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Synthetic Biology Prospective

Synthetic biology for the development of bio-based binders for greener construction materials

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Abstract

The development of more sustainable construction materials is a crucial step toward the reduction of CO_2 emissions to mitigate climate change issues and minimize environmental impacts of the associated industries. Therefore, there is a growing demand for bio-based binders which are not only safer toward human and environmental health but also facilitate cleaner disposal of the construction materials and enable their compostability. Here, we summarize the most relevant bio-based polymers and molecules with applications in the construction sector. Due to the biologic nature of these materials, the existing biotechnologic processes, including synthetic biology, for their development and production have been evaluated.

Introduction

The emissions of the construction industry, which includes the production and use of conventional building materials such as bricks, concrete, and metal, were responsible for 20% of the worldwide CO_2 emissions in 2014.[1] These carbon emissions from the construction industry are projected to contribute more than 31% by 2020 and 52% by 2050.[2] The level of embodied CO_2 in conventional construction materials is very high[3] and urgently needs to be reduced to comply with climate change policies.[4] This embodied carbon of a material (EC, $kgCO_{2e}/kg_{MAT}$) is calculated based on criteria such as the energy required for the extraction and transportation of the raw materials, manufacturing process, building process on-site, use stage, and finally the management of the materials at the end of their service life (e.g., demolition and deposition in landfill or recycling).[5–7] A comprehensive review published recently by Pomponi and Moncaster[7] showed relevant figures that enable the identification of the most relevant factors that influence the EC of building materials; steel for instance exhibits the highest EC (generally over 1.5 $kgCO_{2e}/kg_{MAT}$), whereas the EC of recycled steel is generally well below 0.5 $kgCO_{2e}/kg_{MAT}$. Similarly to steel, high temperatures are required for the production of cement, thus these very energy-intensive manufacturing processes increase the EC of these two very common construction materials. In addition to this, the current technology for the production of high-quality steel relies mostly on coal (70% of global steel production in 2017[8]). The transition to cleaner alternatives such as DRI-H-EAF route (hydrogen-based direct reduced iron which is fed in to an electric-arc-furnace) or PDSP (hydrogen-based plasma-direct-steel-production) would make electricity a crucial input entailing not only high technologic challenges but also with consequences that would need to be addressed at the macroeconomic and social levels.[9] The emission of greenhouse gases is not the only negative environmental effect associated with the manufacturing process of these materials, the production of waste and pollution are also major drawbacks associated with the conventional construction industry.[5,10] For instance, during the extraction, transportation, and processing of raw materials for the production of Portland cement, there is a release of airborne pollutants such as toxic metals (Al, As, Hg, and Pb).[11,12] These toxic compounds are persistent and accumulate in soils, plants, and water, demonstrating a threat to public health and wildlife. In this context, the life cycle assessment (LCA) tool is being widely adopted as a decision tool to identify opportunities for environmental improvement such as a reduction of the embodied carbon in building materials and minimization of other environmental impacts such as pollution, however it is important to take into account that the LCA may show variations solely due to its method of use (e.g., data used and assumptions made[7]).

Thus, there is a need for replacing conventional building materials with greener alternatives as these exhibit lower EC across some of their life stages (e.g., production process and the stage beyond their end of life) while at the same time they may even enable the storage of CO_2e (e.g., hemp-lime walls).[13] Bio-based materials are not only generally more environmentally friendly and sustainable, but also exhibit multifunctional properties. For example, the plant-based building blocks known as agro-concrete, defined as a mixture of vegetable fibers and a mineral binder (usually lime),[14] can exhibit improved hygrothermal characteristics compared to conventional concrete, as well as good sound insulation properties.[15] One of the most common types of agro-concrete is hempcrete, comprised of hemp fibers (shiv), although the fibers of multiple plant species are now being used, such as flax, sunflower,[16] palm, coconut, miscanthus, bamboo,[14] and seagrass.[17] The source of the plant material depends on local availability, often dependent upon local agricultural practices, as this reduces the cost of transport and associated CO_2 emissions, and also supports the local economy by adding value to agricultural waste streams. Material scientists continue to work toward the identification of new lignocellulosic fibrous materials and natural binders to produce biocomposites, aiming to make the most of the natural resources available and to ensure that these materials do not compete for food resources. The study developed by Ferrero et al.[17] is an interesting example, in which the seagrass fibers (seagrass is usually collected while cleaning touristic beaches and disposed of in landfills), together with wheat gluten as a binding agent, were used to make composites exhibiting excellent flexural strength that could replace commodity or even technical plastics.

The LCA of hempcretes has determined that the use of lime as a binder significantly increases the environmental impact of agro-concrete.[18,19] For this reason, with the aim to reduce the carbon footprint and sustainability of agro-concretes, one of the current industry targets is to replace the lime with more eco-friendly binders such as clays,[20] natural pozzolans (siliceous/aluminous materials such as volcanic ash and calcined clays),[21] and other bio-based binders such as rice husk ash (RHA).[22] Between mineral and biologic compounds, the latter are the most sustainable alternative in terms of renewability and biodegradability. Therefore, research in the field of bio-based construction materials, supported by advances in biotechnology and nanotechnology, is looking for alternatives to synthetic adhesives and binding materials, not only to minimize the environmental footprint but also to produce safer compounds (e.g., the replacement of formaldehyde-based resins by natural-based materials). The present literature review aims to cover the most relevant and up to date knowledge available about biologic binders that are totally, or partially, capable of replacing the synthetic or mineral binding/adhesive compounds used for manufacturing biologic construction materials and to highlight the way synthetic biology can contribute to their development and enable to scale-up their production in a cost efficient manner.

Biologic binders

General overview of sources and applications of bio-based binders

Bio-based compounds with adhesive or binding properties are obtained from a wide range of sources (e.g., animal, plants, and bacteria) and processes (Table I). The majority are derived from plants and are very diverse in terms of physicochemical properties (e.g., lignin, tannins, starch, nanosilica), whereas chitin and casein are animal-derived adhesives, and the biologic plastic poly(lactic) acid (PLA) is produced via a microbial fermentation process. Other binding agents such as alginate and nanocellulose may be obtained from both plants and bacteria.

The variety of the compounds reportedly used as binders is very diverse, with many being multifunctional, and a concise description of the most relevant biologic compounds identified in the literature, with useful properties as binders in the construction sector is described here. It is important to consider that the ideal physicochemical properties of binders (e.g., viscosity and mechanical strength) will depend on the material to be glued. However, properties such as resistance to water and biologic degradation, high bonding strength, and storage stability are always desirable traits.[23]

Plant-based binders

Alginate

Alginate or alginic acid is a negatively charged polysaccharide found in brown seaweed and also produced by some bacterial species from the *Pseudomonas* and *Azotobacter* genera[48] (Fig. 1). One of the most characteristic properties of alginate is its solubility in water at low temperatures and the formation of gels, including complexes with divalent and trivalent cations.

Alginate shows the potential as an adhesive for the development of bio-based construction materials with diverse applications, including fire-retardant properties,[42] depending on the fibers used. For instance, bio-composites produced with flexible fibers (e.g., cotton fibers) will serve as flexible filling insulation materials, whereas if harder fibers are used (e.g., wood fibers), the rigidity of the final material will increase offering better mechanical strength properties. Recently Lacoste et al.[41] showed that sodium-alginate can act as a suitable binder for the production of semi-rigid bio-composites (mix of plant fibers and cotton fibers from recycled clothes) with applications such as insulation materials (conductivity was lower than 0.1 W/m/K). When alginate is used as a binder in biocomposites made from crop by-products (rice husk, barley straw, and corn pith), it can enhance the fire-retardant properties of the resulting material. This is due to the low heat release (HR = 2.5 MJ/kg) of the biocomposites, which have even been demonstrated as being much safer than some non-biologic insulating materials such as polystyrene and polyurethane.[42]

Commercially produced alginate is usually brown seaweed derived,[51] however, harvesting alginate from seaweed results in a material with less predictable characteristics due to the biomolecular diversity introduced through the variable growth conditions produced by natural weather systems and seasonal change. To address this, the use of bacterial species can be used to synthesize the binder[48] allowing for greater control over conditions and therefore a more consistent alginate.

The biosynthesis pathways in *Pseudomonas* and *Azotobacter* are very similar[48] and directly comparing the pathways along with any mutations therein has allowed for the development of an *Azotobacter vinelandi*-based process

Table I. Bio-based binders according to their origin and application.

	Application			
	Rigid materials	Filling insulation material	Concrete agro-concrete	Hydrophobic films/ coatings
Source/origin				
Plants				
Lignocellulosic material	Lignosulfonates[24] Lignin[25,26]	Lignosulfonates[27]		
Soft parts of plants	Tannins[28,29]			
Rice husk			Rice husk ash[22]	
			SiO_2 nanoparticles[30]	SiO_2 nanoparticles[31]
Corn	Corn starch[29]	Corn starch[32]		
Wheat		Wheat starch[33,35]; wheat straw powder[36]; wheat gluten[17]		
Plants/microorganisms				
Lignocellulosic material and cotton buds		Nanocellulose[37,38]	Nanocellulose[39,40]	
Seaweed/bacteria		Alginate[41,42]		
Microorganisms				
Bacteria/fungi		Poly(lactic acid) (PLA)[43]	PLA[44]	PLA[45]
Animal				
Exoskeleton of insects and Crustacean/fungi	Chitosan[24,46]	Chitin in mycelium biocomposites[47]		
Milk				Casein[31]

to give increased substrate production[52] and improved properties while still maintaining a high yield.[50] These modifications were produced using randomized and directed transposon mutagenesis.[53,54] While this method of genetic manipulation is good for high throughput screening, the efficiency is very low. The work conducted to date provides only the groundwork for the continued optimization of the process using synthetic biology tools. While few of these tools are available in *Azotobacter* sp. there are many available for *Pseudomonads*, specifically a CRISPR/Cas9 protocol has been developed for use in *Pseudomonas aeruginosa*,[55] which potentially can be used to induce the same mutations and insertions in a more industrially relevant *Pseudomonas* species with greater design and control to further tailor the desirable effects.

Nanocellulose

The term nanocellulose relates to three major forms of cellulosic materials in the nano and micro scale range. The cellulose nanocrystals (CNCs) and cellulose nanofibril cellulose (NFC), also known as microfibrillated cellulose (MFC), are obtained from pure cellulose derived from plant biomass (e.g., wood, cotton, diverse fibrous vegetable material such as straw). The third major group is bacterial nanocellulose (BNC) produced by bacteria[56] via a fermentation process that can be fed from forest, agricultural, and food waste streams.[57,58] These cellulosic nanomaterials exhibit very useful properties such as high surface area, high tensile strength, and a surface chemistry rich in hydroxyl groups that enables their functionalization.[59,60] There are several production processes to obtain plant-derived nanocellulose,[56,61] with acid hydrolysis being the most common technique used for manufacturing CNCs resulting in whiskers of rod-shaped nanoparticles, 100–200 nm in length and 5–20 in diameter. The NFCs are generally produced by high-pressurized mechanical homogenization of the lignocellulosic pulp (vegetable fibers treated under alkaline conditions, e.g., sodium hydroxide and sodium sulfide). The fibrils can be longer than 1 μm in length with an average cross-section of 5 nm.[61] Ng et al.[61] recently published a comprehensive review comparing different aspects of CNCs and NFCs, such as their mechanical, thermal, and hygrothermal

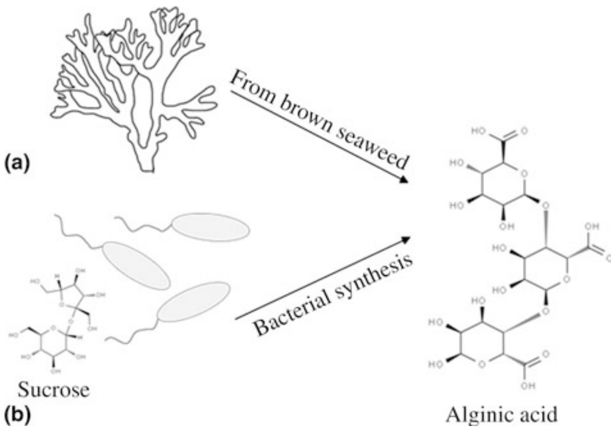

Figure 1. Schematic representation of sources of alginic acid[49]from (A) brown seaweed or (B) from bacterial growing on sucrose.[50]

properties. Overall, these nanocellulosic materials have a very high water holding capacity due to their extremely large surface area and the presence of hydroxyl groups, which trap and bind the water molecules, respectively.[62] Due to this property, nanocellulose is being used in hydrogels and aerogels for multiple applications as they confer enhanced properties in terms of mechanical strength, insulation,[31] and absorbance[32,51] (Table II). Nanocellulose is also being used as a reinforcement agent in nanocomposite materials due to hornification (i.e., upon water removal from the nanocellulose network, an irreversible hardening of the cellulosic fibers takes place which increases the stiffness of the composite). Within the building industry, Claramunt et al.[33] showed that the hornification of lignocellulosic material (kraft pulp and cotton linterns), for the production of vegetable fiber-reinforced cement matrix composites, improved the durability and mechanical performance of the cement mortar.

It is worth noting that BNC may exhibit better mechanical properties than plant-sourced nanocellulose due to its greater crystallinity and a higher degree of polymerization.[65] Lee et al.[40] provided a detailed example of the manufacturing process of sisal fiber composite plates, in which BNC was included as a binder and as a strengthening agent. Recent work in the area of synthetic biology and the cellulose-producing bacterium *Komagataeibacter rhaeticus* may lead to the production of patterned biologic materials with unique properties in terms of macrostructure and function. Walker et al.[66] have engineered *K. rhaeticus* with genetic manipulation tools to insert synthetic circuits into the cellulose pathway which respond to intercellular signaling. This may pave the way for improvements in cell-to-cell communication for engineered living materials, allowing for a greater range of responses to external conditions. Their work also displays the versatile uses of synthetic biology tools for genetic manipulation within cellulose-producing bacteria.

Lignin and lignosulfonates

Calcium and sodium lignosulfonates are polyanions, very water-soluble compounds derived from lignin, an abundant and highly aromatic plant polymer obtained as a waste product from the pulp and paper industry.[67] The chemical composition of lignin and lignosulfonates depends upon several factors, with the plant species (source of the lignocellulosic biomass) and the extraction method used to separate the lignin from cellulose and hemicellulose, being the most important. Essentially, lignosulfonates are sulfonated lignins; very condensed polymers with a high content in sulfonyl, carboxyl, and phenolic-hydroxyl groups[68] as depicted in Fig. 2. Calcium lignosulfonate has been used as a plasticizing and dispersing agent in Portland cement for almost a century[69] and as a binder and dispersant for the production of ceramic[70] and coal briquettes.[71] Currently, lignosulfonate-based compounds are commercialized for a wide range of applications, although scarce information is available in the scientific literature about their uses as binders in agro-concrete or other biologic construction materials. The application of lignosulfonates as components of construction materials are diverse (Table III); they can act as wood adhesives in combination with chitosan[24] and as a dedusting agent in the formulation of vegetable oils, which are an alternative to mineral-based oil emulsions used, for instance, for the production of rock wool.[27]

The method of enzymatically isolating lignin has been in use since 1990.[74] It has been used to isolate lignin from kraft pulp[75] and can be used to recover lignin from a range of waste sources such as the paper industry and sawmill waste streams.[76] This displays the plethora of redirectable sources of lignin that is currently untapped which could be utilized and again, there is the potential for synthetic biology tools to facilitate research in this area through the rapid improvement of enzymes and enzymatic processes.

Rice husk ash and SiO_2 nanoparticles

The high silica (SiO_2) content present in RHA makes this co-product of the rice industry a plant-based alternative to mineral cementitious materials. Work has shown that RHA can replace up to 30% in weight of ordinary Portland cement (OPC), without any loss in binding strength and improves its anticorrosion properties as the presence of RHA reduces water permeability (35%), chloride penetration (75%), and diffusion (28%).[22] In addition to RHA, advances in nanotechnology have enabled the production of SiO_2 nanoparticles that can be obtained from rice husk after HCl-treatment followed by controlled pyrolysis[78] or alkali extraction followed by acid precipitation.[79] To date, the effects of SiO_2 nanoparticles have not been investigated on agro-concrete but numerous studies performed with conventional concrete indicate that nanosilica improves the mechanical properties and durability.[30]

Another potential application of nano-silica in bioconstruction is as a component of latex composite films to

Table II. Nanocellulose-based binders.

Source of cellulose	Application	Output	Reference
Cellulosic fibers (kraft pulp and cotton linters)	Portland cement	Reinforcement	[39]
Bacterial nanocellulose	Sisal fibers	Binder and strengthening agent in sisal composites	[40]
Natural cellulose nanofibers (CNFs) and microfibrillated cellulose (MFC)	Nanocomposite films	• Used to prepare nanocomposite films using an acrylic polymer as matrix • Increase of the stiffness of the acrylic polymer MFC showed higher reinforcing effect compared to CNCs	[63]
Natural cellulose nanofibers (CNFs)	Portland cement	• Enhancer of construction Portland cement • Increase in the flexural and compressive strengths of cement paste	[64]

improve the hydrophobicity and water resistance of the building materials. Xu et al.[31] showed that the addition of SiO_2 nanoparticles to casein–latex composites improved the hydrophobic properties and tensile strength of nano-composite latex, although on the other hand, the flexibility of the latex film decreased.

Starch

Starch is a carbohydrate constituted by long chains of glucose units joined by glycosidic bonds. Wheat starch has been used as a binder for the production of hemp-aggregates (Table IV) and, even though it could not be utilized as a structural material due to its low tensile strength (low elasticity modulus, below 2.16 MPa), it performed well as a filling material being light and exhibiting good mechanical strength (compressive and tensile strength)[33] which can be improved by pre-treating hemp fibers with NaOH and silane.[80] Further studies conducted by Le et al.[34] concluded that smaller hemp shives (also known as hemp hurds, the woody part of the hemp stalk) and lower hemp/starch ratio conferred higher compressive and tensile strength to the plant composite, which exhibited the potential as a sound insulating material (sound absorption coefficient was around 0.7) due to the porosity of this plant fibrous material. Later work showed that a combination of small (0–5 mm, 30%) and bigger shive sizes (0–20 mm, 70%) leads to the best mechanical properties, not to the standard of the hemp-lime composite, but with superior Moisture Buffering Values (MBV).[35] MBV indicate the ability of a material to store or release moisture when the relative humidity (RH) of the air that surrounds the material changes. Materials with MBV >2 (g/m^2%RH) are considered to exhibit excellent buffering capacity.[81] Starch confers good moister buffering properties when used as a binder in hemp-based materials due to its water sorption properties associated to the interaction between the water molecules and the hydroxyl groups (−OH) present in the starch polymer[82] depicted in Fig. 3.

Similar findings to Le's work were obtained in a different study conducted by Belakroum et al.,[32] in which it was observed that including corn starch as a binder in palm fibers resulted in the production of composites more efficient than lime-palm fibers in terms of sound insulating material for high and medium frequencies (between the ranges of 1500 and 6300 Hz, the absorption coefficient for sound exceeds 0.7), and that at increasing concentrations of corn starch the MBV (4.05 $g/m^2/\%RH^1$) improved as well.

Tannins

Tannins are plant polymers present in vascular and non-vascular plants. They are rich in phenolic and aliphatic hydroxyl groups, the second most abundant green source of aromatic compounds after lignin. Tannins are present in the soft tissue of plants (e.g., inner bark and leaves) and have been incorporated as an adhesive in wood panels as an alternative to formaldehyde-based resins.[84] Work developed in this

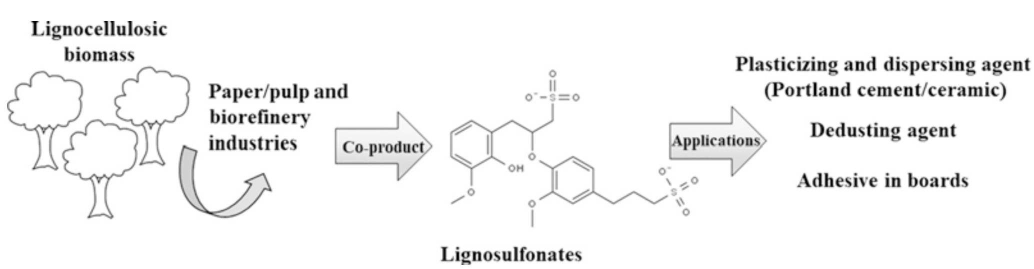

Figure 2. Schematic representation of the most common sources and applications of lignosulfonates and general chemical structure.[77]

Table III. Lignin-based binders.

Source	Application	Output	Reference
Lignosulfonates	Plasticizing agent in Portland cement	The lignosulfonate anions are adsorbed by the cement particles which enhances their dispersion	[69]
Lignosulfonates	A binder and dispersant in ceramic	Patent number US5656562 A	[70]
Ammonium lignosulfonate	Wood adhesives in (MDF)[a]	The addition of chitosan enhanced the improved MOR[b], MOE[c] and impact strength of the boards	[24]
Lignosulfonates	Dedusting agent in the formulation of vegetable oils	Lignosulfonates acted as an emulsifier that enabled the curing of phenol-formaldehyde resins at lower temperatures than mineral-based oils compounds	[27]
Technical lignins and lignosulfonates	Adhesive in wood boards	• The adhesive properties of the lignin polymer are enhanced after its oxidation with enzymes • Patent numbers WO1998031729A1, WO1998031763A1, WO1998031764A1	[25,26,72]
Kraft lignin	Adhesive in corn stalk fiberboards	• Boards containing 20% kraft lignin comply with the relevant standard specifications. Improved modulus of rupture (bending strength), modulus of elasticity (stiffness in an elastic material), and impact strength compared to commercial fiberboard but thermos-mechanical performance	[73]

[a]Medium density fiber.
[b]Modulus of rupture.
[c]Modulus of elasticity.

area has shown that synthetic resins can be partially substituted by using a combination of tannins and another biologic compound, such as corn starch.[29] While more recent work developed by Santiago-Medina et al.[28] demonstrated that formaldehyde can be replaced completely in wood ply boards, by 4-phenoxybenzaldehyde, a bio-based aldehyde, derived from vanillin, a small aromatic compound obtained from lignin.

In recent times, synthetic biology offers an alternative to crop growth for plant-derived products in the form of plant-based in vitro systems such as calluses and plant cell cultures.[85] The production of tannins has been observed in plant calluses as far back as the 1960s[86,87] but while the production of tannins in this method is more industrially favorable, it does result in lower yields compared to plants.[88] Suvanto et al. compared a selection of plant cell cultures for tannin production, this revealed that a combination of three species (*Sorbus aucuparia*, *Vaccinium myrtillus*, and *Empetrum nigrum*) proved an exception to this lower yield.[88] With the advances in synthetic biology, it may be possible to characterize the genes involved in this collaboration and improve the yield under these callus cultivation and cell culture conditions. In vitro plant systems provide the perfect conditions for genetic manipulation with a number of synthetic biology tools, including CRISPR/Cas9[89] and transgenic modification[90] These tools can be used for the synthesis of bioactive secondary metabolites or to develop desirable polymer traits for a more specialized product.[85]

Non-plant-derived biologic binders

Casein

The adhesive properties of casein, the most abundant protein in milk, have been known for centuries. It was utilized as a wood adhesive to be later put aside by synthetic resins.[91] Nowadays this is likely to change as there is an increasing interest for using biologic compounds, such as casein, to manufacture biodegradable plastics[92] as a result of the environmental impact caused by the use of synthetic plastic. In addition to this, casein can be sourced from the waste streams of the milk industry, adding value to the resulting by-products.[93] Powdered casein glues are commercially available, and used for bottle labeling as it makes them easily removable with washing.[94] In addition to being a component in adhesives, casein forms a part of coatings and paints[91,95] (e.g., in silica nano-composite latex[31]), with potential applications for the production of hydrophobic films and coatings. Casein is also useful as a dispersant and a binding agent for the synthesis of PLA-nanocellulose biologic reinforcements.[45]

Chitin and chitosan

Chitin is an aminopolysaccharide, the second most abundant biologic polymer on Earth after cellulose,[96] as it forms part of the exoskeleton of insects and crustaceans, and the cell wall of fungi. Chitin exhibits a similar structure to cellulose, this is glucose molecules linked by β-(1,4) glycosidic linkages,

Table IV. Starch-based binders.

Source	Application	Output	Reference
Corn starch	Binder in date palm fibers composite for sound insulating material	• Better MBV properties than trunk + lime and petiole fiber + lime composites • Palm fiber + corn starch good sound insulating material	[32]
Wheat starch	Binder in starch-hemp composite as a filling material	Very low Young modulus thus not allowed as a construction material but as filling materials	[33]
Wheat starch	Binder in starch-hemp composite as a filling material	• The biocomposite have a good mechanical and acoustical performance and can be used as building materials • Extensive study	[34]
Wheat starch	Binder in starch-hemp composite as a filling material	• 100% plant-based material • Extensive study of the physical and hygrothermal properties and mechanical behavior	[35]
Corn starch	Binder in rice husk, corn pith, and barley straw composites	Improved fire-retardant properties, especially corn pith + corn starch, better than synthetic insulating materials (polystyrene or polyurethane)	[42]
Wheat starch	Binder in hemp-starch concrete	Hemp fibers were pretreated under alkaline conditions followed by a treatment with silane to create cross-linkages between the matrix and the fibers. These pretreatments increased the compressive strength from 0.4 to 0.8 MPa and the Young modules improved from 1.75 to 3.2 mPa	[80]

but it is less exploited, possibly because the cost of its extraction and purification is higher than that of cellulose.[96] Chitosan is derived from chitin by deacetylation under alkaline conditions; it is water soluble in acidic media, whereas chitin does not dissolve in water. The adhesive properties of chitosan have been exploited extensively in products of high value such as biomedical applications.[97] The presence of numerous reactive functional groups in chitosan confers to this polymer important electrolyte properties, high adsorption capacity, and gel-forming capability. These characteristics together with its biodegradability and low toxicity enable its utilization in drug delivery systems, as scaffolds in tissue engineering, for gene therapy and bio-imaging.[98] However, regarding bioconstruction, it has also been used successfully as a glue agent in plywood[46] and mycelium biocomposites,[47] and for the production of plant-based (sunflower stalks) insulating blocks.[99]

While chitin is highly abundant, the difficulty comes from the recovery and purification of the polymer. This is traditionally done with mechanical grinding and extreme shifts in pH,[100–102] which can affect the properties of the polymer such as molecular weight and degrees of acetylation.[103] The biotechnological solution is to use microbial fermentation or enzymatic hydrolysis of the chitin-rich biowaste to purify the

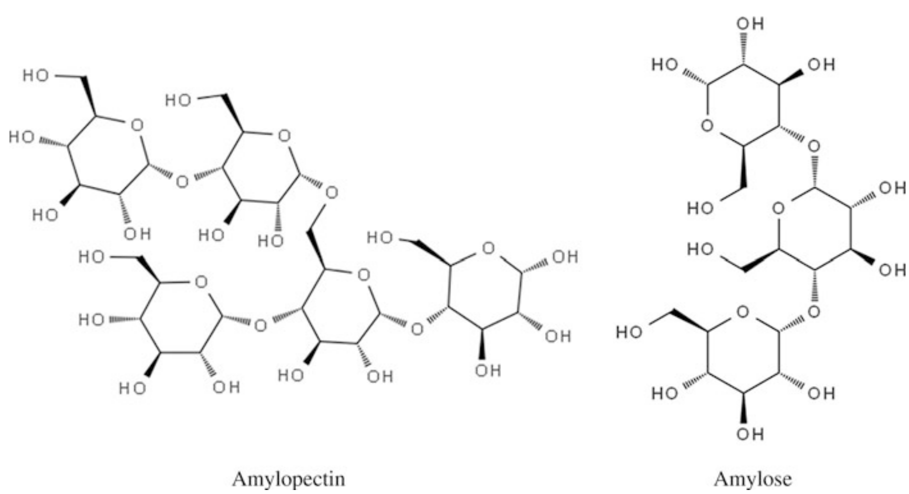

Figure 3. Chemical structure of amylopectin and amylose,[83] the two main molecules that form the starch polymer.

chitin in a form which does not damage the polymer, maintains high yields, and offers a route free of caustic and acidic reagents.[103]

Poly(lactic acid)

PLA or polylactide is a biodegradable polymer, an aliphatic polyester produced from the microbial fermentation of sugars which fungi and bacteria can source from agricultural and food industry waste streams.[104] PLA has been used successfully as a binder for bio-based composite materials, for example, in the construction of a pedestrian bridge,[38] and to improve the compressive strength of hemp composites.[37] PLA is also a component of biological nanocomposites, for example, dispersed with casein in a matrix of nanocellulose that results in efficient reinforcement nanomaterials.[39]

PLA is generally produced chemically from lactic acid, which can be chemically synthesized or made by microbial fermentation,[105] the latter being a more pure product than chemical synthesis which produces a racemic mixture.[106] More recently, organisms have been specifically engineered using synthetic biology to create an original metabolic pathway allowing for long chains of pure PLA to be produced.[107] This process has been further improved in *Escherichia coli* by creating deletions using homologous recombination,[108] introduction of propionate CoA transferase from *Clostridium propionicum*[109] and the enzyme polyhydroxyalkanoates synthase.[110] This combination allows for the removal of the secondary synthesis step and allows for PLA to be produced entirely by *E. coli*.[107]

Other biotechnologic solutions

Self-bonding/binderless boards

The production of self-bonding particleboards, also known as binderless boards, to avoid the use of formaldehyde-based resins has been under study for decades, initially because of the health concerns associated to the formaldehyde emissions indoors, and more recently due to the need for the production of more sustainable materials.[23] In this line of research, one of the most relevant approaches to produce bio-based binderless boards, without the addition of adhesives, relies on the functionalization of the natural fiber surface (wood material or other lignocellulosic particles) that can be obtained from agricultural co-products such as wheat straw[111] or from agro-industries' residues such as leaf sheath fiber bundles from plantain.[112] The functionalization of the fibers is mostly based on the enzymatic oxidation of the native lignin (naturally present in the lignocellulosic material).

In regards to the enzymes required during the pretreatment, laccases are the most common enzymes used to pre-treat fibers, although peroxidases have also been used.[113] These enzymes are synthesized naturally by bacteria and fungi although they can be produced on a much larger scale with genetically engineered microorganisms[114] at a reduced production cost. The research developed by Felby et al. showed evidence that cross-links in the native lignin of the wood fibers and boards were formed after the pretreatment with laccase.[115] Moreover, an increased hydrophobicity of the fiber surface was observed and it is likely that the surface compatibility between the fibers' surfaces was also enhanced.[116]

The use of commercial lignin (e.g., kraft lignin, lignosulfonates) instead of the native lignin treated with laccase as board adhesives has been patented.[25,26,72] Lignosulfonates are not suitable due to their hydrophilic nature[117] and another drawback, pointed out by Widsten and Kandelbauer, could be the high cost of some commercial lignin types if large quantities are needed.[118] With this in mind, Velásquez et al.[119] compared the effects of replacing fibers of steam-exploded *Miscanthus sinensis* with commercial kraft lignin and observed that the properties of the board improved when 20% of *M. sinensis* was replaced by the commercial lignin. This demonstrates that while the use of the native lignin may offer a cheaper alternative, the addition of commercial lignins, which are produced in large quantities and with diverse physicochemical properties,[67] deserves further investigation.

Bacterial-sand bio-bricks

The cementation of sand by bacteria, to produce bricks with the same mechanical properties and features as conventional bricks, has been a great success. Bacteria can produce the cementation media from urea and calcium.[120] In a brick mould, the bacterial growth leads to the precipitation of calcite between particles, cementing the sand particles and creating a solid and stiff material. This bacterial function is also being exploited for crack reparation in conventional concrete[121] known as self-repairing bioconcrete, through the incorporation of living bacteria.[122] After the production of the material, the bacteria used to cement the bricks together are left within the material, and can survive there for several months without food or oxygen.[123] This means that the repairing mechanism is very easy to use and can repair cracks in as little as 28 days.[123] However, there are still several drawbacks as the use of laboratory grade nutrient sources reduces the viability of use in field applications, and the organisms within the material would not survive long term. While there is a great deal of potential for bio-bricks, since the nutrient supply being the highest cost (60% of total operating costs[123]), the durability of the bacteria could be improved. An alternative could be the use of bacterial-free solutions such as bacterial carbonic anhydrase (CA) enzymes responsible for the conversion of CO_2 into calcite. This type of enzyme can be produced by wild-type bacteria[124,125] or bacteria engineered using genetic tools[126] and offers great potential not only for CO_2 atmospheric sequestration but also for the development of environmentally friendly solutions in the construction sector.

Current constraints in the field might be aided by the ongoing research being developed in the area of synthetic biology which is looking at the feasibility of building 3D-patterned living materials with applications in diverse fields including civil engineering[127] and to scale-up the production of promising enzymes such as the CA.[126]

Mycelium biocomposites

The importance of microorganisms to help us design and manufacture new materials is immeasurable, and the biocomposites of mycelium, more commonly known as mushroom roots, depict a perfect example in the areas of sustainable construction and architecture. These blocks exhibit similar properties to polystyrene foams with the advantages of being made of 100% renewable materials (small building blocks of mycelium glued with chitin supported on plywood) that can be disposed of safely, as they are easily biodegradable.[47]

Challenges and opportunities

Existing technology and current knowledge enable the production of bio-based binders and adhesives that allow the production of 100% biological materials. These biocomposites could completely replace some of the conventional materials used in construction, such as filling/insulating materials, coatings, and boards. In this context, biotechnological approaches aided by the use of synthetic biology tools can support the production of the biologic binders by several means: (1) by scaling-up the production of enzymes allowing cost-efficient treatment of feedstock (e.g., functionalization of lignin), (2) through the bioremediation of industrial water and waste streams to enable their valorization,[128] (3) by up-cycling organic material (e.g., food waste) into more valuable compounds such as nanocellulose. The optimization of these processes should lead to the maximized use of resources, as well as the re-purposing of waste as a resource, preventing competition with basic needs such as food and water.

While re-purposing waste as a raw material can decrease the costs involved with biological-based binders and does not compete with food production, where there is not a waste stream to tap into, bacterial production of the polymer could be an alternative. This would allow greater control over the properties of the synthesized polymer, tailoring it specifically for the construction industry, and reduced production costs. Plant in vitro systems can also be used as they have similar growing conditions to those in bacterial production, but they are an alternative in cases where the synthetic pathways are too complex to be transferred to bacteria themselves. Bacterial and plant callus factories are also ideal candidates for gene and pathway characterization.

The production of biological structural building blocks with comparable performance to agro-concrete containing mineral-based binders, or to conventional bricks and concrete is still under development. This is because some mechanical properties (e.g., compressive strength) of biological materials need to be improved. Consumer demand for more sustainable construction materials is a key contributing factor for driving these improvements. The synthetic biology tools mentioned in this review can be applied to support future developments in the field as well as to scale-up their production to make them more competitive and cost-effective. The availability of raw materials for the synthesis of bio-based binders should not be a constraint because they can be obtained from renewable and sustainable feedstocks produced as co-products or sourced from the waste streams of different industries (e.g., agro-food industry, biorefineries, and pulp/paper industry).

A shift in culture in the construction sector is also required as it is notable for exhibiting resistance to new technologies.[129] Action toward a "zero carbon" construction sector is urgently needed to prevent the acceleration of climate change and to ensure the more sustainable use of natural resources to move us toward a more circular economy and secure the availability of materials in the future.[130] Besides this, innovation in the sector will create new export opportunities[131] and contribute to the clean growth of the world economy.

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