Nanocellulose/Nanodiamond Hybrids

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Nanocellulose can be obtained from low-cost sources and has been extensively studied in the last decades due to its biodegradability, biocompatibility, low weight, large specific surface area, and good mechanical and optical properties. The nanocellulose properties palette can be greatly expanded by incorporating different metals, metal oxides or carbon nanomaterials, with the formation of multifunctional hybrids. Nanocellulose–nanocarbon hybrids are emerging nanomaterials that can respond to many current challenges in areas such as water purification, energy storage and conversion, or biomedicine for drug delivery, tissue engineering, antitumor and antimicrobial therapies, and many others. Nanocellulose/nanodiamonds hybrids combine the bio-based origin, biodegradability, good dispersion in water, and non-toxicity of nanocellulose with the high thermal conductivity, excellent mechanical resistance, and great structural stability of nanodiamonds.

nanodiamonds | nanofibrillated cellulose | hybrid materials

1. Introduction

Cellulose, the most widespread biopolymer on the planet, lives a new youth through nanocellulose, the nanomaterial obtained from cellulose by mechanical, enzymatic and/or chemical treatments [1][2][3]. Cellulose can be extracted from a multitude of sources, including plants, algae or tunicates, and can also be synthesized by bacteria. The extraction of cellulose from agricultural, forestry, and industrial wastes has received much attention due to both economic and environmental advantages [1][4][5][6]. Agricultural waste and industrial byproducts such as wheat straw, rice husk and straw, corn cob, sunflower shells, barley straw, sugarcane bagasse, legume straw, fruit seed shells, and others were used in recent works as sources for the production of nanocellulose, demonstrating the huge interest in this new feedstock [5][6][7][8].

Due to the possibility of isolation from low-cost sources, low weight, high strength and rigidity, biodegradability, and biocompatibility, nanocellulose has been extensively studied in the last decades [1][2][3][4][5][6]. Compared to cellulose, nanocellulose presents a much higher specific surface area, superior chemical reactivity due to the greater number of -OH groups located on its surface which are available for chemical modification reactions, superior tensile strength and specific modulus of elasticity, as well as improved optical transparency [9][10]. Nanocellulose is a generic term used to describe the cellulosic materials having at least one dimension in the nanometric range (<100 nm) that include cellulose nanocrystals (CNCs), cellulose nanofibers or nanofibrillated cellulose (CNFs), and bacterial cellulose (BC) (**Figure 1**) [1][3][11][12][13]. The list of nanocellulose's applications is long and it is growing fast [14]. To mention just a few, so far nanocellulose has found its way as a reinforcing agent in (bio)polymer nanocomposites [3][15], as key-component in the preparation of drug-delivery systems, wound dressings, and other biomedical products [1][12][16], in the fabrication of paper or textiles with special properties [17], in the food industry (as stabilizer, emulsifier, or thickener) [18], in water purification [19], cosmetics [20] or electronics [21]. While in most of these applications, nanocellulose acts as filler or modifier for polymeric or non-polymeric matrices, it can also serve as a dispersing agent or matrix.

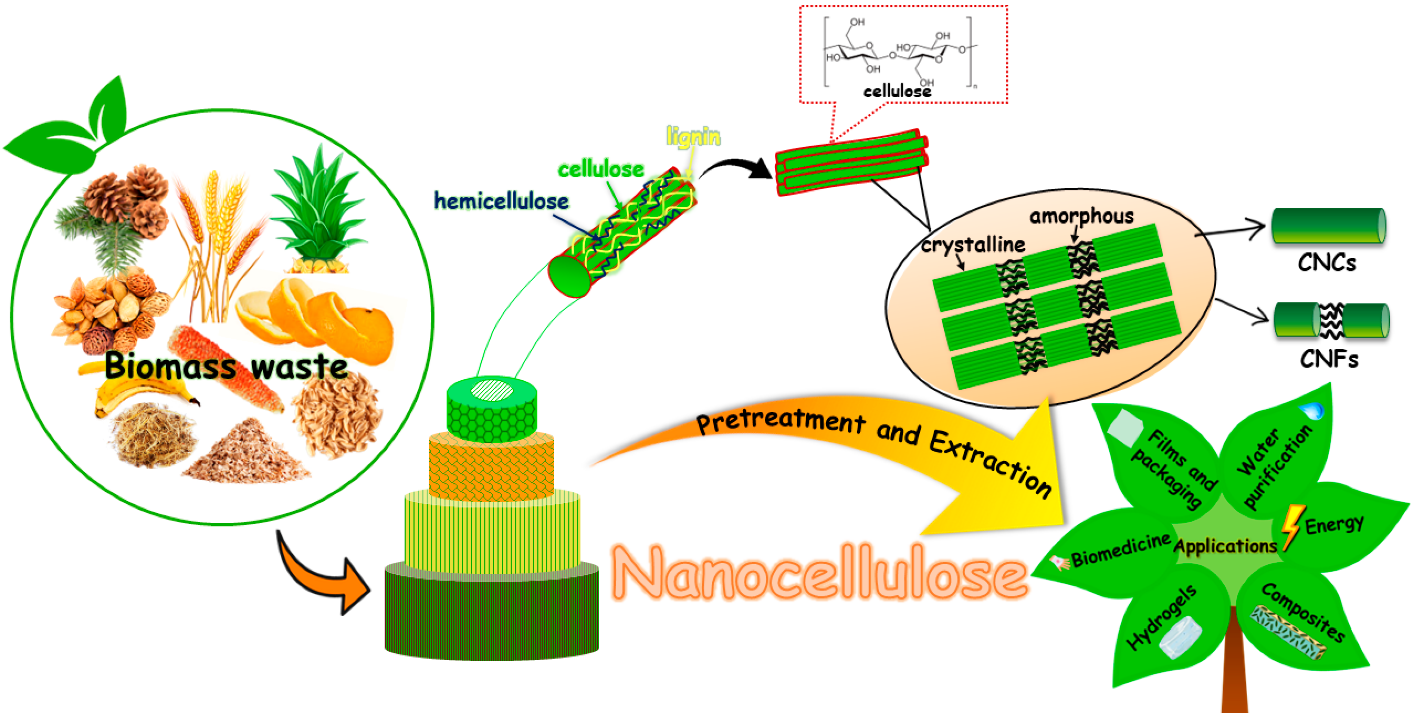

Figure 1. Nanocellulose extraction from agricultural waste, forestry residues and food industry by-products.

Hybrid materials, which are organic–inorganic materials assembled at the nanometer or molecular level, have shown remarkable advances in the last decades due to the progress in nanotechnology [22][23]. Nanocellulose, unmodified or surface-modified by various chemical routes, may be coupled with different metals, metal oxides or carbon nanomaterials with the formation of multifunctional hybrids [24]. From these, nanocellulose–nanocarbon hybrids obtained by the association of nanocellulose (in the form of CNCs, CNFs or BC) with carbon nanomaterials (e.g., graphene (G), carbon nanotubes (CNTs), nanodiamonds (NDs), fullerenes (C_{60}), carbon nanofibers, carbon quantum dots (CQDs) (**Figure 2**) [25] have gained particular interest due to the advantages arising from combining the bio-based origin, biodegradability, non-toxicity, and good water dispersion of cellulose with the remarkable mechanical strength, electrical conductivity, and/or thermal conductivity of the carbon-based nanomaterials. Due to their outstanding properties, these hybrids have potential uses in a variety of applications in biomedicine, as well as in the manufacture of functional composites, sensors, electrically conductive films, energy storage devices, adsorbents, catalysts, coatings, and others [26].

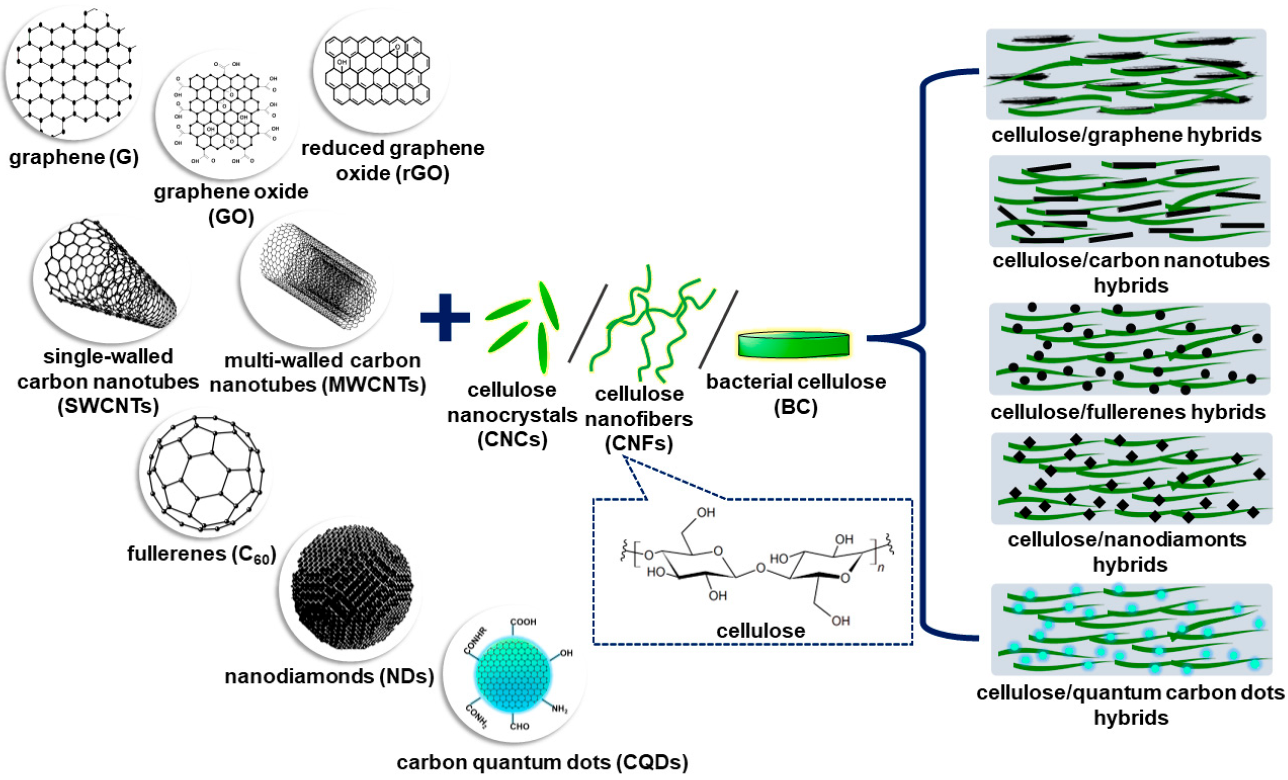

Figure 2. Nanocellulose–nanocarbon hybrids containing different types of carbon nanomaterials.

Graphene consists of a single layer of sp^2 hybridized carbon atoms arranged in a two-dimensional (2D) honeycomb network [27][28]. The special interest given to this material is due to its reduced thickness, low weight, high specific surface area, optical transparency, excellent electrical and thermal conductivity, and particularly high modulus of elasticity, of approximately 1060 GPa [29]. In particular, aerogels obtained from 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized CNFs and graphene showed a specific capacitance of 361.74 F/g at a current density of 0.5 A/g after combustion at 1100 °C, being recommended as electrode materials for supercapacitors [30]. The exceptional thermal and electrical conductivity of G can be attributed to the delocalized π electrons from the graphene plane that can move freely in the graphene structure [28]. A disadvantage of graphene is, however, its strong tendency to agglomerate due to the van der Waals interactions and π–π stacking interactions that arise between the graphene layers. Graphene oxide (GO) is a derivative of graphene resulting from the oxidation–exfoliation of graphite. It can be described as a single layer of graphite bearing carboxyl (-COOH), hydroxyl (-OH), epoxy, and ketone (-C(=O)-) functional groups on its surface [27]. Due to the presence on its surface of these polar groups and the repulsive forces that are established between the negatively charged -COO^- groups, GO presents a better dispersion in aqueous media than graphene and a higher ability to form composites with hydrophilic polymers [31]. However, the electrical and thermal conductivity of GO is much lower compared to those of graphene due to structural defects induced by the generation of oxygen-bearing groups on its surface [32]. Reduced graphene oxide (rGO) results from an exfoliation–reduction process of GO and greatly recovers the good electrical conductivity of pure graphene [27].

Carbon nanotubes are tubular materials formed by rolling a single graphene sheet, in the case of single-walled carbon nanotubes (SWCNTs), or several graphene sheets, in the case of multi-walled carbon nanotubes (MWCNTs). CNTs are characterized by high aspect ratio and specific surface as well as excellent mechanical and electrical properties [33]. Similar to graphene, CNTs are difficult to disperse in water and organic solvents, having a strong tendency to agglomerate due to the multiple van der Waals-type interactions and π–π stacking forces which lead to a decrease in their specific surface area and electrical and optical properties [34]. Fullerenes are another type of carbon nanomaterial that are considered an allotrope of carbon. They have the form of closed hollow cages consisting of sp^2 hybridized carbon atoms [25]. Regardless of their type, carbon-based nanomaterials are expensive and difficult to process due to their strong aggregation tendency [35][36]. Nanocellulose can act as a support or dispersing agent for carbon-based nanomaterials to increase their colloidal stability in aqueous media and thus, their processability into final products [35][37].

2. Nanocellulose–Nanodiamonds Hybrids

2.1. Nanocellulose

CNCs, CNFs and BC are characterized by different aspect ratios and cross sectional morphology, depending on the source of cellulose and the methods used for their synthesis or extraction [38]. CNCs are obtained by the acid hydrolysis of different cellulose sources using strong acid solutions of various concentrations, and controlled temperature [1][5]. Due to being obtained by the acid hydrolysis of the amorphous regions from cellulose, CNCs are characterized by a high crystallinity, superior mechanical strength, and a thermal stability dependent on the type of acid used for hydrolysis. In particular, the acid hydrolysis of cellulose with sulfuric acid leads to the generation of sulphate groups on the surface of CNCs which were shown to decrease the thermal stability of CNCs [5].

CNFs are obtained by the mechanical disintegration of the cellulose bundles from cellulose sources that were previously treated using chemical, enzymatic, or other mechanical methods [5][12][39][40]. As compared to CNCs, CNFs are characterized by a higher aspect ratio and lower crystallinity due to the different processes employed in their isolation. Additionally, as a consequence of the lower degree of crystallinity and higher lengths, CNFs possess superior flexibility when compared to CNCs. However, the morphological characteristics, thermal, and mechanical properties of CNFs strongly depend on the cellulose source [5].

The nanocellulose known under the name of microbial cellulose or bacterial cellulose (BC) is synthesized as an exo-polysaccharide by different species of bacteria following the metabolism of various carbon sources, such as glucose, sucrose, fructose, mannitol, sorbitol, etc. While the most commonly exploited species for the production of BC remains *Komagataeibacter* (formerly *Gluconacetobacter*) *xylinus* [41], BC can also be produced by other bacterial species such as *Aerobacter*, *Agrobacterium*, *Alcaligenes*, *Azobacter*, *Gluconobacter*, *Pseudomonas*, etc. [1][15]. BC consists of an ultrafine network of nanofibers with a ribbon-like appearance, having a diameter of 20–100 nm and a length of 1–10 μm and, therefore, a higher aspect ratio compared to other types of nanocelluloses [42]. Compared to nanocellulose isolated from plants, BC shows a higher purity and degree of crystallinity due to the lack of hemicellulose and lignin impurities, two polymers found alongside cellulose in the plant cell walls [43].

2.2. Nanodiamonds

NDs are three-dimensional carbon nanomaterials characterized by remarkable mechanical properties, optical transparency, fluorescence, high heat conductivity, biocompatibility, and non-toxicity; therefore, they are suitable for multiple applications in both industrial and biomedical areas [44][45]. NDs consist of a tridimensional (3D) lattice of covalently bonded sp^3 carbon atoms (tetrahedral hybridization), which confers excellent hardness, rigidity, incompressibility, a low friction coefficient, and high chemical resistance [46][47][48].

NDs can be obtained by the detonation of a graphite source or a carbon-rich explosive, or by the shock compression of graphite or organic compounds under high pressure and temperature followed, or not, by ball milling, which are the methods preferred at an industrial scale (**Figure 3**) [44][49]. Other methods to obtain NDs include laser ablation applied to a graphite or carbon black source, plasma-assisted chemical vapor deposition, ion irradiation of graphite, and others [44][49].

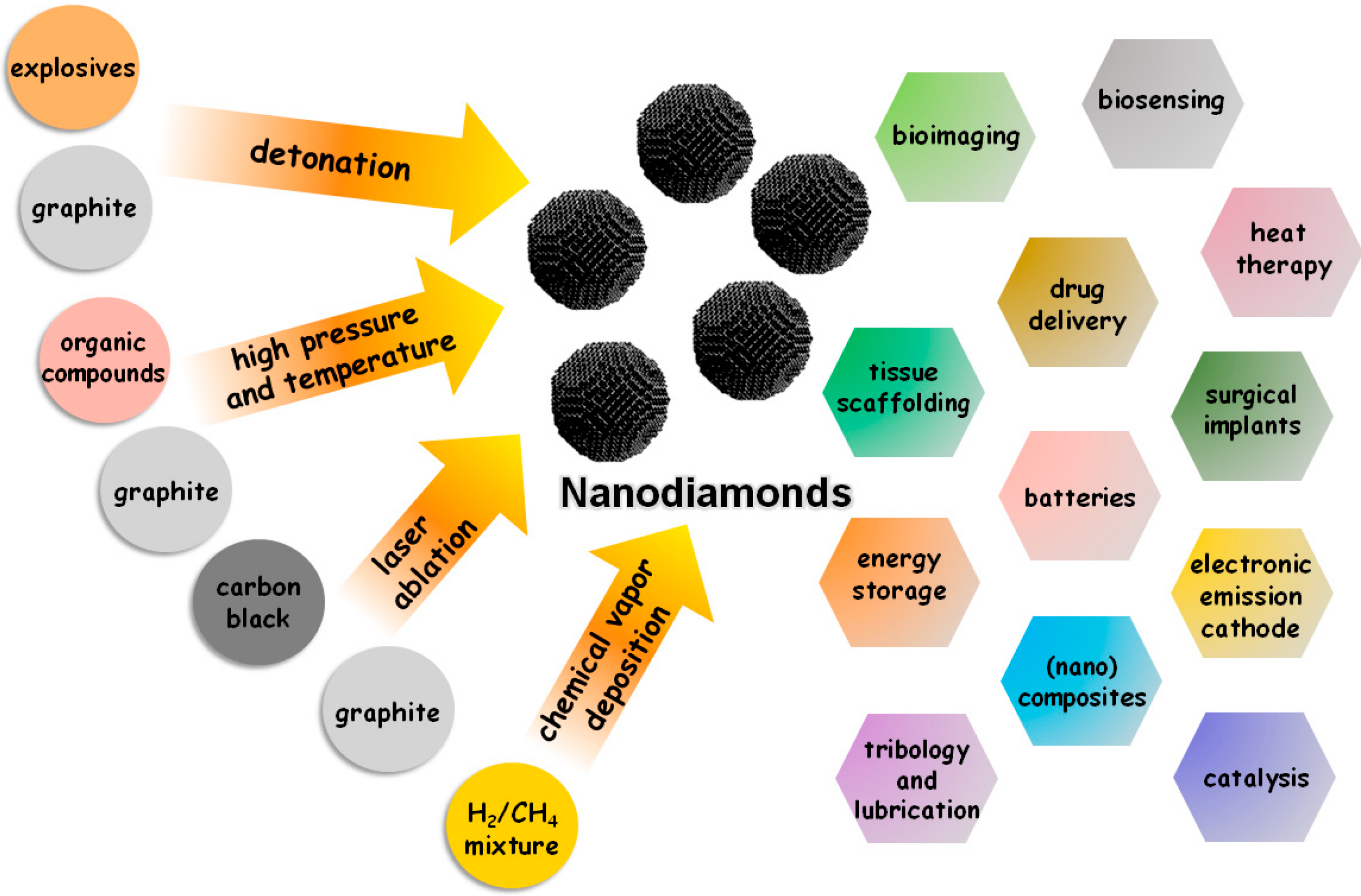

Figure 3. Schematic representation of NDs fabrication routes and main applications of NDs.

As they combine a high thermal conductivity with electrical insulation properties, NDs can solve several problems related to the market needs for efficient heat dissipation and prevention of overheating in electronic devices. Therefore, the addition of NDs improves the thermal conductivity of substrates by removing large amounts of heat or by dissipating the concentrated heat [50]. The high thermal conductivity of NDs may be explained by the highly ordered lattice and long phonon mean free path. This makes NDs induce a higher increase in the thermal conductivity of a substrate when used in lower concentrations than boron nitride nanosheets (BNNS), a common filler employed to increase the thermal conductivity of different substrates or matrices [50].

Besides their high thermal conductivity and dielectric properties, NDs possess special optical and mechanical properties along with biocompatibility and non-toxicity. Due to these cumulated properties, they were tested for drug delivery, biosensing, magnetic resonance imaging, heat therapy, tissue scaffolding, surgical implants, tribology and lubrication, catalysis, energy storage, or as a nanofiller in polymer nanocomposites [44][49].

2.3. Preparation of Nanocellulose–Nanodiamonds Hybrids

In a first attempt, NDs–ethyl cellulose mixtures were obtained for the development of screen-printed films for electron emission cathodes [51]. In this case, nano-graphite, NDs, and ethyl cellulose were mixed in the proportion 2:5:6, and ethyl cellulose was used only as an organic binding material. The first hybrids containing NDs and nanocellulose were produced using chitosan (CS, deacetylation degree 85%), BC nanofibers, and 5 nm NDs and the resulting materials were studied for potential application as wound dressings in biomedicine [52]. A solvent casting approach in which a chitosan solution in acetic acid was mixed with a BC gel dispersed in acetic acid and NDs dispersed in water, stirred for 24 h, sonicated until achieving a homogeneous suspension, and then poured in Petri dishes followed by evaporation of the solvent was employed for the preparation of the BC/NDs hybrids.

Drug releasing, transparent and porous cellulose-NDs hybrids were also developed as wound dressing materials [53]. Prior to the preparation of the hybrids, the NDs were surface functionalized to obtain carboxylated NDs (CNDs) using a mixture of sulfuric acid and nitric acid (3:1), and thermal treatment. Further, NaOH and urea were added to the homogeneous dispersion of functionalized NDs in deionized water, and the mixture was ultrasonicated and cooled to −12.5 °C before the addition of cellulose from cotton linter. The hybrid membrane was obtained by casting the mixed solution and immersing the obtained gel-like sheet in a 5 wt% H_2SO_4 aqueous solution followed by successive washings and freeze-drying [53].

Nanocellulose-NDs hybrids with a porous structure were also obtained by electrospinning. For this, a CS:BC:polyethylene oxide (PEO) (45:45:10) suspension was prepared by mixing an aqueous solution of chitosan in acetic acid with a BC gel dissolved in acetic acid, and a PEO solution in water [54].

For a better dispersion of the NDs in the water suspension of nanocellulose and stronger nanodiamond–cellulose interactions, CNFs were surface modified by two chemical routes: TEMPO oxidation (TOCNFs) and glycidyltrimethylammonium chloride (GTAC) modification (QCNFs) [55]. Hybrid materials containing TOCNFs or QCNFs and NDs of about 10 nm in size in different proportions (1, 2.5, 5, 10, 33, and 50 wt%) were obtained by mixing the water suspensions of the modified celluloses and NDs, followed by filtration [55]. In another attempt, a water suspension of cationic cellulose nanofibers (Q-CNF) obtained using GTAC as a surface modification agent was added over a NDs aqueous suspension, and the mixture was stirred for 48 h and filtered [48]. Hybrid films with a NDs content of 0.5, 1.0, 2.5 and 5 wt% were produced by drying the wet cakes obtained after filtration between metal sheets at 93 °C for 15 min and then under vacuum [48].

2.4. Main Characteristics of Nanocellulose–Nanodiamonds Hybrids

2.4.1. Thermal Conductivity

Nanocellulose–nanodiamonds hybrids have been developed for obtaining materials with new or special properties or for improving the properties of nanocellulose-based materials. Heat dissipation is now a major problem for electronic devices due to the high frequency and high power density of the new systems developed to meet the needs of increased performance, integration, and miniaturization [50]. A higher power density level implies a higher heat flux density, which may raise reliability and equipment lifetime issues, hindering the development of high-performance devices.

Therefore, an increased thermal conductivity for the polymeric materials used in the manufacture of electronics is a major and urgent requirement. Nanodiamonds stand out by their high thermal conductivity at room temperature (2000 $Wm^{-1}K^{-1}$) and remarkable electrical insulation properties, which promote them as a valuable material for electric and electronic devices [50]. Several nanocellulose/NDs hybrids have been developed for this purpose. Thus, CNFs/SCND hybrids showed up to 145.6 times increase in thermal conductivity as compared to the neat nanocellulose film [50]. The thermal conductivity of the hybrids was measured by a laser-flash method, which measured the temperature rise when the sample was heated on one side by a short laser pulse. The improvement in the heat dissipation coincided with an increase in the mechanical properties of the hybrid materials containing up to 30 wt% NDs due to the reinforcing effect of NDs.

The dissipation of heat in highly integrated circuits is currently an important issue because most of the composite materials dissipate heat well only in one direction, being anisotropic materials. An increase of only 10 °C in the temperature of a light-emitting diode (LED) device leads to a reduced luminous efficiency and a halving of the LED's lifetime [56]. Materials showing a high bidirectional thermal conductivity are required in these applications for an efficient in-plane and through-plane spreading of heat in advanced electronic devices. Incorporating microdiamonds (M) in anisotropic nanofibrillated cellulose (CNF)–graphene nanoplatelets (G) films can enhance the thermal conductivity in both in-plane and through-plane directions by constructing three-dimensional heat dissipating pathways and reducing phonon scattering [57]. Thus, more balanced in-plain ($k_{\parallel}$)/through-plain ($k_{\perp}$) thermal conductivity results were obtained for CNF/G/M hybrids due to the addition of M of different sizes [57].

2.4.2. Mechanical Properties

The mechanical properties of the nanocellulose/nanodiamonds hybrids depend primarily on the dispersion of the ND nanoparticles in the hybrids and the NC/NDs interface strength as well as on the ratio between the components in the formulations and the preparation method [22]. In particular, CNFs/NDs hybrid films obtained by the vacuum filtration of the CNFs/NDs mixtures with a NDs content of 0.5–10 wt% showed a decrease in the tensile strength of up to 25% as compared to the tensile strength of the NC film [58]. The tensile properties were determined through dynamic thermomechanical analysis using a Q800 from TA Instruments (USA). The CNFs/0.5 wt% NDs hybrid film was proposed as a lateral heat spreader for portable electronic devices due to its good thermal conductivity, satisfactory tensile strength, good toughness, as well as its electrical insulation and optical transparency properties [58].

Nanocellulose/nanodiamonds hybrids with improved tensile strength and modulus and high heat dissipation capacity were obtained by using up to 30 wt% SCND flakes. An important role in the improvement of the thermal and mechanical properties of these hybrids was attributed to the hydrogen bonds between the CNFs and SCND and the ordered layered structure of the SCND flakes. The CNFs/70 wt% SCND hybrid showed excellent flexibility and mechanical strength, a tensile strength of 113.4 MPa and a tensile modulus of 10.8 GPa that were proven by the easy bending and folding of the film [50].

A remarkable reinforcing effect of the NDs was observed for cationic cellulose nanofibers/NDs hybrids [48]. In this case, the ionic interactions between the electropositive charges on the nanocellulose surface and the electronegative NDs had a significant role in increasing the strength and preserving the ductility of the hybrid material. Thus, the Young's modulus increased from 9.8 to 16.6 GPa with an increase in the NDs content from 0 to 5 wt% [48]. Strong interactions between NCs and NDs were obtained by the surface functionalization of nanocellulose by TEMPO-oxidation [55].

2.4.3. Optical Properties

The optical transparency of the nanocellulose film, also known as nanopaper, is an important property when the application of cellulose as a substrate for electronics is pursued [59]. Although characterized by high optical transparency, NDs may change the optical transparency of the NC hybrid films. Thus, the transparency in the visible region of CNFs/NDs hybrid films with a thickness of 50–60 μm decreased when the concentration of the ND particles in the hybrids increased from 0 to 10 wt% [58]. As a measure of the transparency of the hybrid films, the light transmittance at 550 nm wavelength decreased from more than 75% for the unmodified CNFs film, to about 20% for the CNFs/10 wt% ND hybrid film. This was due to the light scattering created by the ND particles and possible agglomerations when their concentration in the hybrids increased [58].

2.5. Applications of Nanocellulose–Nanodiamond Hybrids

Materials more appropriate for the new electronic devices and, in particular, for power electronics are in great demand. These materials must have very good heat dissipation properties to be used in applications such as portable electronic devices or energy storage systems. Nanodiamonds stand out due to their remarkable thermal conductivity, of 2000 $Wm^{-1}K^{-1}$ at room temperature, which makes them the correct choice when an increase in the conductivity of various polymers is desired. NC/NDs hybrids benefit from the properties of both materials, combining good mechanical properties, high thermal conductivity, and electrical insulation, with biodegradability, and lack of toxicity. Thus, CNFs/NDs hybrid films with a low content of NDs showing good thermal conductivity and mechanical properties as well as optical transparency were developed for the lateral heat spreader in portable electronic devices [58].

Two fillers with different geometry were used in NC hybrids to ensure a high bidirectional thermal conductivity for the development of thermal interface materials. Thus, new materials based on NC, graphene nanoplatelets, and micro or nanodiamonds were designed for this purpose [57]. Similarly, hybrids containing NC, BNNS and micro/nanodiamonds were fabricated and tested with good results in the heat dissipation system of a main processor [60]. Reportedly, the temperature of the processor recorded during 100% utilization was lower than the limit temperature for stable operation (53 °C) when the CNFs/BNNS/NDs hybrid used as a thermal interface material in the computer contained both nano and microdiamonds [60]. An even lower difference between the in-plane and through-plane thermal conductivity was reported for a CNFs/BNNS/NDs hybrid obtained via an electrostatic self-assembly route [61].

CNCs/NDs hybrid materials were also tested for humidity detection and humidity level measurement [62]. The detection and control of humidity are vital in several fields such as food and drug storage, medical health, industry, and agriculture. A humidity sensor should measure humidity over a large range, with high sensitivity and accuracy and it must show cyclic responsiveness [63]. The CNCs/NDs hybrid acting as an adsorption layer was combined with a quartz crystal microbalance (QCM) and its humidity-sensing properties were tested for a wide range of humidity, from 11.3% to 97.3% [62]. The encouraging results, fast response, high sensitivity (54.1 Hz/%RH), and small humidity hysteresis (3.2%RH) recommended this hybrid as a humidity sensor in breath monitoring [62].

The favorable chemical stability, mechanical strength, and biocompatibility recommend NDs for biomedical applications such as wound dressing, wound healing, skin tissue engineering, bone tissue regeneration, and drug delivery [52][53][54][64][65].

CNCs/NDs conjugates obtained by covalently bonding silylated CNCs and oxidized NDs were designed as a biointerface material for bone tissue regeneration [64]. In vitro biocompatibility investigations were conducted by studying the proliferation and differentiation of human fetal osteoblastic cells (hFOB) using the CNCs/NDs conjugates as cell culture substrates. The cytotoxicity tests showed that the CNCs/NDs conjugates induce cell growth and showed no cytotoxic effects after 7 days of culture [64].

Chitosan/bacterial cellulose/nanodiamonds (CS/BC/NDs) hybrid films were recommended as wound dressings [52]. The hybrid films containing 2 wt% NDs showed enhanced mechanical properties and only a slight decrease in transparency as compared to the CS/BC film without NDs. Moreover, the mouse skin fibroblast cells' (L929) viability on this hybrid film (CS/BC/2 wt% NDs), evaluated using the MTT assay, was higher than 90% after 24 h incubation and exceeded 75% after 48 h incubation, showing a good biocompatibility [52].

Nanocellulose/NDs hybrids were also tested for the delivery of drugs, using doxorubicin as a model drug [53]. The addition of CNDs to cellulose greatly improved the modulus of elasticity and tensile strength of the hybrid films without significantly modifying their elongation at break and transparency. This improvement in properties was explained by the good dispersion of the CND particles as well as the strong interactions established between the hydroxyl groups of nanocellulose and the carboxylic groups of carboxylated NDs [53]. The doxorubicin loading was investigated by immersing the hybrid membranes in a doxorubicin solution overnight. A higher amount of NDs in the hybrid material led to a higher content of doxorubicin loaded in the porous films while the drug release profile was influenced by the pH. The cytotoxicity of the hybrid membrane was evaluated by the MTT assay using HeLa cells. The results showed very good cell viability (>95%) in the absence of doxorubicin after 48 h. These results were considered strong evidence of the feasibility of these hybrid materials as systems for the loading and release of bioactive compounds [53].

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