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# Progress in Sustainable Polymers from Biological Matter

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## Keywords

sustainability, biological matter, biopolymers, biocomposites, cementitious materials, renewable resources

## Abstract

The increasing consumption of nonrenewable materials urgently calls for the design and fabrication of sustainable alternatives. New generations of materials should be derived from renewable sources, processed using environmentally friendly methods, and designed considering their full life cycle, especially their end-of-life fate. Here, we review recent advances in developing sustainable polymers from biological matter (biomatter), including progress in the extraction and utilization of bioderived monomers and polymers, as well as the emergence of polymers produced directly from unprocessed biomatter (entire cells or tissues). We also discuss applications of sustainable polymers in bioplastics, biocomposites, and cementitious biomaterials, with emphasis on relating their performance to underlying fundamental mechanisms. Finally, we provide a future outlook for sustainable material development, highlighting the need for more accurate and accessible tools for assessing life-cycle impacts and socioeconomic challenges as this field advances.



**Biomass:** renewable organic material from plants or animals, including individual extracted components thereof

**Biopolymer:** polymer synthesized from biological organisms

**Self-bonded polymeric material:** polymer that does not require an external binder to form a self-standing matrix

**Biomatter:** biomass synthesized by any living organism (plant, animal, bacterium, alga, fungus) that retains a degree of native, hierarchical organization

## 1. INTRODUCTION

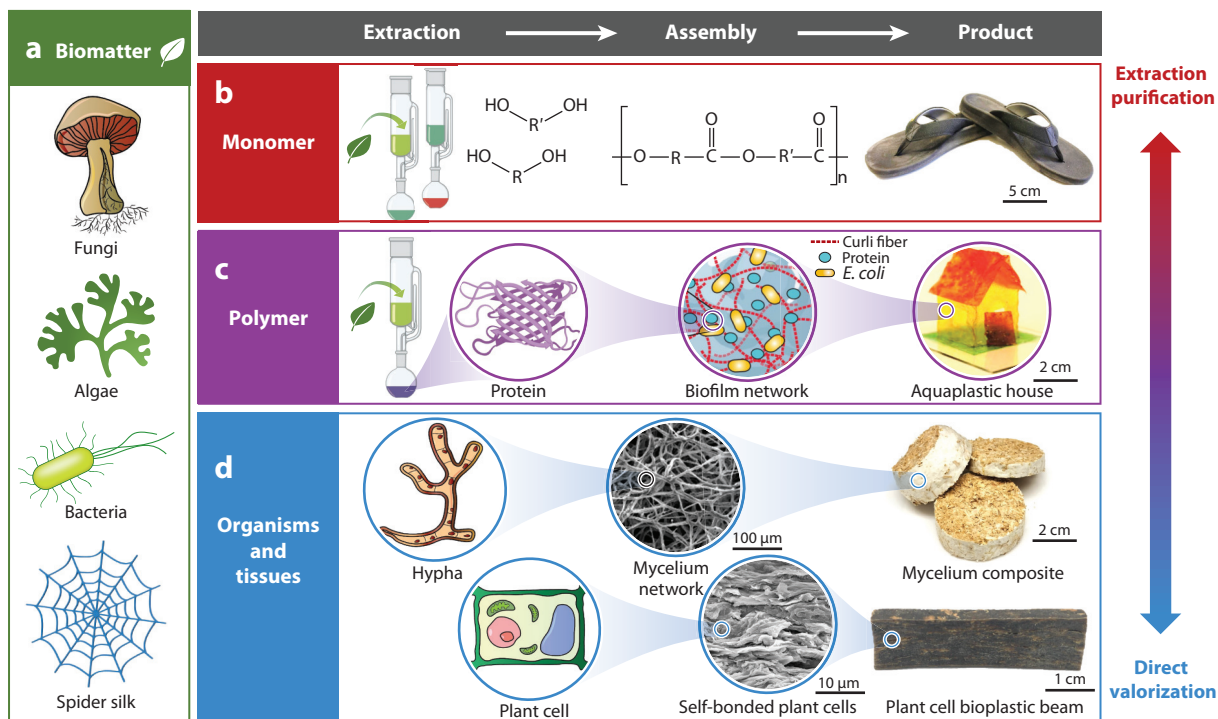
Since the beginning of large-scale production and use of plastics in the 1950s, approximately 8.3 billion tonnes (Bt) of pure plastics (not including fillers and additives) have been produced, from which 6.3 Bt are generated waste (1). Of this plastic waste, less than 10% has been recycled, approximately 12% has been incinerated, and almost 80% (~5 Bt) has accumulated in landfills or the natural environment. Plastics accumulated in the environment will represent 12 Bt by 2050 if current production and waste management trends continue unaltered (1), at which point the weight of plastic waste in the ocean will equal that of fish (2). The negative impacts of the proliferation of plastic waste in the natural environment are multifold, including acute trauma to animals upon ingestion as well as long-term hazards created by concentrating organic pollutants in the environment (2). These alarming data, along with the irreplaceable role played by plastics in our society and economy, motivate the development of sustainable polymers. This broad term includes new and existing macromolecules that are derived entirely or partially from renewable (nonfossil) feedstocks for the production of biodegradable or recyclable polymers (3). To supplant commodity polymers, sustainable polymers must combine performance and scalability (including source feedstock availability, cost efficiency, and ability to be processed with the existing plastics manufacturing infrastructure). In terms of mechanical properties, which are the primary performance metrics we focus on in this review, commodity plastics have an elastic modulus between 0.1 and 1 GPa, strength between 1 and 50 MPa, and elongation to break between 1% and 1,000%, while engineering and high-performance plastics have higher modulus and strength values, 1–10 GPa and 30–200 MPa, respectively, but are brittle, with elongation to break values below 10%.

Here, we provide an overview of current research efforts in creating polymers from renewable feedstocks, offering promising solutions to the ever-increasing pollution problem. We outline three distinct tracks, introduced in **Figure 1**, and present exciting findings that highlight the potential of each approach in providing sustainable polymer solutions addressing the sourcing and end-of-life issues simultaneously. First, we describe monomers derived from biomass or waste to produce existing or entirely novel polymers. Using well-developed polymerization reactions enables seamless integration of bioderived monomers in existing infrastructures, while the derived monomers can also serve as functional organic molecules for other synthetic materials. Next, we present advances in extracting and utilizing biopolymers as self-bonded polymeric materials or as components for synthetic polymers or inorganic structural materials. This approach utilizes the high-molecular-weight biopolymers as produced from organisms and often maintains their secondary or tertiary structure as a template for forming hierarchical materials. Finally, we review recent advances in using entire organisms in the form of cells or tissues as building blocks to create either self-bonded materials or novel composites. This approach can potentially lead to wasteless manufacturing (i.e., where no biomass is wasted) and can be built around local resource utilization and existing processing infrastructures. An example of this emerging approach is developing cell cultures locally as tunable material platforms that eliminate transportation needs, bypass unsustainable supply chains, and are independent of climate and land fertility.

## 2. FROM BIOMATTER-DERIVED MONOMERS TO SUSTAINABLE POLYMERS

Recent innovations in the chemical and enzymatic extraction and polymerization of monomers derived from biological matter (biomatter) and, specifically, from vegetal biomass, organic waste, and microorganisms have augmented the potential for biobased monomers to supplant petroleum-based equivalents (2) (**Figure 2a**). In this section, we discuss examples of abundant and versatile macromolecules of plant biomass such as carbohydrates, fatty acids, terpenes,





**Figure 1**

Research tracks to produce sustainable materials from renewable sources. (a) Examples of biomatter resources. (b) Extracting monomers to synthesize existing or entirely novel polymers. (c) Extracting biopolymers to create self-bonded or composite materials. (d) Using the entire organism as a polymer composite building block. The extraction needs and generated waste increase from bottom to top. Image of flip-flops in panel *b* adapted from Reference 4. Illustrations of extractions in panels *b* and *c* and image of protein structure in panel *c* adapted from images created with BioRender.com. Network illustration and image of the 3D aquaplastic house in panel *c* adapted with permission from Reference 5. Upper scanning electron microscopy snapshot in panel *d* adapted with permission from Reference 6. Image of plant cell bioplastic beam in panel *d* adapted with permission from Reference 7.

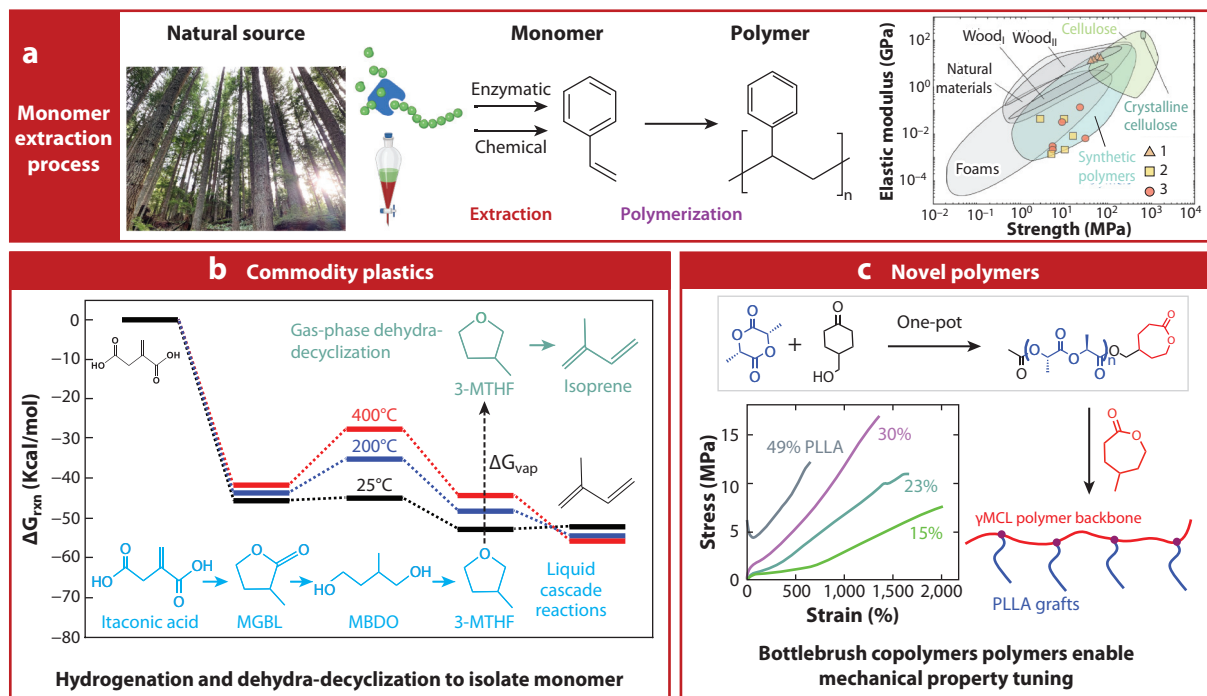
polyphenols, organic acids, and their derivatives, which are used as the principal renewable sources of high-value monomers.

One of the most important monomers for commodity plastics, ethylene, has been derived through the fermentation and dehydration of glucose, extracted from agricultural products such as sugarcane, and used commercially to produce bio-polyethylene (Bio-PE) since approximately 2010 (10). Other industrially significant olefin monomers have also been derived from fatty acids via the decarbonylation of carboxylic acids (11). By using common nickel salts to catalyze deoxygenation, John et al. (11) achieved up to 82% yield of olefins from fatty acids while reducing the number and rarity of reactants and eliminating the need for an acid-activating species. Abdelrahman et al. (8) similarly improved the yield of monomer extraction by hydrogenation and dehydracyclization of itaconic acid to isolate dienes and isoprene with a 72% selectivity (Figure 2b). While these techniques efficiently transform biosourced monomers into traditionally petroleum-derived polymers, they do not improve upon detrimental end-of-life environmental persistence.

Arguably one of the most industrially significant bioplastics in the world (12), polylactic acid (PLA), is obtained by the ring-opening polymerization of lactic acid monomers, which are produced through the fermentation of starch-rich biomass. Unlike commodity plastics such as Bio-PE, PLA can be degraded, albeit slowly, via synthetic hydrolysis of backbone ester groups

**Polyphenol:** biopolymer formed from aromatic phenolic networks

**Bioplastic:** polymer derived from biomass that, at some stage in its processing, can be shaped by flow



**Figure 2**

Monomer extraction and polymerization. (a) Visualization of chemical or enzymatic extraction of monomers from biomass to synthesize polymers and a graphical representation of their mechanical performance from the literature (triangles are from Reference 14, squares are from Reference 9, and circles are from Reference 13). Illustration of extraction adapted from BioRender.com. Ashby plot adapted with permission from Reference 7. (b) The energetic reaction pathway for the isolation of isoprene from itaconic acid and the 3-MTHF intermediate. Panel adapted with permission from Reference 8. (c) The variation in mechanical responses enabled by differing degrees of copolymerization of (red) poly( $\gamma$ MCL) and (blue) PLLA. Panel adapted with permission from Reference 9. Abbreviations: 3-MTHF, 3-methyl-tetrahydrofuran; MBDO, 2-methyl-1,4-butanediol; MGBL, methyl- $\gamma$ -butyrolactone; PLLA, poly(L-lactide).

(2). Other monomers have been isolated from biomass specifically to facilitate degradation, such as  $\beta$ -methyl- $\delta$ -valerolactone (MVL), which can be derived from sugar to produce thermoplastic polyurethane (PU), PU foams (13), and poly(MVL), which is depolymerizable at low temperatures, enabling the recovery and reuse of approximately 97% of the MVL monomer. Other recent examples include work from Manker et al. (14), who synthesized thermoplastic poly(alkylene xylosediglyoxylates) from lignocellulosic saccharides that are chemically recyclable and degradable via hydrolysis. Their results show that the degree of degradation depends on the diol molecule used in the polymerization. Shen et al. (15) promoted degradation by including acetal groups in the backbone of lignin-derived monomers. The resulting polycycloacetals are semicrystalline thermoplastics and can be degraded via the cleavage of acetal groups by hydrolysis in acidic organic solvents.

Novel monomers can also be used to create block copolymers that diversify polymer mechanical performance. The terpene pinene, a product of conifer sap, was used to synthesize thermoplastic elastomers (TPEs) from myrcene and  $\alpha$ -methyl-p-methylstyrene (AMMS) monomers (16). When polymerized into an ABA triblock copolymer, the poly(myrcene)-poly(AMMS) copolymers have elongations and tensile strengths comparable to petroleum-based styrenic TPEs. Fournier et al. (9) synthesized a bottlebrush copolymer elastomer with tunable

mechanical properties from poly(L-lactide) (PLLA) and lignin-derived  $\gamma$ -methyl- $\epsilon$ -caprolactone ( $\gamma$ MCL). By varying the density and length of PLLA grafts, the copolymer mechanical properties can be tuned significantly (**Figure 2c**).

Microbial cultures have also been used as a sustainable route for the isolation of monomers. Liang et al. (17) utilized genetically modified *Escherichia coli* to improve the extraction of styrene by a factor of 3.45, although the resulting polystyrene had a low molecular weight. Microalgal oils have been used to isolate polyols, which serve as polyester monomers, with examples including PU foams that meet the requirements for commercial footwear while demonstrating excellent compostability in soil (4).

### 3. BIOPOLYMERS FROM BIOMATTER

Biological organisms synthesize and utilize hierarchical biopolymers, often of high molecular weight, as structural and functional building blocks. Leveraging the diversity of biopolymers and developing methods for their extraction constitute a promising emerging field within sustainable polymers. In this section, we present advances in sustainable materials utilizing polysaccharides, polyphenols, and proteins.

#### 3.1. Cellulose

Cellulose is the most abundant biopolymer in the world. It is synthesized by plants, bacteria, algae, and tunicates. Its wide availability, well-developed extraction methods, and competitive properties (**Figure 3a**) (18) make cellulose one of the most widely studied sustainable candidates for synthetic polymer replacement. Linear homopolymer chains of covalently bonded glucose rings stabilized through intra- and interchain hydrogen bonding (H-bonding), in addition to out-of-plane van der Waals bonding, give rise to rigid elemental fibrils 3–4 nm wide (18) (structure provided in **Figure 3a**). These fibrils have high tensile strengths (6–7 GPa) and Young's moduli (120–140 GPa) (19) and can be processed to produce nano- and microfibers with different dimensions and aspect ratios, yielding a variety of properties.

Zhu et al. (20) probed the relationship between the diameter of cellulose fibers (CFs) and the mechanical properties of pure cellulose nanopapers and found that the tensile strength scales inversely with the square root of the fiber diameter (**Figure 3b**). Compared with extracted wood fibers (27- $\mu$ m diameter), nanopapers composed of smaller-diameter cellulose nanofibrils (CNFs) (~11 nm) yielded a 40-fold increase in tensile strength (from 6.7 to 275 MPa) and a 130-fold increase in toughness (from 0.13 to 11.68 MJ/m<sup>3</sup>). Instead of increasing strength at the expense of toughness, Zhu et al. showed that the smaller-diameter CNFs facilitate molecular toughening as a result of cascading bonding between abundant surface hydroxyl groups during mechanical loading. Cascading bonding, or the dynamic breaking and reforming of H-bonds between adjacent chains, as well as fewer intrinsic defects causes the dramatic increase in strength and toughness observed with decreased CF diameter.

Besides tuning the fiber diameter, controlling the alignment, interactions, and bonding of CFs also allows for control of the macroscopic mechanical properties. Mittal et al. (21) capitalized on hydrodynamic and electrostatic interactions of CNFs to create highly aligned macrofibers and demonstrated the nonlinear relationship between fiber length and alignment, summarized in **Figure 3b**. The shorter ~400-nm-long CFs had twice the rotary diffusion coefficient compared with the longer 600–700-nm fibers, allowing faster alignment but also disorganization. Thus, macrofibers consisting of the longer CFs showed tensile strength improved by over 90% (up to 1,200 MPa) and modulus by 55% (up to 70 GPa) for the same elongation to break due to better alignment and increased interactions compared with shorter constituent CFs (21). To further

#### Polysaccharide:

linear or branched carbohydrate polymer of monosaccharides (e.g., glucose) bound together through glycosidic linkages (covalent bonds)

#### Nanopaper:

sheet composed of nanofibers (with at least one dimension below 100 nm)

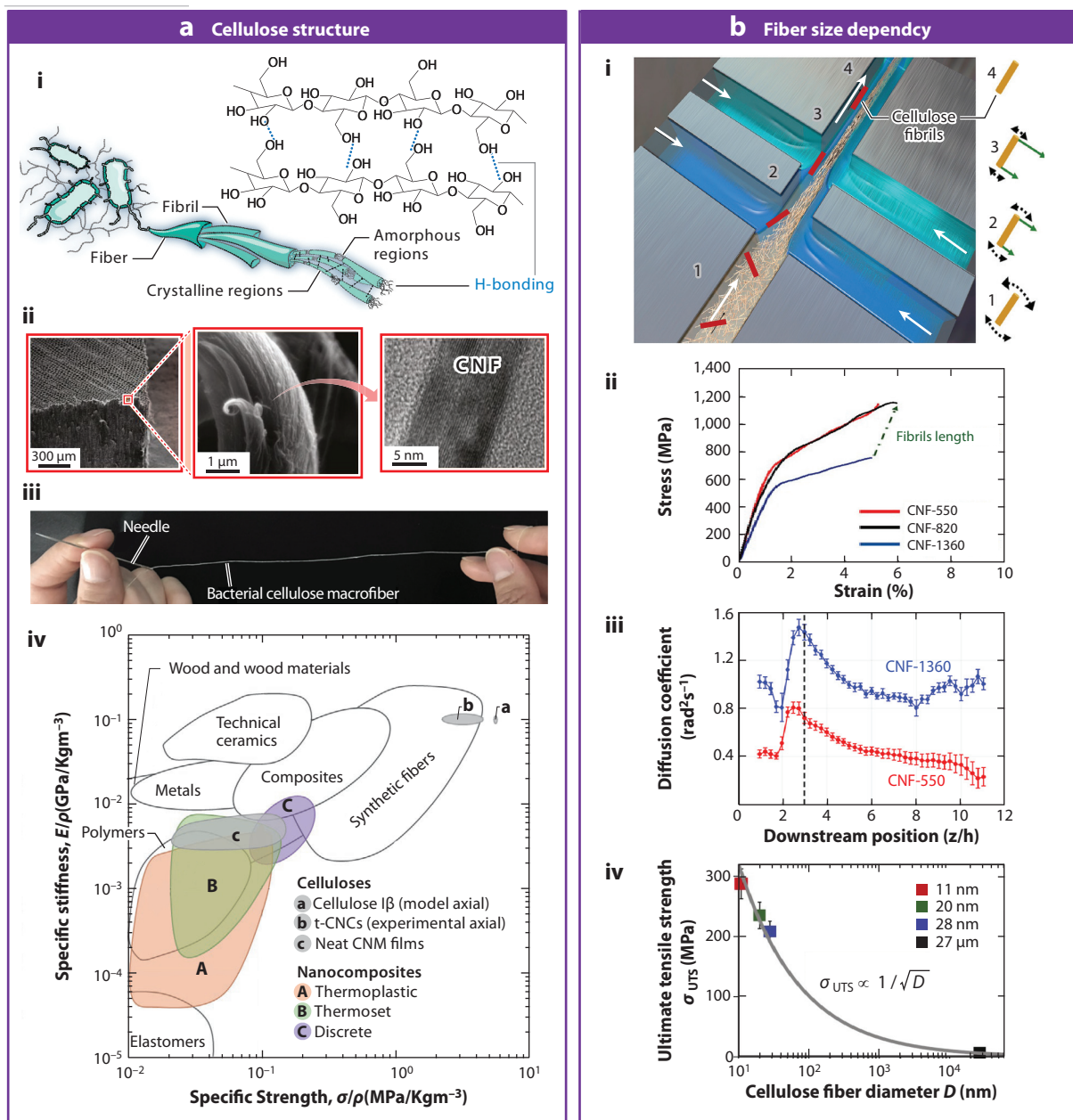
#### Cellulose nanofibril

(CNF): cellulose fibril comprising both amorphous and crystalline regions (<50 nm in width and 0.5–10  $\mu$ m in length)



**Bacterial cellulose (BC):** pure cellulose fiber synthesized by bacteria (20–100 nm in width and an undefined length that can reach hundreds of micrometers)

enhance the interactions between cellulose chains, Mittal et al. introduced chemical crosslinks (covalent bonding created through 1,2,3,4-butane tetracarboxylic acid treatment), which allowed a maximum ~31% improvement in tensile strength at no cost to extensibility. Wang et al. (19) reported another innovative method of improving interfibrillar alignment. By wet-stretching bacterial cellulose (BC) sheets 30% before twisting them into a macrofiber, they were able to increase the BC tensile strength by 620% (825.5 MPa) and modulus by 1,777% (65.7 GPa) compared with the equivalent unstretched macrofiber. These results collectively show that the



(Caption appears on following page)

**Figure 3** (Figure appears on preceding page)

Cellulose-based materials. (a) Illustration of the hierarchical structure of cellulose with (i) SEM and (ii) TEM images, (iii) a photograph of a manufactured macrofiber obtained through wet twisting and stretching of BC, and (iv) an Ashby plot of bulk cellulose and nanocomposites. (b, i) Process and results summarizing the effects of hydrodynamic alignment of cellulose fibrils, where red and yellow lines represent individual fibrils, the numbers correlate to positions within the flow channel, and the green and black arrows depict hydrodynamically induced alignment and electrostatic repulsion, respectively. White arrows show the flow and movement of fluid and fibrils. (b, ii) The stress–strain relationship for cellulose fibers of different lengths and surface charge densities. (b, iii) The effect of the position of cellulose fibers within the flow channel on the rotary diffusion coefficient. (b, iv) Strength as a function of fiber diameter. Abbreviations: BC, bacterial cellulose; CNCs, cellulose nanocrystals; CNF, cellulose nanofibril; CNM, cellulose nanomaterial; H-bonding, hydrogen bonding; SEM, scanning electron microscopy; TEM, transmission electron microscopy. Panel a adapted with permission from (i, ii) Reference 20, (iii) Reference 19, and (iv) Reference 18. Panel b adapted with permission from (i–iii) Reference 21 and (iv) Reference 20.

dimensions and alignment of CFs allow tuning of the interchain and interfiber interactions, which ultimately control the macroscopic mechanical properties of cellulose materials. The same principles apply when CFs are used as a matrix or a filler in plastic composites (see the sidebar titled Cellulose and Natural Fibers as Reinforcement in Plastics) and concrete (see the sidebar titled Cellulose and Natural Fibers as Reinforcement in Concrete).

### CELLULOSE AND NATURAL FIBERS AS REINFORCEMENT IN PLASTICS

Pure cellulose fibers as well as plant-derived natural fibers (e.g., hemp or flax, which contain cellulose mixed with various amounts of lignin, hemicellulose, pectin, and proteins) have long been used as reinforcing agents in plastics (3). The surface chemistry, charge, surface area, and arrangement of cellulose or natural fibers within the host polymer matrix are critical variables in determining the macroscopic properties of the resulting composite materials (110). The abundance of surface hydroxyl groups, which makes cellulose highly hydrophilic, enables strong interactions with water-soluble polymers via H-bonding without requiring surface treatments. On the other hand, the highly hydroxylated surface of cellulose leads to incompatibility with hydrophobic polymers such as polyolefins (111). To combat this filler–matrix incompatibility, which also promotes poor dispersion and agglomeration of the cellulose filler, a number of different physical and chemical modification methods have been developed and reviewed elsewhere (110, 112). In addition, enhancing the axial alignment of cellulose and/or host polymer chains (e.g., via solid-state drawing) has been reported to substantially improve the composite performance (113).

### CELLULOSE AND NATURAL FIBERS AS REINFORCEMENT IN CONCRETE

Natural fibers as fillers in concrete lead to significant gains in thermal and acoustic insulation efficiency, which come at a cost of poor mechanical properties. The mechanical property reductions are driven by the high porosity and moisture uptake of natural fibers, coupled with the alkali penetration from the cement matrix. To mitigate these problems, heat treatments (114), hydrophobic coatings (115), and carbonation treatments (116) have been used. On the other hand, the incorporation of pure cellulose fibers shows competitive advantages in enhancing mechanical properties of cementitious biocomposites. The removal of hemicellulose and lignin allows better compatibility while the hydrophilic and hygroscopic characteristics of cellulose foster homogeneous water uptake and prolong the hydration reactions, ultimately increasing the amount of hydration products. Moreover, the high specific mechanical properties, aspect ratio, and large surface area of cellulose enable a nano-reinforcement effect on the cement matrix, which improves the composite mechanical performance. The positive effects of cellulose fibers are commonly dominant at concentrations below 1 wt% (117–119), while, at higher loadings, the competing mechanism of fiber agglomeration dominates (120), cancelling the reinforcement effects on the mechanical properties of the composite.

**Amylose:** linear, low-molecular-weight macromolecule formed from glucose residues; one of two components of starch

**Amylopectin:** highly branched, high-molecular-weight macromolecule formed from glucose residues; one of two components of starch

**Gelatinization:** disruption of macromolecular interactions between biopolymer chains and swelling in the presence of heat and moisture, causing increased molecular mobility

### 3.2. Chitin

Chitin, another linear chain biopolymer like cellulose with an acetylglucosamine monomer, is produced within crustaceans, insects, and fungi. Similarly to cellulose, the vast network of H-bonded linear chains gives rise to hierarchical fibers composed of elemental fibrils. Crystalline chitin fibrils reach strengths of  $\sim 3$  GPa and moduli of 80–100 GPa (22). Chitin nanopapers have been reported to reach tensile strengths of 77.2 MPa with a 2.6-GPa modulus, with notable  $\sim 20\%$  extensibility (23). Like cellulose, the failure mechanism is dominated by a dynamic cascading H-bonding destruction and reconstruction effect (22). To enhance interactions between chitin fibers, Nawawi et al. (24) have suggested the use of  $\beta$ -glucans, which are naturally synthesized together with chitin fibers in fungal cell walls. The highly disordered  $\beta$ -glucans have strong H-bonding interactions with the chitin fibers and facilitate chain sliding, which improves composite extensibility and ultimately increases flexibility and toughness. Recently, Nawawi et al. (25) demonstrated tunability of mechanical properties by varying the chitin-to-glucan ratios in composites through the use of different fungal sections or species. Specifically, they achieved tensile strengths from 65 to 204 MPa and moduli from 1.2 to 6.9 GPa.

### 3.3. Starch

Native starch, as extracted from biomass, takes the form of granules composed primarily of two bonded macromolecules: amylose and amylopectin. Amylose and amylopectin interact to form a semicrystalline structure stabilized by H-bonding (26). Thermoplastic starch (TPS) is formed when moisture and small molecule plasticizers are mixed with biomass-extracted starch and subjected to thermomechanical processing, causing starch gelatinization (26). Typically, TPS has a Young's modulus of 0.1–1.1 GPa, tensile strength of 1.4–21.4 MPa, and strain to break of 3–60%. Cellulose, lignin, and mineral fillers have been employed as reinforcements to improve the strength and stiffness of TPS (26).

Common drawbacks of TPS include temperature-dependent loss of plasticity over time due to plasticizer leaching and retrogradation (recrystallization) and detrimental sensitivity of mechanical properties to moisture due to the prevalence of available hydroxyl groups in starch molecules (26). To combat plasticizer leaching, Wang et al. (27) synthesized a novel plasticizer through the addition and quaternization of imidazole and epichlorohydrin. The resulting polymer ionic liquid (PIL) consists of repeating imidazolium cation rings and hydroxyl functionalities that replace interchain H-bonding, eliminate crystallinity, and facilitate molecular mobility. The PIL was found to impede retrogradation and leaching through the interactions and entanglement of the plasticizer with starch chains, and the resulting amorphous structure was maintained even after 24 months. An alternative strategy to tackle plasticizer leaching was presented by Zhang et al. (28) who created a covalently crosslinked dialdehyde starch (DAS) that can be thermoformed without the inclusion of a plasticizer. Dynamic DAS–polyimine networks form thermally healable and moisture-resistant films with tensile strengths up to 40 MPa, more than four times greater than TPS tensile strengths (27, 29, 30).

### 3.4. Lignin

Lignin is a widely researched polyphenol extracted primarily as a by-product of wood pulping. While most innovative lignin valorization strategies focus on the depolymerization of natural lignin to retrieve monomers (15), the use of extracted polymerized lignin as a filler or matrix in sustainable polymer composites is rapidly emerging (31). Like the previously mentioned biopolymers, a major challenge in introducing polymerized lignin to composites is controlling the dispersion and enhancing the interactions with the host matrix to prevent aggregation, which can be





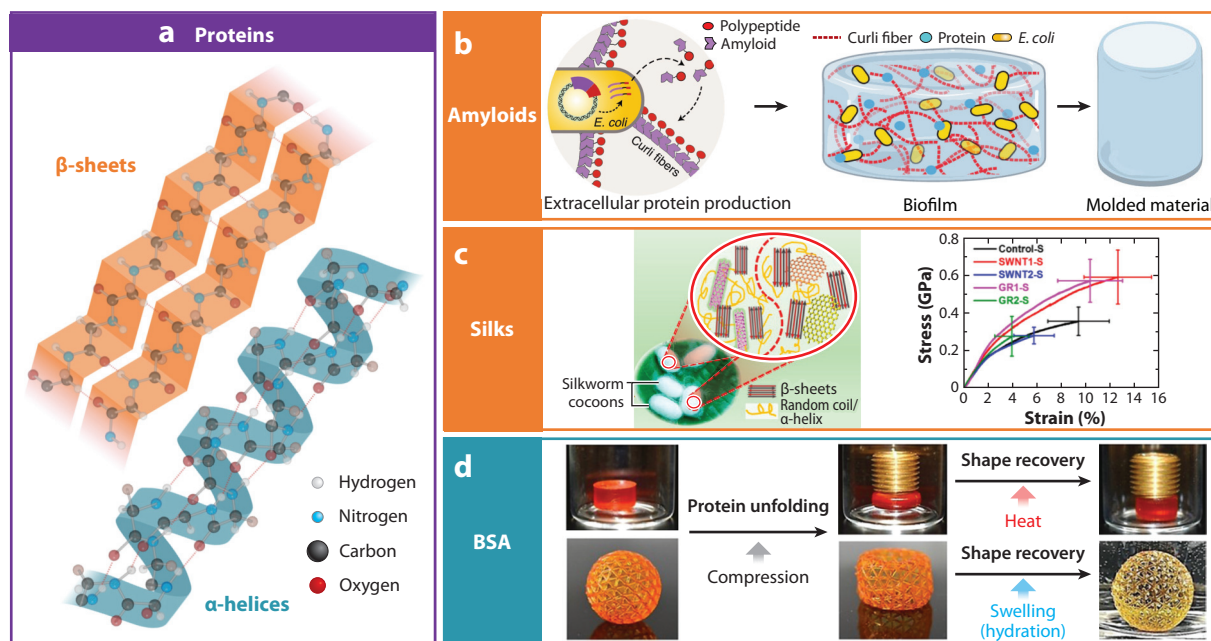
detrimental to the final properties. Tuning the shape, surface chemistry, and charge of lignin to produce high-surface-area lignin nanoparticles is an effective strategy to circumvent agglomeration (32). Capitalizing on polar interactions between lignin and water, colloidal lignin nanoparticles (CLPs) can be self-assembled with hydrophobic phenylpropanoid cores and hydrophilic carboxylic and hydroxylic surface groups (31). Using this method, Farooq et al. (33) prepared different forms of lignin particles and examined the effects of incorporating them as a filler in CNF films at concentrations of 2–50 wt%. When introduced in a CNF matrix at 10 wt%, CLPs with similar dimensions and opposite charges lead to comparable improvements in strength and toughness. The spherical particles act as ball-bearing-like lubricants between CNFs and simultaneously enable (a) effective load transfer between neighboring CNFs, thereby strengthening the matrix, and (b) polymer chain sliding. This facilitates larger strains before failure, leading to composites with toughness improved by 1.2 and 1.9 times for negatively and positively charged CLPs (at 10 wt%), respectively. Interestingly, the addition of nonspherical lignins at the same concentration also improves the ductility and toughness of the composites, but the resulting strength is inferior compared with spherical CLPs, suggesting that the shape (surface area) of the particles is critical for enabling load transfer between the CNFs. A progressive reduction in all mechanical properties was found with increasing lignin concentration, which may indicate that at higher amounts, lignin disrupts the effective network performance of CNFs as it starts forming agglomerates.

In an in situ approach to creating cellulose/lignin composites with nonspherical lignin particles, Xia et al. (34) presented the partial deconstruction of natural wood using a deep eutectic solvent to retain a network of lignin-coated CFs, which can be processed into a film. In this single-step process, the lignin particles acted as a binder for CFs, providing a sevenfold improved strength and eightfold improved toughness compared with fully delignified cellulose papers. This improvement was enabled by well-distributed lignin particles that enhanced the CF H-bonding network, in agreement with Farooq et al. (33). The delicate balance between lignin's function as a stress mediator and reinforcement in strong biopolymer networks (such as those of CFs) and its role as a defect (stress concentrator) is further highlighted in the analysis of Fredricks et al. (35). Their work presents the effects of hot pressing BC/lignin films, revealing increases in specific stiffness and reductions in specific tensile strength and elongation to break when sulfonated and polymerized lignin is distributed in the strong BC matrix. It was observed that during hot pressing, lignin forms aggregates that would hinder cellulose H-bonding and chain sliding, thereby preventing load transmission in the strong CF network and serving as stress concentrators.

### 3.5. Polyesters from Bacteria and Algae

Polysaccharides, proteins, polyamides, polyesters, and other molecules can be extracted from bacteria and algae to be subsequently used as sustainable polymers, as previously described (36). Polyhydroxyalkanoates (PHAs), in particular, represent an emerging class of biodegradable polyesters extracted from microorganisms. And while PHAs have mechanical properties and processability rivaling those of commodity plastics, they cost more than twice as much per kilogram to produce (37). To streamline PHA production, recent efforts have focused on the replacement of pure culturing using valuable substrates with mixed microbial cultures grown on environmental and agricultural waste (37). Alternatively, PHAs can be produced without a carbon-rich substrate if photoautotrophic microalgae are utilized rather than bacteria. Roja et al. (38) were able to extract 2.74 g/L of PHA in this way from four microalgal strains, such as *Chlorella* sp. PHA production can be further enhanced by genetically engineering host microorganisms to augment or repress genes responsible for the polymerization or depolymerization of PHAs, respectively (39). For example, by deleting the *phaB* gene, Bhatia et al. (39) developed a *Ralstonia eutropha* strain that converts approximately 50% of fermented food waste to PHA.





**Figure 4**

Using protein secondary structures for sustainable materials. (a) Macromolecular conformations of  $\alpha$ -helices and  $\beta$ -sheets. (b) A strand of *Escherichia coli* genetically engineered to fabricate aquaplastics from curli fibers. (c, left) Illustration of a silk worm loaded with carbon nanotubes/graphene and (c, right) the corresponding tensile stress–strain curves. (d) Heat- and swelling-induced recovery of stereolithography-printed BSA materials. Abbreviations: BSA, bovine serum albumin; GR, graphene; SWNT, single-walled nanotube. Panel a adapted from images created with BioRender.com. Panel b adapted with permission from Reference 5. Panel c adapted with permission from Reference 40. Panel d adapted with permission from Reference 41.

### 3.6. Proteins as Building Blocks for Materials

**$\alpha$ -helix:** right-handed polypeptide helix where each amino acid is H-bonded to the fourth amino acid along its sequence

**$\beta$ -sheet:** planar structure composed of polypeptide chain sections ( $\beta$ -strands) repeatedly folded onto each other and held together by H-bonds

**Silk fiber:** natural protein fiber composed of load-bearing fibroin fibrils embedded in a compliant sericin binding matrix

The hierarchical organization of proteins involves covalently bonded amino acids called polypeptides (primary structure) being folded into repeated patterns (secondary structure) that form structural motifs that interact to organize a 3D structure (tertiary structure). The most common protein secondary structures are  $\alpha$ -helices and  $\beta$ -sheets (Figure 4a). Disordered structures such as random coils, loops, and turns are also present in proteins, with turns serving as connections between ordered folded secondary structures.

**3.6.1.  $\beta$ -sheet-dominant proteins.** Both amyloids and silks are primarily composed of  $\beta$ -sheets. The appealing intrinsic mechanical properties of these materials, along with their fiber geometry (high aspect ratio) and surface chemistry (which allows for functionalization), make them attractive candidates for use as standalone bulk materials, as scaffolds for hydro- or aerogels, or as reinforcements in composites. Silk and amyloid fibers structurally differ on their  $\beta$ -sheet orientation:  $\beta$ -strands of amyloid  $\beta$ -sheets are orthogonal to the fiber axis while silk  $\beta$ -strands are parallel (42). As a result of this orientational difference, the axial Young's modulus of silk fibers is higher than that of amyloid fibers (68 versus 15 GPa) (43).

Amyloids are a type of protein produced extracellularly by certain bacteria (e.g., *E. coli*) and have recently emerged as promising alternatives to synthetic polymers. For example, Duraj-Thatte et al. (5) fabricated aquaplastics from hydrogels using the amyloid curli fibers produced by a genetically engineered strain of *E. coli* (see Figure 4b). The presence or absence of cells within

the aquaplastics played a major role in determining their macroscopic properties. As expected, aquaplastics without cells were found to be stiffer and stronger than the cell-laden ones because the curli fibers alone show exceptional mechanical properties (with average values of 1.2 versus 1 GPa for the tensile elastic modulus, 29 versus 19 MPa for tensile strength, and 261 versus 102 MJ/m<sup>3</sup> for toughness). Beyond their attractive mechanical properties, the aquaplastics demonstrated exceptional biodegradability, losing more than 85% of their original mass within 45 days. In another study, genetically engineered *E. coli* were used to produce amyloid curli fibers using the curli monomer CsgA as a building block onto which two different protein domains were grafted (44). The resulting monomers, CsgA- $\alpha$  and CsgA- $\gamma$ , self-assembled into high-aspect-ratio nanofibers. Rheological studies showed that these combined hydrogels have 300–600% higher storage modulus and 200% higher yield stress compared with hydrogels made of nongrafted CsgA fibers. The hydrogels demonstrated the ability to serve as microbial inks for 3D printing.

Amyloid hydrogels have been employed as scaffolds for the fabrication of hybrid organic–inorganic aerogels with enhanced properties (45). Notable examples from the Nyström and Mezzenga groups showcase the addition of gold nanoparticles or platelets and CaCO<sub>3</sub> particles that enable pressure sensitivity and stiffening (via ionic crosslinking), respectively, in the resulting aerogels (46, 47). Recently, Cao et al. (48) provided a deeper understanding of the effect of ionic cross-linking in amyloid aerogels, revealing a classic power-law dependence of elasticity and ionic strength with amyloid concentration, with exponents significantly larger than in other semiflexible polymer networks (e.g., actin).

Silk fibers from silk worms and spiders have been extensively studied for their appealing mechanical properties, biocompatibility, and biodegradability. The fabrication of silk-based materials commonly employs regenerated (or degummed) silk fibroin (SF) that is solubilized and extracted before being further processed into the desired shape (e.g., wet spinning for fibers or casting for bulk solids) (49). Depending on the species used for silk production and the postprocessing methods, natural and regenerated silks typically have tensile elastic moduli on the order of 10–20 GPa, with tensile strengths ranging from 200 to 1,500 MPa (50, 51). Even though the primary intramolecular interactions within silk  $\beta$ -sheet nanocrystals are H-bonds, Keten et al. (52) showed that nanoconfinement plays a key role in providing exceptional stiffness and strength to silks. Ling et al. (53) showed that the incorporation of 50% amyloids in pure silk causes a decrease in toughness from 89 to 4 kJ/m<sup>3</sup> but an increase in elastic modulus from 0.94 to 2.25 GPa. The importance of intermolecular interactions was highlighted by Meng et al. (54), who used amphiphilic regenerated SF as a molecular binder between hydrophobic monomers of stearyl methacrylate in a matrix of alginate hydrogel. The addition of Ca<sup>2+</sup> cations enabled an ionic cross-linking between the SF and alginate, thus creating a tough material with self-healing properties. Wang et al. (55) further augmented the mechanical performance of silk materials by using water vapor annealing to create nacre-like graphene oxide (GO)/silk nanocomposites. They illustrated that GO nanoflakes act as hydrophobic nucleation sites to promote  $\beta$ -sheet crystallization in silk fibers. The higher  $\beta$ -sheet content and well-dispersed GO sheets contribute to higher stiffness, strength, and toughness in the GO/silk nanocomposites compared with SF controls. As the GO concentration is increased from 0 to 53.7 vol%, the elastic modulus increased from 13 to 95 GPa, and the ultimate strength increased from 120 to 326 MPa (Figure 4c). Ling et al. (56) demonstrated that the incorporation of Ca<sup>2+</sup> ions in a graphene/SF composite facilitates a staggering plasticization effect, leading to >700% strain to break for a graphene concentration of 10 wt%. However, this large extensibility comes at the cost of reduced Young's modulus (4 MPa) and strength (0.5 MPa). Finally, an unprecedented approach for introducing nanocarbon compounds in silks was adopted by Wang et al. (40) and Lepore et al. (57), who fed nanocarbon materials directly to silkworms and spiders, respectively. The silkworms fed with a 0.2 wt% solution of single-walled carbon nanotubes



**Cellulose nanocrystal (CNC):** purely crystalline whisker of cellulose (3–20 nm in width and 50–2,000 nm in length)

(CNTs) produced a silk that was 639% stiffer and 113% stronger (40). Spiders fed with CNTs produced fibers 1,084% stiffer and 631% stronger than the control (57).

**3.6.2.  $\alpha$ -helix-dominant proteins.** Proteins forming predominantly  $\alpha$ -helix secondary structures have also been used for sustainable materials. The Nelson group (41) developed a resin for stereolithography (SLA) by adding comonomers and a photoinitiator to a solution of a globular  $\alpha$ -helix-forming protein, bovine serum albumin (BSA). Their strategy capitalized on the stimuli sensitivity of the BSA molecular conformation to develop hydrogels with shape memory behaviors. While printed structures retained the native globular BSA conformation, postprinting thermal curing caused  $\beta$ -sheet formation and, subsequently, material stiffening. Moreover, the BSA globules in the printed structures exhibited plasticity during deformation due to protein unfolding, which can be recovered via heating or swelling in water (**Figure 4d**) (41). Smith et al. (58) further enhanced SLA BSA materials by soaking printed structures in tannic acid (TA), a natural polyphenol. Infusing biodegradable methacrylated BSA structures with TA formed an intermolecular H-bonding network that improved toughness almost 10-fold.

**3.6.3. Hybrid  $\alpha$ - $\beta$  protein structures.** Sustainable materials developed from proteins with quaternary organization and mixed secondary structures have also been reported. Lysozyme, for instance, conforms in both  $\alpha$ -helix and  $\beta$ -sheet arrangements. Recently, De France et al. (59) added lysozyme to cellulose nanocrystal (CNC) films and studied the effects of sonication as a means to change the lysozyme conformation from globules to fibers. The  $\alpha/\beta$  ratio of lysozyme remained unchanged and independent of the altered conformation achieved through sonication.  $\alpha/\beta$  ratio stability and strong electrostatic interactions enabled reinforcement of the CNC network by protein fibrils and improved its toughness by 84% (at 10 wt% protein).

Casein, a micellar protein found in milk, has been combined with additives such as glycerol and pectin to prepare films with properties suitable for edible food packaging (60). As discussed previously, the final properties are defined by the interplay between the structural function of protein, its plastic deformability, the interactions with polysaccharides, and the ordered domain disruption facilitated from plasticizers. Building on the anticipated enhanced interactions between lignocellulosic wood particles and casein, durable wood panels were prepared without requiring the use of formaldehyde or other petrochemical binders (61). Gluten, like casein, is a complex mixture of distinct proteins: polymeric glutenins and monomeric gliadins. The network of proteins grants gluten viscoelastic properties that enable thermomechanical processing. By exploiting gluten viscoelasticity and utilizing glycerol as a plasticizer, Jiménez-Rosado et al. (62) produced bioplastics via extrusion and injection molding.

## 4. BIOMATTER AS A MATERIAL BUILDING BLOCK: USING ENTIRE ORGANISMS AND TISSUES

The extraction of biopolymers or monomers, as described in the previous sections, is a costly, energy-intensive, and wasteful process. Recent advances in circumventing extraction processes rely on using raw or minimally preprocessed biomatter. In this section, we discuss innovative utilizations of biomatter as a filler or a matrix material with little or no preprocessing and present emerging approaches such as material farming as viable implementations of sustainable polymers design.

### 4.1. Bacteria

Cultured bacteria have recently emerged as alternative polymer materials. Manjula-Basavanna et al. (63) demonstrated that bacteria, *E. coli* and *Lactobacillus rhamnosus*, or yeast, *Saccharomyces*

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*cerevisiae*, could be cultured, harvested, and air-casted into self-bonded films showing indentation moduli of 5–42 GPa for *E. coli*, 5–30 GPa for *L. rhammosus*, and 1–30 GPa for *S. cerevisiae*.

Rather than culturing a single strain, Das et al. (64) utilized the symbiotic relationship between *Acetobacter aceti* bacteria and *Cblamydomonas reinhardtii* microalgae to create integrated composite biofilms. The by-products of microalgal metabolism were used in the production of BC from bacteria, and the by-products of BC synthesis acted as nutrients for the microalgae. BC was distributed throughout the hybrid material instead of concentrating at the air–medium interface, while varying the component ratio influenced the microalgae distribution. Similarly, Birnbaum et al. (65) designed a bacterial coculture of a BC-producing strain, *Gluconacetobacter hansenii*, and genetically engineered *E. coli* to produce unique composite capsules. By using droplets of growth media, a BC matrix was formed on the droplet surface while intertwined bacteria cells and curli fibers remained at the core of the produced spheres. Further property tuning can occur in this versatile system as a result of bacterial biomineralization; CaCO<sub>3</sub> mineral deposits increase the hardness and stiffness of the composite spheres.

An emerging theme in sustainable materials is capitalizing on bacterial biomineralization, or microbially induced calcium carbonate precipitation (MICP), to develop self-healing construction materials, primarily concrete. When a crack is formed in concrete that contains bacterial spores, air and water come in contact with those spores. Bacterial metabolic processes then alter the pH and carbonate concentration of the surrounding matrix, causing MICP to accumulate and fill the cracks (66). Biomineralization mechanisms include urea hydrolysis performed by alkali-tolerant ureolytic bacteria such as *Bacillus* sp. strains (66) and NO<sub>3</sub> reduction performed by denitrifying bacteria (67). Alternatively, photosynthetic cyanobacteria in mortar induce MICP by metabolizing CO<sub>2</sub>, releasing OH<sup>−</sup>, and increasing the surrounding pH. The associated carbon fixation was reported to promote CaCO<sub>3</sub> precipitation and facilitated 35% strength recovery after microcracking for mortars containing 12 wt% *Spirulina* sp. (68) (the mechanism and self-healing results are shown in **Figure 5a**). Commercialization efforts have been reported, such as BioLITH tiles [from Biomason (<https://biomason.com>)], that show mechanical properties acceptable for structural applications despite consuming only a fraction (namely 3.5%) of the manufacturing energy required for conventional competing materials.

In addition to their use as fillers for crack remediation, living microorganisms have been utilized as binders and compatibilizers in building materials. Raut et al. (73) utilized *Bacillus pasteurii* biomineralization to bind clay and sand and formed bricks with 8-MPa compressive strength after 28 days, which is 30–50% of the strength of conventional bricks. Similarly, Heveran et al. (74) combined *Spirulina*, gelatin, and a sand scaffold to create a living building material (LBM) with 9% cell viability at high humidity (>50%) and low temperature (4°C). Cell viability was further increased to 37% by tuning the component concentrations (69) (**Figure 5b**). The cell viability in LBMs is higher than that of encapsulated microorganisms in cement due to the absence of an alkaline environment, demonstrating the outstanding potential of LBMs as sustainable building materials. Lastly, MICP was used to improve compatibility between 5 wt% recycled plastic filler and mortar and to elicit compressive strengths of approximately 55 MPa (75), exemplifying another strategy to reduce the environmental footprint of cementitious materials.

## 4.2. Fungi

Fungi colonize substrates with filamentous cells called hyphae (2–10 μm in diameter), which form an extended network called mycelium. Mycelia naturally adopt the shape of the substrate as they grow, enabling straightforward shaping of the resulting mycelium/substrate composites. These attractive biomatter-based materials offer diverse mechanical properties and densities, fast growth times, low fabrication costs, and biodegradability.

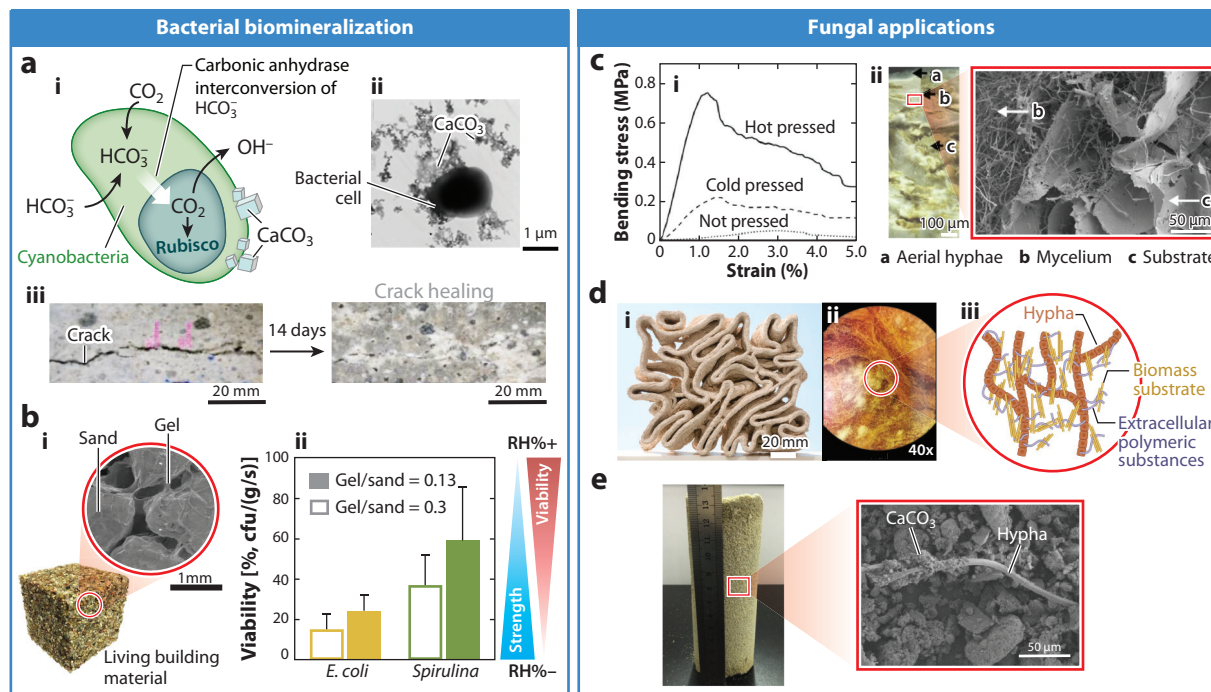
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**Biofilm:** consortium of microorganisms where cells adhere to each other and often to a surface

**Biomineralization:** mineral precipitation, particularly of CaCO<sub>3</sub>, by living cells

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**Figure 5**

Bacteria- and fungi-based materials. (a) Cyanobacteria carry out (i) carbonic anhydrase interconversion of  $\text{HCO}_3^-$ , promoting (ii)  $\text{CaCO}_3$  precipitation that (iii) seals cracks. (b, i) Microbially induced calcium carbonate precipitation combined with sand and gelatin to form a living building material. Higher humidity increases viability while decreasing strength of the living building material. (b, ii) *Spirulina* was found to be more viable than *Escherichia coli* in living building materials. (c, i) Mycelia grown in different substrates were hot pressed at  $150^\circ\text{C}$ , cold pressed at  $20^\circ\text{C}$ , and not pressed, showing up to eightfold increases in flexural strength depending on fungal species, substrate, and processing conditions. (c, ii) Microscopy images of unpressed *Trametes multicolor* mycelium on rapeseed straw. (d, i) 3D-printed mycelium structure with (ii) microscope image. (d, iii) Illustration showing bonding between mycelium and the biomass substrate assisted via the secretion of extracellular polymeric substances consisting of polysaccharides and proteins. (e) Cement-free sandstone bonded by fungi-induced  $\text{CaCO}_3$ . Abbreviation: RH, relative humidity. Panel a, subpanels ii and iii adapted with permission from Reference 68. Panel b adapted with permission from Reference 69. Panel c adapted with permission from Reference 70. Panel d adapted (i,ii) with permission from Reference 71 and (iii) from images created with BioRender.com. Panel e adapted with permission from Reference 72.

The principal structural components of hyphal cell walls are chitin,  $\beta$ -glucans, and proteins. Tuning the relative concentration of the cell wall components by altering growth conditions [e.g., by changing media composition and morphology, incubation temperature, lighting, or humidity (6, 76)] or by genetic engineering (77) allows for the bottom-up control of the macroscopic mechanical properties of the produced material. In addition, the choice of feedstock can influence the composite properties if nondegraded feedstock remains within the final composite (70, 78). Finally, the processing method used to form mycelium-based materials enables further property tuning (70).

**4.2.1. Fungal foams.** Joshi et al. (6) tuned the properties of composite fungi foams by changing the feedstock material on which mycelia of *Pleurotus ostreatus* were grown. Their results showed that pure sawdust and mixed sugarcane-sawdust substrates lead to foams with the highest density and strength,  $0.3 \text{ g/cm}^3$  and  $6.7\text{--}7.5 \text{ MPa}$ , respectively. The high lignin content of sawdust, especially in comparison with other commonly used substrates such as rapeseed straw (79) and

sugarcane bagasse (80), may cause the higher performance of the composite foams. Elsacker et al. (78) examined the effects of varying the feedstock form (loose, chopped, dust, precompressed, or tow forms were tested) on the mechanical properties of *Tinea versicolor* composite foams. Precompressed substrates lead to significantly higher compressive moduli (ranging from 1.1 to 1.4 MPa), compared with loose natural fibers, which consistently lead to softer foams (compressive modulus from 0.1 to 0.6 MPa) for all types of substrates. In composites of *Basidiomycota* sp. mycelium with wood particles, Sun et al. (81) showed that when the mycelium is first grown in culture media and subsequently mixed with wood particles, the produced composite is softer (Young's modulus decreases from 225 to 40 MPa) and weaker (strength decreases from 1.20 to 0.5 MPa) compared with the same species grown directly on wood particles. Moreover, the use of CNFs at low concentrations (2.5 wt%) substantially improves the mechanical performance (modulus increases from 225 to 660 MPa, and strength increases from 1.2 to 3.5 MPa) by enhancing the bonding between the wood particles and mycelium via extensive H-bonding.

Highlighting the influence of the processing method, Appels et al. (70) showed that the elastic modulus and flexural strength for hot-pressed composites of *P. ostreatus* and *Trametes ochracea/multicolor* are 5–35 and 3–8 times higher than unpressed and cold-pressed foams, respectively, under all tested conditions (Figure 5c). Alternatively, Haneef et al. (76) investigated the influence of the culture medium on the mechanical performance of pure mycelium, without a feedstock residing within the final product. They found that adding potato dextrose broth to a pure cellulose substrate altered the macromolecular makeup of hyphal cell walls. These compositional changes caused the Young's modulus and extensibility of *Ganoderma lucidum* films to change from 12 to 4 MPa and 14% to 33%, respectively, owing to the plasticizing effects of lipids. Appels et al. (77) demonstrated a drastic improvement on the mechanical performance of genetically altered *Schizophyllum commune* mycelium foams by modifying light and CO<sub>2</sub> levels during growth. The genetically modified foams ( $\Delta sc3$ ) cultured in high light and high CO<sub>2</sub> flow reached an elastic modulus of 2.73 GPa and a strength of 40.4 MPa (compared with 0.91 GPa and 9.5 MPa, respectively, for unaltered foams). The *sc3* gene deletion in *S. commune* resulted in the highest reported density and mechanical properties among all pure mycelium films. The higher thermal stability results for  $\Delta sc3$  suggest that the comprising biopolymers are either more crosslinked or of higher molecular weight in the case of the mutant. These and other recent successes have encouraged rapid commercialization of mycelium-based materials as demonstrated by 47 patents filed from 2009 to 2018 (82).

**4.2.2. Fungal inks.** Additive manufacturing (AM) can further expand the use of mycelium-based composites (83). Successful demonstrations of 3D-printed fungal materials rely on printing a mixture of growth media and cells as shown in Figure 5d. The same constraints of traditional AM are present in mycelium printing, although the need to preserve cell viability through the control of feedstock type, morphology, distribution, and porosity adds an extra layer of difficulty (84, 85). Burry et al. (71) showed that inter- and intralayer adhesion in mycelium prints can be improved by a cell-secreted extracellular polymeric substance that bonds and physically interlocks with the lignocellulosic substrate, as mentioned in the previous sections.

**4.2.3. Fungi in cementitious materials.** Despite bacterial biomineralization being primarily utilized in self-healing concrete, challenges such as the limited lifetime of bacterial spores (<6 months), high pH environment within cementitious materials, and low nutrient availability restrict the healing efficiency. Therefore, the use of alternative microorganisms such as fungi, which are ubiquitous, highly tolerant to toxic environments, and capable of biomineralization and organomineralization at the same time (86), recently emerged. The metabolic activity of some fungi even improves CaCO<sub>3</sub> precipitation by increasing the carbonate alkalinity and

**Organomineralization:** the precipitation of minerals, particularly CaCO<sub>3</sub>, facilitated by dead biological matter rather than living cells (cf. biomineralization)



calcium cation concentration (87). Luo et al. (88) and Menon et al. (89) observed fungal growth rates of 2.6 mm/day for *Trichoderma reesei* and 3.2 mm/day for *Aspergillus nidulans*, respectively, despite highly alkaline conditions, suggesting possible future uses of fungi in self-healing concrete. The effectiveness of the fungal biomineralization process in providing structural building blocks in noncementitious materials is highlighted by work from Fang et al. (72). They introduced *Penicillium chrysogenum* in sand in the presence of urea and  $\text{CaCl}_2$  and observed the precipitation of  $\text{CaCO}_3$ , effectively binding the sand in mortar-free biosandstones as shown in **Figure 5e**.  $\text{CaCO}_3$  precipitates incorporate with the hyphae fibril network and enhance the interfacial strength between hyphae and sand, resulting in a twofold increase in compressive strength over sandstones made from bacteria-induced  $\text{CaCO}_3$  precipitates (90) (0.7 versus 1.8 MPa).

### 4.3. Cultured Plant Cells

Hybrid biological matrix materials utilizing entire cultured plant cells as matrix and CNTs as binder were first demonstrated for tobacco cells by Di Giacomo et al. (91, 92). These hybrid films had an elastic modulus of 91 MPa and tensile strength of 3 MPa. Using the same cultured cells, Roumeli et al. (7) reported a pressure-induced self-bonding mechanism that enabled strong biological matrix materials to form without the need for additives, as summarized in **Figure 6a**. Compaction of the plant cells enabled cell wall biopolymers to diffuse into neighboring walls, thus facilitating bonding through a combination of fibrillar interlocking and H-bonding. The process keeps cell walls intact, thereby preserving the natural, hierarchical arrangement of CNFs within the cell wall structure. The self-bonded materials had tensile strengths of  $21.2 \pm 3$  MPa and Young's moduli of  $2.5 \pm 0.4$  GPa, which are comparable to commodity plastics of the same density. Furthermore, the composites biodegraded in soil in just 14 weeks.

Natalio et al. (96) presented a plant cell culture system that enables the tuning of the final material performance by taking up functional additives directly from the culture media. Depending on the nature of the functional molecule, properties such as fluorescence and magnetism could be added to CFs synthesized by cultured cotton ovules. Beckwith et al. (97) demonstrated the ability to 3D print living *Zinnia elegans* cells in culture media and maintained over 70% cell viability after 10 days. Postprinting, the viable cells grew in assemblies that filled out their 3D-printed shapes.

### 4.4. Algae

Because of their abundance, cultivability in nonarable lands, and macromolecular complexity, algal biomatter have been used as fillers or matrix materials in bioplastics and biocomposites. Using the entire cell or tissue offers a variety of building blocks to create new composites. As mentioned in the previous sections, polysaccharides can act as structural fibers, while proteins and lipids can act as reinforcements, binders, and plasticizers. Zeller et al. (98) reported the fabrication of bulk bioplastics using solely *Spirulina* and *Chlorella* microalgae. Hot pressing pure *Chlorella* and *Spirulina* resulted in bioplastics with tensile moduli of 270 MPa and 249 MPa and strengths of 5.7 MPa and 3 MPa, respectively. The use of glycerol as a plasticizer in *Chlorella* (at 20 wt%) improved the processability and nearly doubled the elongation to break (from 3.4% to 5.2%) while decreasing the strength and modulus (1.6 MPa and 53 MPa, respectively). Our preliminary results regarding the transformation of pure *Spirulina* cells to bioplastics via hot pressing, without the use of additives, show that their mechanical properties can improve by a factor of 10.4 for flexural modulus and 8.5 for flexural strength (H. Iyer, A.M. Jimenez, P. Grandgeorge, I. Campbell, M. Holden, et al., manuscript in preparation) compared with the previously reported results (98) if the processing conditions are tuned to allow maximization of biopolymer interactions within the algal matrix. In a bottom-up approach to tune the algal biopolymer content, Mathiot et al. (99) used a



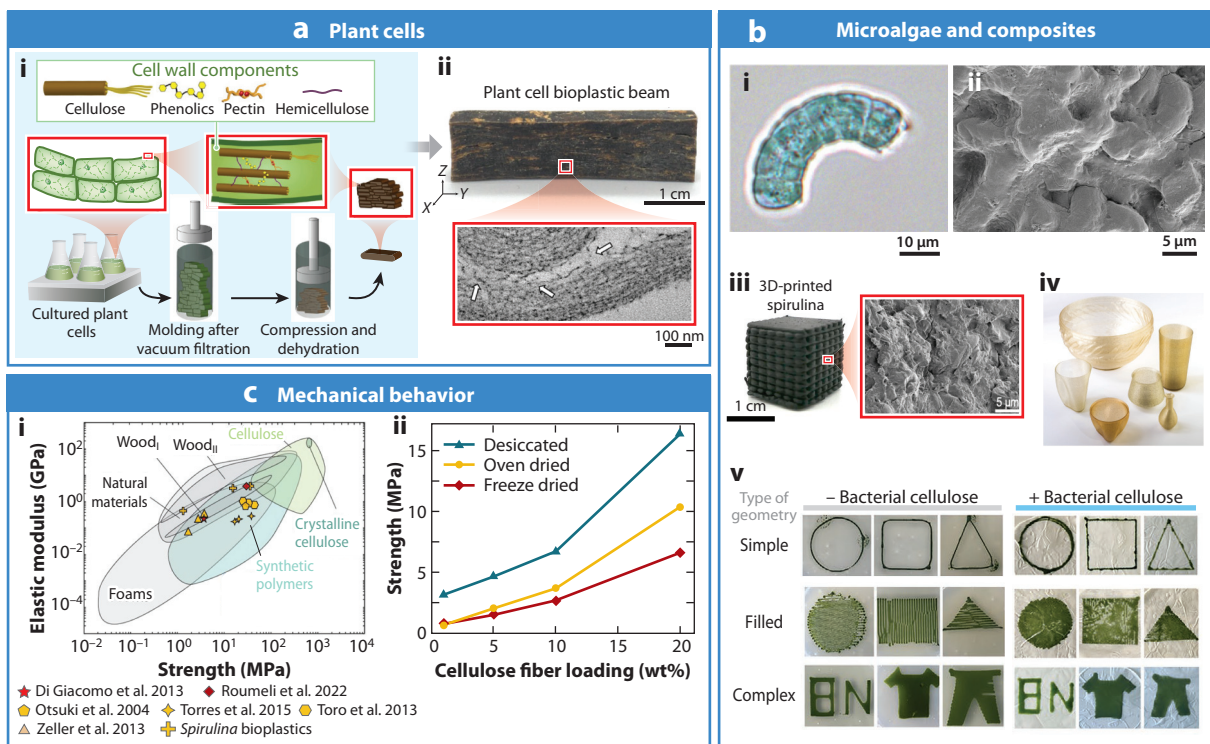


Figure 6

Materials produced from plant and algal biomatter. (a, i) Plant cells are cultured, placed in molds, and compressed to form bulk bioplastics without compromising cell wall structure. (a, ii) Dangling polymer fibrils (white arrows) connect adjacent cell walls and cause self-bonding at the molecular level. (b, i) Optical microscopy and (ii) scanning electron microscopy images of algae structure along with images of millimeter-scale algal-based produces printed via (iii, v) direct ink writing and (iv) fused deposition modeling. Panel adapted from References 94 and 95. (c, i) Comparison of mechanical properties between plant cell/algae materials to known biopolymers. (c, ii) The effect of cellulose fiber loading on the compressive strength of *Spirulina*/cellulose fiber direct ink writing cubes. Panel a adapted with permission from Reference 7. Panel b adapted with permission from (i–iii) Reference 93, (iv) Reference 94, and (v) Reference 95. Panel c adapted with permission from (i) Reference 7 and (ii) Reference 93.

sulfur-depleted medium to promote intracellular starch accumulation in *C. reinhardtii*, a unicellular green alga naturally rich in starch. By shear mixing in a twin screw extruder in the presence of 30% glycerol, the microalgae cell wall was disrupted, releasing starch, which facilitated homogeneous plasticization and improved processability.

Meanwhile, 3D printing of dried and living cell biomatter is an area quickly gaining in popularity (94, 95). Fredricks et al. (93) demonstrated that pure *Spirulina* cells suspended in water form a slurry that can be used for direct ink writing (DIW). The water-mediated interactions between the native biopolymers of the cells facilitated a bonding network, thereby eliminating the need to introduce external binders. The choice of drying method (freeze drying, oven drying, or desiccation) and the use of CFs as additives enabled tuning of the interactions and hierarchical structures of the printed materials (Figure 6b). For example, oven drying resulted in matrix plasticization, while freeze drying created a highly porous matrix. Pure algae prints suffered from shrinkage and associated cracking when dried in an oven or desiccator, which was alleviated by the introduction of CFs. Across all drying methods, the use of CFs consistently improved the matrix bonding and therefore print fidelity and structural integrity (Figure 6c). To mitigate the effect of shrinkage on

DIW prints, Kwak et al. (100) investigated the addition of oil and wax to a *Chlorella*-based ink. Oil aided in the dispersion of algae cells, trapping them at the interface between oil and water, while wax improved interparticle packing and enhanced the cell bonding within the matrix.

Using algae as fillers in plastic biocomposites, Otsuki et al. (101) reported high loadings of *Chlorella* (up to 40 wt%) compounded in polyethylene (PE) via twin-screw extrusion. Their study revealed that the poor interfacial adhesion between the algae and PE could be improved by using maleic anhydride as a compatibilizer, which enabled increases in strength (from 10 to 20 MPa) and modulus (from 0.25 to 0.67 GPa). Capitalizing on the native algal biopolymers, Saha et al. (102) studied the effects of preprocessing *Chlorella* to reduce its lipid content and dissociating the cells via ultrasonication before introducing them as fillers in a PU matrix. The reduction of lipids, which potentially serve as native plasticizers, together with the increase in the contact area between the algal biopolymers and the host matrix enhanced H-bonding between the defatted biomatter and matrix, resulting in progressive increases in tensile strength, modulus, and elongation to break with increasing biomass up to 50 wt%. Lastly, residual microalgal biomass (RMB), generated as waste in biodiesel production, has also been compounded with plastics such as poly(butylene adipate-terephthalate) (PBAT) and poly(butylene succinate) (PBS) in the presence of plasticizers (103, 104). Up to 30 wt% RMB was integrated with plastics via extrusion, leading to improvements in moduli (up to 64%) and reductions in strength (22–44% decrease) and extensibility (46% decrease).

The novel use of algae in structural materials such as concrete can be an effective means to reduce the associated carbon footprint. Chen et al. (105) introduced an aggregated form of *Chlorella* cells in ordinary Portland cement, showing that 0.5 wt%-addition of algae would reduce the embodied carbon of cement by 1% without affecting compressive strength (32 MPa) and processability. Highlighting the importance of surface functional groups of biomatter, preliminary results from our group (M-Y Lin, P. Grandgeorge, A.M. Jimenez, B. Nguyen & E. Roumeli, manuscript in preparation) show that using entire *Chlorella* cells without prior processing, at the same concentration as Chen et al. (105), caused notable decreases in the mechanical properties. We observed that the hydration reactions were inhibited as the carboxyl and hydroxyl groups of algae react with the calcium ions in cement, hindering the formation of calcium hydroxide. Our results suggest that more research is required to understand and modify the interactions between algae and cement to improve the mechanical properties of the biocomposite at higher concentrations.

## 5. FUTURE DIRECTIONS, CHALLENGES, AND OPPORTUNITIES

The growing field of sustainable polymers can provide solutions with significant implications for our society. Major breakthroughs are anticipated to arise from improving extraction processes to derive versatile monomers and designing novel polymers that will combine processability and high performance with enhanced biodegradability or recyclability. In parallel, developing scalable processes to upcycle or degrade existing plastic waste is also a viable solution to alleviate plastic pollution. Cutting-edge advancements that leverage locally available biomass and culturable materials for the manufacturing of biopolymers and/or biocomposites will facilitate fair economic growth while progressing toward circular plastics manufacturing.

Remaining challenges include reducing energy consumption and waste, upcycling plastic waste for the fabrication of biopolymers and biocomposites, improving the processability of materials for use with existing manufacturing methods, and identifying end-of-life options that reduce negative environmental and socioeconomic impacts. Holistic life-cycle assessment (LCA) models are becoming increasingly important in the field of sustainable materials as they provide insights into the energy consumption and environmental footprint of material sourcing, manufacturing, and



disposal of a given product (106). Outputs from typical LCA models include quantifiable parameters such as global warming potential (kilogram of CO<sub>2</sub> equivalent), smog output (kilogram of O<sub>3</sub>), fossil fuel usage (megajoule of surplus energy), water consumption, acidification potential, and less-defined ecotoxicity and human toxicity. Considering that the quality of LCA results is heavily dependent on the available data and the intrinsic conditions imposed by the adopted model, comparing outputs from different LCAs is challenging. In the case of biopolymers, an additional complication arises when accounting for the biogenic carbon sequestration as well as the environmental impacts from growing and harvesting the biomass (107). Still, as more LCA models are developed, and databases become more robust and transparent, the accuracy of LCAs will improve, incentivizing a broader use in estimating the environmental impact of materials and their manufacturing.

While the importance of evaluating environmental impacts of materials has been widely recognized, the socioeconomic aspect of the sustainability equation is often neglected (108). As the excessive heat, flooding, and soil degradation associated with petrochemical production tend to disproportionately impact poorer and underserved communities, evaluating the effect of materials research and development on social equity is crucial (109). Results from studies focused on quantifying the socioeconomic effects of petrochemicals as well as biobased materials are critical and should be considered in conjunction with LCAs in the rising field of sustainable materials.

## DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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