Materials from renewable resources: new properties and functions

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Abstract: Sustainable production requires increasing use of raw materials from renewable sources, processed under mild conditions with minimal effluent production. These requirements are satisfied by using materials derived from biomass, in synergy with food and energy production. The possibilities of biomass are continuously enlarged by new findings, as in the intrinsic nanocomposite properties of natural rubber and the amphiphile behavior of cellulose that translated into new functional materials, including high-performance, flexible and conductive non-metallic materials. Other findings are allowing a better understanding of electrostatic phenomena that play a positive role in electrostatic adhesion and cohesion of nanocomposites made from biomass products. Moreover, this should allow the development of safe electrostatic separation techniques, suitable for the fractionation of crude mixtures of biomass residues. A current study on rubber electrostatics is showing its capabilities as a transducer of mechanical energy while providing clues to understand the performance of the dielectric elastomers used in robotic self-sensing actuators.

Key words: cellulose, electrostatics, nanocomposites, natural rubber.

INTRODUCTION

This is a review of recent progress in two topics relevant to sustainable production (OECD 2013): biomass as a source of materials and soft materials electrostatics. These topics intersect in many ways and the progress in each topic received important inputs from the other, showing the advantage of an interdisciplinary approach to materials research and development.

MATERIALS FROM THE BIOMASS

Biomass is a rich source of renewable materials that are largely made from atmospheric CO₂ and water, with minor contents of minerals and nitrogen. Materials from the biomass predominated in manufacture, arts and crafts, prior to the industrial revolution. They are currently recovering their importance, following a century filled with great successes on their replacement by synthetics. Since the biomass is a renewable resource, the intensification of the use of its products is central among the efforts to build a more sustainable development, with greener production and consumption (Galembeck 2017a). Work in this direction requires concerted action and resources, including much new research and development (Galembeck 2015) in many areas that is not always fashionable or classified as “high impact” using bibliometric tools.
The most common material from renewable resources is wood. It has been used since prehistoric times and the annual consumption continues to grow. For instance, industrial roundwood production grew 3% between 2015 and 2016 (FAO 2016), reaching ca. 2 billion metric tons. It is widely used to make cellulose in the huge paper and pulp industry that produced 180 and 409 million tons of wood pulp and paper/paperboard respectively, in 2016. Although the consumption of some printing paper types declined, other paper and pulp products show a growing demand. Cardboard made from wood plays such an important role that it is often used as an indicator of the trends in the overall industrial production. Wood annual production can still largely increase, making it a current focus of intensive research targeting new industrial products.

Other species are also important sources of cellulose, as for instance grasses like sugarcane, bamboo and others that produce large amounts of straw, yearly (Guimaraes et al. 2009). Another set is formed by plants that have been used as sources of textile fiber, like cotton, jute and some Cannabis species (Struik et al. 2000). There is also bacterial cellulose and other, still unexplored sources. Celluloses from different sources show different properties, even though the basic chemical structure is the same (Pauly and Keegstra 2008). This is not surprising, considering the large effects on the properties of any polymer, caused by minute changes in its macromolecular and supramolecular structures.

Natural rubber is another widespread material from biomass. It was used in pre-Columbian America to make playing balls and chewing gum, latter in Europe to erase pencil writings as a “rubber” and to make impermeable coatings (Hurley 1981). The discovery of vulcanization and its use in tires allowed the widespread use of the automobile. Great efforts were devoted to replace natural rubber with synthetic products, but it still holds an important share in the fabrication of rubber materials, in the 40% range. Natural rubber offers to the user important advantages over the competing synthetics. Thus, many efforts have been devoted to understand the peculiarities of its chemical composition and supramolecular features (Rippel and Galembeck 2009).

Even though they are “natural”, cellulose and rubber have been implicated in serious environmental damage, in the past. Until ca. 1980, liquid and gaseous effluents from the paper and pulp industry plagued many places in the world and large Brazilian cities were affected, e.g. São Paulo and Porto Alegre. On the other hand, rubber tires have been a serious environmental problem in most developed countries, where discarded tires make a significant part of garbage recovered from rivers and coastal sea beds. However, these problems have been effectively eliminated in many places, thanks to wise legislation, recycling and new technology, often based in new scientific knowledge.

Currently, materials derived from biomass appear more and more often as a solution to environmental problems, especially the atmospheric content of CO₂. Even if greenhouse gas emissions are controlled, the current CO₂ concentration in the atmosphere is already much higher than one century ago. Growing plants is an effective way to do atmospheric carbon sequestration, while producing food, energy and industrial raw materials.

Many other important materials derive from biomass as for instance: starch, charcoal, wood tar, oils and resins, diatomaceous earth, chitosan, various proteins and nucleic acids. Some are already used in everyday home or business activities, others may soon become common components of our lives. Beyond, some obvious cases of abundant materials that did not yet find valuable applications but hold great potential are lignin and hemicellulose.

Most materials derived from the biomass are “soft”, sharing an important common feature: their predominant physical behaviors
occur at an energy scale comparable with room temperature thermal energy. At these temperatures, quantum aspects are generally unimportant and the useful temperature range of soft materials hardly reaches 300°C, due to the prevalence of carbon-carbon bonds. They are insulators or poorly conductive, diamagnetic and opaque, which is adequate for some applications but limits their access to other, important applications. Most lack the thermoplasticity that makes polyolefins, vinlylic, acrylic and other polymers processable at a low cost, including the recent additive manufacture technologies. However, current research is showing how new materials can be produced from the biomass, endowed with useful electrical conductivity and other properties that are not usually found or expected from natural materials (Kampioti et al. 2018).

Nearly ten years ago, the use of biomass to replace oil in energy production met with widespread criticism, based on the need to preserve existing land for food production. This was extended to any industrial use of biomass, leading to serious economic and social problems, in some countries. This objection was refuted by data showing steady increase of food production in Brazil, parallel to increasing outputs of ethanol from sugarcane and biodiesel from vegetable oil and lard, for the past 40 years. More recently, a similar conclusion was obtained in Ethiopia, showing that fuel production from agriculture led to increased food safety. The objections to multiple uses of agricultural land are based on the inelasticity of planted area, but even if this is constant, its output may be largely increased by using better technology, introducing good practices and by providing economic stimuli to farmers (Arndt et al. 2016).

Which fraction of the overall biomass production will be transformed in industrial raw materials? This can be estimated, using current data from the petrochemical industry. Synthetic polymers that play an important role in the current materials scene account for nearly one-half of the amount of the products delivered by the petrochemical industry. This in turn uses less than 10% of the overall oil and gas global output but its market value is much more important, 40-50%. Assuming that the same breakdown between energy and raw materials use will prevail in the use of biomass, materials will make an important contribution to the overall wealth produced from biomass, while using only a minor fraction (Galembeck and Abreu Filho 2017, Galembeck 2017b).

This work reviews the recent activity of the authors in this area, showing strategies to enlarge the applicability of the materials derived from biomass, thanks to recent findings that provide better understanding of their structure and properties.

NEW PROPERTIES FROM “OLD” MATERIALS

Cellulose and natural rubber have been studied and used for a long time and they are thus considered to be well known, “mature” materials. Notwithstanding the extensive literature published in the past century, important questions have been answered only recently and others are arising, for both materials.

For instance, cellulose is not soluble in more or less simple liquids that is very unusual behavior, but what is the reason for this remarkable insolvency? A frequently found answer has been the multiplicity of hydrogen bonds that maintains the cellulose chains tightly bound to each other, but the same number of H-bonds is also found in starch, dextran and other polysaccharides that are easily dissolved in water. Recently, the “Lindman hypothesis” (Lindman et al. 2010, Medronho et al. 2012, Kihlman et al. 2013) was raised, based on the amphiphilicity of cellulose that is a result of its particular structure: the rigid chain is formed by two flat hydrophobic surfaces, while the -OH groups are all aligned along the perimeter of the chains. Thus, cellulose is an amphiphile, due to the
spatial separation between the hydrophobic surface and its hydrophilic borders.

The Lindmann hypothesis has been confirmed in different ways. In the authors group it led to the discovery of the ability of cellulose dissolved in alkaline aqueous medium to disperse and to exfoliate the extremely hydrophobic graphite in an aqueous solution (Ferreira et al. 2017). A micrograph of thin graphite sheets obtained in this way is shown in Figure 1. This is now being used to make graphite coatings on lignocellulosic and other materials. (Galembeck and Ferreira 2015). A schematic description of the mechanism of graphite exfoliation by cellulose is in Figure 2.

The solubility of cellulose in alkaline media is being explored in different ways and another contribution from this group was the demonstration that dissolved cellulose makes excellent adhesives for paper, cardboard and wood, with two advantages over any other adhesive: it works very well on wet substrates, where most other paper adhesives fail and it is fully repulpable, since no extraneous polymer is used (Ferreira et al. 2015). Paper impregnated with cellulose solutions is strengthened, because dissolved cellulose adheres to paper fibers, increasing sheet cohesion (Figure 3).

Another important research target is cellulose plasticization, comparable to petrochemical thermoplastics. Cellulose films and fibers can be made using complex solvent media like cuproammonium solutions, in the past and ionic liquids (Pang et al. 2013), more recently. However, the wet-spinning and casting technologies used are based on “dope” coagulation: for instance, a polymer fiber is made from a viscous polymer solution (“dope”) by spinning it through fine bores wherefrom it emerges as thin threads. These enter a coagulating bath, forming filaments that are concurrently pulled and dried, when the polymer chains align. Excellent products are obtained but leaving behind large volumes of liquid effluents with a potentially negative impact in the environment. The processes are slow and more costly than the powerful thermoforming techniques used with thermoplastics. A different approach that was recently disclosed is based on cellulose oxidation with periodate, with promising results but still short of presenting successful extrusion experiments (Leguy 2018).

Cellulose also finds use in specialized niches of low-scale but important applications, as in cell growth scaffolds (Courtenay et al. 2016, Johns et al. 2018) where the supporting material plays a vital role in cell structure and functionality (Da Luz Moreira et al. 2013).

**NANOCOMPOSITES**

Polymer blending and composite formation is a proven, successful approach to create new materials with unprecedented properties that was explored in this laboratory, in different ways.
Blending and compounding have been used together with copolymerization to produce highly diverse materials using a few monomer building blocks. The outcome is the ever-increasing competitiveness of polymers as compared to other materials, since the economics of the chemical industry is strongly dependent on the production scale. Thus, finding more and more different applications for the same building blocks allows the occupation of new niches, stimulating investment for increasing production scale of already important building blocks.

A new, powerful possibility emerged by the end of the past century: the nanocomposites formed by polymers and nanoparticles that display completely new combinations of properties (Mersersmith and Giannelis 1993, Wang and Pinnavaia, 1994). It was already known that carbon black and silica particles contribute unmatched mechanical strength to polyene rubbers used in tires, while silica particles are used in silicone rubber. They are not just “fillers” but rather they perform as strengthening functional additives. Moreover, natural rubber was described as a natural nanocomposite, since it contains a large number of nanoparticles, strongly adherent to the rubber matrix. Adhesion is mediated by proteins and probably also by phospholipids from the rubber tree sap that are incorporated to the rubber latex. The importance of proteins, phospholipids and mineral nanoparticles was previously evidenced by comparing the “skim” and “cream” natural rubber particles whose film-forming capabilities differ largely (Rippel et al. 2003). The availability of carbon nanotubes, graphene, nanoclays, nanocellulose and other nanoparticles created opportunities for developing a large number of polyfunctional polymer nanocomposites, combining different functions (Matos et al. 2014, Galembeck 2017c, Ferreira et al. 2017).

Nanocomposites can be made by mixing dry rubber with the nanoparticle powders but the “latex route” proved very successful. The colloidal polymer particles and the nanofillers are blended together within an aqueous dispersion where their compatibility is determined by interfacial properties, with a small participation of bulk properties that normally hamper the cohesion within multiphasic solids. Interfacial properties may be tuned in many ways to achieve the desired mechanical and other properties, in the nanocomposite as well as in nanoblends. The combination of particle stiffness, polymer plasticity and suitable processing techniques like lyophilization produces exquisite micro-morphologies desired for adsorption and...

**Figure 2** - Left: Representation of cellulose and graphite structures. Right: Disassembly of graphene stacks due to cellulose adsorption that pushes single or multiple lamellae towards the aqueous solution. Cellulose aggregates may also participate in these events (not shown). Reproduced (adapted) from (Ferreira et al. 2017) with permission from The Royal Society of Chemistry.
decontamination purposes, as shown in Figure 4 (Da Silva and Galembeck 2015).

The compatibility in nanocomposites and nanoblends also receives an important contribution from electrostatic adhesion (Rippel et al. 2012, Linares et al. 2013, Morales et al. 2013, Galembeck and Burgo 2017). This adhesion factor was first considered by Deryagin, based on the electrical double layer formation by contact electrification, followed by Coulomb attraction. Other authors recognized its importance but in a few cases, only. More recently, the various scanning electric probe microscopies derived from AFM allowed the direct observation of local charge excess in a solid with nanometer resolution and the detection of electrostatic contributions to adhesion, in several systems (Galembeck et al. 2013). New models of electrostatic adhesion were developed, based on
ion partition not only at interfaces but also in the bulk phases that were successfully verified by measuring the elastic modulus of nanocomposites (Galembeck 2018). A schematic description of electrostatic adhesion where cations hold together the negative surfaces of clay and rubber latex particles is in Figure 5.

The new polymer materials that appeared in recent years are proving suitable for several applications, creating radically new products. A good example is the airless tires that were first announced less than twenty years ago and are already entering the market (Ju et al. 2012).

**ELECTROSTATIC PROPERTIES OF SOFT MATTER**

**CHANGING PARADIGMS**

In many mythologies, controlling lightning was an attribute of the most powerful god in the Pantheon, like Zeus among the Greek and Tupã among the Tupi-Guarani. Today, humankind cannot control lightning, we can only protect ourselves to a limited extent and electric storms continue to bring serious problems that often affect millions of people.

Even so, electrostatics is often viewed as a well-established discipline that slowly lost its importance and was superseded by electromagnetism. For instance, by mid-past century electrostatic machines were relevant as electricity generators playing an important role in the then fashionable area of nuclear physics, but they are now only seen in schools, science fairs, and few other places (Galembeck and Burgo 2017, chap 14). A scientific reason for the fading of electrostatics is that it did not participate from all the huge scientific development resulting from the atomic-molecular theories in the 20th century: current literature still refers to "charge" dissociated from the entities that carry charge. Even more damaging, electrostatic charging is still repeatedly presented as the result of electron transfer that is indeed important in metals and semiconductors but much less so in polymers, colloids, crystal liquids, ionic liquids and other materials that are grouped as "soft materials", including those derived from biomass.

This situation has been changing in the past twenty years, driven by new experimental tools, by the growing interest in energy harvesting, the demand for large numbers of diverse sensors and actuators arising from the Internet of Things (IoT) and robotics, where electroadhesion shows great advantages in gripping devices. However, this is a slow process because it depends on the
abandonment of established paradigms (Galembeck and Burgo 2017).

Recent scientific outcomes are: the growing acceptance of ions as the entities accounting for excess charge in soft materials and the recognition that excess charge is found everywhere, it depends on many ambient factors and it can be controlled in many ways, dismissing the prevalence of electroneutrality (Santos et al. 2011). Other major changes are the replacement of the unidirectional charge transfer in contact electrification by charge pattern formation (Burgo et al. 2014, Burgo and Galembeck 2015) and new mechanisms for electrostatic charging of solids, liquids and gases (Burgo and Galembeck 2016).

The atmosphere is now acknowledged as the site of many phenomena that produce electricity. Water assumes a paramount role in electrostatic phenomena, as a charge carrier across interfaces and as a charge separation tool operating at interfaces. This is a great change from the previously accepted role for water that was seen only as an agent for the dissipation of charge on electrified surfaces, due to its weak but non-negligible conductivity.
Added to that, water ability to impart charge to solid surfaces (Figure 6) is now recognized, in hygroelectricity (Ducati et al. 2010, Gouveia et al. 2012) that designates a broad set of phenomena with a common feature: solids exposed to a moist atmosphere acquire charge due to water vapor adsorption accompanied by charge partition.

This was first evidenced ten years ago but it has been used to explain many electrostatic phenomena, since this time. The most recent case is stretched/relaxed rubber tubing that acquires charge, reaching surface potential in the kV range and is discussed in the next section. Beyond, hygroelectricity is currently explored as a means to scavenge energy (Yin et al. 2014 a, b, Zhao et al. 2015, 2016, Xue et al. 2017, huang et al. 2018).

**RUBBER ELECTROSTATICS**

Interest in the electrical properties of rubber were confined to its insulating properties, including the dissipation factor, \(\tan\ delta\) that were relevant to electric power cable producers. Currently, rubber materials play different essential roles in robot design. An evidence is given by the frequent use of keywords like “dielectric elastomers”, in the mechatronics literature (Berselli et al. 2014, An et al. 2015, Fu et al. 2018).

Electrostatic experiments with rubber are hardly reproducible but an exception was recently found: periodically stretching natural rubber and silicone rubber produces an AC electrostatic potential, in phase with the rubber length. This could be interpreted as the result of mechanochemical reactions in strained rubber, but charge acquisition does not take place during stretching but rather in the following relaxation. The current working hypothesis used in this laboratory is the following: water is adsorbed from the atmosphere, on the newly exposed surface of the stretched rubber, carrying excess negative ions that are trapped when it relaxes and its surface decreases (Burgo et al. 2017). Typical experimental results are in Figure 7.

The appearance of a variable potential on periodically deformed rubber is a cross-effect, symmetrical to the mechanical deformation of rubber membranes that is observed under an applied electric field (Jin and Huang 2016, Dong et al. 2018). This is now used in artificial muscle and robotic self-sensing actuators. The elastomer membranes used in these devices are known for their non-linear behavior that poses difficulties to designers, requiring complex real-time feedback capabilities. Better solutions to this problem may now appear thanks to new physical-chemical models for rubber charging (Santos et al. 2019) and for rubber response to external fields.

The entities responsible for excess charge in a phase repel each other and they are thus driven towards the surfaces, producing deformation and even the Coulombic explosions. This gives greater importance to the knowledge of materials surface properties (Gouveia et al. 2012, Santos et al. 2013, 2018, Burgo et al. 2014) that is often lacking, either...
Figure 7 - Electrostatic potential of (a) natural and (b) silicone rubber under stretching-relaxation cycles. A Kelvin electrode recorded the initial electrostatic potential, for 60 s. The stretching-relaxation cycles followed for 180 s and then ceased, leaving the material at the starting position. Zooms from (a,b) are shown in the inset graphs. (c,d) Voltage vs distance for natural and silicone rubber, respectively. Experiments were performed at 60% RH. Reprinted (adapted) with permission from (Burgo et al. 2017). Copyright 2017 American Chemical Society.
because the needed investigations were not done or because the results are not disseminated among researchers and engineers. Many important metals are coated with a layer of oxide with low intrinsic conductivity. This also helped to understand interesting electrostatic phenomena in isolated metal objects (Ducati et al. 2010).

Another contributing topic is mechanochemistry, the study of chemical phenomena triggered by mechanical agents. This topic held an important status in the past and Ostwald recognized five types of physical-chemical phenomena: thermal, photochemical, radiochemical, electrochemical and mechanochemical. The latter was virtually ignored in the second half of the 20th century but it is currently receiving greater attention due to its growing importance in the pharma and materials industries. (Balestrin et al. 2014). Mechanochemical reactions are often seen as “destructive” but their role in contact and friction charging of soft materials has been demonstrated, recently (Francisco et al. 2012, Burgo et al. 2013, Ruggeri et al. 2013, Balestrin et al. 2014, Galembeck et al. 2014, 2017b, Burgo et al. 2016, da Silva et al. 2017). Triboelectricity is the electricity produced by mechanical action on materials, especially friction, has been known since ancient Greece but its understanding has been very poor (Schein 2007). It is now receiving a firmer mechanistic basis, since charge carriers in tribocharged polymers were identified as ionic species formed during mechanochemical reactions, as in the schematic representation of the mutual electrification of PTFE and polyethylene when their surfaces are sheared (Figure 8). Coupled to the demonstration that charge abatement on electrified polymer surfaces is also related to water adsorption, it can now be much better studied.

An important recent finding on triboelectricity is its participation in a positive feedback loop: electrostatic charge formed by friction in solid surfaces may increase friction coefficients many-fold, as shown in Figure 9.

**PERSPECTIVES**

Perspectives for the use of nanocomposites are always increasing due to their ability to offer good answers to more and more demanding requests. For instance, robotics requires materials that can perform different functions concurrently under variable conditions, like the self-sensing actuation of a robotic skin, arm or gripper. Food production can benefit from self-sensing actuation embedded in an irrigation pipe or a plastic film used to control water evaporation or to deliver nutrients and pest control agents. In a more familiar situation, wall paint makers and researchers work hard to improve the resistance of their products to water and to soiling – and wall paint is a complex multifunctional nanostructured composite.

**ELECTROSTATIC SEPARATION**

Intensive use of biomass is a great challenge, because it involves handling and separating complex mixtures of solid components, which creates the risk of unwanted electrostatic discharges that may trigger fire and explosions in industrial environments. This is a problem also known in mining and some other industries, while fluid handling is a great advantage intrinsic to the oil and gas industry.

Magnetic separation is successful in handling solids, but biomass is diamagnetic, with few exceptions. On the other hand, electrostatic attraction and repulsion are known to every child, but their control is still limited and is be used in a large scale. However, recent progress in this area is showing that solid separation using powerful electrets or blocked electrodes may solve important problems in the processing of biomass residues, municipal waste, as well as in reclaiming polluted areas.
INTENSIVE USE OF ELECTROSTATIC ADHESION

The possibilities of electrostatic adhesion are not yet known to many professionals and researchers that end up resorting to more complex joining techniques. Recognizing its presence in current systems and products and exploiting it rationally to make functional materials can make a great contribution to “green” production and to the improvement of materials performance.

NEW “HARD MATERIALS”

Most materials derived from biomass are soft and this contributes to their attractiveness. However, hard materials are also found everywhere, raising this question: to which extent can biomass be used to make hard materials?

A positive answer is given by materials like glassy carbon, carbon fiber and diamond-like coatings that have been made largely from petrochemicals but can also be made from the
biomass. The current trend to replace metals by carbon fiber composites in aircraft and cars has been strengthened by the benefits in increased safety, weight reduction and energy savings.

**TOWARDS SUSTAINABLE PRODUCTION**

Sustainable production requires materials from renewable resources transformed by technologies that are not energy-intensive, avoiding great departure from room temperature and pressure. Effluent output should be minimal, allowing the insertion of the processes and products in a circular economy. All these requirements are satisfied by materials from the biomass, especially if they are used in conjunction with electrostatic adhesion and mass-processed using electrostatic techniques. These statements are supported by current products and processes but there is several opportunities requiring additional research and development that needs to be done in the near future, prior to the exhaustion of many current resources and raw materials that we all depend on.

**CONCLUSIONS**

Chemistry made an invaluable contribution to our understanding of electrostatic phenomena and this will probably continue, for the foreseeable future. Chemistry is complex, it is not an exact science. It is not responsive to or properly explained by any encompassing theoretical approach; neither are most chemical phenomena predictable by any single theory. Given the importance of chemical phenomena to Electrostatics, the same applies to this discipline.

Electrostatics has some appealing “green” features: large effects are produced using a few Joules, while great changes in the behavior of matter are obtained by adding or removing small amounts of water. These features will allow electrostatics to play a major role in making materials from biomass, that is necessary to advance in the quest for sustainability.

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**AUTHOR CONTRIBUTIONS**

F.G. outlined the paper and wrote parts of the manuscript, with research and writing support from T.A.L.B, D.S.S and L.P.S. All authors provided critical feedback and contributed to its final version.

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