



## Materials from renewable resources: new properties and functions

FERNANDO GALEMBECK<sup>1</sup>, THIAGO A.L. BURGO<sup>2</sup>, DOUGLAS S. DA SILVA<sup>1</sup> and LEANDRA P. SANTOS<sup>1</sup>

<sup>1</sup>Instituto de Química, Universidade Estadual de Campinas, Rua Josué de Castro, s/n, 13083-970 Campinas, SP, Brazil

<sup>2</sup>Departamento de Física, Universidade Federal de Santa Maria, Av. Roraima, 1000, Camobi, 97105-900 Santa Maria, RS, Brazil

*Manuscript received on November 3, 2018; accepted for publication on February 5, 2019*

**How to cite:** GALEMBECK F, BURGO TAL, SILVA DS AND SANTOS LP. 2019. Materials from renewable resources: new properties and functions. *An Acad Bras Cienc* 92: e20181160. DOI 10.1590/0001-3765201920181160.

**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 CO<sub>2</sub>

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.

---

Correspondence to: Fernando Galembeck  
E-mail: [fernagal@unicamp.br](mailto:fernagal@unicamp.br)  
ORCID: <http://orcid.org/0000-0003-4778-5442>

The most common material from renewable resources is wood. It has been used since pre-historic 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 CO<sub>2</sub>. Even if greenhouse gas emissions are controlled, the current CO<sub>2</sub> 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, vinylic, 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.

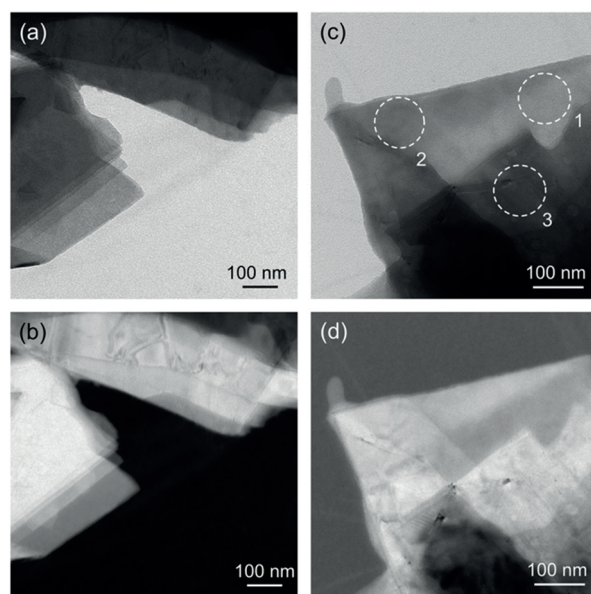
For instance, cellulose is not soluble in more or less simple liquids that is very unusual behavior, but what is the reason for this remarkable insolubility? A frequently found answer has been the multiplicity of hydrogen bonds that maintains the cellulose chains tightly bound to each other, but the 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



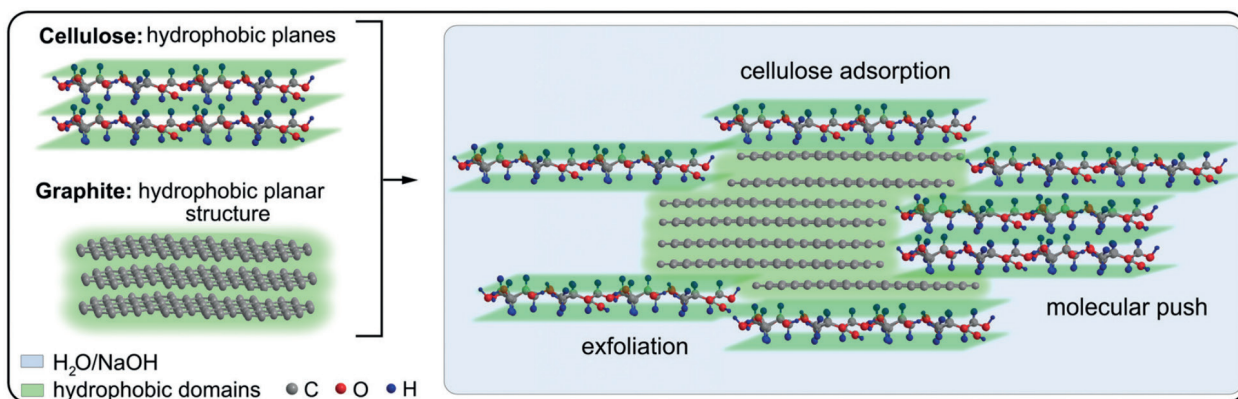
**Figure 1** - Transmission electron micrographs of thin graphite sheets exfoliated in cellulose aqueous solutions. (a, c): brightfield and (b, d): 25 eV EELS filtered images from small graphite particles separated by zonal sedimentation. Particle thickness measured in the marked circles in (c) is: 1, 20 nm; 2, 33 nm; 3, 64 nm. Reproduced (adapted) from (Ferreira et al. 2017) with permission from The Royal Society of Chemistry.

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.



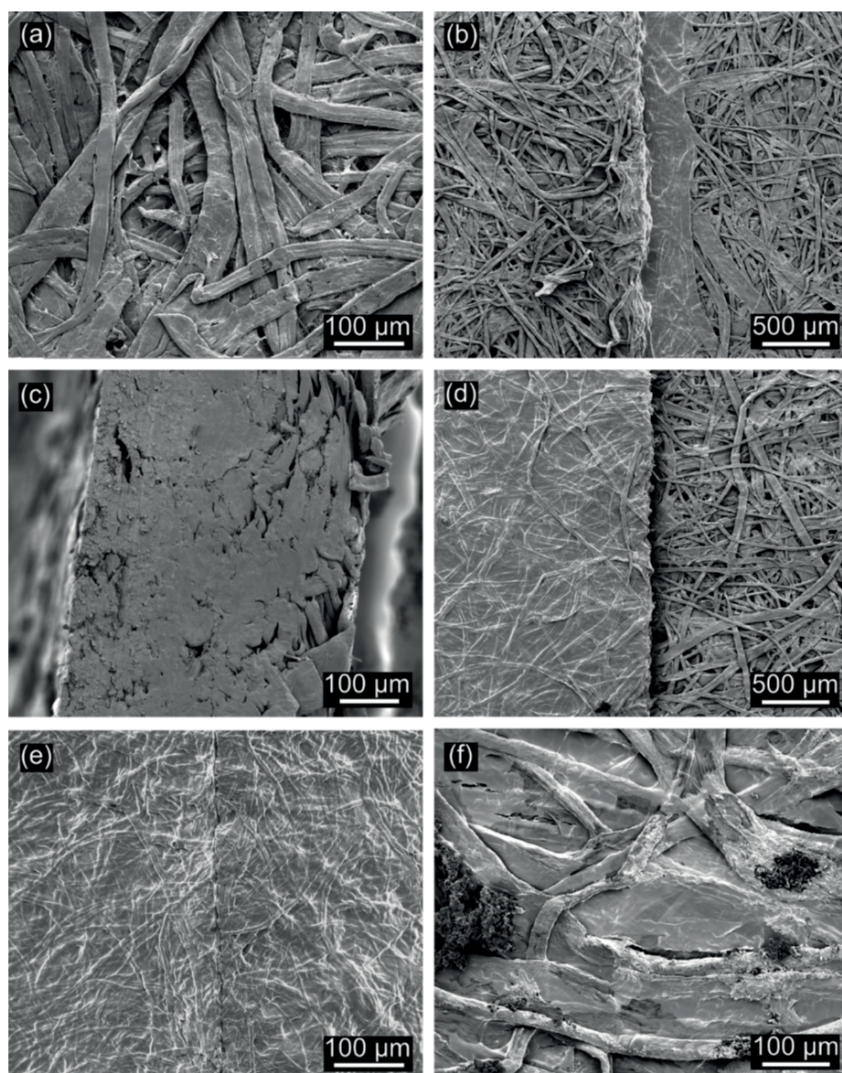
**Figure 2** - Left: Representation of cellulose and graphite structures. Right: Disassembly of graphene stacks due to cellulose adsorption that pushes single or multiple lamellae towards the aqueous solution. Cellulose aggregates may also participate in these events (not shown). Reproduced (adapted)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

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 (Messersmith 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 multiphase 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

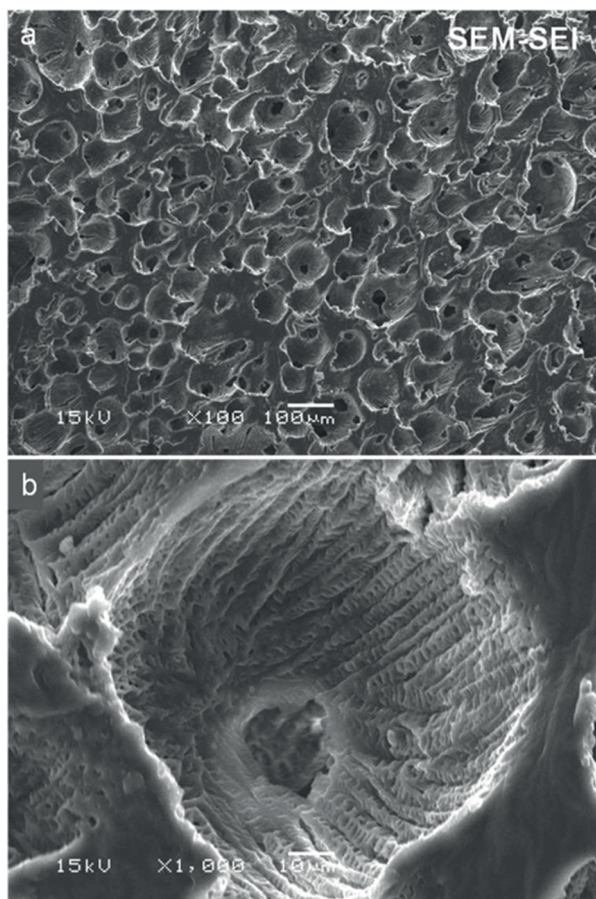


**Figure 3** - Secondary electron micrographs showing results of the application of dissolved cellulose to filter paper: (a) as-received filter paper surface; (b) filter paper strips bonded with cellulose adhesive, single lap joint surface; (c) cross-section view of b; (d) single lap joint prepared with wet paper strips; (e) butt joint; (f) impregnated single strip. Reprinted (adapted) with permission from (Ferreira et al. 2015). Copyright 2015 American Chemical Society.

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



**Figure 4** - SEI micrographs of the freeze-cast foamed poly(styrene-butyl acrylate-acrylic acid) latex show (a) pore distribution and (b) inter-connected pore details. Note the intricate structure of the pore walls in b). Reproduced (adapted) from (Da Silva and Galembeck 2015) with permission from The Royal Society of Chemistry.

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).

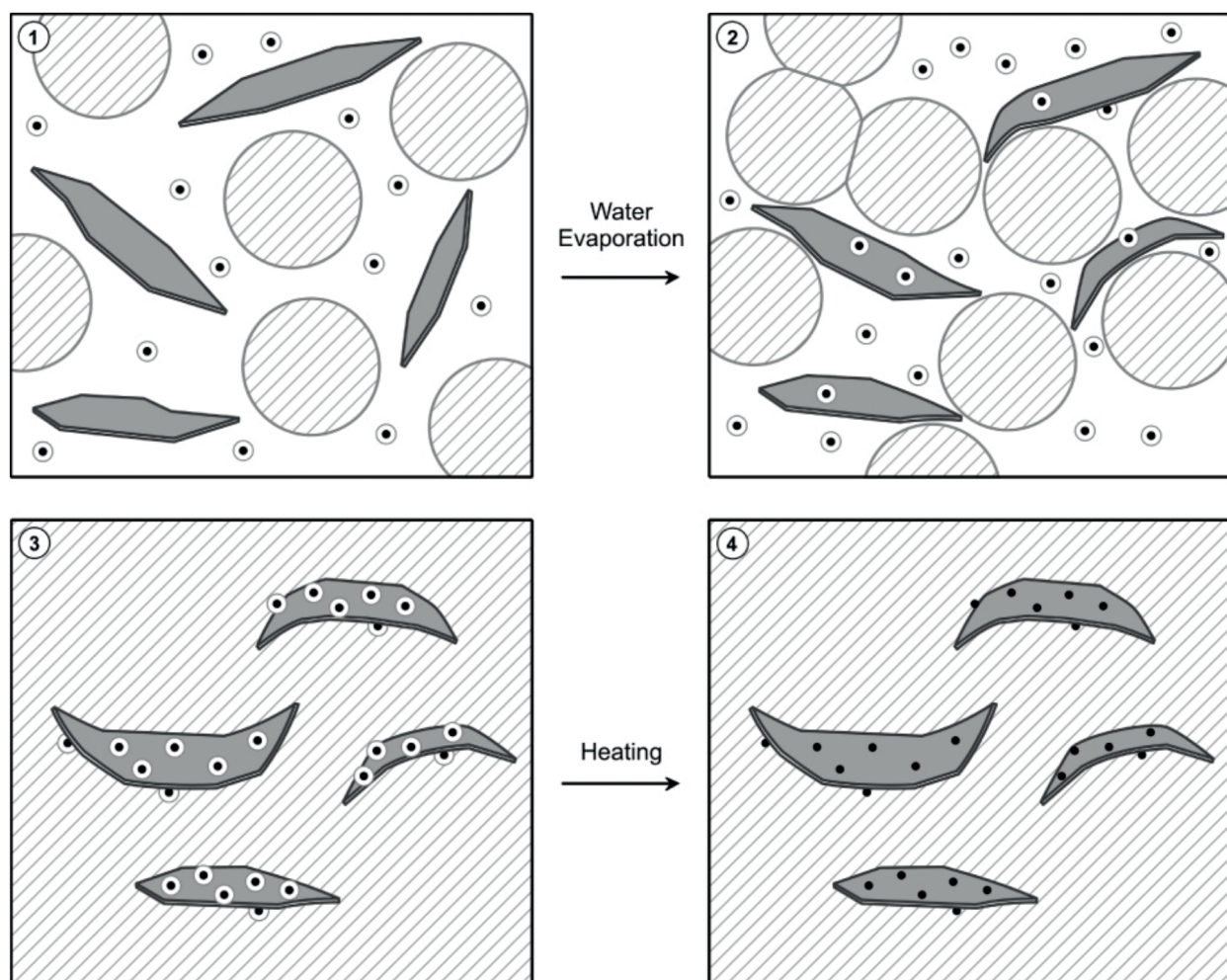
## ELECTROSTATIC PROPERTIES OF SOFT MATTER

### 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 20<sup>th</sup> 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



**Figure 5** - Schematic representation of the role of positive counterions (small circles) on the adhesion between clay lamellae and polymer. (1) Latex and clay dispersion, (2) polymer-clay particles approach during dispersion drying, (3) hydrated counterions bridging clay and the dry polymer matrix, and (4) dehydrated counterions bridge clay lamellae and the polymer matrix. Reprinted (adapted) with permission from Bragança et al. 2007. Copyright (2007) American Chemical Society.

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.



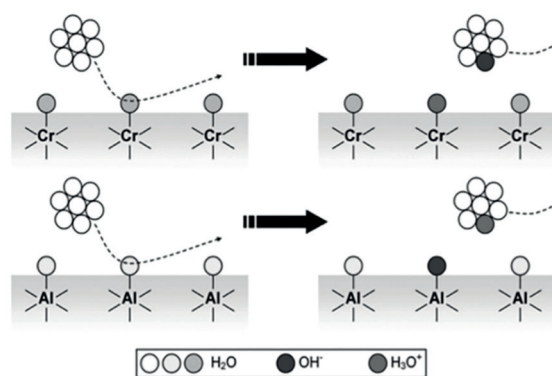
Added to that, water ability to impart charge to solid surfaces (Figure 6) is now recognized, in hygroelectricity (Ducati et al. 2010, Gouveia et al. 2012) that designates a broad set of phenomena with a common feature: solids exposed to a moist atmosphere acquire charge due to water vapor adsorption 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

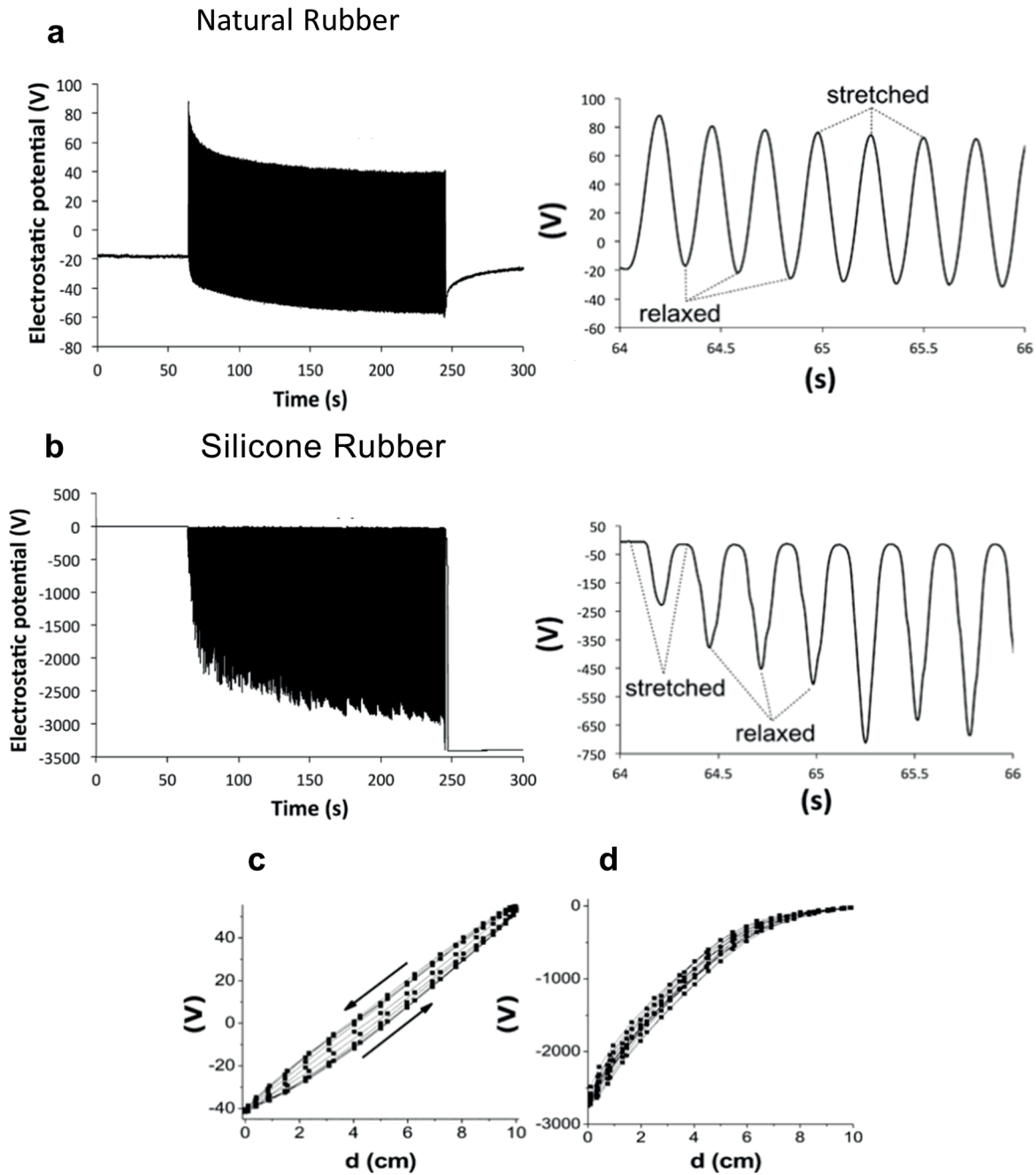


**Figure 6** - How water contributes charge to solid surfaces (hygroelectricity). Upper: a cluster of water molecules approaches a basic surface of stainless steel or other chromium alloy that contains basic chromium oxide at the surface. The oxide picks H<sup>+</sup> ions, acquiring positive charge. Aluminum metal is coated with acidic oxide that picks up OH<sup>-</sup> ions, acquiring negative charge. Reprinted (adapted) with permission from (Ducati et al. 2010). Copyright 2010 American Chemical Society.

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 20<sup>th</sup> 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.

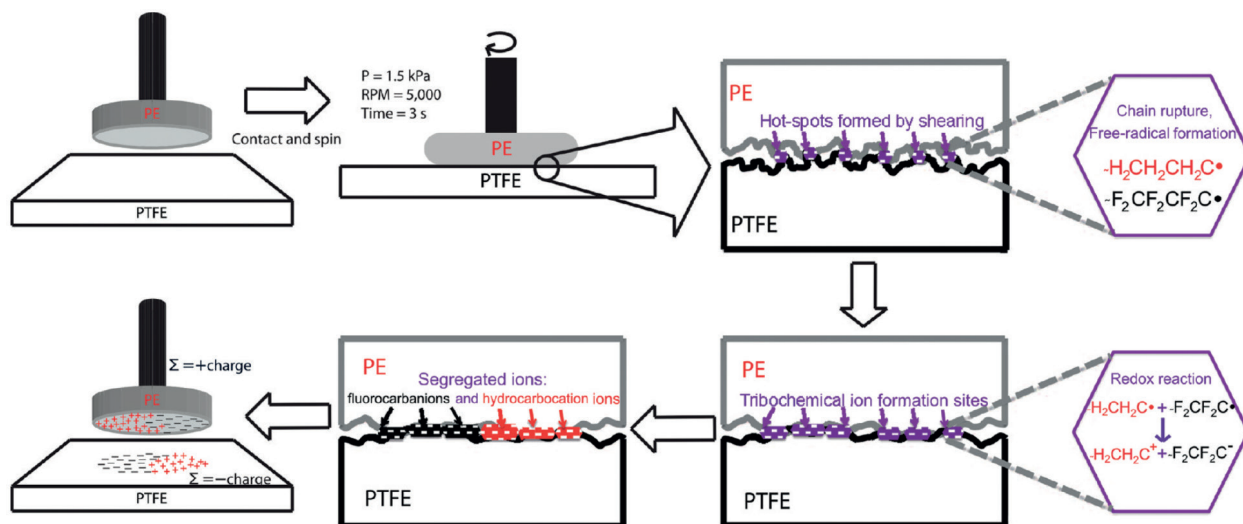
## PERSPECTIVES

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.

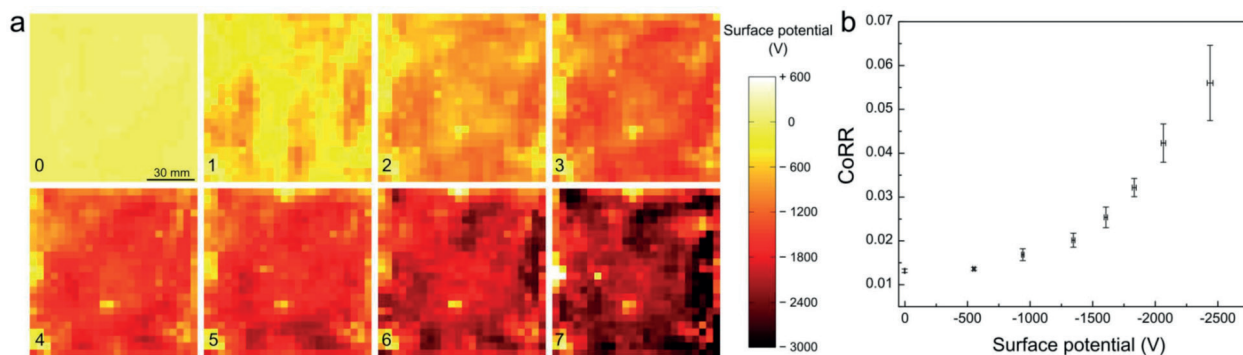
## ELECTROSTATIC SEPARATION

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 to 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.



**Figure 8** - Mechanism for contact triboelectrification of insulating polymers. Shearing the polymer interface heats both surfaces unevenly forming hot spots, due to forced contact on surface hills. Plasticization and melting take place added to chain breakdown and fragmentation. Homolytic scission produces free radicals with markedly different electronegativities that are converted into fluorocarbanions and hydrocarbocations by electron transfer. Ions are segregated due to the chain size, following Flory–Huggins theory and superseding weak electrostatic interactions between highly spaced charges. Reprinted (adapted) with permission from (Burgo et al. 2012). Copyright 2012 American Chemical Society.



**Figure 9** - (a) Potential maps of PTFE plates tribocharged by friction with polyethylene. (b) CoRR (coefficient of rolling resistance) versus average surface potential of tribocharged PTFE plates (Burgo et al. 2013).

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.

#### ACKNOWLEDGMENTS

This work was supported by Brazilian agencies Ministério da Ciência, Tecnologia, Inovações e Comunicações and Conselho Nacional de Desenvolvimento Científico e Tecnológico (MCTIC/CNPq, 465452/2014-0) and Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP, 2014/50906-9) through INCT/INOMAT (National Institute for Complex Functional Materials). LPS thanks Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) to 88887.284776/2018-00.

#### 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.

#### REFERENCES

- AN L, WANG F, CHENG S, LU T AND WANG TJ. 2015. Experimental investigation of the electromechanical phase transition in a dielectric elastomer tube. *Smart Mater Struct* 24: 035006.
- ARNDT C, MSANGI S AND THURLOW J. 2016. Green energy: Fueling the path to food security. In 2016 Global Food Policy Report, Washington D.C.: International Food Policy Research Institute (IFPRI), chapter 7.
- BALESTRIN LBS, DUQUE DD, DA SILVA DS AND GALEMBECK F. 2014. Triboelectricity in insulating polymers: evidence for a mechanochemical mechanism. *Faraday Discuss* 170: 369-383.
- BERSELLI G, MAMMANO GS AND DRAGONI E. 2014. Design of a dielectric elastomer cylindrical actuator with quasi-constant available thrust: modeling procedure and experimental validation. *J Mech Des* 136: 125001.
- BRAGANÇA FC, VALADARES LF, LEITE CAP AND GALEMBECK F. 2007. Counterion effect on the morphological and mechanical properties of polymer-clay nanocomposites prepared in an aqueous medium. *Chem Mater* 19: 3334.

- BURGO TAL, BALESTRIN LBS AND GALEMBECK F. 2014. Corona charging and potential decay on oxidized polyethylene surfaces. *Polym Degrad Stabil* 104: 11-17.
- BURGO TAL, BATISTA BC AND GALEMBECK F. 2017. Electricity on rubber surfaces: a new energy conversion effect. *ACS Omega* 2: 8940-8947.
- BURGO TAL, DUCATI TRD, FRANCISCO KR, CLINCKSPOOR KJ, GALEMBECK F AND GALEMBECK SE. 2012. Triboelectricity: Macroscopic Charge Patterns Formed by Self Arraying Ions on Polymer Surfaces. *Langmuir* 28: 7407-7416.
- BURGO TAL AND GALEMBECK F. 2015. On the spontaneous electric-bipolar nature of aerosols formed by mechanical disruption of liquids. *Colloid Interface Sci Commun* 7: 7-11.
- BURGO TAL AND GALEMBECK F. 2016. Electrified Water: Liquid, Vapor and Aerosol. *J Braz Chem Soc* 27: 229-238.
- BURGO TAL, GALEMBECK AND POLLACK GH. 2016. Where is water in the triboelectric series? *J Electrostat* 80: 30-33.
- BURGO TAL, SILVA CA, BALESTRIN LBS AND GALEMBECK F. 2013. Friction coefficient dependence on electrostatic tribocharging. *Sci Rep* 3: 2384.
- COURTENAY JC, JOHNS MA, GALEMBECK F, DENEKE C, LANZONI EM, COSTA CA, SCOTT JL AND SHARMA RI. 2016. Surface modified cellulose scaffolds for tissue engineering. *Cellulose* 24: 253-267.
- DA LUZ MOREIRA P, GENARI SC, GOISSIS G, GALEMBECK F, AN YH AND SANTOS AR. 2013. Bovine osteoblasts cultured on polyanionic collagen scaffolds: An ultrastructural and immunocytochemical study. *J Biomed Mater Res B Appl Biomater* 101B: 18-27.
- DA SILVA LL AND GALEMBECK F. 2015. Morphology of latex and nanocomposite adsorbents prepared by freeze-casting. *J Mater Chem A* 3: 7263-7272.
- DA SILVA VS, COSTA CAR, BATTIROLA LC, DE FARIAS MA, GALEMBECK F AND DO CARMO GONÇALVES M. 2017. Polymorphic transformation morphology of isotactic poly(1-butene) /poly(propylene-co-1-butene-co-ethylene) blends. *J Polym Res* 24: 22.
- DONG L, GRISSOM MD, SAFWAT T, PRASAD MG AND FISHER FT. 2018. Resonant frequency tuning of electroactive polymer membranes via an applied bias voltage. *Smart Mater Struct* 27: 114005.
- DUCATI TRD, SIMÕES LH AND GALEMBECK F. 2010. Charge Partitioning at Gas-Solid Interfaces: Humidity Causes Electricity Buildup on Metals. *Langmuir* 26: 13763-13766.
- FAO. 2016. Forest Products Statistics. Available at: <<http://www.fao.org/forestry/statistics/80938/en/>>. Last accessed 30 Oct 2018.
- FERREIRA ES, DA SILVA DS, BURGO TAL, BATISTA B AND GALEMBECK F. 2017. Graphite exfoliation in cellulose solutions. *Nanoscale* 9: 10219-10226.
- FERREIRA ES, LANZONI EM, COSTA CAR, DENEKE C, BERNARDES JS AND GALEMBECK F. 2015. Adhesive and reinforcing properties of soluble cellulose: a repulpable adhesive for wet and dry cellulosic substrates. *ACS Appl Mater Interfaces* 7: 18750-18758, 2015.
- FRANCISCO KR, BURGO TAL AND GALEMBECK F. 2012. Tribocharged polymer surfaces: solvent effect on pattern formation and modification. *Chem Lett* 41: 1256-1258.
- FU Y, DORFMANN L AND XIE Y. 2018. Localized necking of a dielectric membrane. *Extrem Mech Lett* 21: 44-48.
- GALEMBECK F. 2015. Thought for Food. *J Braz Chem Soc* 26: 1743-1744.
- GALEMBECK F. 2017a. Synergy in food, energy and advanced materials production from biomass. *Pure Appl Chem* 90: 109-119.
- GALEMBECK F. 2017b. Evolução e inovação no setor químico brasileiro: uma visão dos últimos quarenta anos. *Quim Nova* 40: 630-633.
- GALEMBECK F. 2017c. Multifunctional Nanocomposites of Natural Rubber Latex and Carbon Nanostructures. *Rev Virtual Quim* 9: 73-96.
- GALEMBECK F. 2018. From Aqueous Dispersions to Functional Materials: Capillarity and Electrostatic Adhesion. *Chem Rec* 18: 1054-1064.
- GALEMBECK F AND ABREU FILHO PP. 2017. Perspectives for Biomass Production and Use in Brazil. *Rev Virtual Quim* 9: 274-293.
- GALEMBECK F AND BURGO TAL. 2017. Chemical Electrostatics, Cham: Springer.
- GALEMBECK F, BURGO TAL, BALESTRIN LBS, GOUVEIA RF, SILVA CA AND GALEMBECK A. 2014. Friction, Tribochemistry and Triboelectricity: Recent Progress and Perspectives. *RSC Adv* 4: 64280-64298.
- GALEMBECK F, COSTA CAR, BURGO TAL, BERNARDES JS AND GOUVEIA RF. 2013. Microscopia de sondas: uma caixa de ferramentas da nanotecnologia. *Ciênc Cult* 65: 37-43.
- GALEMBECK F AND FERREIRA ES. 2015. Processo de obtenção de dispersões aquosas estáveis de grafeno, grafite e carbono amorfo, isento de tensoativos e utilizando celulose como dispersante. Patent application: PI 10 2015 026420.
- GOUVEIA RF, BERNARDES JS, DUCATI TRD AND GALEMBECK F. 2012. Acid-base site detection and mapping on solid surfaces by Kelvin force microscopy (KFM). *Anal Chem* 84: 10191-10198.
- GUIMARAES JL, FROLLINI E, DA SILVA CG, WYPYCH F AND SATYANARAYANA KG. 2009. Characterization of banana, sugarcane bagasse and sponge gourd fibers of Brazil. *Ind Crop Prod* 30: 407-415.
- HUANG Y, CHENG H, YANG C, ZHANG P, LIAO Q, YAO H, SHI G AND QU L. 2018. Interface-mediated hygroelectric generator with an output voltage approaching 1.5 volts. *Nat Commun* 9: 4166.
- HURLEY PE. 1981. History of natural rubber. *J Macromol Sci Pure Appl Chem* 15: 1279-1287.
- JIN X AND HUANG Z. 2016. Random response of dielectric elastomer balloon to electrical or mechanical perturbation. *J Intell Mater Syst Struct* 28: 195-203.

- JOHNS MA, BAE Y, GUIMARÃES FEG, LANZONI EM, COSTA CAR, MURRAY PM, DENEKE C, GALEMBECK F, SCOTT JL AND SHARMA RI. 2018. Predicting Ligand-Free Cell Attachment on Next-Generation Cellulose-Chitosan Hydrogels. *ACS Omega* 3: 937-945.
- JU J, KIM D AND KIM K. 2012. Flexible cellular solid spokes of a non-pneumatic tire. *Compos Struct* 94: 2285-2295.
- KAMPIOTI K, MATOS CF, GALEMBECK F, JAILLET C, DERRÉ A, ZARBIN AJG AND PÉNICAUD A. 2018. Highly conducting, sustainable, nanographitic rubber composites. *ACS Omega* 3: 1367-1373.
- KIHLMAN M, MEDRONHO BF, ROMANO AL, GERMGÅRDA U AND LINDMAN B. 2013. Cellulose dissolution in an alkali based solvent: influence of additives and pretreatments. *J Braz Chem Soc* 24: 295-303.
- LEGUY J. 2018. Periodate oxidation of cellulose for internal plasticization and materials design. Material chemistry. Available at: <<https://tel.archives-ouvertes.fr/tel-01852166/document>>. Last accessed 30 Oct 2018.
- LINARES EM, FORMIGA A, KUBOTA LT, GALEMBECK F AND THALHAMMER S. 2013. One-step synthesis of polymer core-shell particles with a carboxylated ruthenium complex: a potential tool for biomedical applications. *J Mater Chem B* 1: 2236-2244.
- LINDMAN B, KARLSTRÖM G AND STIGSSON L. 2010. On the Mechanism of Dissolution of Cellulose. *J Mol Liq* 156: 76-81.
- MATOS CF, GALEMBECK F AND ZARBIN AJG. 2014. Multifunctional and environmentally friendly nanocomposites between natural rubber and graphene or graphene oxide. *Carbon* 78: 469-479.
- MEDRONHO B, ROMANO A, MIGUEL MG, STIGSSON L AND LINDMAN B. 2012. Rationalizing cellulose (in) solubility: reviewing basic physicochemical aspects and role of hydrophobic interactions. *Cellulose* 19: 581-587.
- MESSERSMITH PB AND GIANNELIS EP. 1993. Polymer-layered silicate nanocomposites: in situ intercalative polymerization of  $\epsilon$ -caprolactone in layered silicates. *Chem Mater* 5: 1064-1066.
- MORALES MA, RODRIGUES ECS, AMORIM ASCM, SOARES JM AND GALEMBECK F. 2013. Size Selected Synthesis of Magnetite Nanoparticles in Chitosan Matrix. *Appl Surf Sci* 276: 71-74.
- OECD. 2013. Material Resources. Productivity and the Environment. Available at: <[http://www.oecd.org/greengrowth/MATERIAL%20RESOURCES,%20PRODUCTIVITY%20AND%20THE%20ENVIRONMENT\\_Key%20findings.pdf](http://www.oecd.org/greengrowth/MATERIAL%20RESOURCES,%20PRODUCTIVITY%20AND%20THE%20ENVIRONMENT_Key%20findings.pdf)>. Last accessed 30 Oct 2018.
- PANG J, LIU X, ZHANG X, WU Y AND SUN R. 2013. Fabrication of Cellulose Film with Enhanced Mechanical Properties in Ionic Liquid 1-Allyl-3-methylimidazolium Chloride (AmimCl). *Materials* 6: 1270-1284.
- PAULY M AND KEEGSTRAK. 2008. Cell-wall carbohydrates and their modification as a resource for biofuels. *Plant J* 54: 559-568.
- RIPPEL MM AND GALEMBECK F. 2009. Nanostructures and adhesion in natural rubber: new era for a classic. *J Braz Chem Soc* 20: 1024-1030.
- RIPPEL MM, LEE LT, LEITE CAP AND GALEMBECK F. 2003. Skim and cream natural rubber particles: colloidal properties, coalescence and film formation. *J Colloid Interface Sci* 268: 330-340.
- RIPPEL MM, LINARES EM, BRAGANCA FC, VALADARES LF AND GALEMBECK F. 2012. Electrostatic interactions: an effective mechanism for rubber adhesion and blending. *J Adhes Sci Technol* 26: 767-782.
- RUGGERI G, COVOLAN VL, BERNABÒ M, LI LM, VALADARES LF, LEITE CAP AND GALEMBECK F. 2013. Metal nanostructures with magnetic and biodegradable properties for medical applications. *J Braz Chem Soc* 24: 191-200.
- SANTOS LP, BERNARDES JS AND GALEMBECK F. 2013. Corona-Treated polyethylene films are macroscopic charge bilayers. *Langmuir* 29: 892-901.
- SANTOS LP, CAMPO YAS, DA SILVA DS, BURGO TAL AND GALEMBECK F. 2018. Rubber surface change and static charging under periodic stress. *Colloids Interfaces* 2: 55.
- SANTOS LP, DA SILVA DS, BATISTA BC, MOREIRA KS, BURGO TAL AND GALEMBECK F. 2019. Mechanochemical transduction and hygroelectricity in periodically stretched rubber. *Polymer* 171: 173-179.
- SANTOS LP, DUCATI TRD, BALESTRIN LBS AND GALEMBECK F. 2011. Water with excess electric charge. *J Phys Chem C* 115: 11226-11232.
- SCHEIN LB. 2007. Recent progress and continuing puzzles in electrostatics. *Science* 316: 1572.
- STRUIK PC, AMADUCCI S, BULLARD MJ, STUTTERHEIM NC, VENTURI G AND CROMACK HTH. 2000. Agronomy of fiber hemp (*Cannabis sativa* L.) in Europe. *Ind Crops Prod* 11: 107-118.
- WANG MS AND PINNAVAIA TJ. 1994. Clay-polymer nanocomposites formed from acidic derivatives of montmorillonite and an epoxy resin. *Chem Mater* 6: 468-474.
- XUE G ET AL. 2017. Water-evaporation-induced electricity with nanostructured carbon materials. *Nat Nanotechnol* 12: 317.
- YIN J, LI X, YU J, ZHANG Z, ZHOU J AND GUO W. 2014 a. Generating electricity by moving a droplet of ionic liquid along graphene. *Nat Nanotechnol* 9: 378.
- YIN J, ZHANG Z, LI X, YU J, ZHOU J, CHEN Y AND GUO W. 2014 b. Waving potential in graphene. *Nat Commun* 5: 3582.
- ZHAO F, CHENG H, ZHANG Z, JIANG L AND QU L. 2015. Direct power generation from a graphene oxide film under moisture. *Adv. Mater* 27: 4351-4357.
- ZHAO F, LIANG Y, CHENG H, JIANG L AND QU L. 2016. Highly efficient moisture-enabled electricity generation from graphene. *Energy Environ Sci* 9: 912.