Biocoatings and additives as promising candidates for ultralow friction systems

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ABSTRACT
The achievement of frictionless systems, known as superlubricity, has become of great importance concerning energy saving and emission reduction. In parallel, the drive toward sustainability and environmental aspects has led to intense advances in the research and development of biobased materials. From the standpoint of Green Chemistry principles, this review presents a critical overview of the latest findings and future perspectives on the application of biobased materials aiming at superlubricant pursuits. The progress in the use of biomacromolecules, such as chitosan, cellulose, and lignin, as additives to lubricants or coating materials, are addressed, as well as the advances on sustainable coatings based on diamond-like carbon (DLC). Deeper investigations on the development of non-hazardous processes dedicated to the tribological properties of DLC, such as electrochemical synthesis using environment-friendly solvents to generate molecular precursors, widen the perspectives to achieve sustainable materials. Besides, the exploration of the tribochemical interactions between the DLC surface and lubricants containing biobased materials arises as a promising strategy to achieve green superlubricity as a viable and scalable process, through different pathways: by hydrogen bonds between lubricant and additives, via surface passivation of the functional groups present in these biomacromolecules or by biomimicking natural joints.

1. Introduction
Sustainable processes are a priority demand of industry and can be achieved through the circular economy model, which requires the inclusion of clean technology approaches to minimize the impact of pollution while reducing energy consumption and carbon-neutral emissions (1). Material production must be sustainable from the earliest stages, i.e. from the design, which can be only achieved by adhering to the principles of green chemistry. An efficient way to determine how environment-friendly a chemical process can be is its assessment according to the principles of Green Chemistry developed by Anastas and Warner (2).
The Green Chemistry principles are guidelines to the ‘design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances’ (3) aiming to maximize the efficiency and sustainability in each phase of a chemical’s working life. The concept and principles have been extended to other fields ever since, such as engineering and tribology (4, 5). In the case of the latter, researchers have shown an increased interest in the development of biobased and sustainable coatings and additives, as alternatives to minimize environmental impacts while enhancing the final attributes.

Coating techniques are commonly used to modify the surface properties by creating a thin film on the desired substrate, aiming at the improvement or addition of properties for preserving and/or increasing usability and working life. Unfortunately, one single material does not normally fit entirely all desired functionalities, therefore, synthetic polymers combined with pigments and additives arise as a low cost and specific alternative. Surface coatings have been standard practice for many applications across industries, including automotive, energy, chemistry, and agriculture. Functional coatings are aimed for several purposes, e.g. corrosion and wear resistance, anti-UV, antimicrobial bearing, and anti-fouling; nevertheless, coating processes aiming at lubrication applications have been gained a prominent position. A lubricant is defined as a component capable to reduce friction, generation of heat, and wear between sliding surfaces. Several investigations have proved that the applied operating conditions significantly influence the friction between two surfaces, accounting for a contribution of app. 20% and is one of the major driving forces for the annual global CO2 emission. This emphasizes the importance of efficient lubrication to reduce energy losses up to 40% related to wear. Furthermore, lubrication provides additional required features, such as cooling of the system, while reducing the influence of possible inner contamination (6, 7). In this light, one has to take into account the set of parameters including lubricant viscosity, base oil type, surface roughness, and lubricant temperature related to lubricant regimen, coefficient of friction (COF), and wear. The planning of such conditions should enable researchers to design sustainable processes with predicted friction behavior in a real gear application under decreased emissions level, following the Green chemistry guidelines (8).

Systems with efficient lubrication could save up to 8.7% of the annual global energy consumption, where up to 30% stem from the transportation sector, which is dominated by cars using internal combustion engines. The improvement of current lubrication technologies could reduce the global CO2 emissions in the short term up to 1460 Mt, corresponding to app. 4,50,000 million Euros (9). Although the transition from fossil fuels to green alternatives could reduce the losses originating from friction in energy production up to 60%, vehicles empowered entirely by electricity would still contribute to friction-related energy losses (10). Therefore, to design sustainable lubrication solutions, the whole material’s life cycle must be considered to be environment-friendly and economically feasible.

At first glance, it seems evident that the highest goal should be the achievement of more efficient lubrication and stable operation within the long operation period. Nevertheless, the saved amount of CO2 comes at the cost of creating simultaneously waste in the form of lubricant degradation products, such as volatile organic compounds (VOC), debris, and other particles (11–14). Traditionally, the lubricant industry makes extensive use of oil-based lubricants, mainly originated from mineral (petroleum-based refinery products) and synthetic oils, like polyalphaolefins and polyalkylene glycols, that commonly contain additives or contaminants.

Organophosphates (OP) are a well-known class of additives used in turbine oil lubricants. Despite the efficiency that organophosphorus compounds add to the lubrication systems, they represent a serious problem due to the generation of phosphorus emission and the toxicity of the degradation products (15). We have shown that in the case of lubricants containing functional additives, e.g. zinc dithiophosphate (ZDDP), detergents, dispersants, and antioxidants for engine and gear lubricants, the generated soot matrix particles contain 3–5 nm ZnO,P,S nanoparticles (16). Part of the issue caused by the use of OPs can be managed by substitution with thiazoles without efficiency losses. Another friction modifier widely applied in engine lubricants is the molybdenum di-thiocarbamate (Mo-DTC), which produces a tribofilm with MoS2 sheets that lead to low friction (17). However, this organic lubricant additive is a source of harmful emissions due to its toxicity (18).

In this context, the industry faces the need to keep sustainability standards, aiming to minimize the dependence of mineral oils while reducing waste generation and CO2 emissions through renewable sources and new synthesis paths. Water-based lubricants and vegetable oils arise as potential alternatives to mineral oil-based ones; nevertheless, under specific conditions, it is difficult to achieve the required efficiency due to the lack of oxidation stability or low viscosity. An alternative to overcome this drawback is centered on the use of biobased or sustainable coatings, which has attracted
attention since the Green Chemistry principles were released. Among the different sources of biobased materials, lignin, cellulose, and chitosan are the three most naturally available and biodegradable macromolecules originated from biomass. These materials are presented as sources to produces polymeric/molecules originated from biomass. These materials are presented as sources to produce polymeric/macromolecular films that can be used as coatings and/or lubricants.

The generation of polymeric thin films as coatings can occur in two ways, either by tethering the polymer chains physically, i.e. by physisorption, or chemically (chemisorption) (Figure 1). These methods differ on the strength of the interactions between the substrate and the polymer chains. Polymeric coatings generated by physisorbed thin films are mostly governed by weak electrostatic interactions, which include London forces, dipole–dipole, and van der Waals. Therefore, given the weak nature of these interactions, coatings based on polymer physisorption are more likely to be broken, suffering from major drawbacks, such as displacement, desorption, dewetting, and delamination (19). Conversely, chemisorption occurs via the covalent immobilization of polymers onto the substrate surface, which can be performed via ‘grafting to’ or ‘grafting from’ approaches. Since the sharing/transfer of electrons between the polymer and the surface is typically two orders of magnitude stronger compared to physisorbed polymers, this method leads to more robust coatings.

In the ‘grafting to’ approach, the polymer must present at least one reactive site to be adsorbed, via the formation of covalent bonds with active centers on the substrate surface (19). ‘Grafting from’ approaches requires the surface pre-treatment to generate immobilized initiators, which will be responsible for the polymerization directly from the surface, which can lead to high grafting density polymers coatings (19). Electrostatic interactions based on hydrogen bonds usually present a strength that relies upon between the ones found for physisorbed and chemisorbed species (20). Furthermore, the polymer chains can be crosslinked by using specific agents, comprising their intra and/or intermolecular association through covalent bonds. Crosslinking leads to 3D network structures, either by physical or chemical reactions, which generate matrices in coatings, adhesives, and laminates (20).

Crosslinking the biomacromolecules is a straightforward way to modulate properties while widening their applications. Del Olmo et al. reported on the preparation of antibacterial chitosan coatings onto poly (l-lactic acid) films via both electrostatic and covalent approaches (21). In their study, the stability of the coated films improved in both enzymatic and non-enzymatic medium when the chitosan chains were crosslinked using genipin, which is a natural molecule extracted from gardenia fruits (21). Bongaerts et al. demonstrated the formation of a highly lubricating coating on polydimethylsiloxane surfaces from the crosslinking of chitosan and hyaluronic chains multilayers. The authors reported extraordinarily low friction coefficients, which were comparable to those obtained using human whole saliva physically adsorbed onto PDMS surfaces (22).

Herein, we present a critical review on the latest advances and future perspectives on the application of biobased materials aiming at superlubricant pursuits, from the standpoint of Green Chemistry principles. Superlubricity applications are centered on carbon-based coatings, like diamond-like carbon (DLC), graphene, and related materials due to their compatibility.

2. Sustainable coatings and superlubricity
2.1. Superlubricity

Achieving low friction without the generation of waste would be the desired solution to minimize CO₂ emission; however, this would demand lubricant-free tribological systems (23). Historically, the motivation to minimize friction between two surfaces has led researchers to analyze the phenomena on a molecular scale. The earliest prediction was presented in 1983 when Peyrard and Aubry (24) studied the effects of incommensurability on a mathematical model of a motion system. Almost a decade later, in 1990, Hirano (25) and Sokoloff (26) evaluated a non-dissipation sliding model between incommensurate structures under specific conditions, leading to a frictionless system, nominated superlubricity (27). Figure 2 illustrates a schematic model for nanoscale superlubricity on the example of two planes in different configurations.

This physical state is mainly characterized by the ultra-low coefficient of friction (COF), which is defined by the ratio between the resistive friction force and perpendicular normal force, being useful to quantify the friction between two surfaces. The threshold currently used to characterize a superlubric regime is (COF) < 0.01; however, this parameter itself does not entirely describe the state. A variation in the lubrication regime (elastohydrodynamic to hydrodynamic) or drop of pressure due to wear can result in a low COF. Thus, to characterize superlubricity, besides an ultra-low COF, minimal wear at considerable contact pressure is necessary (28).

Experimental superlubricity was firstly observed by Martin et al. (29) for lamellar material with a thin film of MoS₂ on a steel substrate. The authors obtained a COF lower than 0.01 under a high vacuum (29);
however, due to measuring precision limitations of the equipment, the COF could not be calculated and the regimen was only further confirmed by computer model simulation [30,31]. With a similar approach using atomic force microscopy (AFM), Dienwebel could prove Hirano’s theory with two graphitic surfaces (32). Since then, researchers are aiming to make this regime becoming feasible for direct application in mechanical systems on engineering scale and under ambient conditions (33–36). In 2008, Bergström et al. demonstrated that two surfaces experiencing repulsive surface forces, which deviate within small separation, can achieve slide with a very low COF of 0.0003 (37). Salmeron et al. observed the superlubricity of graphene nanoflakes on a graphene substrate, which originates from the transition between a commensurate to an incommensurate registry (38).

For strongly hydrogenated DLC exhibiting very high H:C ratios of app. 10, extremely low COF values of 0.003 have been demonstrated under inert atmosphere. When being exposed to air, COF increased to 0.6, which points to the complexity of the materials’ composition to achieve the superlubricating behavior (39). The instability of the superlubricating state of a-C:H is related to the disabling of the antifriction capacity by gaseous oxygen molecules; the latter inducing a surface dehydrogenation of the DLC coatings (40). An approach to prevent the surface oxidation of a-C:H thin films is based on doping with silicon, which is more reactive with moisture atmosphere (41).

Under a boundary lubrication regime, superlow friction coefficients of 0.004 have been reported for ta-C coatings on steel in glycerol (Figure 3). Combined AFM and X-ray photoelectron spectroscopy (XPS) investigations revealed a transfer of iron atoms to the outer ta-C layer, forming subsequently a FeOOH layer. The terminal hydrogen atoms of the latter are responsible for dramatically reducing friction between this interface in the presence of glycerol (42). The importance of hybridization of the ta-C coating was later detailed, describing the role of the presence of graphene and graphite in the thin film of glycerol to achieve super-low friction. The carbon coating associated with glycerol acts as a carbon source to produce aromatic lamellar structures in the film formed between the surfaces, through tribochemical interactions. Besides, glycerol also provides hydroxyl groups that help to keep low friction even under more severe conditions (43).
Although superlubricity can be evaluated at the nano- and micro-scales (44), major challenges rely on achieving the same state on the macroscale (45, 46). One prominent example of macroscale superlubricity is known in the case of double-walled centimeter-long carbon nanotubes, which exhibit intershell friction lower than 1 nN (47). A solution to overcome the scale-up problem from nano to macroscale was reached by the combination of different carbon-based surfaces, namely, graphene and DLC, using encapsulated nanodiamonds as additive (48, 49). Macroscale superlubricity with a COF of 0.005 was achieved and subsequently optimized by encapsulation of the nanodiamonds using MoS$_2$ (46). Another promising approach to achieve superlubricity beyond the nano- and micro-scales was introduced by the integration of micro-contacts of modified steel substrates (Figure 4) (50). The tailored microstructured features of the substrate can be further functionalized employing coating with covalent-ionic or ionic-ionic two-dimensional composites in the form of MoS$_2$ and graphene. This results in a superlubricating state of the modified steel-steel macroscale contact, which exhibits a meaningfully reduced friction coefficient in $10^{-3}$ magnitude.

When considering carbon nanostructures for superlubricity, it should be kept in mind that the atmosphere has a strong influence on the performance. When operating under high vacuum, the COF between graphite layers is one order of magnitude lower in comparison to experiments conducted under ambient atmosphere. This is related to the lack of contamination and adsorbed water molecules (51).

Tribochemical synthesis of DLC coatings is a recently investigated approach to obtaining functional coatings that could achieve superlubricity. In this approach, the sliding contact interfaces in the presence of a gas or liquid initiate chemical reactions that can lead to the deposition of thin films. Erdemir et al. obtained different forms of carbon coatings, e.g. graphene, nano-onions, and disordered carbons, by tribochemical conversion on sliding surfaces of nickel and copper in the presence of methane gas (Figure 5) (52). The transfer of the tribochemical approach to biocoatings would be of high interest for anti-wear applications, since customized coatings (vide infra) could be potentially converted to DLC,
providing a way to achieve superlubricity. This approach has been already proven successful to create ta-C coatings by mechanochemical decomposition of organic friction modifiers, e.g. unsaturated fatty acids or glycerol (53).

Although advances were already produced with carbon-based solid surfaces, shift the conventional industrial approach from lubricating oil still faces some challenges that liquid superlubricity could help to overcome. Li et al. have summarized the scientific progress in superlubricity research based on carbon nanostructures as additives for liquid lubricants (54). Furthermore, metal surfaces are the most common material found in industrial contacts, and apply DLC coatings to this huge variety of surfaces is yet very difficult. Conversely, the use of DLC with conventional commercial lubricants, commonly produced for metallic surfaces, entails tribocatalytic interactions that can result in higher adhesion and friction, resulting in wear damage (55). Thus, the development of lubricants compatible with solid surface coatings that also match Green Chemistry principles is crucial.

Concerning the increased awareness of potential hazards of used lubricants for the environment, bio-based materials have been elucidated as coatings that ensure low friction coefficient. In the case of lignin, it has been suggested to exploit the feedstock diversity to tune the tribological properties (56).

2.2. Green synthesis of diamond-like carbon (DLC) as sustainable coating

DLC is a metastable form of amorphous graphite that is characterized by a relatively high degree of sp³ bonds within its structure and it is a potential sustainable coating (57). DLC can be briefly categorized based on the hydrogen content and percentage of sp³ bonding according to: (i) ta-C (80% sp³, 0% H), (ii) a-C:H hard (40% sp³, min. 30% H), (iii) a-C:H soft (60% sp³, min. 40% H), and (iv) ta-C:H soft (70% sp³, 30% H) (Figure 6).

The interest in DLC stems especially from the potential applications in bioinert coatings and protective anti-wear coatings. In the case of the latter, DLCs are also prospective materials for achieving superlubricity (vide supra).

Raman spectroscopy enables to estimate the chemical composition of the deposited carbon films with respect to sp²-hybridized carbon. Whereas graphite is known to have only one sharp peak at 1585 cm⁻¹ (G peak), diamond exhibits only one peak at 1350 cm⁻¹ (D peak) (58, 59). Although DLC can be fabricated by chemical vapor deposition (CVD) process, this approach involves low growth rates of the film and hazardous gaseous precursors, such as methane, acetylene, cyclohexane, ethene, ethane, and propane and their consecutive ionized forms. These hazardous substrates and intermediates, complex and energy-consuming synthesis process, i.e. CVD, do not render DLCs as environment-neutral material and cannot be considered as sustainable. For the fabrication of DLC as a sustainable coating by using Green Chemistry metrics, safe solution-based methods are hitherto required while simultaneously ensuring that the amount of waste is minimized or even completely prevented.

Electrochemical synthesis could fulfill theoretically the green synthesis of DLC coatings by substituting...
gaseous carbon precursors with soluble molecular precursors. Sirk and Sadoway have investigated in 2008 the mechanism of carbon electrodeposition by using metal acetylides as precursors in various solvents, such as liquid ammonia and dimethylsulfoxide (DMSO) (58). Although this study clearly does not represent a sustainable approach, the authors provide a mechanistic understanding of electrochemical carbon deposition by using acetylide anions. By applying an anodic current, the $\text{C}_2^2-$ anion is oxidized on the surface of the working electrode to yield microcrystallites of DLC. Nevertheless, a uniform coating was not obtained regardless of the applied reaction parameters, e.g. temperature, UV illumination, and electrolyte compositions.

Since applying non-toxic substrates is the key to designing green processes for DLC synthesis, attempts have been performed to increase the operating voltage between the electrodes to use the solvent directly as carbon precursor (60). Ethanol/water solutions can be decomposed to carbon structures readily at room temperatures on silicon electrodes in the potential range between 80 and 300 V at a current density of app. 2 mA cm$^{-2}$. The deposited carbon structures can be varied from nanodiamonds, DLC to amorphous carbon, but the lack of characterization and heterogeneous

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**Figure 5.** TEM study of debris particles from methane-derived carbon coatings obtained by tribochemistry. (A) Low-magnification and (B) HRTEM images of large graphene sheet with scattered carbon nano-onions. (C) TEM image showing the side view of carbon nano-onions attached on a graphene sheet (about 10 layers). (D) Low-magnification and (E) HRTEM images of agglomerated nanoparticles wrapped with highly disordered carbon. (F) EELS spectrum from agglomerated debris showing almost no N. (G) EELS spectra of carbon K-edge of disordered carbon compared with glassy carbon (standard), graphene (from image B), and amorphous carbon on the TEM grid. Reprinted (adapted) with permission from (52). Copyright 2020, American Chemical Society.
nature of the deposit makes potential applications challenging. In addition, the deposition process may strongly vary when performed on metallic substrates instead of on silicon. DLC has been also electrochemically deposited previously by decomposition of N,N-dimethylformamide, but the latter does not fulfill the criteria of a green solvent (61).

Acetonitrile dissolved in water can be also electrochemically decomposed to yield on fluorine-doped tin oxide (FTO) electrodes DLC, but the obtained carbon electrodes face the same problem of non-uniformity as previous reports (62). Although acetonitrile seems to be a less toxic solvent, this carbon precursor is considered problematic due to the formation of volatile organic compounds (VOCs) which would pose a potential hazard for any production process beyond the lab scale (63). Comparable risks are accompanied by acetic acid as precursor albeit it can produce DLC and carbon nanotubes via a reductive electrochemical reaction on nickel electrodes (64).

In another approach, LiCl-KCl-CaCl$_2$-CaC$_2$ melts were used to deposit DLC on nickel substrates at 823 K by means of electrochemical deposition (65). Similar to previous approaches, no uniform coating could be obtained at this temperature and the system is far from an atom economy. In addition to the form of the carbon precursor, another important aspect is the choice of conductive substrate (66). Nickel is regarded as a promoter for deposition of carbon film due to (i) formation of a passivating layer during anodic conditions and (ii) solubility of carbon in the metal matrix. However, it is clear that sustainable coatings of metallic components with DLC should be independent of the presence of nickel.

Despite the rapid progress in DLC coatings, none of these processes can be considered green and few research reports on DLC fabrication investigate the coatings concerning tribological properties. Friction and wear on DLC coating were analyzed concerning its hydrogenation degree. Hydrogenated DLC (a-C:H) suffered more wear damage due to the use of commercial lubricants applied commonly for metallic surfaces. This issue is overdue by the use of hydrogen-free DLC (ta-C) which is more commonly used to achieve superlubric regimen (67). The wear dependence of hydrogen concentrations was further evaluated by simulation models on an atomic scale. The observed behavior varies depending on the type of wear mechanism. The chemical wear confirmed the previous studies showing that a higher hydrogen content makes the carbon more susceptible to dissociation. On the contrary way, more hydrogen atoms decreased the mechanical wear due to adhesion suppression of the surfaces. The authors achieved an optimal percentage of 20% of hydrogen for the best anti-wear performance of DLC (68).

### 3. Biobased coatings and additives for lubrication applications

Over the past few decades, lignocellulosic biomass emerged as a promising alternative for the replacement
of petroleum derivatives, being an inexpensive, abundant, and sustainable feedstock, besides fulfilling the demand for carbon-based compounds (69, 70). Lignocellulosic biomass is generally constituted by cellulose (30–50 wt.%), hemicellulose (20–35 wt.%), and lignin (10–30 wt.%). Cellulose and hemicellulose can be both described as polysaccharides differing by the type of monomer. While the first has only glucose as the monomer, the latter is composed of five distinct sugar units, named xylose, arabinose, galactose, glucose, and mannose. In its turn, lignin is a heterogeneous crosslinked macromolecule comprised of more complex phenol moieties, like p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (73–76).

Alongside cellulose and lignin, chitosan completes the set of raw material sources for bio-based coatings analyzed in this review. Mainly obtained from marine waste, chitosan is a polysaccharide obtained by the deacetylation of chitin, which is the fundamental structural component of crustacean shells and fungal cell walls. This polymer is constituted of N-acetylglucosamine (NAG) and d-glucosamine monosaccharide units (77). The molecular structure of these compounds is shown in Figure 7.

In the following topics, we have a summary and discussion on the up-to-date progress related to the use of cellulose, chitosan, and lignin as starting materials aiming at lubricant pursuits. The specific choice for these biomacromolecules as additives to lubricants or as coating materials was addressed from the standpoint of Green Chemistry principles.

### 3.1. Cellulose-based coatings

In 1838, Anselme Payen was responsible for isolating cellulose from wood, by using a simple treatment with nitric acid. Currently, nearly 7.5 million tonnes of cellulose have been produced annually (78), which makes this polymer from biomass the most abundant polysaccharide in the world. Cellulose is a high-molecular weight homopolysaccharide comprised of β-1,4-anhydro-D-glucopyranose units (Figure 7), being found as microfibrils of varied diameters and lengths in the plant cell walls. Due to the presence of several hydroxyl groups on cellulose structure, a complex hydrogen bonding linkage exist between the polymer chains, which results in a macromolecule that is insoluble in water and the most common organic solvents (79).

By breaking the cellulose hydrogen bond network, the dissolution of this polymer can be achieved by using either derivatizing or non-derivatizing solvents. The first one dissolves cellulose by chemically reacting with the hydroxyl groups while breaking partially or fully the hydrogen bond network. The latter act to break the inter- and intra-molecular bonds of cellulose (80). Although cellulose is insoluble in water and common organic solvents, several non-environmental friendly solvents of intermediate properties such as N, N-dimethylacetamide, N-methylmorpholine N-oxide and ionic liquids are well known to be able to dissolve cellulose chains (81). Nevertheless, up to now, researchers could not achieve a common understanding trying to find similarities among all document solvents for cellulose. However, despite the existence of numerous commercially available solvents, it is clear and urgent for the industry sector the need for green alternatives (81).

The incorporation of cellulose and its derivatives into/on other materials has been responsible for boosting their applications in a wide range of different fields, such as energy, environmental, biomedical, among others. In this context, cellulose and its derivatives have been extensively used in different forms, i.e. as fibers, films and membranes, covering a full spectrum of fields: drug delivery, water treatment, biomedical engineering, separation, packing and also acting as stabilizers, as reinforcement agents for composite applications, packing applications, lubricant additives and as biocoating for different materials and surfaces (82–84).

In modern society, there has been an increased search for green lubricant additives aiming at the reduction of energy consumption and the increase of energy efficiency. In this context, cellulose and its derivatives have been widely considered as environmentally friendly candidates. When it comes to the lubricating mechanisms of cellulose, like other biopolymers such as chitosan, we are talking more than simply elastohydrodynamic effects. There is an intimate relationship between the chemical structure of these macromolecules and their lubricating behaviors, as well as related to tribochemical reactions during the tribological process (85). For the case of cellulose, as for other polysaccharides, the formation of a surface-bound water film on the surface of a substrate, due to the strong hydration of the cellulose chains, makes this polymer and its derivatives ideal for lubricant coating applications (86). Although the newest literature has brought important advances on the use of cellulose for the latter application, it has still been observed a clear lack of deeper investigations based on the use of cellulose and its derivatives as coatings aiming at lubricious surface.

Conformal bacterial cellulose coatings have been prepared by using a straightforward and green process consisting of dip-coating 3D objects in suspensions of cellulose-producing bacteria. The authors reported on
the immobilization of *Gluconacetobacter xylinus* and its capacity of secreting highly porous hydrogels, rich in water content, directly to the surface of three-dimensional materials. Due to the perpendicular orientation of the conformal bacterial cellulose (BC) to the coated surface, the materials have demonstrated a load-bearing space filling network with improved mechanical stability, besides energy dissipation under compression and shear. Thus, differently from the common self-supported bacterial hydrogels, this *in situ* grown conformal bacterial cellulose surface has shown enhanced lubricating properties owing to its increased water content and low stiffness (87). Experiments using Poly (methyl methacrylate) (PMMA) surfaces revealed a lowering by

**Figure 7.** A schematic representation of the chemical structure of chitin, chitosan, cellulose, and lignin with its more common moieties.

**Figure 8.** (a) Poly (methyl methacrylate) (PMMA) substrate sliding pairs coated with BC for the friction measurements. (b) Coefficient of friction as a function of time for PMMA coated with a BC layer in comparison to the bare substrate in the dry or wet states. (c) Hernia mesh coated with bacterial cellulose. Reprinted (adapted) with permission from (87). Copyright 2020 American Chemical Society.
a factor of 3 of the coefficient of friction after coating (Figure 8). The authors have also demonstrated the feasibility of using propylene hernia implants as substrates, taking advantage of the bacterial cellulose softness and biocompatibility, as well as its capacity of strengthening the resulting mesh.

Shariatzadeh and Grecov reported on the performance of aqueous suspensions of cellulose nanocrystals (CNC) as water-based lubricants (88). Remarkably, the nanocrystals improved the coefficient of friction and wear when added to water, leading to a friction coefficient of 0.09 (4-fold reduction in the friction coefficient of water) between a stainless-steel cylinder and a chrome steel ball. We should emphasize the existence of several approaches to obtain CNC from lignocellulosic biomass using green routes (e.g. enzymatic hydrolysis and mechanical treatments), which makes all the processes using CNC aqueous suspensions as additive environmentally friend.

Cellulose is also able to work as a lubricant additive, as Martin-Afonso et al. has demonstrated. The dispersion of alkaline-treated cellulose pulp in castor oil leads to considerably smaller friction coefficients compared to commercial lubricating greases under identical mechanical conditions (89). Other modifications in cellulose pulp in order to improve the compatibility with vegetable oils have been often reported, such as methylation and ethylation (90–92). These modifications reduce the cellulose polarity while facilitating the formation of gel-like dispersions with great potential for lubricant pursuits.

Yang et al. have reported on the in-situ synthesis of a novel organic-inorganic nanocomposite based on the growth of calcium borate nanoparticles (CB) onto the surface of cellulose acetate-laurate (CAL), via a green and effective low-temperature hydrothermal method (93). In this investigation, the authors demonstrated the synergistic lubrication effects during the process of sliding between both components, while this novel nanocomposite has been used as a green lubricant additive due to its effectiveness for extreme pressure and anti-wear applications (Figure 9c). When this nanocomposite was used as a lubricant additive in poly-alpha-olefin base oil, results revealed a reduction up to 48.7% in the coefficient of friction and 25.9% in the average wear scar diameter (Figure 9a,b). While the maximum non-seizure load increased 79.6% (93).

It is well known that the anti-wear performance of cellulose esters is not usually effective under high loads. Nevertheless, many investigations have shown the use of these derivatives as additives in order to enhance the efficiency under extreme pressure (EP) and antiwear properties of lubricant materials. Zhang et al. reported on the green synthesis and application of long chain cellulose esters with high degree of substitution as effective and environmentally friendly lubricant additives (94). In their work, cellulose acetate-octanoate (CAO) and cellulose acetate-laurate (CAL) have been prepared via mechanical activation-assisted co-reactant reaction using the corresponded fatty acid, acetic anhydride, and $H_2SO_4$ as catalyst. As regards the average wear scar diameter, the authors showed that long chain cellulose esters reduced wear and friction between contact surfaces and the steel balls. At the same time, maximum nonseizure load was significantly improved, mostly attributed to the higher attraction of the polar heads (−O−CO−R and −OH) in cellulose esters to the metals. CAL has also been used as green additive to improve the lubricating performance of base n-butyl palmitate/stearate base fluid (95).

### 3.2. Chitosan-based coatings

Chitosan, β-(1-4) linked 2-amino-2-deoxy-β-D-glucopyranose, is a natural, renewable, biocompatible, and biodegradable carbohydrate produced by the direct deacetylation of chitin, a naturally occurring cationic polysaccharide (Figure 7). After cellulose, chitin is the next most abundant polysaccharide in the world, which has as the main source of extraction the exoskeleton of crustaceans and several insects. Both chitin and chitosan have chemical structures similar to cellulose, consisting of β-(1-4) linked D-glucose units. While cellulose has a hydroxyl group at C-2, chitin and chitosan have an acetamide group. In an alkaline media, once those acetamide groups are partially deacetylated into primary amino groups, we obtain chitosan, i.e. an N-deacetylated derivative of chitin. Thus, chitosan can be truly defined as a copolymer consisting of β-(1-4)-2-acetamido-d-glucose and β-(1-4)-2-amino-d-glucose units (96).

The solubility of chitosan is highly dependent on the degree of N-acetylation and molecular weight. While being insoluble in water and the most common organic solvents, chitosan solutions can be easily achieved in acid solutions below pH 6.3 (97). Nevertheless, it is important to highlight that concentrations above 2% (wt/wt.) are often reported to lead to very viscous solutions. However, the final viscosity has a strict correlation with the degree of acetylation and molecular weight (98).

Chitosan has excellent film-forming properties, which allows the production of films and coatings materials. Besides good mechanical, antibacterial, and antioxidant properties, chitosan-based materials have a selective permeability to gases, such as CO₂ and O₂. All these
features make chitosan an ideal candidate for a wide range of applications, such as cosmetics, textiles, biomedical devices, emulsifying, drug delivery, and the food industry in general (99, 100). Regarding the application of chitosan as a biobased coating, it is important to emphasize its use for many key applications such as lubrication and anti-wear film formation, anti-biofouling, cellular adhesion promotion, biosensing, drug delivery, among others (101). Chitosan has been demonstrated to be an effective lubricant when freely physisorbed on surfaces under very low-pressure conditions. Conversely, crosslinked chitosan gels have shown not so promising results. The effective boundary lubrication of physisorbed chitosan has been attributed to the weak interpenetration between the layers arising from steric effects and counterion osmotic pressures, along with the presence of hydration sheaths about the charged polyelectrolyte (102).

Nikogeorgos et al. reported on the use of chitosan in combination with porcine gastric mucin (PGM) in order to enhance the lubricating properties of PGM by a synergic effect based on their mucoadhesive interaction (103). In their work, the authors showed a feasible and straightforward way to produce ‘bio-glues’ to enhance the slipperiness of mucins. The combination of chitosan and other materials aiming at lubricating goals has been also frequently reported. While catechol has been long recognized for its high toxicity, the combination of chitosan-catechol has been demonstrated to lead to a biocompatible material with excellent hemostatic ability, tissue adhesion, and lubricating properties. Stable chitosan hydrogel coatings based on chitosan-catechol have been produced on polyurethane (PU) and polyvinyl chloride (PVC) substrates, leading to a considerable reduction in surface friction, at the same time that the coating minimized the binding of bacteria on the surface of the catheters (104).

In the last few years, there has been an increased number of different investigations reporting the generation of lubricious coatings via different strategies, such as covalent coupling, using chitosan as raw material. Niemczyk et al. reported on the development of a coating process to yield amphiphilic, lubricious coatings, resistant to bacterial colonization, based on chitosan and chitosan-fatty acid derivatives (Figure 10a). The authors demonstrated that the presence of these coatings onto PET-DLA (butylene dilinoleate) substrates reduced the coefficient of friction (Figure 10b) up to 47%. Furthermore, the tests were conducted up to 1800 s, whilst no increase in the coefficient of friction was observed, possibly indicating no issues related to

Figure 9. (a) COF (coefficient of friction) of poly-alpha-olefin base oil without and with different additives and (b) variation of WSD (average wear scar diameter) and COF of poly-alpha-olefin base oil without and with different additives (load = 490 N, sliding speed = 1200 rpm, temperature = 75°C, testing time = 60 min, and concentration of additive = 0.6 wt.%). (c) Schematic illustration of a proposed lubrication model with CB/CAL as additive under the condition of high temperature and high load or low temperature and low load (93). Copyright 2020, with permission from Elsevier.
coating delamination or flaking. However, although the researchers demonstrated a particularly promising strategy for biofunctional catheter coatings, it involved many synthesis steps, and many of them involving the use of methanol as solvent \((\text{105})\). The same authors reported on the use of chitosan and the same chitosan-fatty acid derivatives as endovascular catheter coatings, finding that the chitosan derivative coatings presented a clear reduction in the coefficient of friction to levels similar to those of the commercially available ones \((\text{106})\). Nevertheless, the synthesis procedures lacked green routes to produce the chitosan derivatives.

It is well known that the condensation of the free amino group of chitosan with aldehydes or ketones leads to Schiff bases \((\text{107})\). At the same time, these chitosan-based Schiff bases usually present better load-carrying capabilities, as well as anti-wear and anti-corrosion properties, opening up a window of applications as lubricating additives. Murmu et al. reported on the preparation of azomethine-functionalized derivative of chitosan as a bio-lubricant additive for paraffin oil. In this work, Murmu et al. demonstrated that the coefficient of friction was reduced by up to 15 times due to a possible formation of a tribo-film of the chitosan-based Schiff base on the metal surface \((\text{108})\). Again, it is important to emphasize the need for green routes to obtain chitosan-based Schiff bases, which have a ‘bio source’ (chitosan), however, their production goes through not so sustainable pathways. While most of the synthesis procedures have been using methanol as solvent and long-time reactions at high temperatures, many studies have presented green approaches using microwave synthesis, greener solvents (e.g. ethanol) along reduced reaction times \((\text{109})\).
At this point, it is important to emphasize that after discussion, aligned with the Global Harmonized System (GHS) and European regulations, methanol has become a recommended solvent. Since the current occupational exposure and ICH limits for methanol are relatively high, as well as it has a rapid synthesis with low energy-demand, methanol has now been recommended, although it is still ranked as ‘problematic’ (63). Furthermore, even though literature brings different routes approaching pathways to obtain bio- methanol, what happens, in reality, is the opposite, whereas the petrochemical industry has been responsible for most of the production (110, 111).

The synthesis of acylated chitosan Schiff base has been also reported as regards it used as an ‘eco-friendly’ multifunctional biolubricant additive for antioxidant and lubricity properties in N-butyl palmitate/stearate (112). The authors found that the average wear scar diameter decreased significantly, however, it is worth mentioning that the synthesis involved two steps using 3,5-di-tert-butyl-4-hydroxybenzaldehyde, (dimethylamino)pyridine as catalyst and N,N-dimethylacetamide as solvent.

After the examples of advances using chitosan and chitosan derivatives as lubricant materials, we should be careful before labeling a novel material or method as sustainable, ‘bio’ and/or even ‘green’. So far, most of the methods using chitosan derivatives have been using hazardous reactants and solvents, while complex and energy-consuming synthesis pathways are still required. In order to ensure to be under the Green Chemistry metrics, it is important to keep carrying investigations based on greener solvents, non-hazardous materials/reactants, or even solvent-less reaction. Furthermore, special attention should be direct to microwave-assisted methods, which have advantages including energy-saving processes, shorter synthesis time and higher yield, lower processing cost, and rapid and uniform heating.

### 3.3. Lignin-based coatings

Lignin is one of the major components in structural cell walls of higher vascular plants and it is considered the main renewable source of aromatics in nature. Large quantities of technical lignins are annually generated from pulping, paper, and biorefinery industries (113, 114). Unlike cellulose, lignin is a heterogeneous and amorphous phenylpropanoid macromolecule, mainly composed of monolignol derived moieties, e.g. syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units, linked together to form a complex three-dimensional structure (Figure 7) (73, 113). The macromolecular arrangement of lignin differs according to the biomass feedstock and isolation process. Regarding the monomer composition and content of inter-unit types of linkages, phenolic hydroxyl, alcoholic hydroxyl, carbonyl, carboxyl, methoxyl, and conjugated double bonds are the common factor among all of them (94, 95, 113).

Despite lignin macromolecules are characterized by plenty of functional groups, chemical modification is often required to broaden the application areas. Simple activation of hydroxyl groups can improve their reactivity, increasing the compatibility of lignin with non-polar polymer matrices and allowing for the production of a variety of lignin-based coatings (115, 116). For instance, naturally amphiphilic, lignin is widely used as an anti-corrosion protector of metallic surfaces (117, 118), as a water-resistant coating, including wood protection (115, 119–121). Associated with cellulose, this macromolecule plays an important role as a UV light blocker due to its chromophore functional groups (122).

The association of lignin with ionic liquid (IL) triggers a good mechanism for lubrication purposes. The use of lignin as an additive for IL lubricants composed of choline and amino acids (glycine and L-proline) led to an improvement in tribological behavior due to the establishment of strong hydrogen bond interactions. [Choline][Amino acid] ([Ch][AA]) ionic liquids (IL) with 3–7 wt.% lignin fractions showed an amelioration on thermal stability and anti-wear properties, besides a notable enhancement in friction stability. The affinity between the carboxylic acid group present in the IL and a positively charged steel surface by the liberation of low-energy electrons during friction leads to the formation of a lubrication film. Nevertheless, the mechanical strength of the [Ch][AA] coating was notably enhanced concerning to reduction of friction and wear, after adding lignin fractions. The anionic and cationic charges present on the nitrogen and hydroxyls groups of [Ch][AA], respectively, acted as proton acceptor and donator of lignin functional groups, forming reciprocal hydrogen bonds that improved the interfacial separation between metal/metal surfaces (123).

The key role of the H-bond formed between lignin and ionic liquid lubricants have been extended to carbon-based surfaces. On commercial DLC coatings used for automotive components, the L-[Ch][AA] performed strong physical adsorption to form tribofilms, enhancing the lubrication performance when compared to a commercial lubricant for hydrogenated and non-hydrogenated DLC (124). The COF was lowered from 0.12 to approx. 0.07 (Figure 11) and negligible wear was observed.

In addition, chemical functionalization of lignin structure to add heteroatoms (N and P) in a one-pot reaction was performed to intensify the intermolecular bond.
As result, a decrease of up to 30% and 71% was observed in the friction coefficient and wear volume loss, respectively. These results were achieved due to the enhancement of H–bond density and polarity of the lignin-IL lubricant caused by the presence of heteroatoms, which led to stronger adhesion promoting lubrication. Nonetheless, the lignin modification procedure involved POCl₃ and 1,2,4-triazole as solvents, which can generate hazardous intermediates, thus failing to the sustainable design framework proposed by the Green Chemistry principles.

A broader exploration of the enhanced hydrogen bond density allowed the proposition of a friction mechanism of prevention of metal surface contact (Figure 12). Mu et al. evaluated the friction decrease in the presence of lignin associated with gelatin for ethylene glycol (EG) and polyethylene glycol (PEG) (126–128). In their study, the average molecular weight of different types of lignin played an important role in the tribological effects, while achieving remarkable wear reductions up to 89-94% along with enhanced thermal stability.

In a similar approach, lignin can also work as a thickener additive for grease lubricants to replace Mo-based or metallic soaps (129). As aforementioned, lignocellulosic biomass can act as a good thickener agent for lubricating greases. Different types of functionalized lignin added as thickener to biobased oleogels implemented suitable rheological characteristics when compared to commercial greases. Additionally, the additives presented better friction coefficients than a lithium lubricating grease (130–133).

Figure 11. Friction coefficient evolution for one hour test on (A) steel disc, (B) Tribobond 40 disc (Cr+a-C:H:W), (C) Tribobond 43 disc ((Cr+) a-C:H) and (D) Tribobond 44 disc (a-C:Cr). Reprinted from (124) licensed under CC BY 4.0. Copyright 2019, Hua and Shi.

Figure 12. Friction mechanism scheme for EG-lignin-gelatin lubricants in a (a) ball on disk friction test for (b-f) different mass ratio of lignin:gelatin. Reprinted (adapted) with permission from (126). Copyright 2017, American Chemical Society.
4. Summary and outlook: DLC coatings and biobased lubricants, fiction or non-friction?

While current research does not present an absolute answer to this question, the findings summarized in this review suggest that the interactions between these complementary materials may eventually lead to superlubricity. Despite the recent progress on the employment of biomass materials to enhance lubrication on different substrates, the connection to Green Chemistry principles still needs to be augmented. Our review has identified potential bottlenecks that need to be addressed at the stage of chemical synthesis to establish truly green materials. We examined the contribution achieved with carbon-based solid coatings on the nano-, micro-, and macroscales for low and super low friction. The latter is achieved with carbon-based surfaces and we focused on DLC coatings in particular. Despite the capacity to lower friction attained with this material, current DLC synthesis procedures do not fulfill the requirements of a sustainable approach, due to the presence of toxic solvents and/or generation of hazardous waste. Electrochemical synthesis is presented as a possible approach to satisfy the Green Chemistry requirements, but more research must be carried to associate the use of this method to produce tribologically efficient DLC surfaces. After a summary of the advances concerning DLC synthesis and biocoatings, an outlook of the combination of these materials becomes clearer.

The application of the superlubric regime industrially would decrease energy losses and CO₂ emissions caused by friction to minimum levels, attending to the ideal sustainable efficiency. This is still a utopic scenario, however, the development of lubrication systems making use of Green chemistry metrics already helps to establish a sustainable lubrication process. Thus, it is encouraging to pursue research on the advantages of the synergetic effects between the DLC surface and biobased lubricants. DLC coatings have already widespread commercial applications, but their tribological behavior has proven to be strongly dependent on the hydrogenation level of the surface and accompanying environmental conditions. The hydrogen content determines the tribochemical reactivity, making the coating more or less susceptible to structural changes; moisture or stem can promote oxidation in different levels, which can limit the coating usage (134, 135). Hence, biobased lubricants are able to minimize these effects while improving the performance under certain operation conditions, through different surface interactions. We propose three possible mechanisms that could lead to superlubricity encompassing biobased lubricants and DLC coatings, namely anionic interaction, hydration lubrication, and tribochemical reaction.

- Anionic interaction of dissolved lignin in DES with DLC

Studies have proven that superlubricity can be achieved with the use of lubricants (33, 136, 137) as a solution to overcome the constraints of the ambient conditions. Water-based lubricants combined with 2D nanomaterials additives are able to maintain low COF for long periods. Even though limitations still exist related to load-bearing capacity by using water-based lubricants, they could be overcome by substitution with ionic liquids (IL), whose load capacity, electrochemical widow, and thermal stability favor low friction (136, 138–140). Moreover, the association of IL and DLC is attractive to generate lubrication systems with low friction (141, 142). Nevertheless, when it comes to sustainability, ILs do not figure as a good option due to their toxicity and low biodegradability (143, 144). In this context, deep eutectic solvent (DES) appears as an alternative, sharing properties with IL and overcoming the sustainability issues (145, 146). Another promising solvent that is similar to ILs is the natural deep eutectic solvent (NADES), which is a DES composed of natural, readily available, and biorenewable compounds (147). DESs are also known as natural solvents for the delignification process of lignocellulosic biomass in paper industry (148, 149). In that way, making use of the similarity between ILs and DESs for lubrication purposes, combined with lignin as an additive, arises as a promising strategy to reuse and valorize these compounds. Similar to lignin as additive for IL, the high density of H-bonds linked with the existing polarization in lignin-IL solution induces tribofilm formation by physical adsorption, while the charge separation assists friction decrease. Thus, DES is a more sustainable option than ILs, and it could deliver the required charge for interactions with DLC substrate, with less hazardous by-products generation.

- Tribochemical interaction between DLC surface and oxygenated functional groups: saturation of biomacromolecules

A stable superlubric regime has been achieved in the presence of graphene-like 2D nanostructures on DLC surfaces obtained by tribochemical reaction with oleic acid lubricants. The theoretical model for tribofilm formation suggests that a formed graphene-like layer on high-sp³ carbon content DLC could be oxidized, producing carbon rings upon contact with oleic acid and...
leading eventually to super-low friction (150). Later, the important role that unsaturation and carboxylic groups in lubricants play as reactive centers for carbon-based surfaces was suggested by simulation models. The ability of these groups to anchor on ta-C surfaces, creating a crosslinking, enables chemical/aromatic passivation, producing a superlubricious layer. Similar results were achieved for steel/steel and a-C:H/a-C:H, but the mechanism is not yet clarified (53).

One can assume the need for multiple active centers in the lubricant to induce the mechanochemical fragmentation of the ta-C surface, which is responsible for superlubricious layer formation. These active centers are highly present in biobased macromolecules, which have been discussed in this review. Thus, similar interactions between hybridized carbon surfaces and lignin, chitosan, cellulose and their derivatives could be achieved in further investigations (Figure 13).

Albeit a proper understanding of superlubricity mechanism is not yet reached, the field evolved with DLC coatings to envision its macroscale progress and industrial applications. Among the aspects to be investigated, the synergy between DLC surface and lubricant film throughout tribochemical interactions is crucial. With this scenario becoming more feasible, there are enormous opportunities yet to be explored and findings have already been done contemplating green superlubricity using vegetable oils as lubricants (151).

- Biomimicking natural joints through hydration lubrication

Similar to lignin, the ability of cellulose and chitosan to be strongly physically adsorbed could also bring advantages toward low friction on DLC. The strong hydrogen-bond formation is present in both macromolecules and related features could also be explored. The physisorption capability of aqueous suspensions of chitosan or cellulose nanocrystals could enhance the water content in the lubricant layer, which increases wear resistance and decreases friction for a-C coatings (135). The hydration levels also benefit lubricated natural organisms and enable the superlubrication found in natural joints (152,153). An ambitious approach could take advantage of the ability of cellulose and chitosan to produce hydrogels, similar to what Klein et al. (154) reported, aiming at biomimicking the lubrication of natural joints. By loading poly (hydroxyethylmethacrylate) (pHEMA) hydrogel with phosphatidylcholine (PC) lipids, the authors created a lipid boundary layer and reduced up to 99% the friction and wear in comparison to the lipid-free hydrogel. Associating this technique with cellulose-based hydrogel could be even more beneficial to enhance the biocompatibility for biomedical applications. The study has also demonstrated friction reduction on polished stainless steel with lipid-based boundary lubrication surface. Besides the clinical application, the use of cellulose hydrogels loaded with lipids could mimic cartilage-like lubrication on DLC surfaces as well.

Another approach to reach low friction behavior, while mimicking biological systems, would be the molecular design of biocomponents based on the principles of thin film lubrication. The proposed design is based on the combination of surface properties and specified functionalities of biological molecules introduced to the system. Covalent bonding between surface crops of mechanical parts, e.g. hydroxil groups of modified

![Figure 13. Possible formation of superlubricious layer on DLC coating through tribochemical reactions with biobased lubricants that produce 2D carbon nanostructures in the lubrication film throughout surface passivation and promotes superlubric state.](image-url)
oxide films on the passivated metallic surface, enables the formation of a thin self-assembling layer similar to the absorption layer (155, 156). The functionality of the next layers must be selected in order to reduce the interaction between the separate molecules by regulation of their intermolecular interactions. This would start from the strongest chemical interactions, like anchored polymerization, to intermolecular interactions, such as hydrophobic–hydrophilic balance, steric and colloid interaction between the sliding surfaces, ordered layers and multilayered additives. Therefore, the possibility of combining features of biobased materials to produce hybrid lubricant coatings for green DLC aiming at low friction is a promising but untapped approach. Besides the abovementioned biomacromolecules, metal or metal-free phthalocyanines or porphyrins appear also as potential biologic precursors for bioinspired superlubricity.

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