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Biobased fibers and materials in Brazil

Leonardo F Valadares

Abstract

The human evolution is directly associated to the use of materials. During the last century, humanity had significant development powered by the use of fossil resources, which largely impacted the materials discovery and use. However, there are many concerns about the use of fossils, based mainly on economic and environmental issues. These concerns motivate the study, development, and use of renewable resources, including biobased materials. Brazil is one of the largest producers of agricultural commodities, which can be used to produce renewable materials. This review describes actual production of some renewable materials in Brazil and future possibilities to generate them using biomass residual streams of industrial processes.

Keywords: Biobased materials; Renewable fibers; Sugarcane bagasse; Biomass fractionation; Cellulose; Lignin

Introduction

Materials can be defined as the substance, or mixture of substances, with properties that makes it useful in products, devices, structures, and machines [1,2]. Tools and materials have been used by the civilization since the beginning of history registers. The human evolution is directly associated to the use of materials. Food production, clothing, housing, transportation, and every segment of our everyday lives are influenced by the use of materials. Historically, the development and advancement of societies have been intimately associated to its ability to produce and manipulate materials to fill their needs. The development of the production and use of different materials by early civilization landmarks the Stone Age (2.5 million BC), the Bronze Age (3500 BC), and the Iron Age (1000 BC) [3].

Until the latter part of the 19th century, the civilization survived using essentially renewable resources, based on biomass for cooking, heating, and building materials. Nowadays, just least developed countries are still using essentially these kinds of resources. The use of fossil resources took place during the twentieth century and still increasing in the beginning of the twenty-first century. During the industrial revolutions, the demand for energy had increased drastically, and the high use of coal, petroleum, and natural gas leads to the large-scale generation of electricity, heat, and fuels. Today, the fossil fuels correspond to more than three quarters of the primary energy used in the world [4].

Correspondence: leonardo.valadares@embrapa.br
Embrapa Agroenergia, Parque Estação Biológica, PqEB s/n – Av.W3 Norte (final), 70770-901 Brasília, DF, Brazil

However, the reduction in the use of fossil resources is an actual and important issue, driven by two main reasons: the first is related to the cost variation, depletion of reserves, and irregular distribution in Earth, which are the causes of many conflicts; the second reason is related to environmental subjects as the climate changes due to greenhouse gas emissions [5]. The development, commercialization, and use of renewable fibers and materials, together with biofuels, can help to mitigate the usage of fossil resources.

Recent scientific and technological developments enabled a number of opportunities to create new materials from sustainable and renewable resources. These opportunities need to respond positively to a transition from an economy currently based on fossil fuels to an economy based on renewable resources, aiming the sustainable development, and maximizing the resulting social satisfaction [6].

Solid materials have been conveniently grouped into three basic classifications: polymers, ceramics, and metals. This scheme is based primarily on chemical makeup and atomic structure, and most materials fall into one distinct grouping or another, although there are some intermediates. In addition, composites are combinations of two or more materials [1]. Polymers and composites are the mainstream of the renewable materials industry; however, charcoal and biomass can be used as energetic input for metal and ceramic production [7]. Renewable composites have been studied with myriads of formulations [8,9]. Usually, fibers are used as reinforcing agent to a polymer matrix.

Stiffness [10], hygroscopic behavior [11], dimensional stability, strength, and fracture toughness are among the main engineering properties of biocomposites to consider. During conception, design, and engineering of new products, the stiffness is important since it determines the fiber concentration needed to ensure acceptable deformations for a specific application. To effectively predict the properties of a composite for a specific application, it is essential to know the properties of the reinforcing fibers [12].

The worldwide consumption of biopolymers has increased since the nineties, and they have found applications as packaging materials, disposable nonwovens, hygiene products, consumer goods, and agricultural tools. However, the uses of renewable composites are still limited due to their poor physical properties and difficult processability.

Review

Renewable materials in Brazil

Brazil have some comparative advantages in agriculture - plenty of soil, light, temperature, and water supply - which, associated to the technological expertise, enabled the sector to play an important role in the international market [13]. Cellulose pulp, cotton lint, natural rubber, and polyethylene derived from ethanol are examples of important renewable materials produced in Brazil at present. Table 1 presents the production of these renewable fibers and materials.

Pulp and paper

Pulp and paper industries use wood as raw material to produce cellulose-based products. In Brazil, this sector produced a total of 14,401,000 tons of cellulose during 2012. The South and Southeast Regions concentrate most of the production. São Paulo state is responsible for 27% of the national production of paper pulp and 43% of production paper. The wood used by this industry is extracted exclusively from reforestation allocated to this sector, covering, in 2011, an area of 2,200,000 ha, mainly with eucalyptus and pine [14].

Brazilian pulp and paper industries are competitive mainly because of the favorable climatic conditions, which allow the fast growing of the trees. *Eucalyptus*, for example, that comprises the forest base of Brazilian companies can be processed six to seven years after planted. The main companies in Brazil are: Fibria, Suzano, Eldorado, Cenibra, Veracel, International Paper, Bahia Speciality, and CMPC Celulose.

Table 1 Brazilian production of renewable materials during 2012

Renewable material	Production (tons)	Main producing states in Brazil	Reference
Pulp	14,401,000	São Paulo	[15, 16]
Cotton lint	1,638,103	Mato Grosso	[15]
Natural rubber	177,100	São Paulo	[15]
Renewable polyethylene	200,000[a]	Rio Grande do Sul (Triunfo)	[17]

[a]Installed capacity.

The pulp and paper companies in Brazil produce mainly short fibers extracted from softwood (eucalyptus) when compared to long fibers (pinus). The predominant process is the chemical pulping, using the kraft process (*ca.* 80%). For the short fibers production, usually the wood is charged to the digester in the form of chips together with fresh cooking liquor (white liquor) from the chemical recovery line. The liquor is an aqueous solution of sodium hydroxide and sodium sulfide. The principal digester systems are discontinuous (batch system) or continuous. Using batch systems, the cooking time varies 4 to 6 h. The normal kraft cooking is performed at temperatures between 160°C to 180°C and pressure ranging from 7 to 11 bar [18].

After cooking, the pulp and the spent liquor (black liquor) are discharged at the bottom of the digester at reduced pressure into a blow tank. Insufficiently cooked large-size rejects (knots) are screened and generally transported again to the digester for repeated cooking. The spent liquor is removed after countercurrent washing of the pulp and further processed within the recovery line. The pulp is further screened, cleaned, sometimes mildly refined, and thickened. Finally, the pulp can be stored, directed to bleaching, or directed to paper production systems [19].

Cotton

Cotton, extracted from plants of the genus *Gossypium*, is considered the main raw material to textile industries. During 2012, the world's main producers were China (26%), India (20%), USA (14%), Pakistan (9%), and Brazil (6%), with other countries representing 25% of the percentage total production [15]. The Brazilian production reached 1,638,103 tons during 2012 (Table 1) when the Midwest Region was the main producing area of cotton followed by the Northeast Region. Mato Grosso is the main producing state of Brazil. It has the largest area planted and achieves the highest productivity in the country. Most of the production is used for domestic consumption.

Traditionally, the farmer directs the cotton seed without any processing to gins, to separate the cotton lint from seeds. Currently, high-scale producers absorb this step and promote the ginning. The ginned fiber, called lint, is pressed together and made into dense bales weighting about 180 to 200 kg.

The cotton lint is mainly destined for textile industry, which absorbs approximately 60% of world production of cotton fiber [20]. The lint has many other applications:

cotton wool for medical purposes, fillings (for blankets, furniture, etc.), and uses for cellulose applications.

Natural rubber

The natural rubber latex is extracted from the rubber tree (*Hevea brasiliensis*), a plant originated in the Amazon rainforest. The latex is a colloidal dispersion of rubber particles, sizing from 5 to 3,000 nm in aqueous serum. The polymer fraction corresponds to 33% of the fresh latex, consisting of *cis*-1,4-polyisoprene, with mean molecular weight of 5×10^5 g mol^{-1} [21]. For logistic reasons, the latex is usually dried to rubber or stabilized (with ammonia and other substances) and concentrated by centrifugation to a solid content of ~70% [22].

As presented in Table 1, during 2012, Brazil produced 177,100 tons of natural rubber, with São Paulo being the main producer. Brazilian production is increasing since last year but Brazil is essentially a natural rubber importer.

The natural rubber is been used widely in segments as transportation and health. It is currently used in different products such as: adhesives, tires, surgical gloves, health equipment and accessories, condoms, coatings, and floor covering. Natural rubber is an important material because it cannot be replaced by synthetic rubbers in some applications, due to its outstanding elasticity [23].

Vulcanization process of the natural rubber, discovered by Charles Goodyear [24], crosslinks polyisoprene chains, drastically changing its properties. Vulcanized materials are durable and less sticky and have unique mechanical properties [25]. However, the vulcanized rubber is not disposable and easily degradable and cannot be burned outdoors, due to the sulfur-derivative emissions. Scientific effort has been done to modify the mechanical properties of natural rubber without vulcanization. Many composite formulations have been studied using clays [26] and natural fibers [27].

Polyethylene

The petrochemical company Braskem is a pioneer in the large-scale production of a plastic resin made from ethanol. Braskem's renewable ethylene plant was commissioned in September 2010. The production on a commercial scale secured the company's global leadership position in bioplastics. The plant has annual production capacity of 200,000 tons of polyethylene. Braskem receives the sugarcane ethanol from suppliers and it goes through a dehydration process and is transformed into renewable ethylene [16]. The ethylene is a drop-in renewable input that goes to the polymerization plants where it is transformed into plastic with the same specification of polyethylene made of fossils.

Possibilities for future

Brazil is a large producer of agricultural and animal commodities, which generates large amounts of byproducts, residues, and/or wastes. These agricultural residues and animal waste can be transformed into energy, materials, and other products [28] in systems analogous to an ethanol refinery where an integrated process involves conversion for biomass into a variety of products. Forster-Carneiro et al. [29] indicated the sugarcane as the crop with highest agronomic availability (estimated reuse potential of 19,600,000 tons on dry basis), followed by soybeans, rice, maize, orange, wheat, cotton, cassava, and tobacco.

Raw materials

The biobased fibers and material properties, utility, and price are intrinsically linked to their raw material. The first key point for industrial use of any selected biomass is the agriculture development stage of the species. Table 2 presents the Brazilian production of some developed crops which can be used in a biorefinery to generate materials.

During the 2012/13 crop production, 588.9×10^6 tons of sugarcane were produced in Brazil and 387.2×10^6 tons were produced only in the Southeast Region for ethanol and sugar. About one-third of this mass is converted to bagasse, a coproduct generated after the sugarcane juice extraction. This bagasse is usually burned to generate heat and power [30]. Even though, the bagasse is an important substrate that can be used for materials development due to some advantages: availability, it is pulverized and generated in the industry after the sugarcane milling.

There are current scientific and industrial efforts for the production of cellulosic ethanol. Although cost-competitive cellulosic ethanol mostly overcome technical and economic challenges, the possible implementation of these industries will increase the ethanol production and generate lignin and hemicellulose-rich residual streams. These fractions can find use in production of material, chemical, and energy generation, aggregating value to the ethanol productive chain.

The advent of biodiesel as a fuel in Brazil largely impacted the glycerol (propane-1,2,3-triol) production. Today, the use of 6% of biodiesel (called B6) is mandatory for diesel commercialization [31]. This percentage has perspective to increase to 7%. The production of fatty acid methyl ester (biodiesel) and, consequently, crude glycerol largely increased, affecting their prices. Purification of crude glycerol is often necessary before its utilization [32]. Pure glycerol is used in various products. For materials technology, it can be transformed by chemical reactions or microbial fermentation into products such as propene, 1,3-propanediol, succinic acid, citric acid, oxalic acid, poly-3-hydroxybutyrate (PHB), and others [33,34].

Table 2 Brazilian crop production during 2012/2013

Product	Crop production (10^3 tons)	By-products streams	Main producing states in Brazil (production/10^3 tons)
Maize	81.007.2	Stover, cobs	Mato Grosso (19,893), Paraná (17,642)
Rice	11.746.6	Rusks, straw	Rio Grande do Sul (7,933)
Soybean	81.499.4	Glycerin	Mato Grosso (23,532.8), Paraná (15,912.4)
Sugarcane	588.915.8	Bagasse, straw, vinasse	São Paulo (330,694), Goiás (52,727), Minas Gerais (51,208)

Adapted from [35]

Lignocellulosic materials processing

Lignocellulosic materials refer to parts of plants composed mainly of cellulose, hemicellulose, and lignin. The processes of fractionation of biomass aim to isolate these fractions as pure as possible for a specific product. To achieve this goal, sequences of many treatments on the biomass are required. These treatments technologies have currently been getting increased attention as it is one of the main bottlenecks for the commercial production of biorefineries. Many processes have been developed in the last decades and are being continuously improved through research studies [36]. Lignocellulosic biomass pretreatments can have aspects of physical, chemical, and biological processes. These processes have been detail described by some scientific reviews [36-38]. The main fractions of lignocellulosic biomass are described below.

Cellulose

With about 10^{11} tons of cellulose growing and disappearing annually, cellulose is the most abundant renewable organic material on earth [39]. In plant sources such as the wood of mature trees, the content of cellulose is in the order of 35% to 50%. The cotton fibers are almost pure cellulose.

This carbohydrate macromolecule is the principal structural component of the cell wall of most plants. Cellulose is also a major component of wood, as well as textile fibers such as cotton, linen, hemp, and jute. For this reason, cellulose has always played an important role in the life of humans, and its applications could even constitute a landmark in the understanding of human evolution. Method lignocellulose substrates for production for writing and printing go back to the early Chinese dynasties. Exploration, trade, and battles relied for many centuries on man's ability to build wooden ships and making cotton sails and hemp ropes.

Cellulose and its derivatives are materials used by industrial exploitation and they represent a considerable economic investment [40]. Detailed knowledge about the different levels of structural organizations is needed to provide rational ways of conducting chemical modifications while maintaining the biodegradable and recyclable features of the starting raw material, modifying the properties of the cellulose to achieve utility.

Cellulose is a linear homopolysaccharide of glucose residues, composed of α-D-glucopyranose units linked by β-($1 \rightarrow 4$) glycosidic bonds [41]. These pyranose rings have been found to be in the chair conformation $^4C_1$, with the hydroxyl groups in an equatorial position. The two chain ends are chemically different.

The degree of polymerization (DP) of native celluloses depends on the source and is not well established. Indeed, the combination of procedures required to isolate, purify, and solubilize cellulose generally causes scission of the chains. The DP values obtained are therefore minimal and depend on the methods used. Values of DP ranging from hundreds to several tens of thousands have been reported.

Lignin

Lignin is primarily a structural material to add strength and rigidity to cell walls and constitutes between 15% and 40% of the dry matter of woody plants. Lignin is more resistant to most forms of biological attack than cellulose and other structural polysaccharides, and plants with higher lignin content have been reported to be more resistant to direct sunlight and frost. *In vitro*, lignin and lignin extracts have been shown to have antimicrobial and antifungal activity, act as antioxidants, absorb UV radiation, and exhibit flame-retardant properties [42]. All of these features are useful for materials, such as composites.

Lignin is a crosslinked macromolecular material based on a phenylpropanoid monomer structure. Typical molecular masses of isolated lignin are in the range 1,000 to 20,000 g/mol, but the degree of polymerization in nature is difficult to measure, since lignin is invariably fragmented during extraction from living matter.

Purified lignin can be applied to a wide number of products such as: adhesives [43], composites [44], carbon fibers [45], MDF, and others.

Hemicellulose

Hemicelluloses are polysaccharides bearing more irregular macromolecular structures than cellulose or lignin because of the presence of different anhydrohexose and anhydropentose units in their chains and/or branched architectures [46]. As a consequence, these natural polymers are usually amorphous and those present in plant tissues play the role of a gel sleeve around the cellulose fibers providing elasticity and flexibility to the composite assembly, together with lignin. Additionally, their average molecular mass distribution is often lower than those of cellulose.

The principal applications of hemicellulose, after appropriate modifications, are as food additives, drug encapsulation and delivery, hydrogels, and emulsification because they provide useful properties. However, differently from cellulose, hemicellulose has not found a large use in materials.

Conclusions

The research, development, and use of biobased fibers and materials can help to mitigate the use of fossil resources. Some renewable products, such as cellulose pulp, cotton lint, polyethylene, and natural rubber are already produced in Brazil. The production of renewable materials can largely increase due to the availability of raw materials, included lignocellulosic residues that can be fractionated and applied to many products. This can be applied in biorefineries facilities in which the fuel, power, and chemicals are also generated. Brazil has advantages for biorefineries implementation because it is a large raw materials producer, has a strong industrial sector, and has vast experience in biofuels.

Competing interests

The author declares that he has no competing interests.

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