon-free world as it relates to nondegradable packaging is unrealistic but the passage back to carbon neutrality necessarily means a bigger commitment to synchronize materials with nature. The conceptuality of this idea is being developed by adapting nonbiodegradable materials or their composites to resemble structurally and behaviorally natural polymers.

Nanocelluloses lie at intersection of bio- and synthetic polymer engineering. As the number of biosynthetic nanocellulose composites reportedly increase year by year, there is small yet concerted effort to better understand structure-function correlations that reside within nanocelluloses. A greater understanding of structure

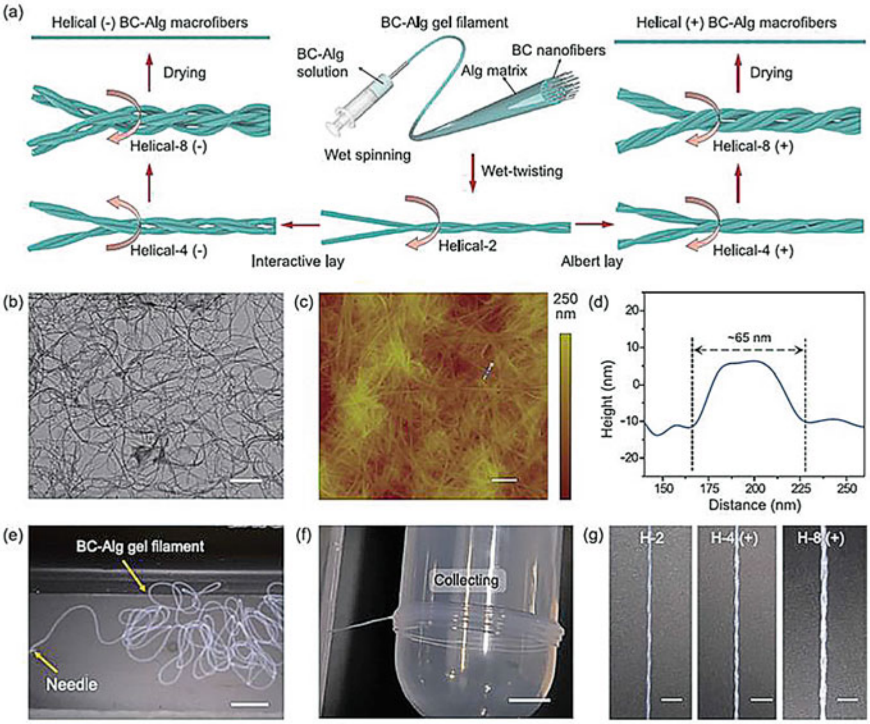


Fig. 16 (**a**) Fabrication of twisted bacterial cellulose alginate. (**b**) Transmission electron microscope images of BC nanofibers. (**c**, **d**) Atomic force microscope imaging and height profile of BC nanofibers. (**e**) BC-alginate gel image after its extrusion through the capillary in the $CaCl_2$ bath. (**f**) Image of a wind roller used for the continuous BC-Alg filament. (**g**) Twisted BC-Alg bundle following wet twisting at different hierarchical levels. (Reproduced with permission from (Gao et al. 2020). This work is licensed under a Creative Commons Attribution 4.0 International (CC BY 4.0))

in terms of bond connectivity across all hierarchical scales is key to elucidate performance-related mechanisms as a potential biodegradable material. An important area gaining attention relates to environmentally responsive structural changes that correlate to weak and strong mechanical performance. Switchable states that reflect mechanical performance of nanocelluloses is complex and requires an in-depth study to ascertain the intrinsic capabilities as a bioplastic. One emerging but insightful area has focused on the interfacial properties and behavior with water. A more extensive appreciation of the chemical and structural synergy with its environment and with other biopolymers could provide more effective solutions in challenging area of biodegradable plastics. To this end, the merger of natural resources and technology is imperative. Natural biodegradables offer considerable opportunity to leverage renewable technologies and related areas to improve plastic recyclability and cost reduction.

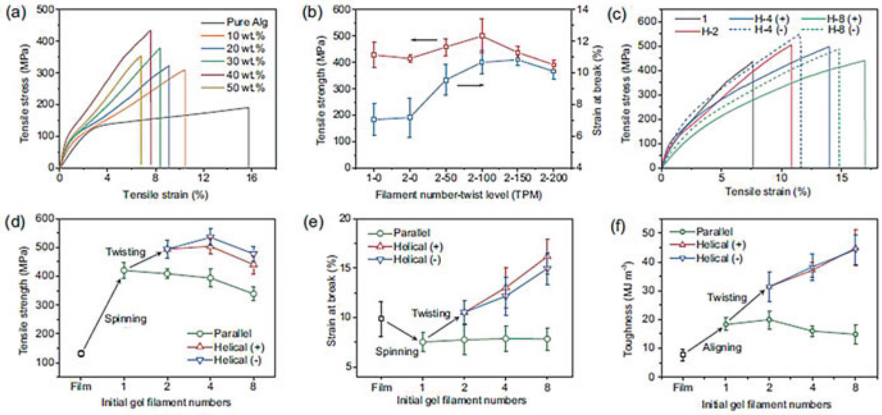


Fig. 17 (**a**) Stress-strain curves of dried single BC-Alg filaments of different compositions. (**b**) Tensile strength profiled against twist level of helical −two fibers. (**c**) Stress-strain curves exemplifying macrofibers of BC-Al hierarchical structures; (**d**–**f**) d showing the tensile strength at strain break shown in (**e**) and toughness in (**f**) as functions of hierarchical levels. (Reproduced with permission from (Gao et al. 2020). This work is licensed under a Creative Commons Attribution 4.0 International (CC BY 4.0))

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