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Introduction to biomass materials

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Biomass is an abundant, renewable feedstock of biological matter that humans first harnessed – as a source of fuels, tools, textiles, materials, and chemicals – long before the earliest human civilizations appeared. The fabrication and wearing of clothing, for example, predates the domestications of dogs and crops by tens of thousands of years. During the Industrial Revolution, biomass fuels were replaced by coal and, later,

petroleum, with the attendant consequences that biomass-derived chemicals and materials were phased out in favor of those derived from coal and petroleum.

Tree- and plant-derived biomass was used to make the earliest synthetic polymers, such as cellulose nitrate and vulcanized natural rubber, but materials prepared from biomass feedstocks were largely supplanted by materials prepared from fossil resources. With a growing understanding of the harmful impacts fossil-derived polymers have on the health of the planet and its ecosystems, the science and engineering community has recognized the urgent need to return to biomass feedstocks as precursors for commodity and high performance materials.

Replacement of fossil-derived fuels for transportation and energy with those

derived from biomass has been an objective of environmental-protection policies, but pursuit of this objective inherently requires contemporaneous and radical transformations of modern chemical and materials industries. To produce chemicals and materials from biomass instead of fossil resources, interdisciplinary research is needed, spanning a fundamental understanding of synthesis and properties to translational studies for targeted applications.

Because biomolecules and biomaterials naturally occur in highly-heterogeneous, complex mixtures of structurally- and functionally-diverse molecules and macromolecules, obtaining a specific, desired compound or material requires one or more chemical interventions to separate it from the

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mixture. Notably, biorefining methods to isolate a desired molecule/macromolecule from its biomass source can also dramatically alter the elemental composition, bond connectivity, chemical microstructure, and/or macroscopic structure of that molecule/macromolecule, potentially rendering its properties unsuitable for its intended purpose.

Optimal biorefining strategies will not only yield the desired molecule/macromolecule from the biomass mixture but will also convert as many other parts of the biomass feedstock as possible into coproducts which are complementary in purpose to the primary product. If this is not possible, alternative uses for these coproducts are sought which would enable them to be employed productively in other applications, a process known as “valorization”. Arguably, the primary focus of modern biomass research is the valorization of biorefining coproducts from unusable into useful forms.

The composition of a biomass mixture is determined by the living system that produced it, thus, it is common to categorize biomass types based on whether they are produced by plants, animals, microorganisms, *etc.* One prominent biomass example is found in the cell walls of trees as heterogeneous mixtures of cellulose, hemicellulose, and lignin, whose compositions and structures may not be conserved even within the same

organism. From this particular mixture, cellulose has been heavily utilized as a source of fiber and sugars for chemicals, but its linear chain structure, relatively crystalline morphology, and well-conserved C/H/O ratios make it an attractive scaffold for the synthesis of polymers and materials that are derived from renewable sources.

Lignin, in contrast, is a dramatically more challenging coproduct to valorize, owing to its highly-crosslinked structure, amorphous morphology, and significantly-variable C/H/O ratios. The predominant strategy to valorize lignin is to depolymerize it into organic, small-molecule aromatics (*e.g.*, coniferyl, *p*-coumaryl, and sinapyl alcohols). Lignin is desirable as a feedstock since it provides access to aromatics without requiring energy-intensive processes such as dehydrogenation, and lignin-derived aromatics have demonstrated their value as carbon-free alternatives in the synthesis of a wide variety of biobased chemicals and materials.

Chitin, chitosan, and silk are biomass feedstocks that are obtained from aquatic life, insects, and some fungi. The linear-chain structures of chitin and chitosan bear closest resemblance to cellulose, whereas silk is an acyclic polyamide that could be considered a regioisomeric structure of nylon. Unsurprisingly, the linear structures, thermodynamically-robust carboxamide linkages, and extensive hydrogen-bonding abilities intrinsic

to chitin, chitosan, and silk translate into biomass-derived materials with exceptional mechanical strength and thermal durability. Current and emerging efforts in synthetic biology will lead to even larger interest in the synthesis, isolation, and use of biomass.

In the context of the emerging interest in and societal need for increased biomass utilization, this themed collection on Biomass Materials contains a diverse set of papers showcasing opportunities for using biomass directly, as a precursor for chemicals and materials, and as a source for nanofibers for use in films and composites. Many papers in the collection highlight opportunities for using lignocellulosic biomass with insight on new high volume applications or on understanding how to use less common sources of lignocellulosic biomass to produce advanced materials and chemicals. To frame this insight, processing-structure-property relationships are explored for materials development. Perspectives on using other biomass such as chitin and bacterial cellulose to produce materials are presented as well.

Finally, we would like to thank the editorial staff at *Materials Advances* for their support in organizing this themed collection. We hope that readers will enjoy learning about the breadth of research occurring in biomass materials from reading these papers and develop new ideas for utilizing these ubiquitous materials.

