


# A Review: On Smart Materials Based on Some Polysaccharides; within the Contextual Bigger Data, Insiders, “Improvisation” and Said Artificial Intelligence Trends

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## Abstract

Smart Materials are along with Innovation attributes and Artificial Intelligence among the most used “buzz” words in all media. Central to their practical occurrence, many talents are to be gathered within new contextual data influxes. Has this, in the last 20 years, changed some of the essential fundamental dimensions and the required skills of the actors such as providers, users, insiders, etc.? This is a preliminary focus and prelude of this review. As an example, polysaccharide materials are the most abundant macromolecules present as an integral part of the natural system of our planet. They are renewable, biodegradable, carbon neutral with low environmental, health and safety risks and serve as structural materials in the cell walls of plants. Most of them are used, for many years, as engineering materials in many important industrial processes, such as *pulp and papermaking* and *manufacture of synthetic textile fibres*. They are also used in other domains such as *conversion into biofuels* and, more recently, in *the design of processes using polysaccharide nanoparticles*. The main properties of polysaccharides (*e.g. low density, thermal stability, chemical resistance, high mechanical strength...*), together with their biocompatibility, biodegradability, functionality, durability and uniformity, allow their use for manufacturing *smart materials such as blends and composites, electroactive polymers and hydrogels* which can be obtained 1) through direct utilization and/or 2) after *chemical or physical modifications* of the polysaccharides. This paper reviews recent works developed on polysaccharides, mainly on cellulose, hemicelluloses, chitin, chitosans, alginates, and their by-products (blends and composites), with the objectives of manufacturing *smart materials*. It is worth noting that, today, the fundamen-

tal understanding of the molecular level interactions that confer smartness to polysaccharides remains poor and one can predict that new experimental and theoretical tools will emerge to develop the necessary understanding of the structure-property-function relationships that will enable polysaccharide-smartness to be better understood and controlled, giving rise to the development of new and innovative applications such as nanotechnology, foods, cosmetics and medicine (*e.g. controlled drug release and regenerative medicine*) and so, opening up major commercial markets in the context of green chemistry.

## Keywords

Polysaccharides, Cellulose, Hemicelluloses, Chitosan, Alginate, Composites, Blends, Hydrogels, Smart Materials, Electro-Active Papers, Sensors, Actuators, Bigger Data, Innovation, Science in Education, Jazz, 4C, CRAC

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## 1. Introduction

### 1.1. Prelude

“The use of biomaterials for industrial applications has increased significantly. Carbon footprints rationalization and food vs. fuel dilemma have been debated and made considerable progress towards a wider acceptance at various levels. Open innovation contributes meaningfully with regards to: softer, milder temperature biochemical processing which includes preconditioning, low stress reactions, “just-as-needed” purifications, zero waste, fallow land exploitation rationalization, usable agri-waste, traceable land use, water consumption minoration vs. agronomical food-related practice, partial detachment from international seasonal trading of agricultural commodities...” [1].

In this context, our journey across the “rurban” zones is evolving. The sightseeing is a planet “responsible” fairytale that is coming closer to reality; locally produced, synergically codependent energies. Piezo (due for example to the unique crystalline structure and piezoelectric behavior of cellulose as described later in Section 2.2) and solar photovoltaic road paving, quietly growing CO<sub>2</sub> harvesting forests, prairie and golden fields ecofuel providers... are among the multi centennial castles, monuments and mills now wind, solar and hydraulic universal converters.

Along this fairy trail, alternative energies (**Figure 1**), as well as new energy usage patterns are promoting innovation in the field of energies’ production, transmission, transformation, distribution and local usages.

“The emotional intelligence has become a recognized essential part of a global ‘balance’, in this virtual-reality.” Let’s see what we said some about 20 years ago, on related skills [2].

“Can we foresee the profile of the next generation of scientists and engineers? The people behind innovation are essential to establish the foundations of the



**Figure 1.** Alternative Energy Illustration designed with author's private art: wind turbines and photovoltaic solar & piezo factories among golden canola fields with forests in the background and centrally, "inspirationally redesigned" old wind mill [1].

future successful businesses. In the chemical industry, the chemist, the physicist, the material scientist, the engineers are playing an important role in the creative process which is required to follow the pace of change. New organizational concepts have been proposed in order to schematize the industry adaptation to this 'new' global environment. We found that most of them require from the people a balance of skills which we propose to abbreviate with the acronym 4C, where the 4Cs represent: Connaissance, Creativity, Competence, Communication. 'Pursuing with', the bubble concept is one way of stimulating innovation. It is possible to combine enterprises or projects A, B, C in a way that the mentors, the promoters, the generators of the enterprise A have a chance to play another role in B or in C..."

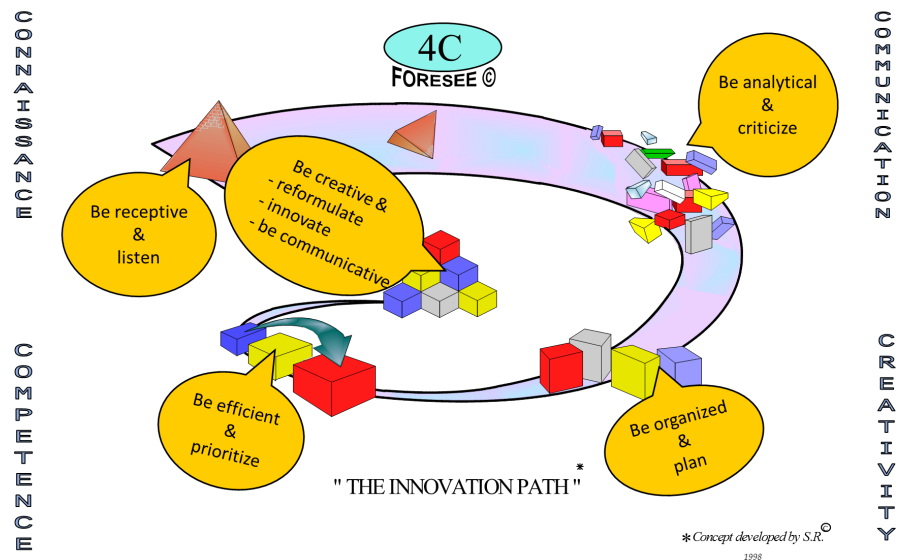
**Figure 2** below helps capture more about the above 4C innovative tetralogy.

The number of current innovation styles, from open to close, disruptive, col-laboratory®, from reverse to inclusive, nested and frugal, are more or less self-explanatory terminologies and further enlightenment can be found, e.g. in Lapray et al. [3] [4] in reviews on the matter, covering some of them [5].

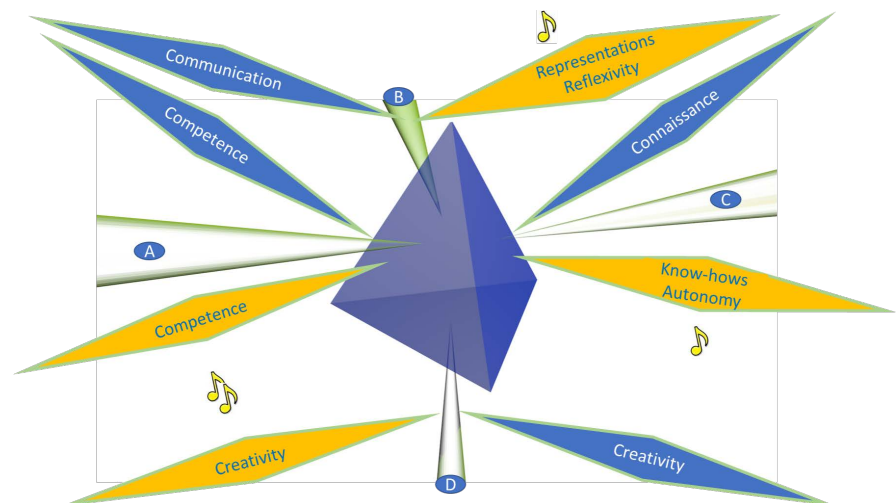
More literature on artistic creation and more expressly musical art is dedicated to the innovation traits of musical production, rather say improvisation; Jazz is of an established relevance.

**Figure 3** attempts to provide the 4C's corresponding Jazz terms and concepts therewith developed by the expert Charles Calamel [6], in the creation, integration, self learning and improvisation model that Jazz culture continues to develop spontaneously.

One may further cite Charles Calamel proposed acronym "CRAC" [6], with stands for Competent, Responsible, Autonomous, Creative... definitely a series



**Figure 2.** “Foresee, 4C, the innovation path” [2].



**Figure 3.** 4C\* concepts in blue diamonds of Figure 2 compared with the Jazz tetrahedral representation of [6], in yellow diamonds.

of traits that innovation in the bigger data surrounding cannot miss.

Charles Calamel, (<http://www.touteduc.fr/fr/archives>), says: “Jazz is a model in that it leads the individual towards a self-direction in learning, a construction of oneself. Due to the conditions of play, the respect and transgression of codes and formats, jazz reverses the traditional pedagogic guidance system to set up a model of autonomy: it is not a question of receiving knowledge but rather of ‘Go find it’”.

Fred Hersch’s song title “Songs without Words” may further highlight the improvisation nature and emotional intelligence of creativity and innovation.

Emotional intelligence which may become more central to diversity innovative approach, to capture developmental potential, may not fit within the trend of bigger data and artificial intelligence interaction; although the later may be a

source of improvisation.

In that domain D. Lapray and S. Rebouillat [3] presented some anticipatory aspects in a review: “‘Bigger Data’ Visualization to Visual Analytics: a path to Innovation. ‘Happening, definitely! Misleading, possibly?’ A review of some examples applicable to IP Discovery.” The authors pointed out that aesthetic may be privileged and can be misled. **Figure 4** below is a clear demonstration.

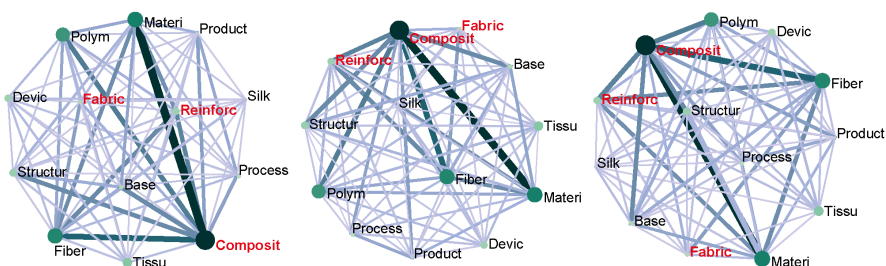
In **Figure 4**, out of [3], “the same analysis was applied to the title of 1000 patents in the field of natural polymers. The 13 top nodes are displayed using the Kamada-Kawai layout (well known force-directed graphs). The three panels represent the exact same data on which the layout was reinitialized three consecutive times. Note that only the nodes, edges size and color are maintained between these three representations. These are the only relevant information, the rest being purely aesthetical.”

No need to be a professional in the advertisement arena or a malicious developer, of fake impression carried by photography angle shot selections, to realize that the above triangles configurations of **Figure 4**, with bold solid heavy black sides, although linking the same matters, Composit (es)-Fiber (s)-Materi (als) & (Polym (ers)) may, take different dimension pending on the persons observing these figures, their mindset of the time.

There is indeed an improvising dimension that may arise from bigger data analysis and visualization. Such as the representation on the left side may give a sharp and central dimension of the three first matters of Composit (es)-Fiber (s)-Materi (als)-(Polym (ers)), the central representation may imply a massive bulk dimension of the four, and the representation on the right may elude to a side lateral importance of the three first. Analogically the jazz player may improvise some mimics and positionings that will attract attention on some elements of his production and interactions.

The improvisation dimension of innovation is certainly a way to liberate the creator away from core dimensions; those are prevalent and revealed in patent analysis wherein a language rarely changes as long as it is in the core corporate language and know hows. Laterals and boundaries are efficient add-ons in an inventive concept presentation.

In a nutshell, the parallel between innovation and art has been progressively



**Figure 4.** Aesthetical tricks do not necessary carry relevant information. The same analysis was applied to the title of 1000 patents in the field of natural polymers.

brought to the attention of the reader from a fairy tale landscape making innovative use of natural resources keeping “monuments in place”. Followed by the foresee, “4C”, dimension of the collaborative skills developed back in 1998 by Rebouillat. Extended to the Jazz science to education breadth and its self-learning integration value; associated with a high degree of intrinsic improvisation. Closing the loop with the bigger data and artificial intelligence emotional limitations and potential for misleadingness that may deserve a longer propos in a review to come.

Instinctive and improvisational innovations are to be added on the list of [4].

Additional references on the above fields with selected technology domains are useful [7]-[13].

## 1.2. More Centrally

The present paper follows up on three reviews [14] [15] [16] that we published on important researches related to the valorization of biomaterials, one of them [14] reached record downloads of 10,500 and 17,500 views, which supports the interest for scientific expert reviews in the context of bigger data; obviously big data consolidation can still improve to be even more useful to the “trained in the art”.

Smart or functional materials form a group of new and state of art materials now being developed that will have a significant influence on many of present-day technologies. Also called active materials, smart materials have the intrinsic and extrinsic capabilities, first, to respond to stimuli and environmental changes and to activate their functions according to these changes [17] [18]. The stimuli could originate internally or externally. Examples of external stimuli can be temperature, pressure, electric and magnetic fields, chemicals, light, humidity, hydrostatic pressure, nuclear radiation, pH and more. Smart material responds to those stimuli with changes in their internal structure and intrinsic properties such as shape, stiffness, viscosity, energy absorption capacity, damping or optical properties like transparency or opacity.

Most smart materials have reversible properties, reverting back to their original state after the stimulus is removed or changed. The cycle can then be repeated. Smart materials are also tailorable and tunable, which means they can be designed for specific, controlled property changes. To achieve a specific objective for a particular function or application, a new material has to satisfy specific qualifications related to technical and technological properties, economic criteria, raw material and production costs, supply expenses and availability, environmental characteristics and sustainable development criteria, implying reuse and recycling capacities.

*If the functions of sensing and actuation are added to this list, the new material is considered a smart material [19].* Since the 1990s, a lot of research efforts have been devoted to the development [20] [21] [22] and industrial application [23] [24] of smart materials. Examples of some well-known smart materials are piezoelectric polymers [25], piezoelectric ceramics [26], shape memory alloys



[27], electro-active polymers [28], covalent adaptive network polymers [22] and electrorheological and magneto rheological fluids [29].

**Many other materials with added functions:** have also been developed. They concern 1) *sensor materials* to detect certain signals, adjust sensitivity according to environmental changes, or restore degraded sensitivity, 2) *catalytic materials* to detect the progress of a reaction or distinguish the reaction of a product, 3) *textile materials* to detect a variety of signals from the human body and weather conditions so as to allow for greater comfort.

**Smart composite materials:** are also manufactured by combining two or more single smart materials in order to utilize synergistically the best properties of their individual constituents. Many of those composites are able to satisfy all of the above specific qualifications. Their advantages and adaptability to the design requirements mentioned above have led to a profusion of new products. There are two essential types of smart composite materials 1) *completely tailored man-made composite materials* which purpose is to improve or add strength or stiffness, 2) *amalgamation of single/composite materials with fibre/reinforced polymers (FRPs) such as the ones* used as reinforcement for concrete, steel or other construction materials. If the FRP is combined with fibre optic sensors, the resulting product will be an attractive and particularly cost effective smart composite.

A smart structure is a system that incorporates particular functions of sensing and actuation to perform smart actions in an ingenious way. It is composed of the following components:

- **Data Acquisition** (tactile sensing) which collects the required raw data needed for an appropriate sensing and monitoring of the structure.
- **Data Transmission** (sensory nerves) to forward the raw data to the local and/or central command and control units.
- **Command and Control Unit** (brain) which manages and controls the whole system by analyzing the data, reaching the appropriate conclusion, and determining the actions required.
- **Data Instructions** (motor nerves) which transmits the decisions and the associated instructions back to the structure.
- **Action Devices** (muscles) which take action by triggering the controlling devices/units.

**The Main areas of R&D involved in smart materials are:**

- **For sensors and actuators:** photo-sensitive materials, fibre optics, conductive polymers, thermally sensitive materials, shape memory materials, intelligent coating materials, chemical responsive materials, micro-capsules, micro- and nano-materials.
- **For signal transmission, processing and control:** neural networks and control systems, cognition theory and systems.
- **For integrated processes and products:** wearable electronics and photonics, adaptive and responsive structures, bio-mimics, tissue engineering, chemi-

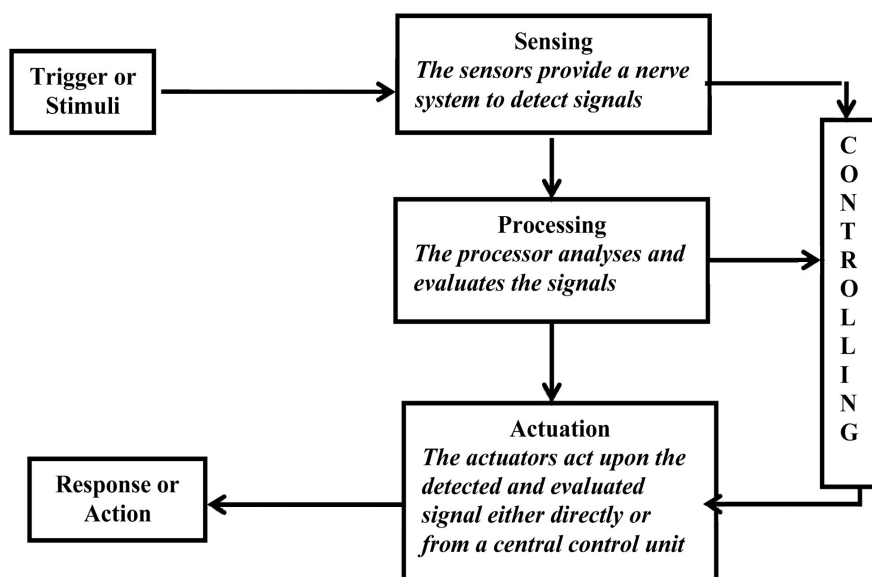
cal/drug releasing.

**Figure 5** summarizes how does a smart material works.

In the last ten years, the field of smart materials has received much attention as a result of the development of new electro-active polymer (EAP) materials that exhibit a large displacement response which changed the potential capability and paradigms of these materials. The main attractive characteristic of EAP is their operational similarity to biological muscles, particularly their resilience and ability to induce large actuation strains [30]. This characteristic is a valuable attribute that has enabled a myriad of potential applications, and it has evolved to offer functional similarity to biological muscles. EAP materials are able to offer a range of performance and characteristics that may not be reproduced by other technologies. Therefore, it is rather certain that EAP materials have a promising future for applications, such as biologically inspired actuators driving various mechanisms for manipulation and mobility including micro-robots, micro-flying objects, and animatronic devices.

Today, the focus is on specialty products engineered for specific end-uses and on creative ways to market these products and the current generation of smart materials has many new dynamic features that enable them to adapt to the environment and make them the materials of the future, mainly, as this will be further outlined in this paper, in the domain of renewable biomass-materials.

The present paper follows upon three reviews [14] [15] [16] that we published on important researches related to the valorization of polysaccharides with the objectives of reducing the fossil resource dependence and producing therefore environmentally-friendly new materials. Indeed, the great biodiversity of nature (*i.e.*, plants, animals, insects, enzymes, microbes, etc.) coupled with the enormous advances developed in biotechnological processes, makes it today possible, through adequate transformations of bio-sourced products, to elaborate high



**Figure 5.** General presentation of smart material actions.



value-added sustainable products endowed with physical, chemical and biological properties leading to particularly innovative applications.

This paper reviews recent works developed on those natural resources with the objectives of manufacturing *smart materials*. The biosourced products which will be considered are polysaccharides, including cellulose, hemicelluloses, chitin, chitosan, alginates, and their by-products (copolymers, blends and composites).

Polysaccharides are the most abundant materials that can be obtained from renewable and sustainable resources. They are biodegradable, carbon neutral with low environmental, health and safety risks and serve as structural material in the cell walls of plants. Some of them (e.g. cellulose and hemicelluloses) are used, for many years, as engineering material in many industrial processes such as *pulp and papermaking* and *manufacture of synthetic textile fibres* (e.g. organic and inorganic esters, alkyl, hydroxy alkyl and carboxyl alkyl ethers) which are important components in coatings, optical films, foodstuffs, pharmaceuticals, cosmetics, additives in building materials, etc. [14].

Moreover, owing to polysaccharides properties, functionality, durability and uniformity, their use continue today in other domains (e.g. *conversion into bio-fuels* such as ethanol as an alternative fuel source and, more recently, in *the design of processes using polysaccharide nanoparticles* for the generation of novel polysaccharide-based biomaterials and composites [14]).

On the other hand, it is noteworthy that chemical modifications of polysaccharides, “tailor-made” towards specific properties can also result in new materials, *including smart materials*. Indeed, owing to their unique and valuable functional properties, modified polysaccharides can confer smartness through somewhat unique mechanisms such as:

- *reversible, stimuli-responsive self-assembly* (gelation),
- *biospecific interactions with enzymes and lectins* (carbohydrate-binding proteins)
- *And interactions that confer nanoscale* (e.g. fibril-forming) and *hierarchical supramolecular assembly*.

Nevertheless, today, the fundamental understanding of the molecular level interactions that confer smartness to polysaccharides remains relatively poor and one can predict that new experimental and theoretical tools will emerge to develop the necessary understanding of the structure-property-function relationships that will enable polysaccharide-smartness to be better understood and controlled, giving rise to the development of new and innovative applications. This would allow making polysaccharides materials of choice in the very promising areas of nanotechnology, foods, cosmetics and medicine (e.g. controlled drug release [31] and regenerative medicine [32] [33]) and so, opening up major commercial markets in the context of green chemistry.

## 2. Cellulose-Based Smart Materials

Cellulose is the major constituent of the plants cell walls [34] [35]. It has many prominent properties such as high modulus and tensile strength, excellent me-

chanical strength, hydrophilicity, biocompatibility, biodegradability and relative thermal-stability [36] [37].

Cellulose is a linear syndiotactic homopolymer composed of *D*-anhydroglucopyranose units which are linked by  $\beta$ -(1 $\rightarrow$ 4)-glycosidic bonds (Figure 6).

The high content of hydroxyl groups along the skeleton of cellulose, is the basis of an extended system made of intra- and inter-molecular hydrogen bonds allowing the formation of highly ordered, three-dimensional crystal structures, making cellulose a semi-rigid polymer made of elementary microfibrils with two structure regions: the crystalline region and the amorphous region [38].

## 2.1. Cellulose Nanofibers and Nanoparticles

Despite its high hydroxyl groups content, cellulose has limited functionalities and, to our knowledge, there are very few reviews on “smart” materials based on cellulose unless hydrogels which were referred to [39] [40] [41]. Nevertheless, the physical structures of cellulose fibers, (*particularly cellulose nanofibers: CNFs*) and nanoparticles (*nanocelluloses: CNCs*), have opened up interesting opportunities to manufacture blends and composites used to make high valued products (Table 1).

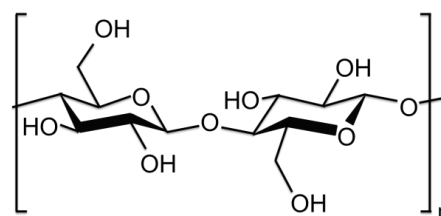


Figure 6. Chemical structure of cellulose.

Table 1. High value cellulose nanofiber and nanoparticle smart materials and corresponding potential applications.

Type of cellulose	Fabricated material	Potential application	Reference
Nanofiber	Optically Transparent Nanofiber Paper	Flexible circuits	[47]
Nanofiber	Transparent nanocomposites	Electronics device industry	[48]
Nanofiber	Transparent cellulose-based nanocomposites	Solar panels	[47]
Nanocellulose	Antibiotics/Carbonated hydroxyapatite coatings on titanium	Implant materials	[49]
Nanocellulose	Scaffold materials	Cartilage tissue engineering	[50]
Bacterial nanocellulose (BNC)	Scaffold materials	Tissue engineering	[51]
Bacterial nanocellulose (BNC),	BNC membranes	Biomedical applications (drug delivery, cytotoxicity against cancer cells)	[52]
Carboxymethylcellulose (CMC)	Spherical CMC nanoparticles	Biomedical applications	[53]

CNFs photo-responsive nature can act as adaptive fillers in soft polymer matrices. CNCs properties such as low density, thermal stability, chemical resistance, high mechanical strength, biocompatibility and biodegradability allowed to consider them as functional materials in actuation systems and sensors for detecting pH, organic vapors, ions and humidity [39] [42].

CNC based smart materials display intelligent behavior in response to environmental stimuli such as light, temperature, electrical input, pH, and magnetic force [43] [44] [45]. Moreover, owing to their high aspect ratio and mechanical properties, CNCs can also serve as renewable reinforcing agents in nanocomposites, as well as a handle for adding stimuli responsiveness [46].

On the other hand, the properties of cellulose enable cellulose to be applied to the vast fields of *smart electroactive polymers* and *hydrogels* which can be fabricated through *chemical modifications* or *physical incorporating/blending processes*.

Chemical modifications of cellulose are realized using homogeneous or heterogeneous processes.

*Homogeneous processes* are mainly carried out by dissolution of cellulose derivatives (e.g. carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), hydroxyethyl cellulose (HEC), and cellulose acetate (CA)) in suitable solvents (e.g. water or common organic solvents).

*Heterogeneous processes* are usually performed, after swelling in suitable solvents, on cellulose nanocrystals (CNCs), films/membranes, fibers, and cellulose particle suspensions.

In the processes of *physical incorporating/blending*, cellulose or cellulose derivatives act as matrices, fillers, or coatings/shells [15].

## 2.2. Cellulose Electroactive Paper

Recently, cellulose has been discovered as a smart material named *cellulose-based electroactive paper (EAPap)* [54] [55] [56] [57]. The electroactive behavior of EAPap is due to the unique crystalline structure and piezoelectric behavior of cellulose [58]. Indeed, cellulose II crystal is monoclinic and non-centrosymmetric in nature and thus it exhibits piezoelectric characteristics [54] [59] [60]. This piezoelectricity is able to induce large displacement output, low actuation voltage, and low electrical power consumption in the application of biomimetic sensors/actuators and electromechanical system.

Moreover, nanocellulose-based EAPap portrayed several superior characteristics such as ultra-lightweight, large bending deformation, low actuation voltage and low power consumption. These characteristics are very appealing for delicate biomimetic actuators and sensors, dynamic wings for flying articles, active sound-absorbing materials, adaptable speakers and smart shape control gadgets [56] [61] (**Table 2**).

In addition, preparation of nano-cellulose-based smart material via chemical modification and physical incorporation or blending in various forms can affect

**Table 2.** Potential applications of EAPap actuators.

EAPap characteristic/quality	Potential application	Reference
Low electrical power consumption	Microwave-driven actuators	[62]
Biocompatible and hydrophilic properties	Biosensors	[63] [64]
Microwave-driven innovations	Controlled actuators, Biomimetic robots	[65]
Reasonable quality	Vibration sensors	[66] [67]
Acoustic characteristics	Acoustic applications	[67]
Stacked and unimorph EAPap actuator	Haptic applications	[68]
Piezoelectric paper	EAPap speakers	[69] [70]
Ultra-lightweight and consumption of less energy $\geq$ response to electrical stimulation	Microscale robotic insects, Tiny flying objects, Wireless power supplies	[71]

responsiveness to pH, temperature, light, mechanical forces, electricity, and magnetic field. The presence of porosity and refractive index variation has made EAPap a feature with extraordinary light-scattering effect (used as a transparent paper) for use in integrated transparent sensors and 3D microfluidic application.

However, even if there are already many potential applications for cellulose EAPap, it must be noted that, today, several important challenges remain and should be considered, for example in terms of reliability, material robustness and force improvement.

### 2.3. Cellulose Hydrogels

Gels are three-dimensional natural or synthetic polymer networks that can swell and absorb large amounts of solvents without dissolving, provided that chemical or physical crosslinks exist among the macromolecular chains.

Hydrogels are, mainly, structures formed from biopolymers and/or polyelectrolytes, and contain large amounts of trapped water. They can be divided into chemical gels and physical gels. Chemical gels are formed by covalent bonds while physical gels are formed by molecular self-assembly through ionic or hydrogen bonds [72]. They have wide potential applications in the fields of food, biomaterials, agriculture, water purification, etc. (Table 3).

Responsive hydrogels can undergo a swelling transition in response to environmental stimuli, such as the changes in temperature, light, pH, etc. Because of this unique feature, responsive hydrogels have received an extensive attention in the fields of drug delivery [82], bioseparation [83], sensors, and optical transduction of chemical signals [83] [84]. For example, the drug release from responsive hydrogels can be remotely controlled by the local heating of magnetic nanoparticles [85]. The same concept has been transferred to the application in catalytic reaction, which is particularly attractive due to the unique tunable and responsive properties as well as the improvement of reactive properties [82] [83] [84]. Specifically, the swelling and deswelling of the hydrogel with temperature

**Table 3.** Examples of some classical hydrogels and corresponding applications.

Hydrogels	Application	Reference
Polymer blends of natural and/or synthetic polymers	Drug delivery	[73]
Supramolecular hydrogels	Drug delivery	[74]
Chitosan and Polyethylenimin	Tissue engineering	[75]
Natural polymers ( <i>collagene, hyaluronic acid alginate, chitosan</i> ) and synthetic polymers ( <i>PEO, PEG and corresponding block copolymers with poly (lactic acid)</i> )	Tissue engineering	[76]
Methacrylate/acrylic acid (AA) copolymers	Inverse opal pH sensors	[77]
Poly(acrylic acid)/poly(vinyl alcohol)	Piezoresistive pH sensors	[78]
GM3 material (terpolymer, based on high-purity glycerol methacrylate) from Contamac, UK (49.3% Water content)	contact lenses	[79]
Nanofilm-encapsulated silicone-hydrogel	contact lenses	[80]
Ni <sup>2+</sup> -poly (2-acetamidoacrylic acid) hydrogel	Purification of histidine-tagged green fluorescence proteins	[81]

change can control the loading/unloading of reactants in the hydrogel network, which, in turn, changes the reactivity.

There are plenty of methods for preparing hydrogels. The mixing of anionic and cationic polymers solutions is widely used for preparing reversible hydrogels. The final properties of the 3D network of physical hydrogel should depend on several factors such as the anionic/cationic charge ratio, the pH and the existence, or not, of stirring and the respective speed during the preparation, as well as several other parameters.

After these basic definitions and examples, the following paragraphs aim at highlighting some of the most recent developments in cellulose-based hydrogels materials, including *pure cellulose*, *cellulose composite* and *cellulose hybrid hydrogels*.

### 2.3.1. Pure Cellulose-Based Hydrogels

Two routes have been thoroughly developed for their preparation:

- **Direct preparation from native cellulose**

Due to its highly extended hydrogen bonded structure, *native cellulose* is very difficult to be dissolved in common solvents. Recently, new solvents have been developed to dissolve cellulose providing great opportunities for the preparation of cellulose hydrogels. The main solvents used for those hydrogel preparations are: LiCl/dimethylacetamide (DMAc), N-methylmorpholine-N-oxide (NMMO), Ionic liquids (ILs), Alkali/urea (or thiourea) aqueous systems.

- **Cellulose derivatives-based hydrogels**

Cellulose derivatives such as MC, HPC, HPMC and CMC have been used to fabricate cellulose-based hydrogels through physical and chemical cross-linking. Physical cross-linked gels are formed by ionic bondings, hydrogen bondings, or

associative polymer-polymer interactions. Chemical cross-linked hydrogels are prepared by cross-linking two or more polymer chains with a functionalized cross-linker.

With the development of cellulose derivatives, mainly cellulose ethers, some stimuli-responsive hydrogels have been developed leading to temperature sensitive hydrogels and pH sensitive hydrogels from MC, HPC, HPMC and CMC.

Cellulose-based hydrogels have many favorable properties such as hydrophilicity, biodegradability, biocompatibility, transparency, low cost, and non-toxicity. Therefore, cellulose-based hydrogels have many applications (**Table 4**).

### 2.3.2. Cellulose-Polymers Composite Hydrogels

Cellulose (or its derivatives) has been blended with both natural biodegradable polymers and synthetic polymers. Combining the different properties of cellulose and other polymers has given rise to novel hydrogel smart materials with specific applications. Various composite hydrogels were designed in wide size from macroscopic materials such as membranes, fibers, and beads to microscopic materials such as microgels, and nanogels (**Table 5**).

**Table 4.** Examples of cellulose-based hydrogels and their applications.

Cellulose-based hydrogel	Application	Reference
Si-HPMC	Tissue engineering	[86]
Na-CMC and cellulose	Controllable delivery systems	[87]
Cellulose acetate and phospholipids	Blood purification	[88]
Crosslinked (HEC) and (CMC)	Sensors and actuators	[89]
CMC/Acrylamide	Super absorbents for agriculture and horticulture	[90]
Poly[(N-tert-butylacrylamide)-co-acrylamide]/HPC	Swelling temperature-sensitive agents	[91]
Cellulose/chitin beads	Water purification	[92]
Regenerated cellulose beads modified with silane	Chromatographic supports	[93]

**Table 5.** Examples of cellulose-polymers composite hydrogels.

Cellulose-polymers composite hydrogels	Application	Reference
CMC/Chitosan	Cells immobilization	[94]
Starch/Cellulose-based polymers ( <i>sodium alginate, HPMC, NaCMC</i> )	Thermal behaviour	[95]
CMC/Starch	Textile sizing and flocculation agents	[96]
Na alginate/gelatin, and Na alginate/NaCMC blend beads	Release of carbaryl	[97]
Alginate/MC	pH-sensitive hydrogels	[98]
Hyaluronic acid/HEC; Hyaluronic acid/NaCMC	Use in prevention of postsurgical soft tissue adhesion	[99]



### 2.3.3. Cellulose Hybrid Hydrogels

In recent years, polymeric-inorganic hybrid materials have attracted increasing attention due to potential applications in electric, optical, magnetic, and biological fields. Introduction of inorganics into cellulose hydrogel networks is an effective way to develop materials with high functionality. Indeed, cellulose hydrogels have been used as matrices to incorporate inorganic nanoparticles for preparing cellulose-inorganic hybrid hydrogels [100] [101] [102] [103] [104]. It is worth noting that with the development of nanotechnology, this strategy is suitable for fabricating novel cellulose-based hydrogels with multifunctional properties. The smart behaviour of some cellulose derivatives (e.g., NaCMC, HPMC) in response to physiologically relevant variables (i.e., pH, ionic strength, temperature) makes the resulting hydrogels particularly appealing for *in vivo* applications.

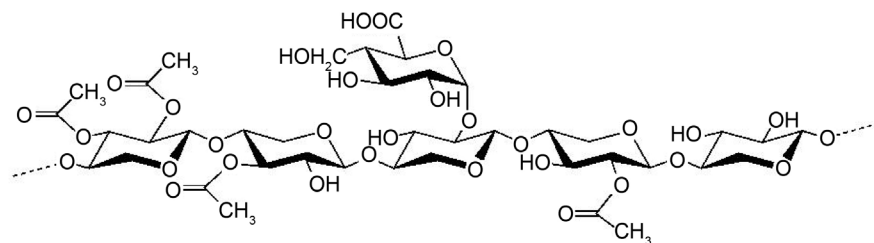
On the other hand, even if cellulose is known to be non-bioresorbable, it seems possible to functionalize cellulose-based hydrogels with bioactive and biodegradable extracellular matrix domains. This suggests that, *in the near future*, such hybrid hydrogels might constitute ideal platforms for the design of scaffolding biomaterials that could be used in the fields of tissue engineering and regenerative medicine.

## 3. Hemicelluloses-Based Smart Materials

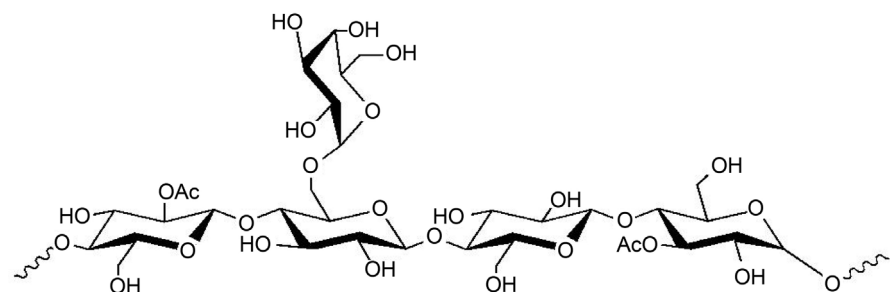
Hemicelluloses, as natural polysaccharides, are categorized as the second most abundant components of the plants after cellulose and constitute about 20% - 30% (w/w) of the total weight of the lignocellulosic biomass [34] [105]. Hemicelluloses have a random, amorphous structure. They are hetero-polymers with various chemical linkages between different monomer units such as pentoses (xylose, lyxose, arabinose, ribose...) and/or hexoses (glucose, fructose, galactose, mannose, rhamnose...). Different hemicellulose chemical compositions, structures and amounts are present in biomass. Hemicelluloses are polysaccharides that have beta-(1→4)-linked backbones with an equatorial configuration and include mainly xyloglucans, xylans, mannans, glucomannans, galactoglucomannan, O-acetyl-(4-O-methylglucurono)-xylan, O-acetyl-galactoglucomannan etc. **Figure 7** and **Figure 8** show, as examples, the chemical structure of two main hemicelluloses present in *hardwoods* and in *softwoods* respectively.

It is worth noting that the pendant hydroxyl groups of the polysaccharide backbone offer a number of possibilities for the chemical modification of hemicelluloses and for the preparation of materials with new profiles that can increase the utility of these biopolymers. Several methods are applied to extract hemicelluloses from biomass (**Table 6**).

Increasing attention has been concentrated on the development and application of hemicellulosic products because of their numerous inherent advantages, including non-toxicity, biocompatibility, biodegradability, and anti-cancer effect [111] [112].



**Figure 7.** Main hemicellulose of hardwoods: O-acetyl-(4-O-methylglucoron)-xylan.



**Figure 8.** Main hemicellulose of softwoods: O-acetyl-galactoglucomannan (AcGGM).

**Table 6.** Principal methods developed to separate hemicelluloses from the other constituents of biomass.

Raw material	Extraction method	Advantages/Disadvantages	Reference
Softwood	Single- and two-stage diluted-sulfuric acid pretreatment	Degraded dissolved sugars	[106]
Corn stalks	Autohydrolysis and alkaline extraction processes	Hemicellulose of high purity	[107]
Biomass	Hot water treatment and water/acetone extraction	Cleavage of hemicellulose acetate groups	[108]
Spruce	Microwave oven or steam treatment	Successful extraction of hemicellulosic oligosaccharides	[109]
Kraft pulp	Extraction with ionic liquid/cosolvent systems	Hemicellulose with high purity	[110]

Firstly, hemicelluloses have been used as fermentation feedstocks in production of ethanol, butanol, and xylitol [111] [113] and as raw materials in the preparation of food packaging films [114] [115].

Secondly, due to their large content of hydroxyl groups, hemicelluloses can be modified by both chemical reactions and physical interactions. The main chemical reactions are etherification, esterification and chemical crosslinking which allow preparing many materials such as *packing films*, *oxygen barrier* [114] and *water-resistant coatings* [115] [116].

Nevertheless, most of the materials made with hemicelluloses are smart hydrogels. Many kinds of hemicelluloses from different of plants such as birch

wood, aspen wood, spruce, bamboo, straw etc., have been used for the preparation of such materials. However, these hydrogels display weak thermostability, brittle properties and weak mechanical properties which restrict their application in material field. Nevertheless, this can be partially overcome through blending hemicelluloses with compatible products, as shown in **Table 7**.

#### 4. Chitin and Chitosan-Based Smart Materials

**Chitin** is the most widespread aminopolysaccharide and is the second natural polysaccharide after cellulose that can be obtained as a cheap renewable biopolymer from marine sources. As shown in **Figure 9**, chitin is a poly- $\beta$ -1,4-*N*-acetylglucosamine. It is found in arthropod exoskeletons, tendons, and the linings of their respiratory, excretory, and digestive systems and in the cell wall of fungi.

Due to its intermolecular hydrogen bonds, chitin is insoluble in water and in organic solvents, which, despite its enormous availability, limits its use. Nevertheless, several attempts have been reported to solve this problem owing to chemical modifications which allowed giving rise to derivatives such as chitosan or carboxymethyl chitin. Indeed, most of those derivatives are soluble in aqueous media and can be used as fibers, hydrogels, beads, sponges, and membranes [133].

The main applications of chitin and chitosan materials have been thoroughly reviewed by some researchers [133] [134].

Nevertheless, chitin-based smart materials or composites have also been created. Among those materials, shape memory materials containing polyurethanes molecules, are gaining more attention. Indeed, polyurethanes present good shape memory effect at room temperature. But polyurethanes cannot bear repeated changes in the shape memory, and retention will decrease by increasing the number of cycles of shape memory. Consequently, chitin-based polyurethane shape memory materials have been developed to overcome those problems [135] [136].

**Chitosan** is a linear polysaccharide composed by two kinds of randomly distributed  $\beta(1\rightarrow4)$ -linked structural units: 2-amino-2-deoxy-d-glucopyranose (*D*-glucosamine) and 2-acetamid-2-deoxy-d-glucopyranose (*N*-acetyl-*D*-glucosamine). It is obtained by extensive deacetylation of chitin.

Considering its low toxicity, biocompatibility, biodegradability and *indirect* abundance in nature, chitosan has attracted much research interest and has found potential applications in pharmaceutical, paper, textiles, cosmetic, and food industries, as well as in agriculture and medicine [137] [138].

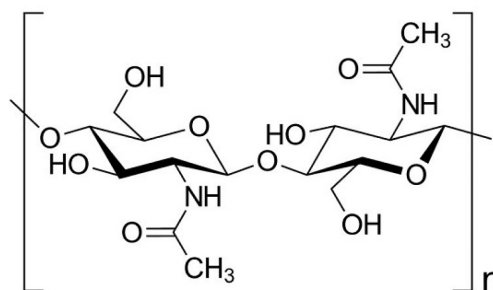
Moreover, chitosan is known for its absorption of exudes, anti-fungal, anti-microbial, anti-viral and wound-healing properties and is useful as a wound management aid to reduce scar tissue.

There is an increased interest in preparing chitosan and various macromolecules blends for mitigating undesirable properties and a rapidly growing list of

**Table 7.** Hemicellulose-based hydrogels: origine, properties and potential applications.

Raw material	Hemicellulose	Hydrogel synthesis	Hydrogel properties and potential applications	Reference
Bambo	Xylan	Grafting with AA + Crosslinking	High swelling, sensitive to pH	[117]
Spruce pulp	AcGGM	Grafting with MA + Crosslinking	Drug release	[118]
Crude spruce hydrolysate	AcGGM	Free radical graft copolymerization and cross-linking of poly(amidoamine)/AcGGM	High absorption capacity for heavy metal ions	[119]
Dextran	AcGGM	<i>In situ</i> Michael-type addition using vinyl sulfone	Thermosensitive injectable hydrogels	[120]
Birch wood	Xylan	Introduction of allyl groups + reaction with thioacetic acid, + free thiol-thiol oxidative coupling	3D hydrogel scaffolds and cross-linked foams	[121]
Crude spruce hydrolysate	AcGGM	Direct incorporation of hemicellulose into a semi-IPN matrix obtained by crosslinking polymerization of MA-CMC with AA	Appreciable mechanical performance and high swelling ratio	[122]
Crude spruce hydrolysate	AcGGM	Synthesis of Hemicellulose full IPN by free-radical polymerization and a thiol-ene click reaction	Fast swelling rates and highly porous structure	[123]
Spruce TMP	AcGGM	Functionalization of carboxylated AcGGM with GMA and covalent immobilization of conductive AT onto GMA.	Electrically conductive hydrogels with high and controllable swelling	[124]
Spruce TMP	AcGGM	Cross-linking of AcGGM in a One-pot reaction with E in the presence of AP	Conductivity, swelling and mechanical properties for biomedical applications	[125]
Spruce TMP	AcGGM	<i>In situ</i> fabrication of microgels by chemical cross-linking during spray drying	Conductivity, mechanical properties, biomedical applications	[126]
Eucalyptus (Acid acetic pulping)	Xylan and glucomannan	Grafting maleic MA to hemicellulose and UV photo-crosslinking with NIPAAm	Temperature responsive	[127]
Birchwood	Xylan with glucuronic acid functionalities	Network formation by complexation between glucuronic acid of xylan and amino groups of chitosan	Porous structure, sensitive to pH.	[128]
Bamboo	Xylan with glucuronic acid functionalities	Use of Freeze-thaw process to obtain reinforced hybrid hydrogel of Hemicelluloses/PVA/Chitin Nanowhiskers	Improved mechanical and thermal properties (applications in tissue engineering)	[129] [130]
Beech	Xylan	Mixing of Xylan, kappa-carrageenan and oat spelt	Improvement of gelling and melting temperatures of Kappa-Carrageenan hydrogels	[131]
Pinewood, Switchgras and Coastal bermuda grass	Various hemicelluloses	Grafting with DTPA and cross-linking with chitosan	Biosorbent for Water Desalination and Heavy Metal Removal	[132]

**Abbreviations:** AA: Acrylic acid; MA: Maleic anhydride; AcGGM: *O* acetyl-galactoglucomanan; AP: Aniline pentamer; AT: Aniline tetramer; DTPA: Di-ethylene triamine pentacetic acid; E: Epichlorohydrine; GMA: Glycidyl methacrylate; IPN: interpenetrating polymer network; MA-CMC: Methacrylated Carboxymethylcellulose; NIPAAm: N-isopropylacrylamide; TMP: Thermo-mechanical pulping.



**Figure 9.** Chemical structure of chitin.

biomaterial applications. Examples are chitosan blends with cellulose, cellulose acetate, xanthan, gelatin, silk, polyamide, poly (acrylic acid), poly (vinyl alcohol), polyamide, gellan, collagen, glycine, poly (N-vinyl pyrrolidone).

On the other hand, chitosan structure can be modified through its amino group and the hydroxyl groups. These chemical modifications improve chitosan mechanical properties and solubility or bring new functional properties and promising applications. In this sense, a wide variety of chitosan thermosensitive materials has been generated, like nanostructures, scaffolds, membranes, cryogels and paramagnetic beads, to cite some of them [139].

Moreover, because of the polyelectrolyte nature of chitosan, several chitosan-based materials are also sensitive to changes of pH, ionic strength etc, and hence have an advanced interest due to specific technological potential applications as sensors, actuators, controllable membrane for separations and modulators of drugs delivery for use in medicine, biotechnology and other fields.

On the other hand, chitosan can also be induced to undergo reversible sol-gel transition forming *hydrogels* or films by changing chemical or pH gradients [140]. These materials offer a versatile platform and customizable functionality to interface and interact with labile biologics (biomolecules, proteins, enzymes, cells) in aqueous environment. They are widely used in composite film coating, tissue engineering and drug delivery for creating functional materials with desired physical, chemical properties and even biological functionalities (Table 8).

## 5. Alginate-Based Smart Materials

Alginate is a natural polysaccharide that has two main sources: bacteria and seaweed (brown algae). It is composed of mannuronic acid residues (M-blocks), guluronic acid residues (G-blocks) and alternating M and G residues (MG-blocks). This chemical composition shows that alginate is a polymer with a polyelectrolyte nature.

Alginate, exhibits excellent biocompatibility and biodegradability and has many different industrial applications linked to 1) its ability to absorb water 2) its gelling, viscosifying and stabilizing properties. Alginate is used in several industrial fields such as textiles, food, pharmaceuticals, cosmetics, waste water treatment and paper industry together with biomedical supplies.

Alginate is readily processable for applicable three-dimensional scaffolding

**Table 8.** Chitosan-based stimuli-responsive hydrogels: functionalization, synthesis, properties and applications.

Functionalization	Synthesis	Characteristic	Application	Reference
Cross-linking	With glutaraldehyde and sulfosuccinic acid	Protonic conductivity	Membranes for Fuel cells	[141]
Cross-linking	With di- and tri-carboxylic acids	nano-hydrogels	Drug release	[142] [143]
Graft copolymerization	Copolymerization of metacrylic acid with chitosan in the presence of APS	Improved water solubility	Antibacterial activity	[144]
Graft copolymerization	Copolymerization of maleic acid with (CMCTS) and (HPCTS)	Improved scavenging ability	Antioxidant activity	[145]
Graft copolymerization	Copolymerization of aniline with chitosan	Protonic conductivity	Conductive films and fibers	[146]
Carboxymethylation	Monochloroacetic acid	Solubility depends on pH	Antimicrobial activity, affinity with metal ions, Controlled release of drugs	[147]
Phosphorylation	Heating chitosan with orthophosphoric acid in DMF or with phosphorous pentoxide in methanesulphonic acid	Solubility in water under neutral conditions	Bactericidal, biocompatible, bioabsorbable, osteoinductive and metal chelating properties	[148]
Esterification	Reaction of acyl chlorides with chitosan ( <i>synthesis of N,O-Acyl chitosan derivatives</i> )	Reaction mainly occurred on the OH group and not on the NH <sub>2</sub> group	Highly improved antifungal activity	[149]
Etherification	Synthesis of N-phthaloyl chitosan. (MPEG) iodide	Soluble in water and aqueous solutions of wide pH range	Extremely low reduced viscosity	[150]
Self-rearrangement of polymer networks	chitosan/chondroitin sulfate formed by polyelectrolyte complexation	Crystallinity, higher thermal stability, porosity, and water uptake capacity	pH sensitive material which can be tailored to several specific applications	[151] [152]
BC/Ch composite preparation	Immersing wet BC pellicle in chitosan solution followed by freeze-drying	porous network structure and large aspect surface	Wound dressing or tissue-engineering scaffolds	[153]
Reversible blending	Mixing of chitosan/PHEMA	Swollen structure	Electrically sensitive behavior	[154]
Electrospun chitosan fibers	Electro-wet-spinning ( <i>submicron scale</i> )	Fast and reversible electroactuation	Application in artificial muscles	[155]
Blending of chitosan and Cellulose	Preparation of chitosan/cellulose blend beads	Blend beads with rough and folded surface morphology	Odor treatment and metal ions adsorption	[156]
	Casting of a TFA solution of chitosan and cellulose	Large bending displacement under low voltage	Blended dry and durable actuator	[157]
Blending of chitosan with PCL	Chitosan and PCL homogeneously dissolved in acetic acid/water and processed into uniform membranes	Blends with chemical bonds	biological and anti-bacterial properties	[158]
Preparation of poly(AA-co AM)/(O-CMC) interpenetrating polymer network	Synthesis of a semi-IPN by AA and AM copolymerization in the presence of O-CMC then synthesis of a full-IPN through cross-linking	Superporous hydrogel	Mucosal drug delivery system, especially for peroral delivery of peptide and protein drugs	[159]

**Abbreviations:** APS: Ammonium persulfate; BC: Bacterial cellulose; Ch: Chitosan; CMCTS: chitosan-carboxymethyl chitosan; DMF: N,N-dimethylformamide; HPCTS: hydroxypropyl chitosan; IPN: Interpenetrated Network; MPEG: Poly (ethylene glycol) monomethyl ether; NMMO: N-Methylmorpholine-N-oxide; PCL: poly ( $\epsilon$ -caprolactone); PHEMA: poly (hydroxyethyl methacrylate); TFA: Trifluoroacetic acid; AA: Acrylic acid; AM: Acrylamid; OCMC: O-carboxymethyl chitosan.



materials such as hydrogels, microspheres, microcapsules, sponges, foams and fibers that provide responses to internal/external stimuli.

Alginate-based biomaterials can be utilized as drug delivery systems and cell carriers for tissue engineering, control release, matrix for living cells, immobilization of microorganisms [160]. Recently, there is a growing research interest in the applications and development of novel sustainable hydrogel materials for waste water treatment [161], and as an alternative to smart electrolytic gels for rapid electroencephalography monitoring and easy cleaning procedures [162].

As cellulose, hemicelluloses and chitosan, alginate can be easily modified via chemical reactions and physical interactions, to obtain derivatives with various structures, properties, functions and applications. Various techniques such as 1) oxidation, sulfation, copolymerization and coupling of cyclodextrin units, 2) esterification, use of Ugi reaction and amidation, are employed for chemical modification of the hydroxyl groups and carboxyl groups of alginate, respectively [163].

Moreover, owing to its structure and properties, alginate can be achieved through 1) combination with other biomaterials, 2) immobilization of specific ligands such as peptide and sugar molecules, and 3) physical or chemical crosslinking (Table 9).

## 6. Conclusion and Perspectives

This paper reviews the recent progress developed to produce and characterize smart materials using the most abundant products of the biomass, i.e. polysaccharides which include cellulose, hemicelluloses, chitin, chitosan, and alginates and their by-products. Owing to their low density, thermal stability, chemical resistance, high mechanical strength, biocompatibility, biodegradability, functionality, durability and uniformity, those products are materials of choice for the preparation of smart products that can be used in the very promising areas of nanotechnology, foods, cosmetics and medicine (mainly controlled drug release and regenerative medicine) and so, opening up major commercial markets in the context of green chemistry.

The resulting smart materials are generally prepared through direct utilization and/or after chemical or physical modifications of the polysaccharides.

Cellulose and its different physical structures (*particularly cellulose nanofibers and nanoparticles*, i.e. *nanocelluloses*) can be transformed into high value-added *smart blends and composites* with applications in important industrial areas such as those of flexible circuits, solar panels, implant materials, cartilage tissue engineering, drug delivery, etc.

Moreover, owing to its unique crystalline structure and its piezoelectric behaviour, cellulose has also the characteristics of an *electroactive polymer*, with potential applications in biomimetic sensors/actuators and electromechanical biosystems.

Together with hemicelluloses, chitosans and alginates, cellulose can give rise

**Table 9.** Main smart alginate derivatives obtained by functionalization processes.

Functionalization	Experimental strategy	Material characteristics	Application	Reference
<i>Oxidation</i>	Controlled reactions on-OH groups of C-2 and C-3 with sodium periodate	Cleavage of carbon-carbon bond of cis-diol groups and formation of acetal groups	Powerful material for tissue engineering, Drug-controlled delivery systems	[164] [165]
<i>Sulfation</i>	Reaction of sodium alginate with a sulfating agent (N (SO <sub>3</sub> Na) <sub>3</sub> )	Sodium alginate sulfate with DS of 1.87	Anticoagulant activity	[166]
	Reaction with ClSO <sub>3</sub> H in formamide	Alginate sulfate and its quaterized derivatives	Anticoagulant activity and potential application as anti-HIV	[167]
<i>Reductive-amination of oxidized alginate</i>	Synthesis of APSs with a linear alkyl group (C8, C12, C16)	Low interfacial tension value	Surfactant activity and adsorption of heavy metal	[168]
	Syntheseis of (HM-alginate) via reaction of sodium alginate with dodecyl glycidyl ether	Zeta-potential of HM-alginate higher than that of sodium alginate. Very low viscosity	Ecology-safe material to encapsulate lipophilic substances	[169]
<i>Copolymerization</i>	Synthesis of a copolymer of sodium acrylate with sodium alginate	Water absorbency of the hydrogel $\geq$ 85 times its own mass	Superabsorbent resistant to salinesolution	[170]
	Microwave-initiated synthesis of SA-g-PAM	M <sub>w</sub> and Intrinsic viscosity greater than that of SAG.	Polymeric flocculant	[171]
	Graft copolymerization of VSA onto alginate in the presence of (PDP)/thiourea	Thermally more stable than alginate	Metal ion sorption, Flocculant, Resistant to biodegradability	[172]
<i>Esterification</i>	Synthesis of derivatives of sodium alginate, by chemical binding of long alkyl chains onto alginate backbone via ester functions	Increasing of the hydrophobic nature of native alginate	Protein carrier with High encapsulation yields and important release properties	[173]
	Esterification of alginate by butanol	Very stable material with gelling and non-toxic properties	Encapsulation of both hydrophilic and hydrophobic molecules	[174]
<i>Ugi reaction</i>	Sodium alginate dissolved in water + formaldehyde, octylamine and cyclohexyl isocyanide	Self-aggregated micelles with high thermal stability and good amphiphilic functionality	High potential in pharmacology and tissue engineering	[175]
<i>Crosslinking</i> Preparation of poly (AA-co AM)/(SA) interpenetrating polymer network	1) Synthesis of a semi-IPN by copolymerization 2) Crosslinking with Bis	IPN with a superporous structure, good mechanical properties, pH sensitivity	Potential candidate in the field of Drug delivery system	[176]
Preparation of poly (AA)/(SA) interpenetrating polymer network	1) Synthesis of SA beads 2) Synthesis of hydrogels hybrids by polymerization of AA and crosslinking	Strong and elastic superporous hydrogel, high network density, good mechanical properties	Various pharmaceutical, biomedical and industrial applications	[177]

**Abbreviations:** Bis: *N,N*-methylenebisacrylamide; DS: degree of substitution; APSs: alginate-derived polymeric surfactants; HM-alginate: hydrophobic modified alginate; M<sub>w</sub>: Weight average molecular weight; SA: sodium alginate; SA-g-PAM: sodium alginate grafted polyacrylamide; VSA: vinyl sulfonic acid; PDP: potassium peroxydiphosphate.

to several types of stimuli-responsive *hydrogels* (e.g. temperature responsive, pH-sensitive, protonic conductor, etc.) able to be used in numerous applications such as tissue engineering, absorption of heavy metal ions, odor treatments, liquid and gas absorption, polymeric flocculation, energy storage etc.

All those investigations clearly show the great potential of polysaccharides for the production of cheap, disposable and environmentally friendly devices. However, as shown in different sections of the present review, still more comprehensive studies are required to broaden the fundamental understanding of molecular level interactions that confer smartness to polysaccharides. This would allow manufacturing new materials with new applications, able to bring more technological impacts to markets.

Regarding innovation and bigger data: in a nutshell, the parallel between innovation and art has been progressively brought to the attention of the reader from a fairy tale landscape making innovative use of natural resources keeping “monuments in place”. Followed by the foreseeing, “4C”, dimension of the collaborative skills developed back in 1998 by Rebouillat [2], now extended to the Jazz science to education breadth [6] and its self-learning integration value, associated with a high degree of intrinsic improvisation serving innovation, the loop on the innovation subject matter, in the present work, is closed with the bigger data and artificial intelligence, and, its emotional intelligence limitations and potential for misleadingness that may deserve a longer propos in a review to come.

Finally, Smart Materials are along with Innovation attributes and Artificial Intelligence among the most used “buzz” words in all media. Central to their practical occurrence, many talents are to be gathered within new contextual data influxes. Has this, in the last 20 years, changed some of the essential fundamental dimensions and the required skills of the actors such as providers, users, insiders, etc.? This is a preliminary focus and prelude of this review which shall not be ignored.

The era of smart materials may deserve an artistic warning-illustration to complete the picture of its tremendous potential with some level of disruptive improvisation in **Figure 10**.



**Figure 10.** “The hand-footed, to travel a New Universe.” Private art to illustrate smart technologies approaches on smart gloves and augmented natural abilities, © Letibarlou, 2018.

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## Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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