Biomass conversion into recyclable strong materials

We review the conversion of waste biomass into recyclable materials using different methods of materials treatment such as thermal, mechanical and chemical processes. Renewable and sustainable biomaterials are increasingly becoming alternatives for synthetic strong materials, e.g. composites. The type of treatment of biomass will determine the form to which the biomass is converted and its subsequent applications. It is anticipated that the transformation will produce materials that have superior qualities, properties and characteristics. These include biopolymer materials such as cellulose and hemicellulose, which have all been obtained as products of treatment and extraction from plant materials such as lignocellulose. The main reason for inefficient biomass conversion has been found to be poor manipulation of composite properties during biomass treatment process. The treatment processes are expected to facilitate dehydration, dehydrogenation, deoxygenation and decarboxylation of the bulk biomass materials to target the formation of new compounds that may be used to make strong materials.

Significance:
This work demonstrates that plant material, as a solid-state biomass material for strong structural applications such as in biocomposites, is affected by factors that include the alignment of fibres, orientation of fibres, and mass density distribution. However, biocomposite materials have been found to be non-toxic, corrosion-resistant, low-cost, and renewable. They are preferred because the materials possess high thermal stability, are biodegradable and recyclable, and have high biocompatibility, performance, strength, water-resistance, specific surface area and aspect ratio to qualify them for applications including biobricks for construction, slabs for paving, vehicle internal components, ultra-high temperature aerospace ceramics, and energy storage devices.

Introduction
Global demand for and usage of materials has grown over the past century and the environmental impacts associated with materials management are projected to more than double in the coming decades, with adverse consequences for human health, ecosystems, and the economy. As more materials are used, more wastes are generated and the recycling and recovery rates of these wastes remain low, with most of the waste landfilled or down-cycled and used as lower-value materials. The process of moving biomass waste materials up the green economy hierarchy requires a deep understanding of the nature of the waste materials in terms of their respective physical and chemical properties and characteristics. These parameters determine how the waste materials may be taken up the hierarchy – either as bulk material, broken down into unit components that will be used in different applications, or as a usable form converted through chemical processing of the components of the materials. Biomass may also be converted into recycled materials that have added value with advanced applications either as the bulk material or processed product. Agriculture has been conceptualised into a phenomenon called dual cropping, in which the ability of crops to supply grain for food and then feed and straw or residues for bio-refining is being prioritised. Thus, there is a shift in the breeding of crops to increase grain yield and quality while decreasing straw yield by selection of dwarf-lines, to the practising of programmes that consider harvesting index, a measure of the grain yield relative to total biomass yield.

This work highlights the principal purpose of the waste hierarchy as a way to convert 100% of biomass waste from different waste streams, with the conversion process generating none or the minimum amount of waste, and derive maximum practical benefits from the products that are higher up the bioeconomy hierarchy. Waste hierarchy offers the following advantages: new sources of materials for strong materials fabrication, reduction in pollution, decreasing greenhouse gas emissions, energy conservation, resource preservation, job creation opportunities and stimulation of the growth of green technology. Waste conversion to high hierarchical bioeconomic products is systematic, and serves as an holistic approach to waste management during the life cycle of waste material. Based on the schematic in Figure 1, the waste biomass hierarchy addresses reduction and avoidance, re-use, recycling, recovery, treatment, bulk conversion to strong materials, and safe disposal. An application of the waste hierarchy is interlinked with a circular economy.

![Illustration of the waste management hierarchy](https://doi.org/10.17159/sajs.2022/9747)

Figure 1: Illustration of the waste management hierarchy.
A transition to a circular economy (Figure 2) to increase resource efficiency can lower resource demands and environmental impacts and contribute to economic and social recovery. The circular economy concept involves the use of materials for as long as possible through recycling and material resourcing, as presented in Figure 2. The bio-economy is described as the set of economic activities in which biotechnology contributes centrally to primary production and industry, especially where the advanced life sciences are applied to the conversion of biomass into materials, chemicals and fuels. An effective bio-economy must mobilise large quantities of biomass from a range of resources, including agricultural and forestry residues, and organic fractions of domestic waste.

Lignocellulose is made up of carbohydrate polymers, namely cellulose, hemicellulose and lignin, which is an aromatic polymer. It is the most abundant raw material for bio-based products. Preliminary studies have been conducted on the properties of different lignocellulosic biomasses to determine how to modify biomass for moving it up the hierarchy. It was determined that the use of acidified and non-acidified sodium chlorite to treat wood chips and sugar cane bagasse produced cellulose products that were devoid of aromatic compounds to give high quality lignin and hemicellulose. The moving of biomass up the hierarchy may take a wide range of forms, starting from molecular levels such as in the extraction of active medical or cosmetic ingredients, to whole or bulk biomass such as in the pulp and paper industry. For example, Eucommia ulmoides Oliv. is a widely cultivated medicinal herb with a leaf that is a hyper-accumulator of chlorogenic acid, a type of phenylpropanoid, and it possesses a large number of biological activities such as antibacterial, antioxidant and anti-obesity, and lowers blood pressure. The organic plant material was studied for adsorption and desorption of chlorogenic acid using macroporous adsorbent resins during the extraction of the E. ulmoides leaves.

Treatment and extraction: From soluble to solid-state biomass materials

Biomass from different sources — such as wood, waste plant materials, microalgae and terrestrial energy plants — has been converted into either alternative liquid biofuels or solid-state biomass as bulk or as macromolecules and nanosized particles. Many technical pathways have been developed, including extraction and hydro-treating, pyrolysis, gasification and Fischer–Tropsch synthesis. Biorefinery processes, such as ultrasound and microwave-assisted ternary deep eutectic solvents pre-treatment, were developed to deconstruct the recalcitrant structure of biomass materials for further lignocellulose fractionation and cellulose enzymatic hydrolysis. Similarly, a chemical-free pre-treatment method involving extrusion and ultrasound is also applied to enhance enzymatic hydrolysis of agricultural biomass-rich resources such as rice hull, crop straw and vegetable wastes. Cellulose nanocrystals have also been prepared from oil palm frond by acid hydrolysis preceded by autohydrolysis treatment.

Many other traditional methods have been used previously to extract active materials from different types of plant species biomes. Figure 4 shows the methods of biomass conversion in materials for energy production. Different extraction and treatment processes such as combustion, pyrolysis and gasification can generate the thermochemical conversion of the plant biomass energy. Biological conversion can be obtained through alcoholic fermentation and digestion, while physical conversion occurs by squeezing. The use of methods such as solvent partitioning and Soxhlet extraction prior to enzymatic processing (e.g. cellulases or pectinase) was developed to improve yields and extraction efficiencies of active materials. Latest developments include the advancement of a novel procedure of radio frequency heating-assisted enzymatic
extraction as a more efficient method of solvent extraction of materials such as polyphenolic flavonoids called anthocyanins.16,17

The choice of treatment and extraction method for lignocellulose biomass depends on the target material available in the biomass resource of interest. This is because lignocellulose biomass materials contain structural polymeric resins comprising cellulose (40–50%), hemicellulose (20–30%), and lignin (15–25%). Thus, cellulose is the major component in most lignocellulosic resource materials.18 Several methods of treatment of biomass materials have been applied and reported in the preparation of biocomposites.19 Methods such as wood fibre and coupling agent extrusion, injection moulding process, lignin precipitation using the lignin-boost process, black liquor Kraft lignin extraction, wet pulp disintegration and TEMPO-mediated oxidation of cellulose beers at neutral pH have been applied in different preparation processes.19

Solid-state biomass for strong materials

There is a need for utilisation of sustainable low-cost carbon-derived materials from abundant and renewable natural resources for various applications. The biomass feedstock can be derived from lignocellulosic materials such as energy crops, agricultural biomass residues, and forest biomass.20 The biomass-derived materials have strong physical and chemical adsorption properties and are sustainable and environmentally friendly.21 Given the existence of different plant biomass categories – such as sugar-based biomass, starch-based biomass, oil-based biomass (oleaginous crops), woody and non-woody lignocellulosic biomass and algal/microalgal biomass – more consideration has been given to lignocellulosic biomass in the making of cost-effective solid materials.22

A previous study showed that there is no limit to the source of biomass. It is apparent that different materials present different types of biomass that may be used and modified in one or more similar processes to produce valuable materials that are in a high hierarchical position in the bio-economy.19 Nanosized biomass was prepared from a modification involving bio-inspired self-bonding nanofibrillated cellulose composite. This was done using a simple mechanical thermal rubber milling and the hot-pressing methods. The methods have a response surface procedure for the optimisation of processing variables. This has been applied in binderless biomass materials produced from wheat-straw lignocellulose.23 Previous studies have revealed that the preparation of activated carbons may be achieved by chemical activation with potassium carbonate (K₂CO₃) from five types of nutshells: almond shell, coconut shell, oil palm shell, pistachio shell and walnut shell.24

A detailed study on the evaluation of the extraction of sugarcane bagasse and soft wood celluloses with alkali treatment followed by bleaching using sodium chlorite at different times,19 produced bulk solid-state biomass materials used in many different applications such as pulp and paper technologies. There are several targets set to affect, improve, and change physicochemical characteristics of the solid biomass such that there is increased usability, thus adding value and accessibility to biomass materials.15,25-27 Concerns about global warming and environmental pollution and degradation have triggered a shift in the focus of research institutions towards the development of sustainable, biodegradable and recyclable constituted materials. Biocomposites have potential in the construction industry as renewable building materials and are called natural fibre-reinforced polymers.28

The application of solid-state biomass for strong materials includes the high energy density and low-cost lithium-sulfur (Li-S) batteries for energy storage systems, capacitors (or supercapacitors), bio-degradable composite materials, aerogels/or hydrogels. Biomass materials are of great interest in high-energy rechargeable batteries due to the fact that they are sustainable, their use has environmental benefits and, importantly, they are structurally and compositionally versatile with abundant functional groups and many other unique physicochemical properties.29 An example is a functional biomass carbon with hierarchical porous structure derived from bamboo, which is a low-cost renewable material (Figure 5), for supercapacitor electrode materials.30 The bamboo-derived porous carbon with boron and nitrogen co-doping was fabricated through successive carbonisation, activation, and heteroatom doping.

Cellulosic biomass is favoured in the development of aerogel materials because of its biodegradability and sustainability, which is important in their regeneration technique and physical dissolution from non-derivating cellulose solvents.21 Chen et al.20 prepared a highly porous lignocellulosic biomass-derived aerogel directly from a bagasse solution (bagasse dissolved in DMSO/LiCl). Bagasse aerogel displayed sheet-like skeletons with Brunauer–Emmett–Teller surface areas of 185 m²/g and pore volumes of 0.46 cm³/g.30 Some biomass materials are derived from cross-linked hydrophilic polymers that are technically referred to as hydrogels. These hydrogels are classified as materials with large volumes of water in their three-dimensional hierarchical structures. Biomass-derived hybrid hydrogel evaporators are built from Konjac galactomannan and iron-based metal-organic components. Their framework is derived from photothermal nanoparticles after being introduced into polyvinyl alcohol networks to form cost-effective hydrogel evaporators.30 Hybrid hydrogel evaporators have application in heavy metal ions removal
and wastewater-purification processes. A cheap biomass, Konjac galactomannan enhances the hydration ability of hydrogels for water activation and provides plenty of hydroxyl groups for the formation of hydrogen and chelating bonds to remove contaminants effectively.30

The fabrication of solid-state biomass strong materials involves the use of biomass derivatives that sufficiently and efficiently fuse with biocomposite materials and bind them together to make strong structural materials of different forms. 5-hydroxymethylfurfural (5-HMF) is a material derived from lignocellulose biomass and is convertible, thus promising for biofuels and a variety of useful derivatives which have been previously produced from petroleum. The 5-HMF compound has been considered a fundamental material serving as a mediator between carbohydrate chemistry and mineral oil based industrial materials chemistry.34 A slightly water-soluble biomass material called rutin – a flavonoid naturally present in many plants, with the highest content of 10.5% found in the dried fruit of the inedible shrub of the smoke tree (Rhus cotinus) – is also abundantly found in banana leaves (Musa balbisiana)35 and may be used specifically as a binding material and water-resistant agent in solid-state biomass strong structures.

Figure 6 shows some of the conversions of biomass and the solid-state materials produced through the extraction and treatment processes. Hemicellulose, extracted from sugarcane bagasse using the alkaline-alcoholic method, produced a compact, dense-structured, homogeneously thick, highly water-soluble material which exhibited high tensile strength with an increase in hemicellulose content. However, the increase in hemicellulose content also has the consequential effect of reduced tensile strain and thermal stability.37 Most biocomposites in solid-state biomass strong materials have found applications in structural artefacts such as pallets, locomotive interior components or biocomposites used in the fabrication of solid-state biomass strong materials.40

Detailed studies explored an alternative material to use as a modifying filler towards enhanced inherent properties and characteristics of biocomposites used in the fabrication of solid-state biomass strong structural materials.37-39 Hemicellulose is also a good candidate for biocomposites for solid-state biomass strong materials. Tannin, a natural macromolecular biomass resource mainly found in fruits, seeds, flowers and bark, has found wide application, including in leather tanning. Tannins are characterised by phenolic groups that can form chemical bonds with the functional groups of the matrix in the biocomposites. In leather, the chemical bonds are formed on the carboxyl and amino functional groups along the cross-linking collagen peptide chain of the leather matrix.42

Wood undergoes massive bulk biomass conversion into a high-value material during pulp and paper making, as shown in Figure 7. The use of paper produces hundreds of millions of tons of wastepaper from which cellulose nanocrystals can be extracted in a high-value secondary fibre utilisation in recyclable strong biomass and biocomposite materials. Methods applied for extraction had an impact on the morphology, properties and characteristics of the cellulose nanocrystals that influenced their binding and filling role in the biocomposites fabricated for strong structural material application.43

Recent research in biomass and biocomposites has been driven by a need for the development of sustainable energy, materials and chemicals.44 However, the solid-state biomass strong materials are being managed right from the plant growth in which a high harvesting index is favourable. Arundo donax is one of the plants that is being preferentially cultivated as a C4 energy plant and a lignocellulosic biomass feedstock. It is characterised by fast growth and adaptation to severe soil and climatic conditions. A. donax has superior biomass qualities due to its chemical composition characterised by a high
content of cellulose, hemicellulose and lignin. This material is known to  
competently substitute conventional synthetic fibres such as glass fibre,  
carbon fibre and aramid that are widely used as fillers in composites  
because of their high strength and stiffness. The drive to replace these  
synthetic fibres is mainly due to their non-biodegradability, high initial  
processing cost, non-recyclability, and high energy consumption as  
measured against natural fibres that are biodegradable, renewable, low  
density, cost effective, non-abrasive, and have high filling levels.

Mathematical modelling of biomass conversion

Mathematical models are used in the study of a wide range of  
parameters involving complex processes and mechanisms, especially  
in science, engineering and geo-environmental studies and analyses.  
In science, the mathematical models provide an instrument to measure  
and compare theoretical predictions against experimental determinations  
and deductions. One such study was on mathematical modelling of  
bioassimilation gasification in which tar formation threatened the efficiency of  
the gasification process. Thus, mathematical models were developed  
to advance the optimisation of gasification reactors in relation to the  
tar formation mechanism and the decomposition pathways. Complex  
processes have been deconvoluted using mathematical models for  
the purposes of optimisation and further process development of the  
technological applications thereof. Thus, mathematical models ranging  
from less complex models to highly sophisticated models have been  
developed for various purposes including process assessment, control  
and performance evaluation. Single-compound models, kinetic models,  
and lumped models have been developed for calculating energy  
and mass transformation. Similarly, modelling of anaerobic digestion has  
evolved radically with variations starting from very simple models that  
consider digestion as a fermentation process from sugars, to advanced  
and extended models such as anaerobic digestion model 1 (ADM1).

Mathematical models have been developed to describe processes with  
a reduced set of parameters, state variables and processes. The anaerobic  
model number 2 (AM2) is one such mathematical instrument which  
describes the degradation of soluble organic compounds and is best  
apt in process control and optimisation. The AM2 was developed by  
Bernard et al. and the model efficiently reproduced the biological  
aerobic digestion process as simulated by the ADM1. Mathematical  
modelling in biomass transformation processes provides more  
intrinsic information that may be used to set parametric precedence  
for experimental determinations, with more access to control and  
manipulation of internal factors in the processes. Thus, the production  
of quality target biomass materials may be modelled and achieved;  
for example, a compromise between a kinetic model, that contains as  
much far species as possible to represent lignin devolatilisation, and a  
mechanism that leads to the formation of tars with minimum reactions  
stands as a solution for tar simulation during biomass gasification.

Optimisation and formulation ratios of biocomposites

Materials fabricated from biomass to give solid-state biocomposites for  
strong materials present a wide range of properties and characteristics.  
It is anticipated that strong biocomposite materials must exhibit qualities  
such as non-toxicity, corrosion resistance, high thermal stability, low  
cost, renewability, degradability, recyclability, high biocompatibility,  
high performance, high strength, high water resistance, high specific  
surface area and high aspect ratio. Previous studies have reported on  
nanoglenccellulose/chitin composites with superior mechanical properties  
and thermal stability fabricated from poplar wood fibre effectively cross-  
linked with chitin by the simple mechanical thermal rubber milling  
method. Similarly, layered densified nanoglenccellulose/calcium  
hydrogen phosphate composites and nanoglenccellulose/polyvinyl  
 alcohol/titanium dioxide composites were prepared by mechanical  
thermal rubber milling-water directional assembly and hot pressing.

The formulation composition proportions of biocomposites give the  
materials their inherent intrinsic properties that qualify the materials  
for applications in solid-state strong biocomposite materials such as  
in construction and other erectile structures as shown in Figure 8.

Contemporary studies on the influence of the ratio of components on  
properties of wood/thermoplastic polymer composites varying between  
10% and 25% wood/plastic, determined that thermal stability and  
mechanical properties (tensile strength and Young’s modulus) increased  
with an increase in wood content. Similarly, investigations into the  
natural fibre reinforced biopolymers as construction materials were done  
by comparing the biocomposites with glass fibre reinforced polymers.  
The natural fibres gave a tensile strength similar to that of glass fibres (of  
mass density 2500 kg/m³) at a mass density of approximately 1500 kg/m³  
– far below the density at the same structural weight as biocomposites,  
and thus exhibited a higher reinforcement factor. Biocomposites may  
be hybridised by fusing them with other natural materials that modify  
and enhance inherent properties and characteristics in materials. Jute  
is one such material that is fused into solid-state biomass materials  
for structural applications. A previous study revealed that jute showed  
more significant acoustic attenuation properties as well as flammability  
properties than glass fibre in terms of limiting oxygen index.
at the break of the cellulose fibres compared to the glass fibres.46 Understanding the isotropic and anisotropic nature of lignocellulosic materials in the fabrication of biocomposites determines pre-packaging of several properties of the materials that will enable their application in the development of new types of composite materials for constructive biomass strong materials.42 Use of high aspect ratio biomass is known to significantly change the composite’s physical properties in contrast to particulate resin fillers which provide isotropic properties for the material. Different types of biomass in specific compositions, various orientations and lengths, have been exploited in engineering applications to construct devices and structural artefacts with high strength and fracture toughness.

Conclusions
It was determined that different extraction and treatment processes such as combustion, pyrolysis solvent partitioning, Soxhlet extraction and gasification can generate the thermochromic conversion of the fluidised plant biomass. Cellulose is the major component in most lignocellulosic resource materials. Lignocellulose biomass materials contain structural polymeric resins comprising cellulose (40–50%), hemicellulose (20–30%), and lignin (15–25%). The fabrication of solid-state biomass strong materials involves use of biomass derivatives that sufficiently and efficiently fuse with biocomposite materials and bind them together to make strong structural materials of different forms. Methods such as wood fibre and coupling agent extrusion, injection moulding process, lignin precipitation using the lignin boost process, black liquor Kraft lignin extraction, wet pulp disintegration and TEMPO-mediated oxidation of cellulose beers at neutral pH have been applied in different solid biomass preparation processes. Sugarcane bagasse and soft wood cellulosics have been processed to produce bulk solid-state biomass materials. Most biocomposites in solid-state biomass strong materials have found application in structural artefacts such as pallets, automotive interior components, construction or building boards, bioenergy, 3D-printing materials, and ceiling and flooring panels. Strong building biocomposite materials for structural construction are expected to be dense and water resistant and have high tensile strength and tensile strain and, more importantly, very high thermal stability. It was determined that formulations determined by percentage composition of components in the biocomposites do not entirely influence the inherent properties of the material as a solid-state biomass material for strong structural applications. Factors such as alignment of fibre, orientation, and mass density distribution directly affect and influence the nature and performance of the fabricated biocomposites. Thus, it may be concluded that weight-related mechanical properties enable biocomposites to be used in applications that are still dominated by glass fibre reinforced plastics. Thus, understanding the isotropic and anisotropic nature of lignocellulosic materials in the fabrication of biocomposites determines pre-packaging of several properties of the materials that will enable their application in the development of new types of composite materials for constructive biomass strong materials.

Future research
This review precedes future work that may be designed under focus areas crafted in line with the Sustainable Development Goals (SDGs), covering SDGs 1, 6, 7, 8, 9, 11, 12 and 15. These SDGs fall under areas crafted in line with the Sustainable Development Goals (SDGs), This work was supported by the Durban University of Technology through a Post-Doctoral Fellowship supported by the Technology Transfer and Innovation Directorate under the office of the Deputy Vice Chancellor for Research Innovation and Engagement. Heartfelt thanks and appreciation are extended to Prof. Sibunasio Moyo for her extensive reviews and contributions to this work.

Competing interests
We have no competing interests to declare.

Authors’ contributions

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