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Review

Biodegradable polymers: A promising solution for green energy devices

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ABSTRACT

With the rapid advancement of science and technology, there is an increasing focus on critical issues such as energy scarcity and environmental pollution caused by energy waste. To address these challenges, the exploration of biodegradable polymers and their application in the development of green energy devices has become a prominent research area. Biodegradable polymers, including starch, cellulose, silk fibroin, and polylactic acid, offer several advantages such as abundant sources, low production costs, biodegradability, and flexible design, making them highly promising for the fabrication of environmentally friendly energy devices. Notably, the utilization of biodegradable polymers in the production of piezoelectric and friction nanogenerators, supercapacitors, and other devices demonstrates their significant potential in mitigating issues associated with energy waste pollution and energy scarcity. This comprehensive review pemphasizes the merits of various biodegradable polymers and provides an overview of their current applications in the development of green energy devices. It also describes the basic structure and properties of both natural and synthetic biodegradable polymers. Furthermore, it addresses the challenges encountered during the development process and presents prospects for future advancements.

1. Introduction

In recent years, various energy devices such as nanogenerators and supercapacitors have gained considerable attention, and with technological advancements, the demand for these energy devices has increased significantly. Traditional energy devices are predominantly composed of non-biodegradable materials and metals, leading to severe environmental issues: the non-degradability of these energy devices upon disposal results in environmental pollution; furthermore, these devices often contribute to the wastage of valuable metal resources [1]. To mitigate the negative environmental impact and meet the diversified functional requirements of energy devices, recent studies have turned their focus towards utilizing biodegradable polymers for the fabrication of energy devices. Energy devices based on biodegradable polymers can fulfill the original performance requirements during usage, maintain stability throughout their lifespan, and undergo chemical structure changes within a short period under natural conditions after use, resulting in performance degradation. Eventually, they can be completely decomposed into CO_2 and H_2O by environmental microorganisms, thus reducing their harm to natural ecosystems [2]. Moreover, energy devices fabricated using biodegradable polymers can meet the demand for multifunctionality, serving roles in energy provisioning [3], human health monitoring [4,5] and smart wearables [6,7], and other domains [8–10] as shown in Fig. 1. In the field of smart wearables, most electronic devices rely on external power sources, limiting the flexibility of wearable devices and leading to additional power losses [11]. However, employing flexible biodegradable polymer-based energy devices can convert the energy generated by human body movements into electrical energy through material properties such as piezoelectricity, frictional power generation, and electrostatic induction, thereby providing energy for smart wearable devices [12] (Fig. 1).

Biodegradable polymers refer to a class of polymers that can be decomposed or degraded into CO_2 and H_2O by microorganisms or their secretions through enzymatic or chemical actions under certain natural conditions [13]. Biodegradable polymers can be classified into natural polymers and biocompatible synthetic polymers based on their sources,

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which can be regenerated into hydrogel, fiber, foam, film, tube, particle and other shapes (Fig. 1) [14]. Natural polymers primarily originate from renewable or biological resources such as animals, plants, marine organisms, and microorganisms, while synthetic polymers are chemically synthesized [15]. Natural polymers include polysaccharides such as starch, cellulose, chitosan, and its derivative chitosan, as well as protein-based polymers such as silk fibroin (SF), collagen, spider silk, and plant proteins. Biodegradable synthetic polymers typically contain ester, amide, or ether bonds and include polylactic acid (PLA), polycaprolactone (PCL), polyurethane (PU), polyethylene glycol (PEG), poly (lactic-co-glycolic acid) (PLGA), polybutylene succinate (PBS), and polyvinyl alcohol (PVA), among others [16]. Among these materials, the main polymers used for the fabrication of green energy devices are starch, cellulose, chitosan, chitin, silk fibroin, collagen, spider silk, soy protein from natural polymers, and PLA, PCL, PU, and PEG from synthetic polymers (Fig. 2). Most of the biodegradable polymers mentioned here are also bio-resourced, making them important for the sustainable society.

This review provides an overview of the structure, peculiarity of the representative natural and synthetic biocompatible polymers mentioned above, as well as their applications in green energy devices. In addition, the challenges encountered during their development are discussed, and future prospects are presented.

2. Biodegradable polymers

2.1. Natural polymers

Biodegradable natural polymers are commonly produced by organisms in nature and are environmentally friendly and renewable resources. The most common natural polymers are polysaccharides such as starch, cellulose, and chitin. Other important natural polymers include protein-based polymers such as silk fibroin, collagen, spider silk, and soy protein (Fig. 2) [17].

Starch is a semi-crystalline polymer composed of glucose molecules and its basic structural unit is α-D-glucose pyranose. Starch is a renewable raw material with low cost and abundant sources, typically extracted from the roots, stems, and seeds of potatoes, corn, wheat, rice, and other crops [18]. Starch is easily processable and can be prepared into films or gels. For example, after heating and stirring a starch solution in a water bath at 90 °C for 35 min, and then spreading it on dishes followed by drying in a forced-air convection oven at 35 °C for 24 h, the film is obtained [19]. Due to its inherent film-forming properties, starch films are often used as flexible and transparent substrates [17,18]. Conductive materials can be easily coated or printed onto starch films, making them suitable for manufacturing smart wearable devices [6,15], among other applications [6,17,19]. Starch hydrogels can also be processed into various shapes through injection or 3D printing, and further carbonized to form three-dimensional structured conductive materials

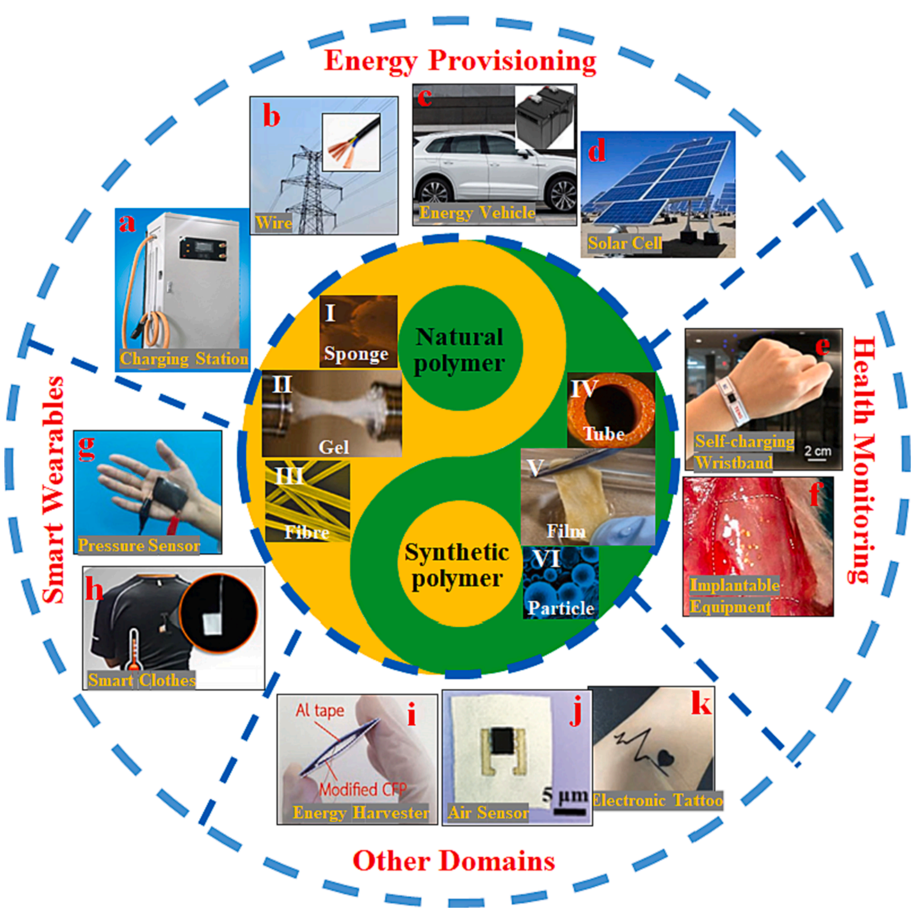

Fig. 1. Energy devices crafted from biodegradable polymers find broad applications in areas of energy provisioning (a-d), health monitoring (e-f), smart wearables (g-h), and other domains (i-k). These biopolymers can be regenerated into sponge (I), hydrogel (II), fibre (III), tube (IV), film (V), particles (VI), etc. (a) Reprinted with permission from reference [3]; Copyright (2020) Wiley-VCH. (e) Reprinted with permission from reference [4]; Copyright (2019) ACS. (f) Reprinted with permission from reference [5]; Copyright (2009) American Institute of Physics. (g) Reprinted with permission from reference [6]; Copyright (2022) ACS. (h) Reprinted with permission from reference [7]; Copyright (2019) Springer Nature. (i) Reprinted with permission from reference [8]; Copyright (2020) Wiley-VCH. (j) Reprinted with permission from reference [9]; Copyright (2020) Wiley-VCH. (k) Reprinted with permission from reference [10]; Copyright (2019) Wiley-VCH. (I), (II), (III), (IV), (V), (VI) Reprinted with permission from reference [14]; Copyright (2014) ACS.

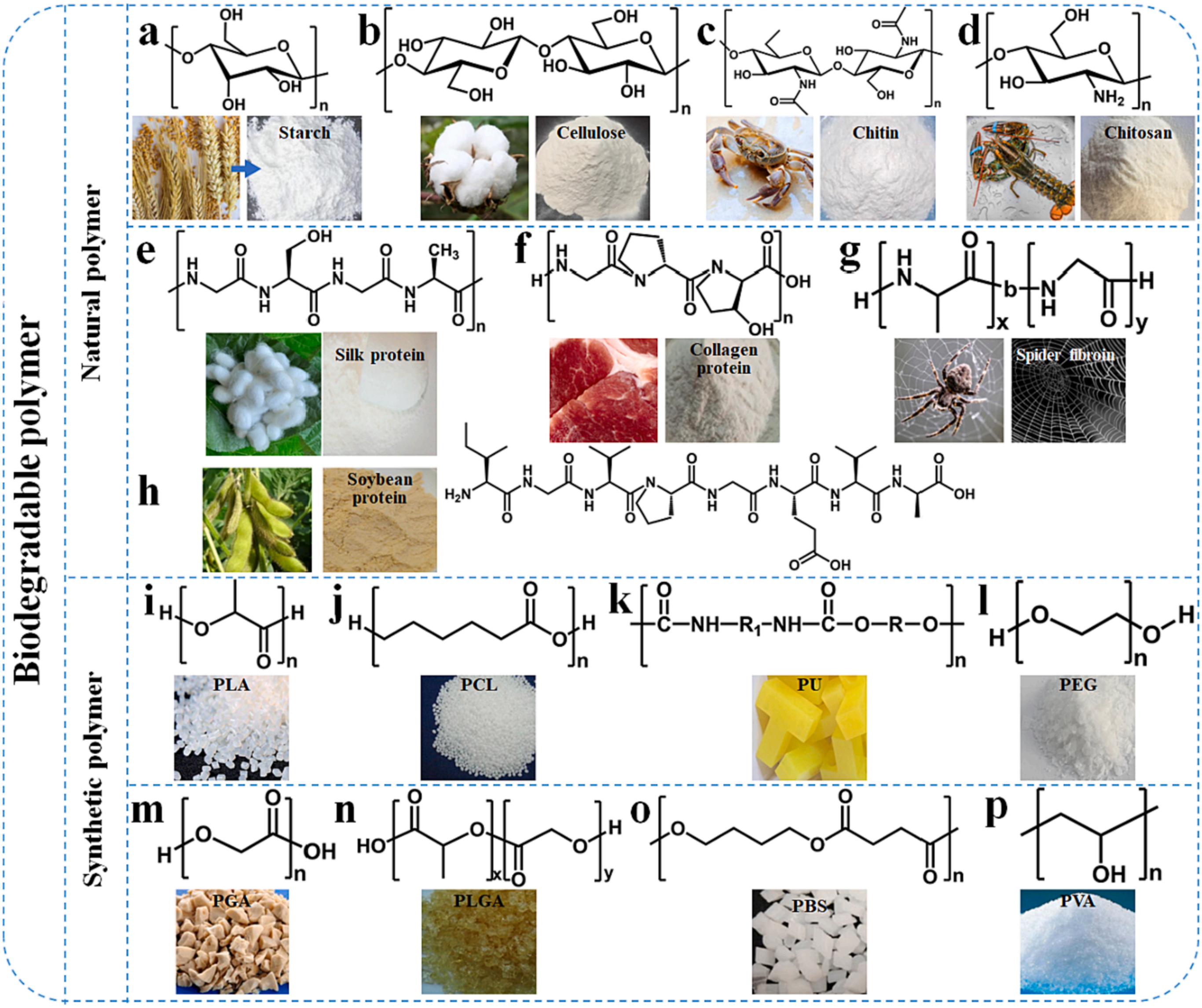

Fig. 2. Classification of biodegradable polymers, schematic representation of typical raw samples, and their molecular structures.

[19]. Additionally, starch exhibits excellent biodegradability and biocompatibility, making it widely applicable in various industrial purposes.

Cellulose is the most widely distributed and abundant polysaccharide in nature. It is composed of linear chains of glucose connected by β-1,4-glycosidic bonds, with each glucose residue rotating in the opposite direction [20]. Cellulose possesses renewable nature, high strength, stiffness, eco-friendliness, good biocompatibility, and low weight. It can also be chemically modified by substituting its hydroxyl groups with functional groups such as specific acids, chlorides, and oxides to introduce desired properties. Consequently, many cellulose derivatives, such as methyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, and carboxymethyl cellulose, have been developed [21]. Cellulose and some of its derivatives exhibit good biodegradability, which makes them suitable replacements for non-degradable polymers as dielectric materials in friction-based nanogenerators. Furthermore, due to the internal rotation of polar atomic groups associated with asymmetric carbon atoms, cellulose also possesses certain piezoelectric properties. However, pure cellulose exhibits relatively weak piezoelectric performance [22]. Therefore, the addition of some materials with good piezoelectric properties to the cellulose matrix can improve its piezoelectricity.

Chitin, also known as poly(N-acetylglucosamine), is a polymer formed by the interconnection of N-acetylglucosamine residues through 1,4-glycosidic linkages. It is the second most abundant polymer in nature after cellulose and is mainly found in arthropods (such as shrimps, crabs), mollusks, seaweed, and fungi [23]. Chitin exhibits excellent biodegradability and biocompatibility. Its molecular structure contains chemical functional groups, such as $-NH_2$, that contribute to its outstanding electron-donating properties. Chitin can be modified to make its surface positively charged, making it an ideal friction-positive polymer for the fabrication of triboelectric nanogenerators (TENGs) [24]. Chitin's structure is similar to cellulose, and due to its non-centrosymmetric crystalline structure, it also possesses certain piezoelectric properties [25]. The deacetylation product of chitin, called chitosan, is a cationic natural polymer and the only alkaline polysaccharide among natural polysaccharides [26]. It has a molecular structure and chemical properties similar to cellulose and chitin. Chitosan exhibits excellent biodegradability and biocompatibility, and the amino groups in chitosan molecules have higher reactivity, making it easier to undergo chemical modification reactions. Therefore, chitosan is considered a widely applicable functional biomaterial [27].

Proteins are polymers composed of α-amino acids arranged in a specific sequence and combined by one or more peptide chains to form a macromolecule [28]. Common proteins such as silkworm silk fibroin, collagen and spider silk have excellent biodegradability and biocompatibility, and can be easily processed into films. Proteins contain abundant electron donors, which can be used to fabricate the frictional layer of bio-triboelectric nanogenerators [29]. Additionally, proteins are natural piezoelectric materials. Their piezoelectric properties originate from the internal rotation of the dipole moment of the C(=O)NH groups associated with asymmetric carbon atoms and the formation of strong intermolecular C–H bonds between peptide chains [30].

Silkworm silk is a protein polymer with excellent mechanical properties, good biocompatibility, processability, and degradability [31]. Silk fibers are mainly composed of two central silk fibroin fibers and an outer layer of sericin. One silk fiber is composed of two core silk fibroin protein fibers, along with an outer adhesive glycoprotein coats (Fig. 3 (a)-(c)) [14]. The glue-like glycoproteins are known as sericins, which ensure the cohesion of the cocoon by sticking the twin filaments together. Sericin constitutes 25–30 % of the weight of the fiber (14), and can be removed by heat or alkaline treatments, resulting in more than 300 m of fibroin fiber from each cocoon [14]. Silk fibroin can be obtained through processes such as degumming and dissolution. Silk fibroin molecules are composed of highly repetitive amino acid sequences, mainly consisting of glycine (Gly), alanine (Ala), and serine (Ser), which account for approximately 85 % of the total amino acids [32]. Silk fibroin contains two crystalline forms: one is a monoclinic crystal system composed of helical structures and repeating β-turn structures (Silk I), and the other is an orthorhombic crystal system composed of β-sheet structures (Silk II) [33]. Due to the non-centrosymmetric crystalline structure of these two forms, silk fibroin exhibits certain piezoelectric properties, and the piezoelectric performance is related to the content or orientation of β-sheet structures [34]. Additionally, silk fibroin demonstrates strong electron-donating tendencies and can be used as the positive frictional material in triboelectric nanogenerators (TENGs). TENGs based on silk fibroin show excellent biocompatibility, enabling direct contact or implantation into human skin [35]. Furthermore, the multifunctionality of silk fibroin has demonstrated unique advantages in addressing the energy supply and multifunctional integration of flexible electronic devices [35]. Spider silk protein is another natural protein biomaterial primarily composed of glycine, alanine, and a small amount of serine. The Major Ampullate (MA) spider silk fibers (of ca. 250–350 kDa) have a diameter between 1 and 20 μm, and are comprised of four different layers: the core of major ampullate spidroin, the skin of minor ampullate like protein, a lipid coat and a glycoprotein coat (Figure 3(d)-(f)) [14]. Multiple secondary structures, including β-sheet structures composed of alanine and α-helices rich in proline, are tightly packed together, forming a semi-crystalline molecular spring-like structure that greatly enhances the elasticity and strength of spider silk protein [36]. Furthermore, spider silk protein not only possesses unique mechanical properties but also exhibits good biocompatibility. It can undergo degradation under certain acidic conditions or ultraviolet irradiation, and the degradation products are harmless to the human body and can be absorbed by the body [37]. Due to the lack of a centrally symmetric crystal structure, spider silk protein exhibits certain piezoelectric properties, which refer to the ability to convert mechanical energy into electrical energy. Therefore, spider silk can be used as a piezoelectric material for the preparation of piezoelectric nanogenerators [38].

Collagen is the main component of animal connective tissue and the most abundant and widely distributed functional protein in all animals, accounting for 25 ~ 30 % of the total protein content, and in some organisms, even exceeding 80 % [39]. Collagen is a fibrous protein composed of three peptide chains twisted into a helical structure, with the basic structural unit being tropocollagen. The amino acids in tropocollagen peptides are arranged in a regular pattern, typically as a Gly-Pro-Y repeat sequence, where Gly represents glycine, Pro represents proline, and Y represents hydroxyproline (Hypro) or hydroxylysine (Hylys) [40]. Collagen exhibits good biocompatibility, biodegradability, and bioactivity. Additionally, collagen has certain piezoelectric properties, which may be a result of the hydrogen bonding between collagen

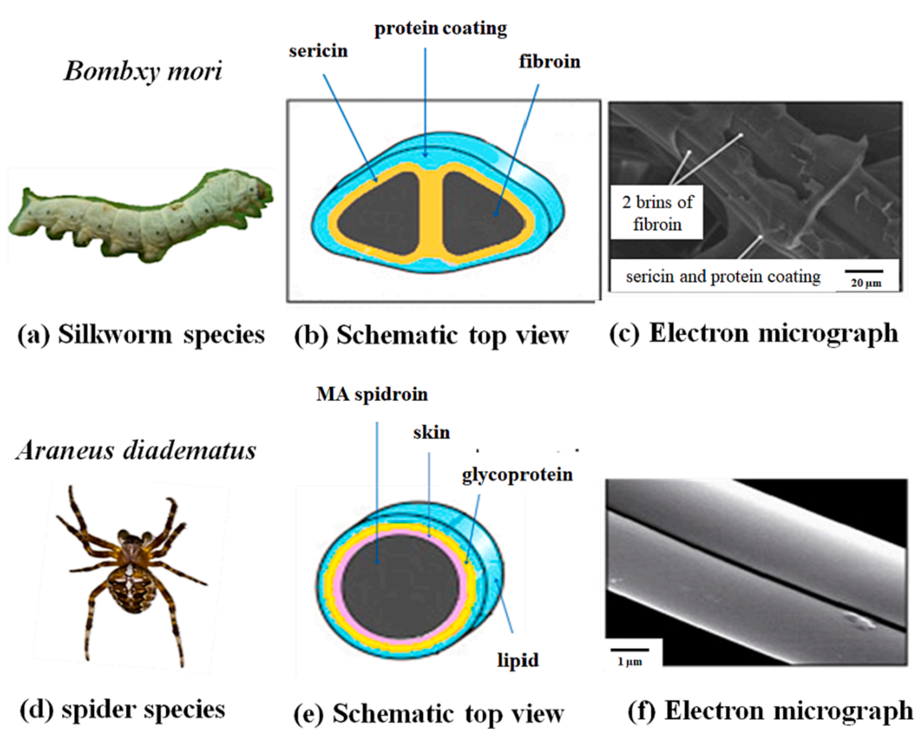

Fig. 3. a) A Bombyx mori silkworm, b) schematic illustration of the composite structure of a cocoon fiber, in which the two fibroin fibers are coated with sericins and other proteins to protect the cocoon against microbes and predators, and c) scanning electron micrograph of a single B. mori silkworm cocoon fiber, d) an Araneus diadematus spider, e) schematic illustration of the composite structure of a major ampullate (MA) fiber, and f)scanning electron micrograph of major ampullate fibers. (Reproduced with permission from Reference 14. Copyright (2014) ACS.)

chains, generating a uniaxial orientation of molecular dipoles. The highly ordered arrangement of α-helices and their inherent polarization contribute to the piezoelectricity of collagen [41]. Moreover, the diversity of collagen types provides more options for the development of collagen-based piezoelectric devices.

Common grains, legumes, nuts, and other sources contain abundant proteins, including soy protein, corn protein, etc. Compared to synthetic polymer materials, these plant proteins not only serve as natural polymer materials but also have low cost and widespread availability. Plant proteins have attracted significant attention in various fields due to their good biodegradability, processability, and mechanical properties [42]. For instance, soy protein (SP) is the only plant-based complete protein, containing 18 amino acids, with glutamic acid being the highest in content, followed by aspartic acid, arginine, leucine, and lysine. SP has abundant charge-supplying functional groups. When used as the positive frictional layer in triboelectric nanogenerators (TENGs), it can enhance the electrical output potential of TENGs [43]. Its isolate, soy protein isolate (SPI), is a sustainable, biodegradable, and biocompatible natural polymer material. However, the mechanical properties of SPI are generally poor, which limits its application in smart wearable devices and energy devices. Therefore, the mechanical properties and conductivity of SPI composites can be enhanced by embedding inorganic/organic conductive nanofillers into SPI substrates, leading to the development of soy protein-based electronic products with good toughness and strength [44].

2.2. Biodegradable synthetic polymers

Apart from natural polymers, most polymers are designed and synthesized in laboratories. These synthetic polymers can offer greater versatility in terms of functionality, such as improved processability, excellent mechanical properties, and electrical performance. Through this approach, various polymers such as polylactic acid (PLA), polycaprolactone (PCL), polyurethane (PU), and polyethylene glycol (PEG) have been widely applied in different fields such as aerospace, electronics, sensors, actuators, as well as tissue and biomedical engineering (Fig. 2) [45].

Polylactic acid (PLA) is a product of α-hydroxy acid condensation and is a thermoplastic polyester made from renewable plant resources such as wheat and corn starch. It belongs to the family of aliphatic polyesters. Lactic acid monomers exist in two optical isomeric configurations, L-lactic acid and D-lactic acid [46]. PLA possesses many properties required by industries, such as good biodegradability and biocompatibility, low production cost, flexibility, and versatility. Most of these properties can be adjusted and modified under different processing conditions. As a result, PLA is often used in fields such as implantable devices, disposable biodegradable plastics, and biodegradable medical tools [47]. Additionally, PLA is considered one of the most promising polymers to replace traditional piezoelectric materials. The piezoelectricity of PLA arises from the internal rotation of polar atomic groups associated with asymmetric carbon atoms in its structure. Research indicates that the piezoelectric constant of PLA is directly proportional to the crystallinity and molecular chain orientation of the polymer [48].

Polycaprolactone (PCL) can be prepared by ring-opening polymerization of β-caprolactone using various anionic, cationic, and coordination catalysts. It can also be synthesized through the free-radical ring-opening polymerization of 2-methyl-3-dioxolane. PCL is a thermoplastic crystalline polyester [49]. PCL dissolves well in aromatic compounds, ketones, and polar solvents. It also exhibits good biocompatibility, making it suitable as a material for cell growth support. It has excellent compatibility with various conventional materials and exhibits good biodegradability, with complete degradation occurring in natural environments within approximately 6–12 months [50]. Furthermore, due to the presence of five nonpolar methylene units and one polar ester group in its repeating unit, PCL possesses good flexibility and processability. Products made from PCL exhibit excellent shape memory and thermal control properties, making it widely used in drug delivery systems, novel self-healing nanogenerators, and biodegradable materials [51]. Polyurethane (PU) is a special type of polymer material typically prepared by the reaction of different isocyanates and polyols in the presence of a chain extender. Therefore, PU can be tailored for specific applications by using different raw materials and production processes [52]. For example, polyurethane was successfully synthesized by reacting 1,6-hexamethylene diisocyanate with ethylene glycol in dimethyl sulfoxide at room temperature using the positive polymerization method [52]. PU contains various functional groups such as alcohol, ether, ester, urea, and some aromatic compounds, allowing for the enhancement of the properties and performance of PU-based materials through reactions with these functional groups. PU also exhibits a wide range of physical and chemical properties, including good strength, excellent biocompatibility, biodegradability, and synthetic versatility, meeting the diverse demands of modern society [53]. Additionally, PU demonstrates outstanding adhesion, aging resistance, abrasion resistance, electrical performance, and industrial weatherability to various substances, making it widely applied in fields such as medicine, plastics, construction, and transportation [54].

Polyethylene glycol (PEG) is an amphiphilic polymer composed of repeating ethylene oxide subunits. It can be synthesized by stepwise addition polymerization of ethylene oxide with water or ethylene glycol, and its end groups contain two hydroxyl groups that can be chemically activated [55]. PEG exists in various molecular weights, and its properties differ depending on the average molecular weight. The degradation performance of PEG is also correlated with its average molecular weight, with higher molecular weight resulting in slightly lower degradation performance [56]. PEG is non-toxic, has good water solubility, and exhibits compatibility with many organic components, making it widely used as a precipitant and extraction solvent in industries such as medicine, textiles, plastics, and food processing. Moreover, PEG is a multifunctional phase change material (PCM) with high latent heat, and its molecular weight can be controlled. By mixing PEG with different molecular weights in specific proportions, the thermal performance parameters can be adjusted, enabling its application in thermal energy storage devices under different conditions [57]. Table 1 lists the examples of morphologies, properties, and material source for various biodegradable polymers used for green energy devices.

Natural polymers, while having structural stability akin to synthetic polymers, offer superior biocompatibility and bioactivity. This helps mitigate toxicity and host immune response-related issues in biomaterials, enhancing their safety. However, biological materials derived from polysaccharides and proteins have their own drawbacks, including variability in material properties based on different sources, risk of microbial contamination, and weakened mechanical strength after regeneration. Some synthetic degradable materials such as PLA, the flexibility of a single component is poor and the impact strength is low due to its high molecular polarity and strong intermolecular force [47]. Consequently, to enhance their various properties, blending and copolymerization with different materials are commonly employed in most cases [18,19,27,33].

3. Applications in energy devices

Energy devices made from biodegradable polymers possess excellent biodegradability, biocompatibility, flexibility, environmental friendliness, and processability, playing a significant role in fields such as smart wearable devices and clinical medicine [58]. The following discussion will focus on piezoelectric nanogenerators, triboelectric nanogenerators, and supercapacitors.

3.1. Piezoelectric nanogenerators

Piezoelectricity is generated by the displacement of ions and atoms

Table 1
Characteristics of biodegradable polymer materials utilized for green energy devices.

Source	Material	Morphologies	Properties	References
Natural polymers	Starch	Film, Fibre, Gel	Processability, Frictional power generation	[19]
	Cellulose	Film, Fibre, Gel	Renewability, High strength, Frictional power generation	[20,21]
	Chitin	Film, Gel	Electronicity, Environmental stability	[24,26,27]
	Silk fibroin (SF)	Film, Fibre Gel	Electronegativity, Piezoelectricity	[31,34,35]
	Collagen	Film	Biological activity, Piezoelectricity	[41]
	Spider fibroin	Fibre	Strength, Excellent elasticity, Mechanical properties	[36,37,38]
	Soybean protein	Film	Processability, Electronegativity	[42,43,44]
Synthetic Polymers	PLA	Film	Flexibility, Modification, Piezoelectricity	[47,48]
	PCL	Film	Material compatibility, Shape memory, Flexibility	[50,51]
	PU	Film	High strength, Synthetic versatility, Electrical	[53,54]
	PEG	Sheets, Liquid	Organic solubility, Water solubility, High latent heat	[56,57]

in non-centrosymmetric unit cells of materials. Piezoelectric materials can generate voltage between their two surface faces by undergoing slight deformation due to compression or shear forces [59]. For instance, in piezoelectric nanogenerators (PENGs), which consist of a piezoelectric layer and two conductive layers, mechanical deformation occurs in the piezoelectric layer when subjected to external force. This deformation leads to the generation of piezoelectric polarization charges on the opposite surfaces. The density of these polarization charges can increase as the external force on the PENG increases. A current is then formed when electrons flow through an external circuit between the electrodes [59,60]. Although piezoelectric ceramics or semiconductors such as lead zirconate titanate and zinc oxide exhibit good piezoelectric performance, their mechanical brittleness and rigidity limit their applications in smart wearable devices [60]. Therefore, piezoelectric nanogenerators (PENGs) can be prepared using flexible and biodegradable piezoelectric polymers, which can harvest mechanical energy from human motion and provide power for smart wearable devices [12].

The piezoelectric properties of cellulose are caused by the internal rotation of polar groups associated with asymmetric carbon atoms. However, cellulose exhibits weak piezoelectric performance, so it needs to be combined with materials that have good piezoelectric properties to improve its piezoelectricity. Alam et al. [61] prepared a flexible hybrid piezoelectric generator (HPG) based on native cellulose nanofibrils (NCMF) and polydimethylsiloxane (PDMS). This NCMF-based HPG exhibited an open-circuit output voltage of approximately 30 V and a short-circuit output current of around 500nA when pressed by hand, corresponding to a power density of approximately 9.0 $\mu W/cm^3$. It can power multiple LEDs or smart wearable devices. Furthermore, the device is non-toxic, exhibits biocompatibility, and can be implanted in the human body to generate electricity from activities like heartbeats. This method does not require any chemical treatment of cellulose; it only necessitates mechanical stirring. Another approach for creating PENGs involves incorporating piezoelectric materials, which have high piezoelectric coefficients and excellent mechanical properties, into cellulose. Wu et al. [62] prepared a biocomposite piezoelectric thin film by the water dispersion method, using 2,2,6,6-tetramethylpiperidine-1-oxyl-oxidized cellulose nanofibers (TOCNs) and molybdenum disulfide (MoS_2) nanosheets. A brick-and-mortar structure can be formed by intercalating one-dimensional cellulose nanofibrils between the layers of MoS_2 nanosheets. This is possible because the high aspect ratio of TOCNs (templated organic carbon nanomaterials) allows for the easy formation of a three-dimensional network, facilitating the dispersion of MoS_2 nanosheets. Such a regular layered structure can significantly enhance the mechanical properties. This nanocomposite film exhibited excellent mechanical properties, and when the MoS_2 content was 4 wt%, the longitudinal piezoelectric constant (d_{33}) of the composite film reached a maximum value of 31 pC/N, which was much higher than that of pure TOCN film and other reported cellulose-based piezoelectric films. Moreover, the piezoelectric nanogenerator fabricated from this composite film achieved a maximum output voltage of 4.1 V and a short-circuit current of 0.21μA. Humans typically move at low frequencies of less than 2 Hertz. Addressing this, Yan et al. [63] enhanced the piezoelectric properties of cellulose by incorporating Ti_3C_2Tx (MXene) into cellulose nanofibers (CNFs), thereby preparing a high-performance flexible PENG. They posited that the improvement in piezoelectric performance was due to the numerous hydrogen bonds between CNFs and MXene nanosheets, which caused the CNFs to align parallel to the MXene layers, forming stacked structures. Additionally, the cellulose chains in the amorphous regions might preferentially adhere to MXene nanosheets in a parallel orientation. This alignment could better organize the dipole moment vector of the cellulose, potentially inducing local polarization by adjusting the orientation of the CNFs and rearranging the conformation of the amorphous cellulose chains. Consequently, this method significantly improves the piezoelectric properties of cellulose, offering an alternative to conventional, energy-intensive methods like electrical poling. Under low-frequency stimulation, the open circuit voltage and current of CNF/MXene PENG containing 10 wt % MXene were 30.8 V and 0.49μA. Its excellent performance in the low-frequency range made it a promising candidate product for human motion energy collection. However, repeated bending may lead to cracking of the surface metal electrode in PENGs. Therefore, research into safe and flexible electrodes is recommended.

Silk fibroin possesses piezoelectricity due to its non-centrosymmetric crystal structure, and silk-based piezoelectric nanogenerators have long been widely used in smart wearable devices. In 1956, Fukada [64] first measured the piezoelectric constant of silk to be approximately 1 pC/N, close to the piezoelectric constant of quartz crystal, which is 2 pC/N. Vitor et al. [65] prepared silk fibroin fiber membranes using electrospinning and exposed them to gaseous methanol to maintain the stability of the silk fibroin membranes in water. The piezoelectric activity of silk fibroin was evaluated using piezo-response force microscopy (PFM). They found that the methanol-treated silk fibroin membranes exhibited higher apparent piezoelectric coefficients and demonstrated good electrical activity. Macroscopic evaluation of the piezoelectric properties showed that the nanoscale energy harvester could generate voltages as high as 8 V in an open circuit. Additionally, it exhibited a power density of 5 $\mu W/cm^2$, excellent dynamic pressure sensitivity of 0.15 V/kPa, and a relatively high energy conversion efficiency of approximately 21 %. These properties make it suitable for powering low-power smart wearable devices. Powering implantable devices without batteries presents a significant challenge. Nanogenerators need to convert mechanical energy from human movements, such as heartbeat or muscle stretching, into electricity. Additionally, they should be able to dissolve harmlessly when no longer needed. Kim et al. [66] demonstrated a biodegradable composite nano-generator film based on silk fibroin through electrodeposition fabrication, whose lifespan could be controlled by varying the concentration of glycerol. This research suggests that implantable electronic devices with controllable degradation hold great potential for future development. Lisa et al. [67] prepared a piezoelectric ultrathin silk-based flexible nano-generator using electrodeposition. This silk-based nano-generator could generate a maximum open circuit voltage of 1.02 V and a short circuit current of 0.8 mA under bending conditions. It also exhibited good stability and reliability in terms of electrical output. The process was simple, safe, robust, repeatable and cost-effective. Collagen possesses certain piezoelectric properties due to its unique triple helical structure, as shown in Fig. 4c. Fig. 4b represents a single chain of collagen, with each chain consisting of a GXY repeat sequence (Fig. 4a), including glycine (G), proline (P), and various other amino acids (Y) [68]. Other researcher [68] created a piezoelectric nano-generator based on collagen membranes (Fig. 4e, 4f). By employing a polypropylene lamination process, they attached aluminum electrodes to both the top and bottom surfaces of the collagen membrane. This design allows for its implantation in shoes, harnessing energy generated from human movement (Fig. 4g) [69]. Fish waste is a good source of collagen with piezoelectric properties. Ghosh et al. [70] extracted collagen from fish processing waste to manufacture a bio-piezoelectric nano-generator (BPNG). The BPNG was able to generate an open circuit voltage of 10 V and a short circuit current of 51nA under a normal stress of 1.4 MPa. It also exhibited a power density of 4.15 μW/cm^2 and an inherent high piezoelectric energy conversion efficiency of approximately 0.3 %. This makes it suitable for applications in the biomimetic functional devices field, such as bionic electronic skin units for detecting breathing, heartbeat, blood circulation, and other life activities. Ramalingame et al. [71] extracted collagen from fish scales and incorporated it into a biocompatible polydimethylsiloxane polymer, developing a flexible and biocompatible piezoelectric nano-generator. It provided an output voltage of 8 V and a short circuit current of 136 mA under a compression stress of 30 Hz, with a corresponding maximum output power density of 649 mW/cm^2. This biocompatible piezoelectric nano-generator is well-suited for harvesting energy from human motion. These two studies demonstrated that waste from fish processing can be recycled more efficiently to prepare PENGs with excellent biocompatibility. Such PENGs could be utilized in human implants, including pacemakers and artificial eyes. The structure of silk fibroin is semi-crystalline, resembling a molecular spring, and it possesses excellent mechanical properties and biocompatibility. Due to its lack of a centrally symmetric crystal structure, silk fibroin exhibits piezoelectricity. These properties make silk fibroin highly promising for applications in piezoelectric nano-generators. Pan et al. [72] confirmed the piezoelectric effect of spider silk by using energy harvesters made from spider silk and measuring their voltage and current outputs. Karan et al. [73] designed a mechanically robust piezoelectric nano-generator (PENG) using spider silk, which demonstrated high energy conversion efficiency (~66 %), high output voltage (~21.3 V) and current (~0.68μA), and an instantaneous power density of approximately 4.56 μW/cm^2. It also exhibited high sensitivity to physiological signals such as arterial pulse response, making it suitable for potential biomedical applications.

Poly(lactic acid) (PLA) possesses excellent biocompatibility, biodegradability, and processability, showing significant potential for green energy devices. The piezoelectric properties of PLA are related to the crystallinity and molecular chain orientation of the polymer. For raw polylactic acid, the absence of piezoelectricity is due to the random distribution of the C = O dipole direction. However, when the dipoles are aligned perpendicular to the molecular chains through the application of external tension or an electric field, polylactic acid can exhibit piezoelectricity [48,74]. Techniques such as melt spinning and electrospinning can be employed to stretch or apply electric field polarization to PLA during the preparation of piezoelectric PLA materials, thereby enhancing their piezoelectric performance [74]. Ma et al. [75] polarized PLA through hot pressing and corona charging, developing a flexible and green disposable sensor based on piezoelectric PLA films. The sensor exhibited notable sensitivity to longitudinal compression and transverse stretching, a pressure range of 0.03–62 kPa, robust mechanical durability exceeding 1.08 million cycles, and the potential for large-scale production. Gong et al. [76] prepared a biocompatible hybrid nano-

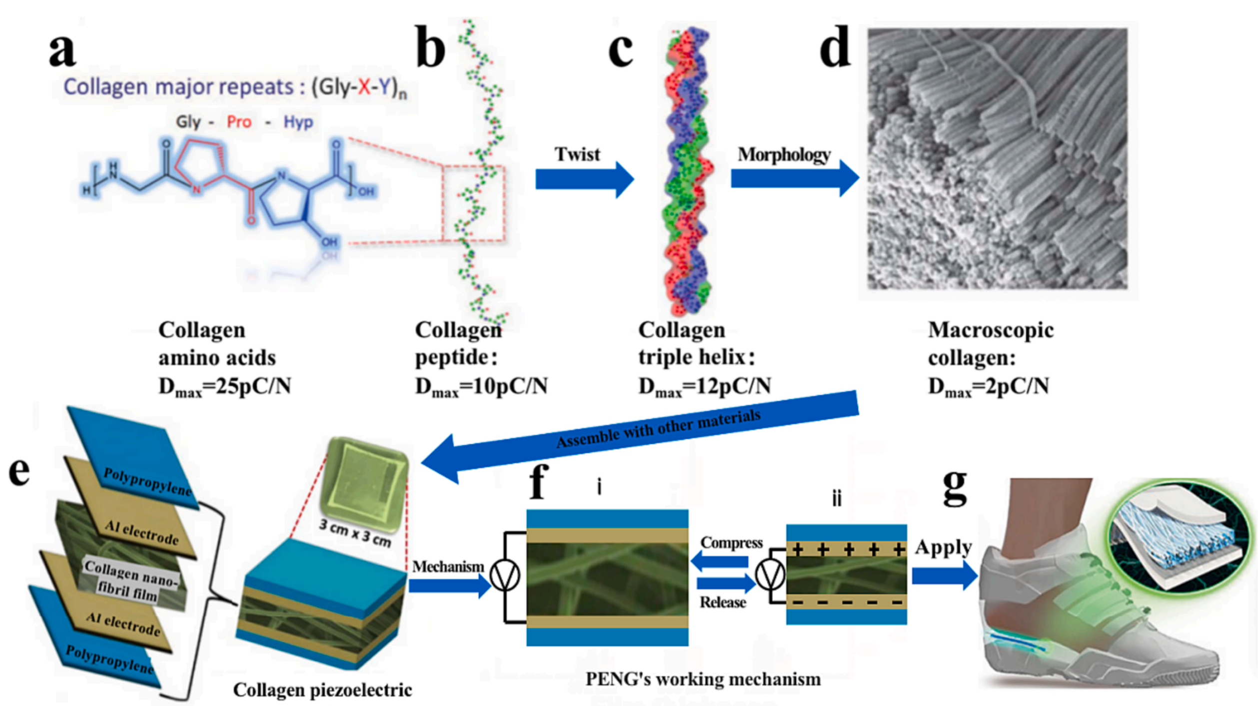

Fig. 4. (a) Amino acid composition of collagen: Glycine (G), Proline (P), and Y usually represents Hydroxyproline (H). (b) Single peptide chain of collagen. (c) Triple helical structure formed by three peptide chains of collagen. (d) Macroscopic morphology of collagen. (e) Layer-by-layer schematic diagram of collagen piezoelectric nanogenerator. (f) Working mechanism of collagen piezoelectric nanogenerator. (g) Schematic of a piezoelectric nanogenerator inserted into a shoe. (a), (b), (c), (d), (e), (f) Reprinted with permission from reference [68]; Copyright (2018) ACS. (g) Reprinted with permission from reference [69]; Copyright (2016) Elsevier.

generator based on stretched PLLA films by incorporating treatments such as film stretching. Under compressive recovery conditions, this nano-generator achieved an output power density of 7 W/m^2 with a resistance of 6MΩ, and its maximum power density reached 65.3 mW/m^2 under bending conditions. Furthermore, this PLLA film-based electronic skin device generated an output signal of 35 V and 1μA during elbow bending tests. Zhao et al. [77] successfully manufactured high-performance piezoelectric nanogenerator (PENG) using $BaTiO_3$ (BT) and polylactic acid (PLA) through a rotating coating process. When the BT content got 6 %, the maximum output voltage of this PENG was reached to 11.97 V, and the short-circuit current to 560nA, which could power small electronic devices. And this generator could a maintain stable output for 2000 cycles, demonstrating its applicability, reliability and durability. In addition, the organic components of the generator could be completely degraded in diluted alkaline solution, thereby achieving harmless treatment of waste PENG. Overall, these PLA-based PENG devices offer great promise for future applications in self-powered electronic devices and electronic skins (e-skins).

3.2. Friction-based nano-generators

Friction-based nano-generators (TENGs) operate differently from piezoelectric nano-generators (PENGs). TENGs utilize the principles of triboelectric charging and electrostatic induction. During the contact-separation process between two objects with different frictional polarities, the charges generated by friction are promptly transferred to an external circuit, converting mechanical energy into electrical energy [78]. And a greater ability to gain and lose electrons between the two materials can lead to higher output performance in the TENG [78]. Starch, with its high content of amorphous regions in thin film form and abundant –OH groups, can serve as a suitable matrix for dissolving cations and ions, thereby enhancing the performance of TENGs. Ccorahua et al. [79] prepared a starch-based electrolyte composite by incorporating starch polymer with the cationic salt $CaCl_2$, resulting in a TENG (Fig. 5a, 5b) with good stability and reliability. This composite film improved the frictional electrical performance of TENGs, with a voltage output of up to 1.2 V for the 0.5 % $CaCl_2$ concentration in starch films, three times higher than that of pure starch polymer (0.4 V) (Fig. 5c). The final device can be harnessed to power sensors in smart clothing, facilitating continuous data collection and real-time monitoring (Fig. 5d) [9]. To improve the hydrophobic properties of starch, Khandelwal et al. [80] enhanced the hydrophobicity of starch by introducing an edible Laver filler, creating a biodegradable TENG. Results demonstrated that a 1 wt% starch/laver (SL) composite material achieved a contact angle of 107°, indicating improved hydrophobicity. Moreover, the increased surface potential led to an increase in the TENG's voltage output. Additionally, this SL-TENG could harvest mechanical energy from human motion, providing power to low-power smart wearable devices.

Due to its excellent biocompatibility, mechanical properties, and potential for chemical modification and reconstruction, cellulose is often used as a substrate or friction material for constructing friction-based nano-generators [81]. Luo et al. [82] converted natural wood into flexible wood through hydrolysis and hot-pressing, developing a flexible and durable high-performance wood-based TENG (W-TENG). This W-TENG achieved a charge transfer density of 36μC/m^2, which is over 70 % higher than that of TENGs based on natural wood. Additionally, the W-TENG exhibited high strength, lightweight (0.19 g), thin thickness (0.15 mm), and cost efficiency. Zhang et al. [83] demonstrated a new method for synthesizing cellulose-based aerogels, which were used to

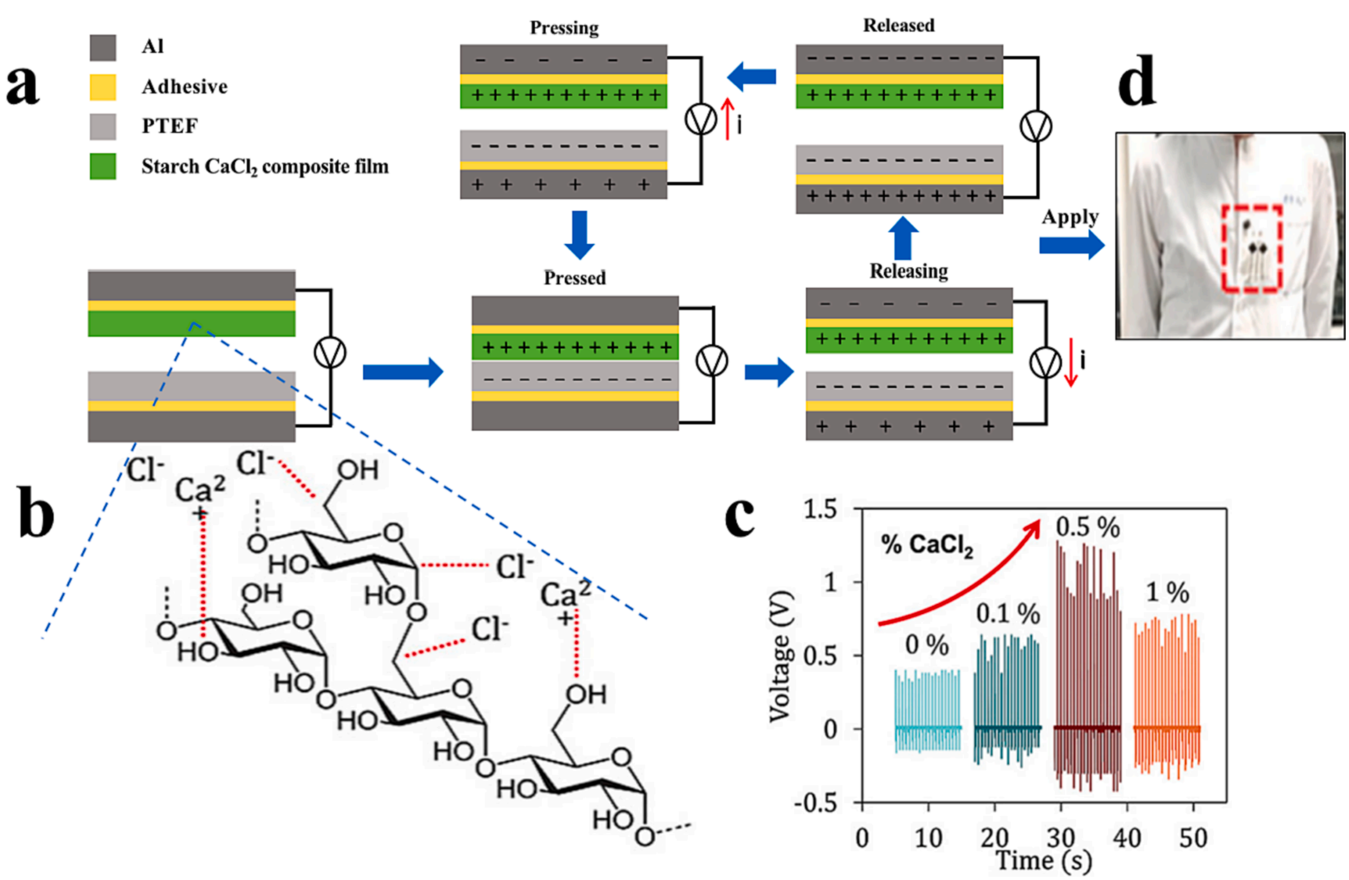

Fig. 5. (a) Working mechanism of starch-based TENG (triboelectric nanogenerator). (b) Illustration of the salt-starch interaction in starch electrolyte membrane. (c) Influence of $CaCl_2$ salt concentration on the voltage output of starch-based TENG. (d) Intelligent clothing equipped with friction nanogenerator. (a), (b), (c) Reprinted with permission from reference [79]; Copyright (2019) Elsevier. (d) Reprinted with permission from reference [9]; Copyright (2020) Wiley-VCH.

fabricate TENGs that can serve as mechanical energy harvesters and self-powered sensors. Normally, when TENG material is compressed, it can induce charge transfer at the contact surface of the network. When the force is released, the gap between the layers widens, separating the friction charges of opposite polarity and resulting in an increase in electric potential. This potential can drive the induced electrons from the bottom electrode to the top electrode. Periodic mechanical loading and unloading processes cause electrons to flow back and forth in the external circuit. The TENGs prepared using cellulose II aerogels exhibited excellent mechanical responsiveness and high electrical output performance. These TENGs could be used to light up LEDs, charge capacitors, power calculators, and monitor human motion, among other applications. Lin et al. [84] prepared a PEO/cellulose composite paper (PEO/CCP) by mixing polyethylene oxide (PEO) with cellulose fibers. This composite paper demonstrated high frictional electronegativity and charge density, leading to outstanding output performance when used in a TENG based on PEO/CCP. Its maximum voltage, current, and power density reached values of 222.1 V, 4.3μA, and 217.3 mW/m^2, respectively. Moreover, the peak voltage, current, and power density of this TENG can be modulated by varying the content of amino groups. Compared to the conventional dense films, the aerogel structure can improve the properties of the TENG by reducing its effective thickness, improving surface roughness, and utilizing a multi-pore structure [83,85]. Chen et al. [85] fabricated a friction nanogenerator using bacterial cellulose (BC) and hydroxyethyl cellulose (HEC) aerogel through an environmentally friendly liquid nitrogen freeze-drying method, resulting in a stable three-dimensional network structure. This design offers biocompatibility, cost-effectiveness, and impressive output performance. Even after 6,000 test cycles at a 5 Hz frequency, the TENG sustains an output voltage close to 25 V, showcasing its reliable output stability. It can convert mechanical energy from knocking and tapping into electrical energy to illuminate a commercial light-emitting diode (LED). These nano-generators have the potential to assist hearing-impaired individuals in promptly detecting knocks at the door, demonstrating their significant potential in intelligent bionic functional devices.

Amino groups in chitosan possess excellent electron-donating capabilities, which can be modified to impart a positive charge to the chitosan surface, making it an ideal friction-positive polymer for the fabrication of TENGs. The chitosan derivative, chitin, contains numerous free hydroxyl and carboxyl groups along its molecular chain, facilitating hydrogen bonding. Chitin can be directly used as a friction layer or combined with other materials to further enhance the performance of biocompatible TENGs. Zhang et al. [86] used a non-freezing dissolution method to produce flexible and transparent chitin films, which were used as the tribo-positive material to assemble TENGs. TENGs with chitin films as the friction-positive layer achieved high electrical performance, with an instantaneous power density of 1.25 W/m^2, surpassing most nanogenerators based on biodegradable materials. This new non-freezing method of dissolving chitin not only saved energy but also reduced equipment requirements for dissolution, contributing to sustainability and potential for industrial mass production. Although chitosan-based TENG smart wearable devices and biomedical electronics have begun initial applications, the influence of the external environment remains a significant challenge for their use [86]. Jao et al. [87] developed a chitosan-based friction-based nano-generator (C-TENG) that exhibited wearability, shape adaptability, and environmental stability. The output characteristics of the C-TENG remained stable under various humidity conditions. Furthermore, this C-TENG could be further applied in smart clothing and healthcare sensors for humidity, sweat, and gait phase detection. Gao et al. [88] developed a friction electric nanogenerator using a chitosan-poly(vinyl alcohol) (CS-PVA) nanofiber membrane for creating antimicrobial e-skin by electrospinning technology, which had a larger surface area due to its microporous and nano-porous structure. With its enlarged surface area, this nanogenerator can achieve a maximum open circuit voltage of 115 V and a power density of 37.5 mW/m^2. It is capable of monitoring joint movements and physiological signals. Additionally, it can be integrated inside a mask to autonomously monitor human respiration. Ren et al. [89] crafted a triboelectric nanogenerator using chitosan cotton paper (CCP-TENG). By incorporating cotton fibers into chitosan films, they enhanced its triboelectric properties. This generator can produce an open circuit voltage of 162 V, a short circuit current of 7.2μA, and a peak output power density of 322.56 mW/m^2. It holds potential for harvesting biomechanical energy and tracking human movement. It is commendable that this chitin or chitosan based TENG preparation processes are simple and safe. These materials can be quickly and easily degraded after the completion of their work cycle, without polluting the environment. The electronic sensors and electronic skins prepared using these materials exhibit excellent biocompatibility and comfort. However, further optimization and improvement are needed to enhance their response to environmental temperature and humidity changes, pollutant attachment, and overall safety.

Silk fibroin protein, as a novel material for triboelectric nanogenerators (TENGs), exhibits excellent electron-donating capabilities. Wen et al. [90] developed a printed silk fibroin-based triboelectric nanogenerator (PS-TENG) that selectively absorbs liquid water molecules, distinguishing the existing state of water molecules in the air. Moreover, it can harness the energy generated by human motion, achieving a high power density of up to 412 μW/cm^2, which can support most smart wearable electronic devices. Gogurla et al. [91] utilized nanostructured silk fibroin and silver nanowires (AgNWs) to fabricate efficient, flexible, transparent, and skin/textile-compatible TENGs and strain sensors. The strain sensor exhibited a remarkably high strain coefficient and could reliably detect joint bending and straightening. The TENG generated a considerable power density of 2 mW/cm^2, capable of powering light-emitting diodes. The strain sensor and TENG were integrated on a single chip, connected to the skin and fabric, enabling simultaneous monitoring of strain and mechanical energy harvesting. Candido et al. [92] developed a flexible, green, and low-cost TENG by incorporating silk fibroin into a polyvinyl alcohol film. This TENG exhibits high transparency, robust mechanical properties, and flexibility. It can achieve a maximum output voltage, short-circuit current, and power density of 172 V, 8.5μA, and 1.304 W/m^2, respectively. These characteristics make it suitable for integration into self-powered sensors for use in bionic prosthetic devices and haptic sensing systems. Furthermore, it's capable of powering electronic calculators and multiple LED lamps. Tan et al. [93] crafted a high-performance friction nanogenerator using silk fibroin (SF) and MXene. The introduction of MXene into SF increases the specific surface area of the aerogel, enhancing the output performance of the TENG. At an SF:MXene ratio of 1:1, the nanogenerator attains a peak open circuit voltage of 545 V and a maximum short circuit current of 16.13μA.

Plant proteins possess excellent triboelectric properties and are often recycled to form the triboelectric layer. For instance, soy protein (SP) is a friction-positive material. Bo et al. [94] doped soy protein with $CaCl_2$ to prepare a friction layer film with enhanced friction positivity and stretchability. TENGs based on this friction layer film exhibited an open-circuit voltage of 130 V, a short-circuit current of 4.4μA, and an instantaneous power density of 1125 mW/m^2, capable of powering 28 LEDs and continuously charging capacitors. Furthermore, even after one year of storage, the device maintained its electrical output integrity. Jiang et al. [95] used five representative plant proteins, including rice protein (RP), peanut protein isolate (PPI), soy protein isolate (SPI), wheat gluten (WG), and corn protein, as the tribo-positive layer in TENGs. They obtained the triboelectric series of these representative plant proteins and demonstrated the significant potential of these bio-TENGs in agriculture.

Synthetic polymers such as polylactic acid (PLA), polycaprolactone (PCL), and polyurethane (PU) can also be used as the friction layer in green TENGs. Pan et al. [96] fabricated a bio-degradable triboelectric nanogenerator (BD-TENG) based on gelatin film and electrospun polylactic acid nanofiber membranes. This BD-TENG exhibited excellent mechanical stability, good biocompatibility, and degradation characteristics, with all the materials completely degrading in approximately 40 days. If used in implantable devices, it can harness energy from blood circulation and heartbeats without any harm to the human body. Gaurav et al. [97] prepared a fully biodegradable TENG using PLLA fibers and chitosan as the active layer. This TENG, based on PLLA fiber, delivers exceptional electrical output, achieving a peak voltage of 45 V and a current of 9μA, with a power density of 6.5 mW/m^2. Additionally, the PLLA TENG maintains stable output for up to 24,000 cycles. The self-healing friction nanogenerator exhibits very high durability, reliability, and safety, effectively reducing mechanical damage. Generally, the self-healing properties of materials are achieved through dynamic interactions between non-covalent and covalent bonds. This process is predominantly based on the dynamic chemical action of hydrogen bonds, functioning as reversible covalent bonds. Polycaprolactone and polyurethane have been widely used in the manufacture of self-healing TENGs due to their versatile and flexible design possibilities in molecular chains [98–100]. Luo et al. [98] developed a novel self-healing TENG based on flexible silver nanowires and polycaprolactone (PCL). This method significantly prolonged the lifespan of the TENG. When the TENG electrode surface was damaged, the PCL polymer or flexible silver nanowires flowed to the damaged area during the heating process, achieving self-healing. This self-healing TENG maintained stable and high output performance even after multiple damage-healing cycles. Sun et al. [99] developed a novel self-repairing triboelectric nanogenerator (TENG) based on polyurethane (PU). When the friction layer of the TENG was damaged, the polyurethane polymer chains reconnected through hydrogen bonding, achieving self-healing. The healed TENG maintained significant and stable output performance. Furthermore, they constructed a cathode protection system that utilizes the current provided by the self-healing TENG. This system transfers the negative triboelectric charges to the protected metal surface, effectively preventing corrosion by converting mechanical energy into electrical energy. Wang et al. [100] introduced a self-healing TENG with a random assembly based on Zwitterion polyurethane (Z-PU). This TENG exhibits superior triboelectric properties and efficient energy harvesting, achieving an output voltage of 90 V and a short circuit current of 14μA. It reaches a peak power density of 1.4 W/m^2. Notably, its commendable mechanical self-healing performance, with a healing efficiency of approximately 96 %, coupled with excellent breakdown self-healing, makes it apt for deployment in challenging environments and as self-assembled splicing materials.

Compared with nano-generators made of traditional materials, biodegradable nano-generators offer excellent safety, biocompatibility, minimal pollution upon degradation, and significant sustainable advantages [12,58]. For example, the mechanical stability of cellulose-based triboelectric nanogenerators (TENGs) not only facilitates the use of flexible electrodes [63] but also improves the cycle stability of electrodes during continuous charge–discharge processes, thereby prolonging the service life of the equipment [61,84]. However, the output power of most nanogenerators is typically in the range of μW to nW, which is insufficient for some high-power smart wearable devices [61,65,70,73,90]. Therefore, further optimization of their structure is necessary to achieve various desired output performances.

3.3. Supercapacitors

Supercapacitors (SC) are a research hotspot in the field of energy storage due to their high specific capacitance, power density, fast charge/discharge rates, and excellent flexibility. Supercapacitors mainly consist of four components: electrodes, electrolyte, separator, and current collectors (Fig. 6a). The capacitance mechanism of supercapacitors is illustrated in Fig. 6b and 6c. During the charging process, electrons flow from the negative electrode to the positive electrode through an external load. In the electrolyte, cations move towards the negative electrode, while anions move towards the positive electrode. The reverse occurs during discharge [101].

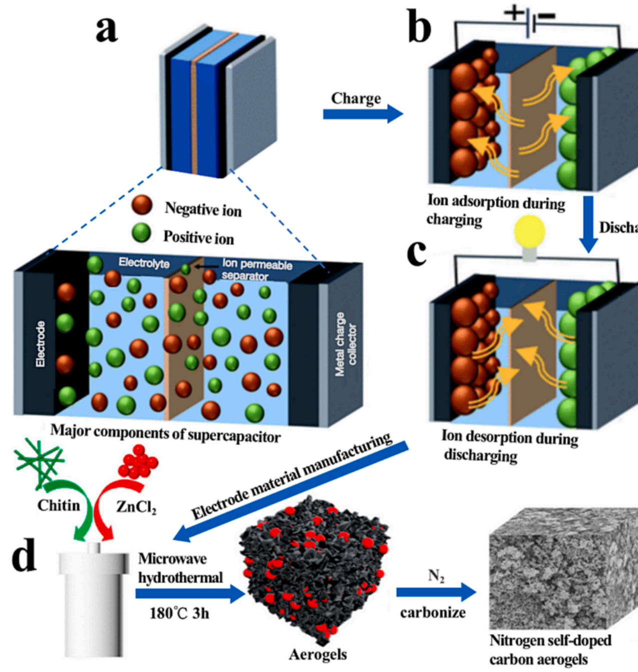

Fig. 6. (a) Schematic diagram of different components of a supercapacitor (electrode, electrolyte, separator, and current collector), (b) ion adsorption during the charging stage, and (c) ion desorption during the discharging stage. (d) Schematic diagram of the manufacturing process of nitrogen-doped carbon aerogel, an ideal electrode material for supercapacitor.(a), (b), (c) Reprinted with permission from reference [101]; Copyright (2021) RSC. (d) Reprinted with permission from reference [108]; Copyright (2021) Elsevier.

The electrodes and electrolyte materials of traditional supercapacitors are mostly made from various non-renewable polymers, which can lead to environmental issues when discarded. Therefore, the use of biodegradable polymers as substitutes for these traditional polymers can reduce environmental pollution and offer better performance to meet the energy demands [102].

In recent years, researchers have started to use biodegradable polymers such as starch, cellulose, and chitosan to fabricate supercapacitors. These bio-based supercapacitors not only possess the performance of traditional supercapacitors but also exhibit characteristics such as renewability, non-toxicity, biocompatibility, pliability, transparency, and biodegradability. Supercapacitors utilize a double electric layer energy storage mechanism, storing charge through the double electric layer formed at the interface between the electrode and electrolyte [101]. Consequently, the specific surface area and porous structure are the main factors affecting the electrochemical performance of carbon-based electrodes [101,103,104]. Yang et al. [103] used starch as the raw material and employed Na_2CO_3 templating and KOH activation methods to prepare hierarchical porous carbon as supercapacitor electrodes. Electrochemical measurements demonstrated high capacitance (234F/g at 2A/g), excellent rate capability (212.6F/g at 20A/g), and good cycling stability (98 % of initial capacity after 1000 cycles). Wang et al. [104] successfully prepared high-porosity carbon nanofibers as supercapacitor electrodes by using a blend of polyacrylonitrile (PAN) and hydroxyalkylated starch (HAS) as precursors. The CNF-20 electrode (with 20 % HAS content) exhibited a high specific capacitance of 344F/g at 1.0A/g, and the resulting supercapacitor maintained a capacitance retention of around 99 % after thousands of cycles, indicating its high cycling durability. This demonstrates that the green and low-cost HAS can be used as a pore-forming agent to prepare porous carbon nanofibers and applied in supercapacitors.

Cellulose possesses numerous unique advantages, such as renewability, good biocompatibility, and eco-friendliness. Since 2012, research on cellulose-based supercapacitors has significantly increased [105]. In supercapacitors, cellulose can be used as: (a) a lightweight mechanical substrate, providing flexibility and strength; (b) a coating material or a template for other carbon species; (c) a diaphragm between the electrodes; and (d) an electrolyte or medium [105]. Cao et al. [106] employed a phosphorization process to modify cellulose acetate (CA) and lignin via a cross-linking reaction. They discovered that esterification with H_3PO_4 diminished the hydrogen bond interactions between lignin molecules, thereby enhancing the flexibility of the precursor molecular chains and improving the spinnability of the solution. Through pre-oxidation and carbonization treatment, they obtained biomass-based carbon fibers (CFs) with intact fibrous morphology, high surface area, excellent flexibility, and outstanding energy storage capability. CFs were successfully utilized to fabricate supercapacitors with high energy density and specific capacitance. This indicates that the introduction of H_3PO_4 can effectively reduce the energy consumption of the pre-oxidation process while improving the energy storage performance of supercapacitors. Lei et al. [107] synthesized porous, nitrogen-doped cellulose-based carbon aerogels with an interconnected honeycomb-like structure using a simple and environmentally friendly method. These cellulose-based carbon aerogels exhibited several desirable characteristics, and the supercapacitors prepared from them demonstrated high specific capacitance (160F/g), good charge/discharge rates, and excellent cycling stability. Zhai et al. [108] prepared internally structured aerogels from chitosan and zinc chloride using a microwave hydrothermal method, followed by high-temperature carbonization to obtain nitrogen self-doped carbon aerogels (Fig. 6d). During the microwave hydrothermal process, $ZnCl_2$ acted as a dehydrating agent, strengthening the internal structure of the aerogel. Additionally, it served as an activator in the carbonization process, ensuring that the resulting carbon aerogel possesses a high specific surface area and an effective pore structure. NSCA-1000 (nitrogen self-doped carbon aerogel carbonized at 1000 °C) exhibited simple preparation, low production cost, environmental sustainability, and excellent electrochemical performance, making it an ideal electrode material for supercapacitors. At current densities of 1.0A/g and 10A/g, NSCA-1000 demonstrated specific capacitances of 249.4F/g and 164.9F/g, respectively. In symmetric dual-electrode supercapacitors, NSCA-1000 achieved energy density and power density values of 26.15Wh/kg and 0.95 kW/kg, respectively, at 1.0A/g.

Polylactic acid (PLA) exhibits good biodegradability, biocompatibility, low production cost, and flexibility, making it suitable for application in supercapacitors. Vargun et al. [109] prepared porous polylactic acid membranes as separators for supercapacitors. At room temperature, the ion conductivities of RF-PLA (radio frequency) separators in 1 M H_2SO_4 and 1 M Na_2SO_4 were measured to be 1.1×10^{-1} S/cm and 0.6×10^{-2} S/cm, respectively. Additionally, they found that PLA separators possessed excellent mechanical strength, and the electrochemical impedance spectroscopy of RF-PLA SCs exhibited low solution resistance and internal resistance. Wang et al. [110] fabricated PLDA (poly(L-lactide)) films for high-energy density capacitors. They found that stretching the PDLA film helps to form a uniform and stable α-phase, thereby enhancing the material's energy density. Their research results demonstrated that, under the same heat treatment at 100 °C, the energy density and efficiency of stretched PDLA films were 1.03 times and 53 % higher, respectively, than those of stretched poly(vinylidene fluoride-co-hexafluoropropylene) films, and 1.98 times higher than those of high-temperature polyimide materials. This indicates that supercapacitors based on PLA materials have significant potential for high-temperature applications.

3.4. Other energy devices

Polymer electrolytes play a crucial role in the safety of lithium-ion batteries. Due to their high energy density, lithium-ion batteries are at risk of spontaneous ignition or explosion in cases of overcharging, overdischarging, or temperature rises. On the other hand, solid polymer electrolytes (SPEs) have a significant impact on the performance of lithium batteries, offering advantages such as a high ion transport rate, a low electrode electrochemical window, and high electrochemical stability. Lin et al. [111] prepared an electrolyte primarily based on starch that exhibited excellent lithium-ion transport properties. They developed a solid-state lithium-sulfur battery that demonstrated outstanding performance in terms of capacity, cycling, temperature, and safety. This polymer electrolyte had a high melting point and thermal stability, which could improve the battery's safety performance and reduce the risk of thermal runaway. Besides, this electrolyte has a wide range of sources, economic advantages over most other solid polymer electrolytes, and is environmentally friendly. Starch can also be used to prepare conductive gels for batteries. For example, Jeżowski et al. [112] used starch as a binder to prepare conductive gels and electrode materials. No toxic or harmful substances were generated throughout the manufacturing process. They found that starch-based conductive gels could reduce the internal resistance of the devices, enhance their electrochemical performance, and exhibit excellent charge propagation and capacitance retention capabilities. Du et al. [113] prepared a mechanically robust and environmentally friendly cellulose gel membrane as a gel polymer electrolyte (GPE) for lithium-ion batteries. This cellulose membrane based GPE exhibits excellent mechanical properties, thermal stability, and outstanding electrochemical performance. Moreover, the membrane fabrication process is convenient, environmentally friendly, and pollution-free, making it widely applicable in the field of safe and high-performance lithium-ion batteries.

Phase change materials (PCMs) provide high latent heat for thermal energy storage. Polyethylene glycol (PEG), as a typical organic PCM, has been extensively studied due to its high latent heat and environmentally friendly nature [57]. Karaman et al. [114] prepared a PEG/diatomaceous earth mixture as a novel PCM using vacuum impregnation. The PEG/diatomaceous earth composite material exhibits high latent heat, good thermal reliability, and chemical stability, offering significant potential for energy storage material preparation. Dong et al. [115] synthesized PEG/polyvinylpyrrolidone (PVP)/copper sulfide (CuS) composite phase change materials with enhanced photothermal conversion functionality via melt blending. The PEG/PVP/CuS composite material exhibits good dispersion stability, thermal stability, as well as high energy storage and conversion efficiency. This indicates its tremendous potential applications in solar energy utilization and biomedicine.

4. Conclusion and outlook

Biodegradable polymers offer significant advantages over traditional non-biodegradable materials, including controllable biodegradability, processability, and acceptable biocompatibility. These properties position biodegradable polymers as crucial components in the development and design of green energy devices. Through chemical modification and processing techniques, a wide range of natural and synthetic polymers can be transformed into biodegradable energy devices, such as piezoelectric nanogenerators, friction nanogenerators, supercapacitors, conductive materials, and energy storage materials for smart wearable devices and biodegradable electronic products. These advancements present extensive application prospects. By harnessing biodegradable polymers, we can mitigate environmental pollution caused by energy and electronic devices while catering to diverse functional requirements. This review summarizes the characteristics of biodegradable polymers from different sources and the green energy devices prepared (Table 2). Their experimental data and applications have demonstrated their potential for use, and these studies have played an important role in the future development of biodegradable electronic devices.

Table 2
Energy devices fabricated from different biodegradable polymers highlighted in this review.

Components	Method	Electrical Property	Application	References
Starch/$CaCl_2$	Blend	1.2 V [a]	Friction nanogenerator	[79]
Starch/Laver	Cast	50 V [a]		[80]
HAS/PAN	Electrospin	344F/g [b]	Supercapacitor	[104]
Starch/Na_2CO_3/KOH	Template method	212.6F/g [b]		[105]
Starch/LiTFSI	Blend	3.39×10^{-4}S/cm [c]	Battery Electrolyte	[111]
Cellulose/LiBr·$3H_2O$	Freeze-drying	65 V [a]	Friction nanogenerator	[83]
Cellulose/PEO	Freeze-drying	222.1 V [a]		[84]
BC/HEC	Freeze-drying	25 V [a]		[85]
CNF/Ti_3C_2Tx	Freeze-drying	30.8 V [a]	Piezoelectric nanogenerator	[63]
Cellulose/PDMS	Blend	30 V [a]		[61]
Oxidized Cellulose/MoS_2	Blend	4.1 V [a]		[62]
CA/Lignin	Phosphorization	346.6F/g [b]	Supercapacitor	[106]
Cellulose/Polypyrrole	Blend	160F/g [b]		[107]
Cellulose/ Epichlorohydrin	Cast, Cross-linking	6.34×10^{-3}S/cm [c]	Battery Electrolyte	[113]
Chitin/KOH/Urea	Non frozen dissolution	182.4 V [a]	Friction nanogenerator	[86]
Chitosan/PVA	Electrospin	115 V [a]		[88]
Chitosan/Cotton Fibre	Cast	162 V [a]		[89]
Chitosan/Glycerol	Blend	130 V [a]		[87]
Chitin/$ZnCl_2$	High-temperature carbonization	249.4F/g [b]	Supercapacitor	[108]
SF/MeOH	Electrospin	8 V [a]	Piezoelectric nanogenerator	[65]
SF/Formic Acid	Electrodeposition	1.02 V [a]		[67]
SF/Ferroelectric Particles	Blend	2.2 V [a]		[66]
SF/AgNWs	Cast	110 V [a]	Friction nanogenerator	[91]
SF/PVA	Blend	172 V [a]		[92]
SF/MXene	Blend	545 V [a]		[93]
Collagen Protein/PP	Freeze-drying	50 V [a]	Piezoelectric nanogenerator	[68]
Fish Collagen/PDMS	Blend	10 V [a]		[71]
Spider Fibroin/PDMS	Coat	21.3 V [a]	Piezoelectric nanogenerator	[73]
Soybean Protein/$CaCl_2$	Blend	130 V [a]	Friction nanogenerator	[94]
Meso-PLA/PLLA	Cast	70 V [a]	Piezoelectric nanogenerator	[76]
PLA/$BaTiO_3$	Blend	11.97 V [a]		[77]
PLLA/Chitosan	Coat	45 V [a]	Friction nanogenerator	[97]
PLA/Gelatin	Coat	500 V [a]		[96]
Porous PLA/PEG	Blend	3.13×10^{-1}F/cm^2 [b]	Supercapacitor	[109]
PCL/Ag NWs	Cast	800 V [a]	Friction nanogenerator	[98]
Z-PU	Blend	90 V [a]	Friction nanogenerator	[100]
Silicone-Modified PU	Blend	517.5 V [a]		[99]
PEG/Diatomite	Vacuum Impregnation	87.09 J/g [d]	Phase change materials	[114]
PEG/PVP/CuS	Melt Blending	175.7 J/g [d]		[115]

Note: HAN-hydroxyalkyl starch; PAN-Polyacrylonitrile; LiTFSI-Lithium bis (trifluoromethanesulfonic acid) imide; PEO-Polyethylene Oxide; BC-Bacterial Cellulose; CA-Cellulose Acetate; HEC-Hydroxyethyl Cellulose; PP-Polypropylene; PDMS-Dimethylsiloxane; CNF-Cellulose Nanofiber; PVA-Poly (vinyl alcohol); Z-PU-Zwitterionic Polyurethane; a. is the maximum output voltage of the nanogenerator, in V; b. is the maximum capacitance of the supercapacitor, in units of F/g and F/cm^2; c. is the ion conductivity of the material, in S/cm; d. is the latent heat of the material, in J/g.

Despite the continuous design and development of biodegradable polymers with new functionalities and green energy devices, further obstacles and challenges must be addressed:

While biodegradable energy devices possess unique advantages over traditional counterparts, only a few biodegradable natural and synthetic polymers are actually employed due to complex processing conditions, high costs and also the issue of the safety of degradable materials in use. Therefore, extensive research is needed to enhance existing biodegradable polymers, optimize production processes, and improve performance. Simultaneously, deeper investigations into their degradation mechanisms are necessary to achieve precise control over degradation.

In certain cases, specific characteristics are also required for biodegradable energy devices, necessitating the incorporation of additional materials. However, these additional materials may compromise biocompatibility or degradability, hindering their practical applications. Examples include metals, nanowires, or polymers used to enhance conductivity. Therefore, it is essential to prioritize research and studies on such materials.

In addition, biodegradable energy devices and the production of green electronic products are still in the early stages, predominantly confined to the laboratory without widespread practical applications. Further research and exploration by scientists are necessary to transform these green products into viable solutions applicable in everyday life.

CRediT authorship contribution statement

Xincheng Zhuang: . **Fang Wang:** . **Xiao Hu:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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