

Hydrogel-Based Flexible Electronics Devices as Human Motion Sensors and Triboelectric Nanogenerators

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Flexible electronics is an emerging discipline in recent years because of its outstanding flexibility. It can be adapted to particular scenarios such as folded or bent, where conventional electronics are complex to apply. Flexible electronics are proliferating in areas, such as sensing, biomedicine, and energy harvesting. However, its development still needs to be improved due to weak biocompatibility, degradability and difficult-to-regulate mechanical properties. Flexible electronic devices need a new material that overcomes the above drawbacks to facilitate their development. Hydrogel is a kind of 3D cross-linked hydrated polymer network whose Young's modulus is close to the biological tissue. Its environmentally friendly properties make it a strong candidate for the next generation of flexible electronics. Currently, hydrogel-based flexible electronic devices are used as sensors for physicochemical and biological fields and energy harvesting and storage devices. This thesis focuses on applying hydrogel based flexible electronic materials in human motion sensing and as triboelectric nanogenerators to power electronic devices. In Chapter 2, flexible and mechanically strong wood-based hydrogels were successfully synthesized by combining cellulose backbone with PVA-Borax-TA hydrogel solution. It exhibits enhanced mechanical properties with a breaking strength of 19.8 MPa and it also has a good self-healing ability and excellent water retention properties, and its response time is as fast as 20ms when used as a flexible motion sensor. In Chapter 3, gelatin-based hydrogel was synthesized through a liquid nitrogen freezing process, after which the properties of the hydrogel were precisely controlled by adding different salt ions. A triboelectric nanogenerator (TENG) was then made by encapsulating the hydrogel in silicone rubber. The device has an open-circuit voltage of up to 160 V and a short-circuit current of 2.6 μ A, as well as a tensile fracture strength up to 1.5 MPa. In addition, it is also highly biocompatible and harmless to the human body, and it is a multifunctional material.

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Chapter 1 Introduction to Flexible Electronics

1.1 Background and Development of Flexible Electronics

Flexible electronics is an electronic device that can maintain its work state when deformation occurs. Regardless of bending, rolling, folding, or stretching, flexible electronic devices remain in good working condition.^[1] The concept of flexible electronics first appeared in the early 20th century.^[2] People started using thin-film electronic components such as thin-film resistors and capacitors for electronic devices.^[3] In 1903, Dr. Ken Gileo patented a flexible circuit which described an electronic device with flat metal conductors mounted on paraffin-coated paper.^[4] In the 1960s, the development of flexible electronic displays made of organic materials laid the foundation for later flexible display devices.^[5] Then, in the 1970s, researchers began to explore printable electronics which allowed electronic components to be fabricated using inkjet printing or other printing methods to reduce costs.^[6] Moving into the 1990s, printable organic electronics technology made significant progress and the development of organic semiconductor materials drove the growth of flexible electronic devices which made it possible to have semiconductor device functionality on flexible substrates.^[7] With the advent of the new century, the application areas of flexible electronic devices have expanded to medical care, wearable technology, foldable electronic devices, and smart labels. Products such as foldable screen cell phones and e-ink readers begin to enter the market.^[8] Flexible electronics make significant breakthroughs in the 2010s widely developed in printable batteries, flexible electronic skin sensors and wearable medical devices.^[9] More research and development are being put into this field to meet the needs of different application areas. Flexible electronics are now widely used in healthcare, smart wearables, e-paper, smart labels, wearable devices, and many other areas.^[10-16] Flexible electronic devices provide unique advantages compared to rigid and tough conventional electronic devices, such as being lightweight, portable, flexible, bendable, foldable, and adaptable for different applications. The continuous development of these devices portends more exciting applications of flexible electronics in the future.

With the advancement of technologies such as smart wearables, IoT, and AI, as well as the growing awareness of personal health management, there is a huge demand and potential for flexible electronics connecting biological tissues in living bodies with synthetic electronic systems.^[17] Currently, common flexible electronic materials include metal nanoparticles/nanowires, organic materials, low-dimensional semiconductor materials and carbon materials.^[18] However, excessive

cost, poor biocompatibility and mechanical properties have restricted their wide application.^[19] The enormous difference in Young's modulus between conventional flexible electronic devices and biological tissues has been a major limiting factor in its development.^[20] Living organisms comprise a series of hydrated, flexible tissues and organs whose Young's modulus typically varies between a few kilopascals and tens of megapascals (**Figure1.1**^[21]). While synthetic polymer materials such as polyethylene (PE), polyethylene terephthalate (PET), Polytetrafluoroethylene (PTFE), rubber, and silicone have the potential to be substrates for flexible electronics, but they either have an excessively high Young's modulus (up to a GPa) or lack sufficient biocompatibility.^[22]

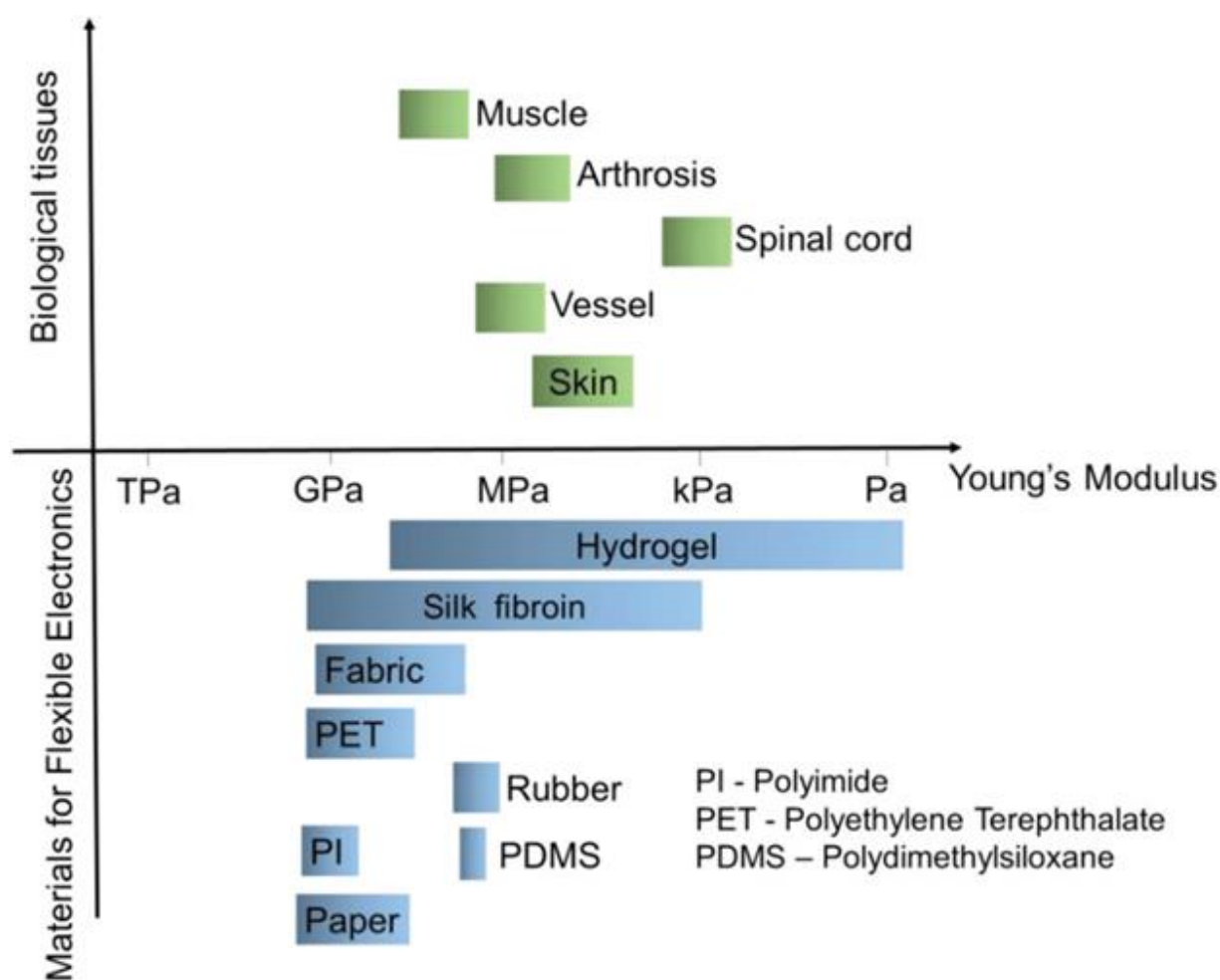


Figure1.1 Young's modulus of biological tissue (green), common flexible electronic materials (blue) and hydrogels. Adapted from Advanced Materials with permission ^[21-22]. Copyright of Wiley publishing group and American chemical society.

1.2 Hydrogel based flexible electronics applications.

1.2.1 Hydrogel-based wearable sensors

Hydrogel has become an ideal material for applications that meet the needs of flexible wearable sensors due to their excellent properties, such as flexibility, stretchability, and biocompatibility.^[14] In recent years, notable progress has been achieved in utilizing hydrogels in the domain of flexible wearable sensors.^[26] These advancements encompass self-healing wearable sensors, wearable sensors with adhesive characteristics, wearable sensors with resistance to low temperatures, multifunctional wearable sensors, energy harvesting wearable sensors, and biomedical wearable sensors.^[115]

1.2.1.1 Self-healing wearable sensors

Self-healing capability is a desirable property for wearable sensors because, in practice, they can sense and quickly repair damage through their self-healing capability, which maintains the integrity of their networks and other potential properties, including mechanical strength and elasticity. This will effectively prolong the life of the sensor. Therefore, many flexible wearable sensors based on self-healing hydrogels have been widely developed to improve their reliability and lifetime.^[49]

The dual-network structure of hydrogels has been proven to be an effective method for preparing wearable sensors with high sensitivity, wide strain range, and self-healing capability. Inspired by nature, Zheng *et al.* developed a novel hydrogel strain sensor with high sensitivity, wide strain range and self-healing capability.^[116] This hydrogel-based strain sensor consists of supramolecular sodium alginate nanofibers and chemically crosslinked polyacrylamide, and this dual network structure of multiple physically cross-linked supramolecular nanofiber networks and covalently bonded polyacrylamide networks gives it excellent performance. In practical settings, strain sensors composed of such hydrogels are employed to gauge physiological signals like human limb motions, subtle contractions of the lip muscles, and wrist pulses.

1.2.1.2 Self-adhesive wearable sensors

Conventional wearable sensors typically require materials such as tape to attach them to human organs or clothing, and this separation from the substrate limits their sensing performance in practical applications. Conversely, the characteristics of hydrogels enable them to adhere directly to human skin without the necessity for supplementary materials like adhesive tape, and they can be easily removed from the skin.^[117]

Incorporating functional additives into a hydrogel network can enhance its self-adhesive characteristics, rendering it precise and stable enough for detecting human activity. For example, researchers have devised a bilayer polyacrylamide hydrogel featuring both self-adhesive and priming properties.^[118] The adhesion layer within this hydrogel includes components like acrylate adenine and thymine, which enhance the hydrogel's adhesion to various surfaces through multiple physical bonding interactions. However, the poor mechanical properties of the adhesive layer limit its application in high-performance, long-lasting wearable sensors for monitoring human activities.^[119] To solve this problem and enable hydrogels self-adhesive, nanofillers or polymer chains capable of physically interacting with different substrates can be introduced into the hydrogel network.^[120] Nano clay, as a self-adhesive filler in hydrogels, effectively enhances the adhesion strength and resilience of the hydrogel through electrostatic interactions and hydrogen bonding with various substrates.^[121] Researchers have proposed a nanocomposite hydrogel, comprised of nano clay, multi-walled carbon nanotubes, and N-isopropyl acrylamide crosslinking.^[122] This hydrogel can adhere to a range of inorganic and organic materials, such as pig skin, glass, and rubber, and can support substantial weight at room temperature (up to 100g). This feature endows the hydrogel with promising applications in portable devices and wearable electronic equipment.

1.2.1.3 Frost resistant wearable sensors

Many hydrogels typically use pure water as the dispersing medium. As the time of use increases, the water content of the hydrogel may decrease due to evaporation, which may lead to a decrease in properties such as electrical conductivity and tensile strength of the hydrogel.^[123] To overcome the problem of water loss, one strategy is to encapsulate the hydrogel by adding an elastic substrate or applying silicone oil.^[124] However, it is worthy of note that this approach has the risk of triggering an allergic skin reaction and can hinder the direct contact of the hydrogel with the skin, thus reducing the sensitivity of the sensor.^[125] In addition, the water in the hydrogel freezes when the temperature falls below 0°C, which can have a severe adverse effect on the electronic and mechanical properties of the hydrogel, limiting its usability in cold environments.^[126] The development of hydrogels with antifreeze and moisturizing features has therefore become an imperative to drive the development of flexible wearable sensors in a variety of applications.

Antifreeze hydrogels can be effectively prepared using glycerol, ethylene glycol (EG), and sorbitol. These solvents can establish robust hydrogen bonds with water molecules, thereby retarding both ice

formation and water evaporation. To enhance the performance of antifreeze conductive organic hydrogels, some researchers have employed a binary solvent system comprising water and glycol.^[127] The resulting hydrogels exhibit remarkable flexibility and exceptional strain sensitivity, even under extremely low temperatures, such as -40°C.^[127] Furthermore, these hydrogels possess outstanding thermoelectricity and self-healing characteristics,^[127] owing to their physical crosslinked network structure, which includes hydrogen bonding and interactions between crystalline domains. These distinctive properties render this conductive organic hydrogel highly promising for diverse applications in wearable devices, particularly in environments with extremely freezing conditions.

1.2.1.4 Multifunctional wearable sensors

In recent years, there has been notable advancement in the realm of multifunctional wearable sensors based on hydrogels. These sensors exhibit a diverse range of characteristics, including exceptional mechanical properties, the capability for self-healing, self-adhesion, resistance to freezing, and biocompatibility.^[51] Traditional hydrogels may only possess one specific property or react to a single stimulus, which may need to be revised in addressing the demands of complex real-world applications. Consequently, contemporary research is focused on creating hydrogel wearable sensors with integrated multifunctional properties which enables these sensors to utilize multiple advantageous properties simultaneously, thereby adapting to a wide range of application requirements.^[128] These efforts have contributed to the wide range of applications of hydrogel sensors in various fields such as medicine, health monitoring and wearable electronics.

Liu *et al.* have developed conductive nanocomposite hydrogels through the *in-situ* polymerization of poly(ethylene glycol) methacrylate monomers within a binary solvent comprised of glycerol and water.^[128] Within this hydrogel, inorganic clay serves as a physical cross-linking agent, imparting exceptional mechanical strength to the hydrogel and facilitating the conduction of ions. This hydrogel exhibits remarkable mechanical flexibility, stretchability, and electrical conductivity. As a result, wearable sensors constructed using this hydrogel can swiftly and sensitively detect subtle skin movements and activities. Moreover, the presence of abundant hydrogen bonding interactions between poly (ethylene glycol) methacrylate and clay grants this conductive hydrogel-based sensor impressive self-healing capabilities, allowing it to repair itself to a certain extent following damage. These characteristics make this hydrogel a promising candidate for a wide array of applications in wearable sensors and skin-contact devices.

The development and formulation of multifunctional hydrogels for wearable sensors represent a multifaceted approach, involving the incorporation of various components into the hydrogel polymer network, each serving a distinct purpose. These components encompass the addition of glycerol for antifreeze capabilities, polydopamine to enhance adhesion and self-healing attributes, and amphoteric ions to facilitate self-adhesion and bolster mechanical properties. Through the introduction of diverse additives, hydrogels can acquire additional functional and structural features while retaining their fundamental properties. Future efforts will result in more comprehensive and multifunctional hydrogels that can fulfill the needs of flexible wearable sensors in intricate and practical environments. These multifunctional hydrogels are expected to be useful in a wide range of applications such as medical, health monitoring, sports, and other fields, thereby improving the performance and versatility of wearable devices.

1.2.2 Energy Harvesting Device

With the escalation of global warming, the world's attention is increasingly drawn to environmental and energy concerns. Presently, fossil fuels remain the predominant energy source in our daily lives. Nonetheless, it is imperative to acknowledge that fossil fuels are finite resources, necessitating an immediate focus on the development of novel energy harvesting devices. These devices aim to tap into previously untapped energy sources or curtail energy consumption, ensuring sustainability for future generations.^[130] Additionally, it is paramount to remain vigilant about the potential environmental repercussions of using fossil fuels.

In recent years, the advancement of flexible electronic devices, including electronic skin, soft robots, and flexible medical monitoring devices, has given rise to the emergence of flexible energy harvesting devices. Hydrogels, owing to their exceptional biocompatibility and high-water content, have facilitated the integration of electronic devices with living organisms. Hydrogel-based devices exhibit a range of unique attributes, encompassing biocompatibility, high flexibility, elasticity, biodegradability, and rapid diffusion.^[42] These properties enable them to harness various forms of energy, thereby accomplishing the objective of energy recovery. Notably, certain hydrogels possess self-healing capabilities and outstanding tensile strength, further enhancing the adaptability of energy harvesting devices.^[131] In this context, hydrogels are primarily employed as electrodes, particularly in triboelectric nanogenerators, where the exceptional electrical conductivity of hydrogels is paramount.

The hydrogel triboelectric nanogenerator is a device capable of converting mechanical motion into electrical energy. It works by utilizing the deformation of hydrogel material under mechanical pressure to create charge separation and current flow. However, the hydrogel triboelectric nanogenerators often exhibit low efficiency, making it impractical to complement them with other energy harvesting methods to meet power requirements. Moreover, external factors such as ambient humidity can influence the performance of hydrogels.^[132] Therefore, the selection of appropriate hydrogel materials for the fabrication of triboelectric nanogenerators is of paramount importance.

Muhammad Toyabur Rahman *et al.* have pioneered the creation of an exceptionally stretchable and durable electrode for wearable triboelectric nanogenerators.^[133] They achieved this by incorporating ZIF-8 as a reinforcing nanofiller within a hydrogel that also contains a LiCl electrolyte.^[133] The addition of ZIF-8 nanocrystals improved the hydrogel's mechanical properties by forming hydrogen bonds with the copolymer chains, resulting in a remarkable 2.7-fold increase in stretchability compared to a pure hydrogel.^[133] To further enhance the performance, the hydrogel electrode is enveloped by a microstructure silica layer, which serves both as a frictional electrical material and as a barrier to prevent water loss from the hydrogel.^[133] These optimized ZIF-8-based hydrogel electrodes contribute to the triboelectric nanogenerator (TENG)'s improved output performance by maintaining a dynamic equilibrium of the double electric layer (EDL) during contact initiation. As a result, the constructed TENG demonstrates an outstanding power density of 3.47 Wm^{-2} , a remarkable 3.2 times higher than that of TENGs based on pure hydrogel.^[133] These developed TENGs are proficient at harvesting biomechanical energy even at sub-zero temperatures. They are suitable for powering small electronic devices and as efficient self-powered pressure sensors for human-machine interfaces (HMIs).

1.2.3 Biomedical device

Hydrogels find a multitude of applications in the biomedical sector, spanning from tissue engineering, drug delivery, biosensors, and ophthalmic applications to trauma dressings, cell culture, medical imaging, controlled release devices, and beyond. Their biocompatible nature and exceptional water-absorbing capabilities render them exceptionally well-suited for facilitating tissue growth, controlled drug release, sensitive biosensing, and the production of medical devices. One of the widespread applications of hydrogels in the biomedical field today is implantable devices. In applications within the human body or as implantable devices, it is essential that conductive

hydrogels exhibit high biocompatibility, possess an appropriate elastic modulus, and can securely adhere and remain stable within highly dynamic organs like the heart, stomach, and lungs. Therefore, the advancement of conductive hydrogels that combine the desired elastic modulus, toughness, biocompatibility, and tissue adhesion is of utmost significance and ultimate goal in the field of medical and healthcare technologies.^[8] Yang *et al.* developed a graphene nanocomposite conducting hydrogel for assembling bioelectronic devices.^[135] This GO nanocomposite conductive hydrogel-based electro-bioadhesive can form adhesion within 5 seconds and has an interfacial toughness greater than 400 Jm^{-2} , enabling it to adhere bioelectronic devices to different wet dynamic tissues.^[135] In addition, the electrical conductivity of the electro-bioadhesive is greater than $2.6 \text{ S}\cdot\text{m}^{-1}$,^[135] further supporting bidirectional bioelectronic communication.

1.3 Characterization of hydrogel based flexible electronics.

1.3.1 Properties of hydrogel materials

Hydrogels are cross-linked 3D network structures of water-rich hydrophilic network polymers which can store and retain enormous amounts of liquid within their own structure.^[23] Hydrophilic groups on the polymer chains ensure the swelling capacity and high water retention of hydrogels.^[24] Intermolecular interactions between the crosslinked network and the polymer chains create cohesive forces that prevent further penetration of water molecules.^[25] Furthermore, the most fundamental property of hydrogels is that they are water-absorbent but not water-soluble.^[26] Hydrogels have many properties like natural soft tissues, including excellent biocompatibility, biodegradability, and adjustable physical and chemical properties.^[27] For this reason, hydrogels have become one of the most widely used biomedical materials. Today, hydrogels are widely used in many fields such as drug delivery, contact lenses, wound dressings, and tissue engineering.^[28-29] Hydrogels can also respond to various stimuli such as light, temperature, pH, and ionic concentration by expanding or contracting in volume.^[30-32] This property has been applied in sensing and actuation. Through the multifunctional and adjustable molecular composition of hydrogel and by combining functional micromaterials or nanomaterials in a rational design, the hydrogel can achieve many further exciting functions.

1.3.2 Sources of hydrogel polymers

The sources of hydrogel polymers can be categorized into three, which are synthesized from natural polymers, synthetic polymers, or a combination of natural and synthetic polymers. Natural

hydrogels are synthesized from polymers obtained from natural sources such as plants or animals.^[33] Some natural materials have inherent water-absorbing and moisturizing properties and can be used as hydrogel polymers.^[34] One of the best-known natural hydrogel polymers is sodium alginate which is usually derived from brown algae. Other natural materials, such as gelatin, agar, and tapioca starch, and can also form hydrogels under certain conditions.^[35] Natural hydrogel polymers offer a lot of benefits, including biodegradability. This means that they decompose in the natural environment, which do not cause lasting environmental pollution.^[36] This is important for disposables and sustainable production. Some natural hydrogel polymers, such as gelatin and sodium alginate, are usually biocompatible and non-toxic to humans, plants, and animals.^[37] They are therefore often used in the medical and food industries. A photo-crosslinked gelatin hydrogel was prepared by Xin Zhao *et al.*^[38] It was used to design an epidermal hydrogel for skin tissue engineering which supports the growth, differentiation, and stratification of keratinocytes to reconstruct multilayered epidermis with adequate barrier functions. The keratin-forming cell-filled hydrogels can be used as epidermal substitutes, wound dressings, or substrates for constructing various in vitro skin models. Synthetic hydrogel polymers are prepared by synthetic chemistry from various monomers or polymer precursors.^[39] Common synthetic polymers include polyethylene, polypropylene, polyethylene glycol, polyvinyl alcohol, sodium polyacrylate and polyacrylamide.^[40] They are usually powders, granules or flakes and can be dissolved in water to form hydrogels. Synthetic polymer hydrogel has a stable hydrogel structure and high chemical resistance.^[41] When synthetic polymers absorb water, they can form a stable gel structure which is able to lock moisture firmly inside.^[42] It usually has good resistance to most chemicals, which helps its application in different environments.^[43] Masanori Kobayashi *et al.* synthesized a hydrogel meniscus that can replace the function of the human meniscus by using polyvinyl alcohol and because of its good mechanical properties and biocompatibility, it maintained an exceptionally good condition one year after implantation in the organism.^[44] Combinations of natural and synthetic polymers can be used to form hybrid hydrogels, which often have the advantages of both and are highly biocompatible while still having a stable structure. Huanyang Yu *et al.* developed a hydrogel consisting of a mixture of polyvinyl alcohol, borax and gelatin which not only has good biocompatibility, but also has enhanced mechanical properties and self-healing ability due to the introduction of borax and polyvinyl alcohol.^[45]

1.3.3 Crosslinking of hydrogel polymers

Crosslinking polymer chains with each other forms the three-dimensional structure of hydrogels, and this crosslinking method is particularly important for the properties and uses of hydrogels. The cross-linking of hydrogels can be divided into two main types: physical cross-linking and chemical cross-linking (**Figure 1.2**^[46]).

Physical cross-linking means the bonding of polymer chains through non-covalent interaction forces. It is a reversible process which means that it can be reversed by altering conditions such as temperature or pH, without causing any damage to the polymer chains.^[47] Physical crosslinking methods include hydrogen bonding, van der Waals force interactions, electrostatic attractions, and hydrophobic interactions.^[48] Hydrogen bonding crosslinking involves the connection of polymer chains through hydrogen bonding interactions.^[49] Van der Waals crosslinking, on the other hand, pertains to the attraction of polymer chains due to van der Waals forces. In cases where polymer chains carry an electrical charge, they can be crosslinked through electrostatic interactions, such as the ionic crosslinking in gelatin. Hydrophobic interactions refer to the binding of polymer chains via the hydrophobic repulsion of water molecules, which also observed in the cellulose-based hydrogel.^[50] Physically cross-linked hydrogels have the advantage of being very responsive to external stimuli such as changes in pH or temperature. This responsiveness gives them valuable properties such as self-healing ability and the ability to be injected at room temperature.^[51] In addition, these physical cross-links can be broken down under physiological conditions, making the hydrogels biodegradable.^[52] However, they typically exhibit limited mechanical strength, due to weak intermolecular interactions. Jiezhou Pan *et al.* successfully prepared a triple physically cross-linked hydrogel with ligand bonding, hydrogen bonding and electrostatic interactions by a one-pot preparation method.^[53] By employing aluminum ions and carboxymethyl chitosan nanoparticles for crosslinking with polyacrylic acid chains, they effectively produced hydrogels that exhibit both antimicrobial qualities and are non-cytotoxic. The hydrogel exhibited a degree of self-healing capability, achieving complete self-healing within 24 hours with an impressive healing efficiency of 92.9% for stress and 98.8% for strain.^[53] Remarkably, the hydrogel proved resistant to surface aging or erosion, including exposure to acids, bases, and salt solutions. Moreover, because of its entirely physically crosslinked structure, the prepared hydrogel can be readily recycled without contamination. However, the notable drawback remains its modest mechanical properties.

Chemical cross-linking entails the binding of polymer chains through covalent bonds, which are permanent and enhance the stability of the hydrogel.^[54] Chemical cross-linking encompasses various methods, including radiation cross-linking, in which polymer chains are bonded using radiation sources such as gamma rays, UV light, or electron beams to initiate the cross-linking reaction.^[55] It also involves the use of cross-linking agents, such as cross-linker molecules or cross-linker initiators, which induce covalent connections between polymer chains.^[56] Another approach is thermal cross-linking, in which the cross-linking reaction among polymer chains is initiated by heat, as exemplified by thermoplastic polyvinyl alcohol (hot-melt PVA). Dongdong Ye *et al.* introduced a chemical double-crosslinked cellulose hydrogel.^[57] This hydrogel was synthesized through a sequential reaction involving cellulose and both low-molecular-weight and high-molecular-weight cross-linkers, resulting in the formation of networks with short and long cross-linked chains. In tensile and compression tests, this hydrogel exhibited fracture stresses of 1.7 and 9.4 MPa, respectively.^[57] These values were significantly higher, being 26.3 and 83.9 times greater,^[57] compared to those of the chemically single-crosslinked cellulose hydrogel. The dual network structure significantly contributes to the enhancement of the mechanical properties of cellulose hydrogels.

Different cross-linking techniques have an impact on the characteristics of hydrogels, including their water absorption capacity, stability, and reversibility.^[56] The selection of the appropriate cross-linking method is contingent upon the specific application needs of the hydrogel. Physical cross-linking is usually reversible and suitable for specific applications, whereas chemical cross-linking is usually more stable and suitable for applications requiring ruggedness and solubility resistance. In certain scenarios, hydrogels can be designed with multiple physical network cross-links, multiple chemical network cross-links, or even physicochemical dual network structures which are used to create hydrogels that exhibit both biodegradability and improved mechanical properties.

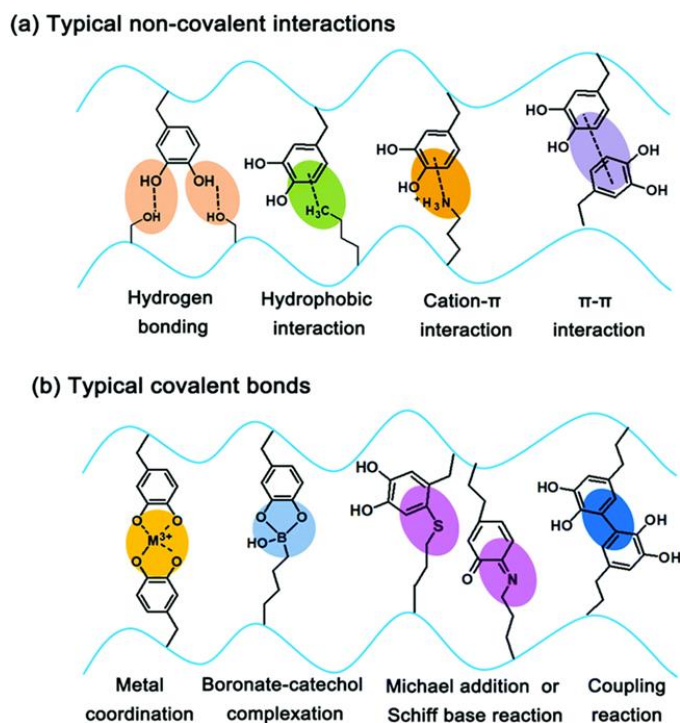


Figure 1.2 Schematic representation of typical noncovalent interactions and covalent bonds in hydrogel. Adapted from chemical society review with permission.^[46] Copyright of Royal Society of Chemistry.

1.3.4 Network structure of hydrogel

Hydrogels are made of monomers (small molecules, biomacromolecules, nanostructures, and metal or ligand units) or polymers and these components come together to create crosslinked networks that allow for the passage of water.^[58] The same or different monomers can be mixed to form repeating structures, thus starting the initial phase of network structure formation. The polymer backbone establishes most of the functional groups, which contribute to the basic structure and intrinsic properties of the hydrogel. Different synthesis methods integrating one or more monomers or polymers produce hydrogels with different properties and functions, which plays unique roles in different fields.^[59] Currently, there are three main types of hydrogel network structures, which are homopolymerized hydrogel, copolymerized hydrogel, and interpenetrating hydrogel. (**Figure 1.3**^[60])

Homopolymerized hydrogels are synthesized from only one type of monomer. For example, transparent PVA hydrogels can be formed by chemical cross-linking or thermal crystallization, which is prepared using only one monomer.^[61] Homopolymer hydrogels typically have a homogeneous

network structure that ensures consistent properties such as water absorption and physical characteristics. This consistency makes them valuable in various applications in the medical, hygiene, agricultural, food industry and cosmetic fields.^[62]

Copolymer hydrogels are polymers that are crosslinked through covalent or ionic bonds.^[63] They are synthesized using two or more diverse types of monomers, which can be organized in random, block, or alternating configurations, and they must include at least one hydrophilic component.^[64] The intricate chemical structure of copolymer hydrogels enables precise adjustments and optimization of their water absorption properties, physical attributes, and chemical characteristics.^[65] In contrast to homopolymer hydrogels, copolymer hydrogels have greater versatility which can find application in a wide range of uses, including water absorption, drug delivery, stabilization, and thickening.^[66]

Interpenetrating network hydrogel, also known as IPN hydrogels, is a single structure formed by intertwining two different cross-linked polymer networks.^[67] IPN hydrogels are typically synthesized via either a simultaneous or sequential process. In the one-step simultaneous process, all monomers and crosslinking agents polymerize and crosslink concomitantly. In the sequential process, a network is first formed, then a second monomer is immersed into the formed network to start second polymerization and cross-linking. In contrast, copolymer and homopolymer hydrogels are formed directly through monomer polymerization.^[67] This interpenetration enhances the mechanical strength of the hydrogel, and a key feature of interpenetrating networks is the ability of each polymer network component to retain its unique properties.^[68] The composition of the polymer components can be flexibly changed to customize the overall performance of the interpenetrating network.^[70] In a recent study, Ren and his team developed a physically crosslinked interpenetrating network hydrogel using PVA and gelatin, which also incorporates the antimicrobial properties of salicylic acid.^[71] Their experimental data showed that this hydrogel has excellent physical properties and is capable of sustained drug release, which has significant potential for medical applications like wound dressings. In addition, such interpenetrating network hydrogels show promise for various applications in physiological signaling sensors. For example, Ye and his team used a simplified process to prepare multi-walled carbon nanotube-poly (3,4-ethylenedioxythiophene) /poly (styrene sulfonic acid)-polyacrylamide-poly (vinyl alcohol)/borax composite hydrogels to form an interpenetrating polymer network.^[72] This hydrogel possesses the characteristics of injectability, high stretchability, electrical conductivity, and adhesion, thus enabling reliable detection of physiological signals. A semi-interpenetrating network is a structure in which a component with a linear molecular structure

penetrates another crosslinked network rather than being covalently bonded to it.^[73] Typically, constructing of semi-interpenetrating networks is a convenient method for integrating additional functionality or properties into single-component hydrogels.^[74] For example, Zhang *et al.* used N, N'-methylene bisacrylamide as a cross-linking agent to prepare a semi-interpenetrating network consisting of a copolymer of linear polyallylammonium chloride and acrylamide/acrylic acid by template co-polymerization.^[75] In this semi-interpenetrating network, the covalent bonds in the copolymers maintained the three-dimensional structure of the hydrogel. In contrast, the ionic bonds between the carboxyl and amine groups conferred higher mechanical strength and pH-stimulation response properties.

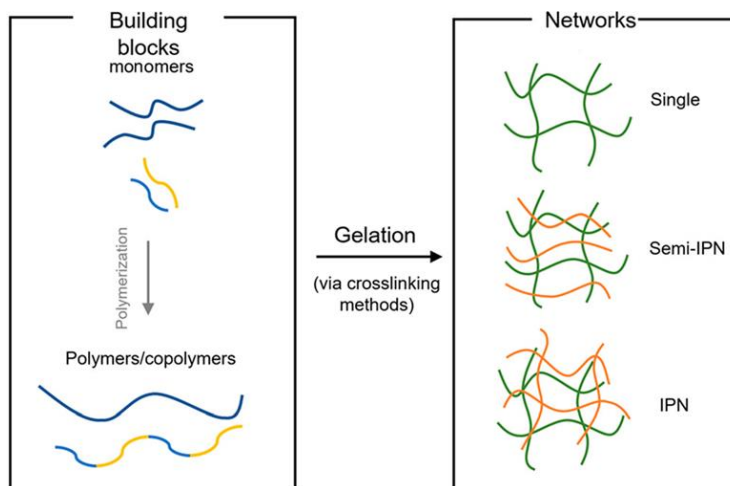


Figure 1.3 Schematic diagram of structural units and polymer networks of hydrogels. Adapted from chemical reviews with permission.^[60] Copyright of American Chemical society.

1.4 Factors affecting the properties of hydrogel.

1.4.1 Conductivity

The porous structure of a hydrogel allows water molecules to flow freely through the polymer network, facilitating the high-frequency movement of molecules in water, which offers a practical approach to creating conductive hydrogels.^[76] Hydrogels primarily serve as conduits for achieving ionic conductivity by integrating of charged salts or conductive elements within a resilient three-dimensional hydrogel matrix.^[77] This entails the incorporation of intrinsically conductive polymers,

metallic nanoparticles, and carbon-based nanomaterials into the hydrogel, facilitating electronic conductivity.^[78] Diverging from conventional conductive materials, the conductivity of ion-conducting hydrogels arises from the controlled movement of free-charged ions, which are generated within the hydrogel by charged salts or conductive materials.^[79]

Conductive materials that produce charged ions in water can usually be divided into three categories: acid (such as HCl, H₂SO₄), metal salts (such as LiCl, NaCl, and Na₂SO₄), and ionic liquids.^[80] These conductive materials produce free charged ions that move directionally in the hydrogel, providing the hydrogel with electrical conductivity.^[81] The most widespread method of preparing electrically conductive hydrogels is to incorporate electrically conductive materials directly into the hydrogel substrate.^[82] Electrically conductive materials can be broadly classified into three categories: metallic materials, including nanoparticles and nanowires like silver and copper; carbon-based materials, such as carbon nanoparticles, carbon nanowires, graphene, and graphene oxide; and conductive polymers like polystyrene.^[83]

In ion-conductive hydrogel networks, freely moving charged ions function as the primary solvent in the hydrogel network, and the high concentration of freely moving charged ions provides continuous electrical conductivity to the hydrogel during the deformation process.^[84] However, due to the high concentration of ions, the risks of ion leakage, high-temperature evaporation and low-temperature freezing easily present during the hydrogel deformation process.^[85] Electrically conductive hydrogels contain a high concentration of non-transparent conductive filler material, resulting in poor transparency of the electrically conductive hydrogel.^[86]

Conductive hydrogels have been developed by combining various conductive materials with hydrogels. The fundamental methods for fabricating conductive hydrogels include:

- (1) Self-polymerization of conductive materials, resulting in a singular network hydrogel.
- (2) Self-assembly of conductive materials into ion-conducting channels, yielding a conductive hydrogel.
- (3) Introduction of conductive fillers or charged salts into non-conductive hydrogel matrices through doping.

(4) Establishment of interpenetrating networks of conductive hydrogels by doping conductive polymers or fillers with non-conductive polymers.^[87] **Figure 1.4** shows the electrical conductivity of standard hydrogels and their applications.^[88]

Conductive type	Conductive component	Network structure	Conductivity	GF	Application
Ion conductive hydrogels	H ₃ PO ₄	Single network	>17 mS·cm ⁻¹	N.A.	Supercapacitor
Ion conductive hydrogels	Li ⁺	Double network	2.25 S·m ⁻¹	N.A.	Supercapacitance
Ion conductive hydrogels	Al ³⁺	Single network	10 ⁻² S·cm ⁻¹	2.84	Ionic skin
Ion conductive hydrogels	PDMAPS , IL	Single network	10 ⁻² S·m ⁻¹	N.A.	Deformable sensory systems.
Ion conductive hydrogels	PDES , MA/ChCl	Double network	4.0 × 10 ⁻⁴ S·cm ⁻¹	N.A.	Stretchable electronics
Ion conductive hydrogels	PDES , ChCl/PA	Single network	7.8 × 10 ⁻⁴ S·cm ⁻¹	3.43	Human motion sensors
Ion conductive hydrogels	[NTI2]	Single network	N.A.	1.83	Wearable optoelectronic devices
Ion conductive hydrogels	PMMA- <i>r</i> -PBA	Single network	1.33 mS·cm ⁻¹	2.73	Healthcare devices
Electron conductive hydrogels	PANI	Double network	5.12 S·m ⁻¹	1.05	Human motion sensors
Electron conductive hydrogels	PANI; PSS	IPN	13 S·m ⁻¹	3.4	Wearable devices
Electron conductive hydrogels	CNTs	Double network	8.2 S·m ⁻¹	N.A.	Self-adhesive bioelectronics
Electron conductive hydrogels	CNT	Double network	7.8 × 10 ⁻² S·m ⁻¹	N.A.	Multifunctional bioactive dressings
Electron conductive hydrogels	Ag NPs	Single network	5.72 × 10 ¹ S·m ⁻¹	N.A.	Nanoelectronics devices
Electron conductive hydrogels	MXene	Double network	1.1 mS·cm ⁻¹	8.21	Human motion sensors
Electron-ion conductive hydrogels	PEDOT; PSS; Poly(HEAA-co-SBAA)	IPN	0.625 S·m ⁻¹	2	Strain sensor

Figure 1.4 Conductivity of common hydrogels and their applications. Adapted from chemical of materials with permission.^[88] Copyright of American Chemical society.

1.4.1.1 Ion conductive Hydrogel

The transmission of electrical signals by the movement of freely charged ions, which is also known as ionic conduction, is a common occurrence in living organisms. The electrical conductivity of ion-conducting hydrogels is generated by the oriented movement of free ions in the hydrogel network.^[89] Flexible wearable electronic devices usually consist of energy storage elements and conversion devices, such as supercapacitors and triboelectric nanogenerators.^[90] Ion conductive hydrogel can be made by dissolving acid into the hydrogel, which is commonly used to prepare portable supercapacitors. Cai *et al.* used vinyl hybridized silica nanoparticles (VSNPs) to cross-link polyacrylamide (PAM) to form a hydrogel and phosphoric acid was added to the hydrogel, which provided ion conductivity.^[91] The hydrogel's conductivity was significantly enhanced by introducing acid, which is extremely useful for developing stretchable and compressible supercapacitors.

The most common method for preparing ion-conducting hydrogel is to dissolve metal salts into the hydrogel. Qin *et al.* synthesized PAM/CNF/LiCl hydrogels by adding cellulose nanofibers (CNF) and lithium chloride (LiCl) to acrylamide (AM) solution by using a one-step polymerization method.^[92] This hydrogel has anti-freezing and excellent water retention properties, and the low-temperature operating range is -80~25 °C.^[92] Supercapacitors based on PAM/CNF/LiCl hydrogel can work under low-temperature conditions. Wen *et al.* created a hydrogel with sensing capability, resistance to UV radiation, good water retention, and frost protection.^[93] This was achieved by uniformly dispersing tannic acid-coated hydroxyapatite nanowires (TA@HAP NWs) and poly (vinyl alcohol) (PVA) in a binary solvent consisting of ethylene glycol (EG) and water. In this combination, TA @ HAP NWs functioned as a UV filter and improved the mechanical properties of the material. AlCl₃ can be fully ionized in water but not in EG and the binary system of EG and water helps Al³⁺ to move freely in ionic water channels which are separated by EG molecules. The dual system of EG and water improves the sensing sensitivity of the hydrogel and alleviates the problem of water freezing easily below 0 °C and evaporating easily at hot temperatures.

Using ionic liquids to provide conductivity for hydrogels is also an effective way to prepare ion conducting hydrogels. Zhang *et al.* synthesized two Polymerizable Deep Eutectic Solvent (PDES) monomers, namely acrylamide/choline chloride (Am/ChCl) and maleic acid/choline chloride (MA/ChCl), and they are using intramolecular and intermolecular multiple bonding interactions construct a supramolecular network structure.^[94] The transparent and conductive elastomeric Poly(Am/ChCIMA/CCI) was prepared by photoinitiated *in situ* co-polymerization. The material has a good transparency of about 95.1%, the strain of up to 450% and stress of up to 0.3 MPa, an ionic conductivity of $4.0 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, and excellent self-healing ability which self-healing efficiency was 94% at room temperature, and 73% at 23°C.^[94] It also can maintain high transparency, stable mechanical properties, and good electrical conductivity in a wide temperature range of -23~60°C,^[94] which ensure the stable and continuous operation of the electronic skin in extreme environments.

1.4.1.2 Electron conductive Hydrogel

Another common strategy to improve the conductivity of hydrogels is to add conductive fillers such as carbon nanotubes, graphene, or metal nanoparticles to the hydrogel.^[95] In addition to providing conductivity to the hydrogel, the introduction of electronically conductive materials also

improves the mechanical strength of the hydrogel.^[96] Conducting polymers receives increasing attention for the preparation of electron-conductive hydrogel.^[97]

Wang *et al.* fabricated a conductive hydrogel with a dual synergistic network that is easy to stretch for wearable resistive strain sensors.^[98] The dual synergistic network consists of a polyacrylic acid (PAA) network, which is formed by crosslinking amphiphilic block copolymers, and a rigid conductive polyaniline (PANI) network, which is formed by chemical doping and ionic crosslinking of phytic acid (PA). These two networks are interlocked by physical entanglement, hydrogen bonding and ionic interactions which are formed through a photoinduced free radical polymerization reaction. This design improves the poor transparency of conventional electron conductive hydrogel and has superb stretchability which has up to 1160% strain and 0.3 MPa stress and controlled conductivity ($5.12 \text{ S}\cdot\text{m}^{-1}$).^[98] Electron conduction applied to this electron conductive hydrogel have excellent sensitivity and a wide sensing range.

Carbon nanotubes (CNT) and graphene oxide (GO) are commonly used conductive materials to prepare electrochemical hydrogels. A typical experimental approach is to disperse the conductive components (CNT/GO) in a hydrogel substrate. Inspired by the natural freeze and heat-resistant mechanisms, Xie *et al.* designed a self-adhesive electronically conductive hydrogel using principles derived from mussel chemistry.^[99] This innovative hydrogel not only possesses long-lasting moisture retention capabilities but also demonstrates remarkable resilience to hot temperatures. Incorporating polydopamine (PDA)-decorated carbon nanotubes (CNTs) enhances its performance. Furthermore, this hydrogel exhibits exceptional resistance to both extreme heat and frost, maintaining its properties even over extended periods within an extensive temperature range, spanning from -20°C to 60°C .^[99] The direct incorporation of metallic materials into hydrogels can impact their elasticity. This is why metallic fillers are typically introduced as nanoparticles or nanowires.

Silver nanoparticles exhibit exceptional electron transport properties. Dawadi *et al.* synthesized electron conductive hydrogels by utilizing hydroxymethylurea (MU) to reduce silver ions (Ag^+) and employing *in-situ* polymerization of acrylic acid (AA) as the raw material at room temperature. This method achieved a remarkable conductivity of $5.7 \times 10 \text{ S}\cdot\text{m}^{-1}$.^[100]

1.4.1.3 Electron-ion Conductive Hydrogel

Enhancing the conductivity of hydrogels can be achieved by introducing electronic conductivity alongside their ionic conductivity. Wang *et al.* synthesized an innovative all-polymer conductive

hydrogel featuring an interpenetrating polymer network (IPN) structure.^[101] This hydrogel incorporates electronic conductive PEDOT: PSS polymers and amphiphilic ionic poly(HEAA-co-SBAA) polymers, resulting in an elongation capacity of 4000% to 5000%, a tensile strength of 0.5 MPa, rapid self-healing within 3 minutes,^[101] and adhesion to various rigid and soft substrates. Furthermore, this hydrogel has been designed as a strain sensor with exceptional sensitivity and stability, enabling precise monitoring of slight deformations and body movements resulting from strain and pressure.

1.4.2 Mechanical property

The high-water content of hydrogels makes them highly like extracellular matrices, making them ideal for tissue engineering. However, this characteristic also causes its weak mechanical properties.^[102] To overcome the mechanical weaknesses of hydrogels, researchers have invested a great deal of work that can be achieved by adjusting cross-linking density and monomer selection. Several methods have been explored to enhance hydrogel mechanical properties, including but not limited to the addition of fillers or dopants, the utilization of anisotropic materials, and the construction of dual network structures.

A frequently employed technique involves the incorporation of fillers or dopants, which filler is used to improve its structural integrity, strength, and stiffness to enhance the mechanical properties of hydrogels. In contrast, a dopant is a substance introduced to modify the properties of the hydrogel.^[103] Nanoparticles such as silica, clay, carbon nanotubes can strengthen the structure of hydrogels by increasing their tensile strength, stiffness, and resistance to deformation.^[104] The addition of dopants, such as ionic compounds or polymers, can affect the swelling behavior of hydrogels.^[105] By controlling the degree of swelling and introducing ionic interactions, it can help adjust the mechanical properties of the hydrogel to meet specific needs.

The establishment of dual-network structures is a pivotal method for enhancing the mechanical properties of conductive hydrogels. In a typical dual-network (DN) hydrogel, the "first network" is typically rigid, brittle, and tightly crosslinked, accounting for most of the energy absorption during deformation. These bonds can be viewed as "sacrificial bonds." On the other hand, the "second network" is usually soft, ductile, and loosely crosslinked. It plays a role in preserving the integrity of the DN hydrogel once the first network breaks. These bonds are considered a source of "hidden elasticity."^[106] Cui *et al.* designed a dual network hydrogel by chemically and physically crosslinking

polyacrylamide-polyvinylpyrrolidone (PAM-PVP).^[107] They introduced a lithium chloride electrolyte to confer electrical conductivity to the hydrogel. This DN conductive hydrogel displayed exceptional ductility of about 1800%, remarkable toughness, effective compression recovery, and electrical conductivity at $2 \text{ S} \cdot \text{m}^{-1}$ and maintaining a tensile strength of $(179 \pm 28.1) \text{ kPa}$.^[107]

Another popular method to improve the mechanical properties of hydrogel is the use of anisotropic structures. Zheng *et al.* have sufficiently aligned the randomly oriented PVA molecular chains by a combined stretching-salt immobilization strategy. At the same time, the salt solution immobilizes the oriented molecules and forms more muscular molecular bundled fibers together with CNF.^[108] The oriented molecular fiber bundles and extended dimensions give the hydrogel excellent mechanical properties, with a breaking strength of more than 40 MPa, a strain close to 250 %, a toughness of more than 60 MJm^{-3} , and excellent tear resistance.^[108]

1.4.3 Self-adhesion and self-healing

The self-adhesive properties of hydrogel have the potential to improve the reliability and functionality of flexible electronic devices, especially in adhering to dynamic and highly deformable tissues such as skin. In addition, the self-healing capability can effectively extend the lifetime of the conductive hydrogel, which is essential to ensure the durability of flexible electronic devices.

Mussel-inspired conductive hydrogels have excellent self-adhesion. Zhang *et al.* developed a dopamine-triggered gel (DTG) strategy to fabricate transparent conductive hydrogels inspired by mussels.^[109] The dopamine has dual functions as polymerization initiator and dynamic cross-linking mediator. The microscale adhesion properties of DTG hydrogels were characterized by shear adhesion tests. The results showed that the adhesive strength of the DTG hydrogels increased with the increase of dopamine dosage up to 20.4 kPa.^[109] In addition, the DTG hydrogels also exhibited high adhesion to tissue surfaces, such as pig skin (adhesion strength of $10.3 \pm 0.5 \text{ kPa}$).^[109] The DTG hydrogels possessed unique dopamine-mediated dynamic interactions and self-healing capabilities. When two broken pieces of DTG hydrogel came into contact, they automatically healed into a complete block within seconds.

Another type of dynamic covalent bond that can be introduced to realize self-healing hydrogels is the borate bonds. Polyvinyl alcohol and borax can create borate bonds in hydrogel that are able to cleave and regenerate without any external stimuli. Xylan/PVA/Borax DN hydrogels were prepared using a one-pot method by Ai *et al.*^[110] Hydrogen bonding between PVA chains and hydroxyl groups

on Xylan builds the physical network, and PVA reacts with borax to form reversible borate bonds which provide the chemical cross-linking network structure. The hydrogel has an intense strength of 81 kPa, a high toughness of 1652.42 kJ/m³, and excellent self-healing properties with a self-healing efficiency of 85.8% in 30 seconds.^[110] This study successfully addressed the incompatibility between hydrogel toughness and self-healing.

1.4.4 Freezing resistance and water retention

The freezing resistance of hydrogel refers to its ability to maintain its structure and properties at low temperatures. Water is a major part of hydrogel compositions, with 80% to 90% of the volume consisting of water. In cold climates or frozen storage, the hydrogel may experience freezing.^[112] Some hydrogels can keep their original structure and properties after thawing, which is important for freezing and preserving biological samples, medical devices, or frozen drug delivery systems. The freezing resistance of hydrogel usually relates to their degree of cross-linking and the design of their molecular structure. The water retention of a hydrogel is its ability to absorb and retain water. Hydrogels can absorb enormous amounts of water, often up to their own weight in water which makes it extremely useful for moisturizing, wetting, and maintaining water balance. Water retention is important for a lot of applications such as medical dressings, cosmetics, agriculture, soil moisturizers, and cell culture of organisms.^[113]

Jian *et al.* developed a novel ion conductive hydrogel with anti-freezing, water retention and self-regeneration properties by introducing highly hydrated LiCl into the crosslinked network structure of poly(sulfobetaine) and poly(acrylic acid).^[114] This ion conductive hydrogel was not frozen after more than 30 days of storage at ultra-low temperature (-80°C), and its initial water content was maintained at about 100%.^[114] In addition, the dehydrated ionic conductive hydrogel, obtained by vacuum drying and placed at -40°C,^[114] can regenerate itself by spontaneously collecting water molecules from the surrounding environment. These properties allow the hydrogels to operate over a more comprehensive temperature range and have a longer service life.

1.5 Summary

Hydrogel has unique materials with significant advantages such as flexibility, biocompatibility, transparency, and controllable adsorption properties. Moreover, it has a wide range of potential applications in areas such as flexible wearable technology, energy storage devices and biomedicine.

In the realm of motion sensing and triboelectric nanogenerators, the unique properties of hydrogel enhance their applicability. Regarding motion sensors, the flexibility and biocompatibility of hydrogel materials render them highly suitable for monitoring human movement. They accurately capture parameters such as muscle activity, joint angles, and body temperature. Simultaneously, hydrogel proves invaluable for energy harvesting in triboelectric nanogenerators, where they efficiently convert the friction generated by human movement into electrical energy. The innovative use of hydrogel materials opens new possibilities in wearables and sustainable energy.

1.6 Objectives and scope of the research project

The distinctive physical and chemical attributes of hydrogels have catalyzed burgeoning interest and accelerated advancements in their utilization for human motion detection and energy harvesting applications. The mechanical properties of hydrogels are very similar to human tissue, making them an ideal substrate for the fabrication of flexible wearable sensors. These sensors can be easily integrated with an external power supply, and they can be attached directly to the human epidermis. The incorporation of conductive materials within the hydrogel matrix significantly augments its sensitivity to mechanical stimulus, as evidenced by modulations in electrical conductivity in response to applied stress. This phenomenon is particularly obvious during human movement. Human movement will cause changes in the shape of the hydrogel, thereby changing the resistance of the hydrogel. When a stable voltage is applied, different current signals will be generated to detect human movement in real time. The inherent elasticity and flexibility of these hydrogels is crucial for applications that require conformity to human movement. In addition, the biocompatibility of these materials highlights their suitability for prolonged skin contact, thus enhancing their potential in the burgeoning field of wearable technology.

In the field of energy harvesting, hydrogels have shown the potential to convert mechanical energy into electrical energy and this process is mainly realized by assembling hydrogels into triboelectric nanogenerators (TENG). TENG exploit the triboelectric effect, a phenomenon wherein electrical charge is generated through friction between two dissimilar materials. Upon contact and subsequent relative motion, these materials undergo charge separation, inducing an electric current within an external circuit during their separation. Within the TENG framework, hydrogels are primarily employed as electrodes. Their role is pivotal in the collection and transference of triboelectric charges, which are elicited from the frictional interaction within the layered structure of the

nanogenerator. The hydrogel's intrinsic properties, such as its high electrical conductivity, flexibility, and robust mechanical stability, render it an ideal candidate for this purpose. Hydrogel-based TENGs are particularly advantageous in capturing energy from low-frequency and irregular body movements, which is an area where rigid materials are usually not up to the task. The combination of hydrogel and TENG represents a synergistic fusion of materials science and energy harvesting technology, paving the way for innovative applications in the fields of self-powered devices and sustainable energy solutions.

Based on the extremely promising potential and application value of hydrogels in human motion sensing and triboelectric nanogenerator, two different hydrogels were designed and synthesized for these two applications. The first type of hydrogel is synthesized by combining the cellulose skeleton from natural wood with a PVA-Borax hydrogel solution. It is not only flexible but also has excellent mechanical properties, high sensitivity and can be effectively used as a human motion sensor. The second type of hydrogel is synthesized by freezing gelatin hydrogel solution with liquid nitrogen and then mediated with different salt ions to obtain different properties. TENG assembled using this hydrogel can be efficiently used to power small electronic devices.

1.7 Outline of the thesis

In the first chapter of this thesis, we delve into the evolving landscape of flexible electronics, with a particular focus on the burgeoning role of hydrogel-based technologies. This includes applications of hydrogels in wearable sensors, including self-healing, self-adhesive, anti-freeze, and multifunctional types, as well as their role in energy harvesting and biomedical devices. Additionally, the chapter thoroughly examines the characteristics of hydrogel-based flexible electronics, covering aspects like the properties of hydrogel materials, sources of hydrogel polymers, their crosslinking, and network structure. It also discusses factors affecting hydrogel properties, such as conductivity (ion, electron, and electron-ion conductive hydrogels), mechanical properties, self-adhesion, and self-healing capabilities, along with freezing resistance and water retention. Following this comprehensive overview, Chapters 2 and 3 transition to specific types of hydrogel flexible electronics.

Chapter 2, "High Sensitivity Flexible Sensing of Human Motion Using Strong, Self-Healing Wood-Based Hydrogel Composites," focuses on innovative flexible sensors crafted from wood-based hydrogel composites, characterized by high sensitivity and self-healing features. This chapter introduces the synthesis of wood-based hydrogel and the characterization of its material structure and

composition. Its mechanical properties and sensing performance as a human motion sensor are also tested. Chapter 3, " Study on the performance of flexible triboelectric nanogenerators using anion-mediated hydrogel," shifts the focus to gelatin-based hydrogels which inspired by the anion-mediated effect, and their application in triboelectric nanogenerators. This chapter focuses on the synthesis of gelatin hydrogels and the assemble of gelatin based TENG device. The mechanical properties of the gelatin hydrogel and the output performance of the TENG device were also analyzed. These chapters not only provide a deeper insight into the field of flexible electronics but also showcase the diversity and potential of hydrogel technologies in pioneering applications.

Chapter 2 High Sensitivity Flexible Sensing of Human Motion Using Strong, Self-Healing Wood-Based Hydrogel Composites

2.1 Overview

By amalgamating the intricately aligned and anisotropic cellulose structure found within natural wood with the PVA-Borax-TA hydrogel, we successfully synthesized hydrogels derived from wood that exhibit exceptional flexibility and bolstered mechanical properties. The mechanical resilience of these hydrogels reaches an impressive 19.8 MPa, marking a staggering 45-fold enhancement over the PVA-Borax-TA hydrogel. Moreover, these hydrogels not only display superb electrical conductivity, boasting a mere 20ms response time, but also possess remarkable self-healing capabilities, rendering them suitable for prolonged deployment in high-salinity regions. This underscores the significant potential of wood-based hydrogel flexible human motion sensors, offering sustained functionality in a multitude of intricate environmental conditions.

2.2 Introduction

In recent years, the rapid advancement of flexible electronic devices has underscored their remarkable attributes, including flexibility, portability, and adaptability across various contexts.^[136] Within this burgeoning landscape, flexible motion sensors have emerged as essential components of flexible electronics, adeptly accommodating bending, folding, and deformation to detect human motion. Typically, these sensors incorporate flexible electronic components onto pliable substrates, enabling the detection and measurement of human motion under a wide range of conditions, such as it adapts to the body's complex movement patterns, such as stretching, bending and twisting, to maintain accuracy and consistency across a wide range of movement conditions.^[137] These substrates often consist of synthetic polymers such as rubber, PET substrates, and elastomers, providing the necessary flexibility but possess limitations in terms of biocompatibility, thus hindering their seamless interaction with human motion.^[138]

Simultaneously, the rise of hydrogels in the field of flexible sensing has been notable, owing to their inherent characteristics of flexibility, stretchability, and biocompatibility.^[139] Hydrogels, with their 3D mesh structure, are polymer matrices with a high-water content, capable of absorbing or losing water while remaining insoluble.^[140] By carefully controlling the polymer type and water content, we aim to synthesize biocompatible sustainable hydrogels that offer both mechanical strength

and ecological safety. However, conventional hydrogels have faced challenges related to mechanical integrity and limited reusability.^[141]

Amidst this tapestry of innovation, wood emerges as a plentiful natural resource, primarily composed of cellulose, hemicellulose, and lignin. Cellulose serves as the primary scaffold of the wooden framework along its growth axis, with hemicellulose and lignin enveloping the cellulose matrix, collectively providing structural support.^[142] The fusion of the mechanically flexible hydrogel structure with the formidable strength of wood gives rise to a novel entity: the wood-based hydrogel. Wood-based hydrogel combines the pliability of hydrogels with the mechanical robustness of wood, resulting in a hybrid material that offers not only flexibility but also considerable mechanical strength.^[143] However, the presence of lignin and hemicellulose necessitates their removal, leaving behind a cellulose skeleton within wood, allowing enough space for the wood to be combined with other material.^[145]

This study utilized cellulose from wood as the main scaffold of the hydrogel network, while taking advantage of the abundance of hydroxyl groups in PVA to hydrogen-bond with the hydroxyl groups on the surface of cellulose.^[146] Strategic incorporation of borax and tannic acid bolsters the hydrogel's intrinsic self-healing capabilities with dynamic borate bond. Meanwhile, the fusion of hydrogel with cellulose culminates in a composite manifesting exceptional flexibility and robust mechanical properties. This is attributed to the intricate cross-linking of PVA and borax via boronic acid diester bonds, thereby engendering self-healing potential through continual fracture and reorganization.^[147] The infusion of tannic acid further accentuates tensile attributes, underscoring its pivotal role.

Elevating the hybrid's utility, introducing sodium sulphate salt solution during the initial hydrogel precursor formulation imparts commendable electrical conductivity, thereby rendering the wood-based hydrogel eminently suited for human motion sensing applications. The present study thus pioneers an innovative approach at the nexus of material science and nature's ingenuity, yielding a wood-based hydrogel amalgam that not only surmounts existing limitations but also forges ahead to redefine the landscape of flexible sensing technology.

2.3 Experimental Methods

2.3.1 Chemicals

Basswood purchased from Amazon. Poly vinyl alcohol (Mw 89,000-98,000, 99+% hydrolyzed), Sodium tetraborate decahydrate (ACS reagent, $\geq 99.5\%$), Tannic acid (ACS reagent), Sodium sulfate (ACS reagent, $\geq 99.0\%$, anhydrous, granular), Sodium chlorite (technical grade, 80%), Sodium hydroxide (ACS reagent, $\geq 97.0\%$, pellets), Acetic acid (glacial, ReagentPlus®, $\geq 99\%$) and other chemical reagents were all purchased from Sigma-Aldrich Corporation (Canada). 3D hydrogel molds were printed by Fortus 360mc at the Rapid Prototyping Centre at the University of Waterloo.

2.3.2 Removal of lignin from natural wood

Natural wood was precisely cut into small pieces measuring 3×3 mm with a thickness of 1 mm (**Figure 2.1**). Subsequently, 5 grams of sodium chlorite (NaClO_2) were meticulously dissolved in water to make a 2 wt% solution and subjected to sonication for thirty minutes until the solution attained a clarified state. Following this, acetic acid was gradually added dropwise to the sodium chlorite (NaClO_2) solution until its pH reached approximately 4.6.^[147] The NaClO_2 solution was then subjected to heating in an oil bath, raising its temperature to 130 °C until it reached a boiling point. Following this, the prepared wood slices were immersed in this solution for two hours, leading to a transformation of their color from yellow to white. It is noteworthy that the NaClO_2 solution may undergo evaporation during this process, necessitating timely replenishment with NaClO_2 solution and acetic acid.^[148] Once the wood chips had completely transitioned to a white hue (**Figure 2.1**), they were removed from the solution and subsequently washed three times with ethanol and deionized (DI) water, respectively, to ensure complete removal of all chemicals. Following this, the wood chips were subjected to drying in an oven set at 80 °C for 4 hours. To prepare a 15 wt% sodium hydroxide (NaOH) solution, 15 grams of sodium hydroxide pellets were introduced into 85 mL of DI water. The NaOH solution was then subjected to sonication for one hour until it achieved a clear and clarified state. The previously dried "white wood" was immersed in this NaOH solution for two hours, after which it was removed and subjected to several washes with ethanol and DI water to ensure the complete removal of all chemicals. Finally, the "white wood" was once again placed in an oven set at 80 °C for 4 hours to complete the drying process.

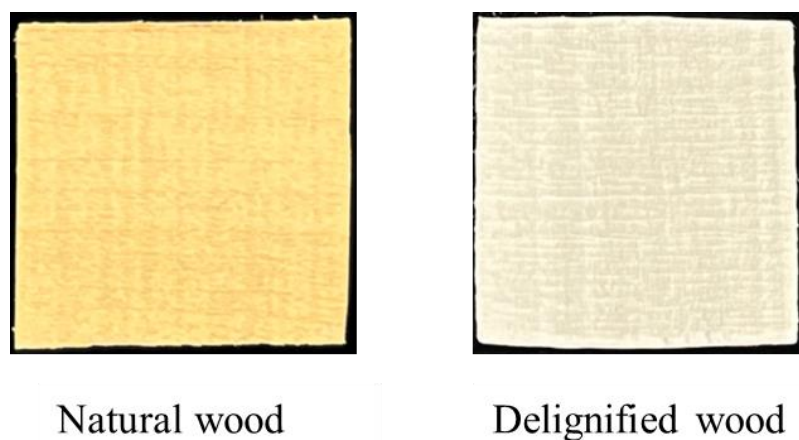


Figure 2.1 Optical images of natural wood and delignified wood.

2.3.3 Synthesis of WPBTS and PBTS hydrogels

Firstly, 6 g of PVA powder was dissolved in 54 mL of UP water, the temperature was maintained at 90 °C during the dissolution process while the solution was stirred at 400 r/min until a clear and clarified PVA solution was formed. After that, 0.6g of sodium sulfate powder and 0.6g of TA powder were added to the solution respectively and stirred continuously until completely dissolved. In parallel, 0.4 grams of Borax powder were dissolved in 9.6 mL of UP water, and the solution was sonicated for one hour to ensure complete dissolution. Subsequently, 4 mL of the Borax solution were added to the PVA solution. The mixture was then stirred at 600 r/min for one hour to yield the clarified hydrogel precursor solution. The prepared "white wood" was immersed in this precursor solution and subsequently placed in an oven at 90 °C for half an hour to evacuate air bubbles from the solution. Following this step, the beaker containing the hydrogel precursor solution with the "white wood" was placed in an oil bath at 90 °C and heated for 12 hours to allow complete immersion of the hydrogel solution into the wood chips. Subsequently, the wood was removed from the hydrogel solution and positioned between two glass pieces. It was then transferred to a -20 °C refrigerator and frozen for 12 hours. Finally, the wood was removed from the refrigerator and allowed to thaw at room temperature for 1 hour, resulting in the formation of the Wood-PVA-Borax-Tannic Acid-Sodium Sulfate (WPBTS) hydrogel. For the preparation of PVA-Borax-Tannic Acid-Sodium Sulfate (PBTS) hydrogels, a similar process was followed. The hydrogel precursor solution was synthesized and poured into pre-prepared 3D printed molds, followed by freezing in a refrigerator for 12 hours and

subsequent thawing at room temperature. The molecular structural formula of WPBTS hydrogel is shown in **Figure 2.2**.

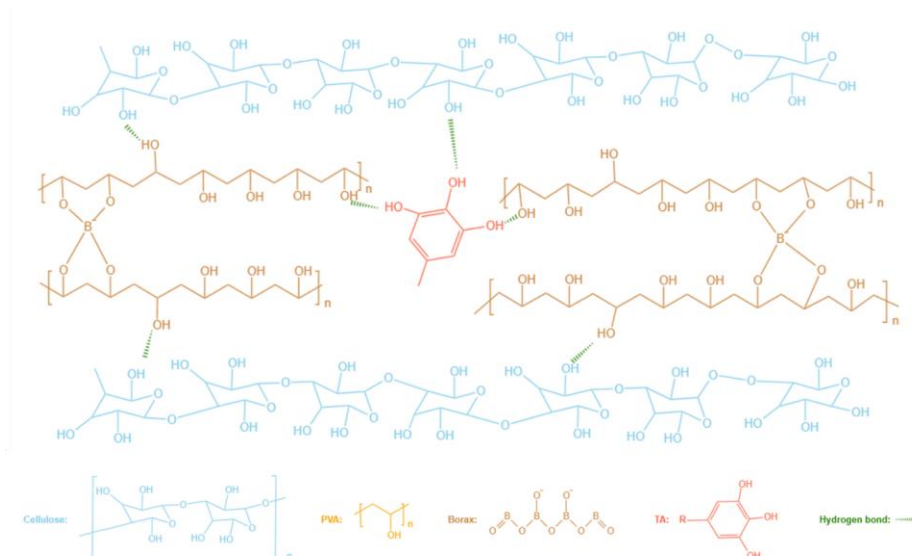


Figure 2.2 Molecular formula of WPBTS hydrogel.

2.3.4 Characterization

Optical images of natural wood, de-lignified wood and hydrogel wood are taken by an mobile phone camera. Their microstructures were characterized by scanning electron microscopy (SEM). The crystal structures of natural wood and de-lignified wood were obtained by X-ray diffraction (XRD) patterns. Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet iS10 FTIR spectrometer (Thermo Scientific Inc., America) equipped with a reflectance attenuated total reflection (ATR) system. All samples were analyzed at 500-4000 cm^{-1} wavenumber using 16 cumulative scans with a resolution of 2 cm^{-1} . The water retention of WPBTS and PBTS hydrogels in the same environment was obtained by weighing the masses at different times. Synchrotron based small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) of natural wood, delignified wood, and hydrogel wood were measured at the Canadian Light Source to determine its directionality. To measure the sensitivity of the hydrogel, the hydrogel was placed on a PET substrate wrapped with two pieces of copper tape at the top and bottom, connected to an electrochemical workstation (Gamry Instruments Inc.), and fed with a steady 1 V Voltage. When an external action deforms the hydrogel, it causes the length, width and height of the hydrogel to change, thus changing

its electrical resistance. When the external voltage is kept constant, the current will change. Afterwards, different masses of weights were used to press the hydrogel separately to detect the change in sensitivity. Sensitivity is defined as $S = \Delta I / m$ and $\Delta I = (I - I_0) / I_0$. I_0 is the initial current, I is the current after the weight is touched, and m is the mass of the weight. WPBTS hydrogels were immersed in a salt solution of simulated saline soil for 14 days, and the changes in morphology and quality were examined to determine their salinity resistance. The hydrogels were cut into strips of equal size (3x1x1mm) and clamped on an Instron (ADMET Inc., USA) at a stretching rate of 20mm/min. Each hydrogel with a different content of PVA was measured three times to determine its mechanical properties. The masses of natural wood, de-lignified wood, and different ratios of hydrogel wood were weighed separately using a balance to determine the content of each component in the hydrogel. Sensing performance was measured by the following procedure. The hydrogel is placed on the PET substrate and the top and bottom ends are wrapped with copper tape, respectively. Afterwards, it is connected to the electrochemical workstation (Gamry Instruments Inc.), with a constant voltage output. The hydrogel is then attached to each joint of the human body with double-sided tape to detect changes in the current signal before and after human movement.

2.4 Results and discussion

In nature, wood is characterized by a complex, three-dimensional layered framework comprising hollow fibers.^[149] These fibers have cell walls composed of robust cellulose fibrils embedded within a softer, amorphous matrix consisting of hemicellulose and lignin.^[149] In nearly all types of wood, these fibers are oriented primarily in the direction of tree growth, creating a highly anisotropic structure. Each wood fiber contains numerous microfibrils, each of which can be further broken down into nanofibers, including cellulose nanofibers (CNF).^[150] Through a process known as de-lignification, lignin can be extracted from wood, resulting in the release of tight connections between bundles of CNF while preserving the inherent structure of the aligned cellulose backbone.^[151] By introducing a PVA-Borax hydrogel solution in conjunction with the cellulose backbone, a flexible PBTS hydrogel is formed, exhibiting significantly improved mechanical properties.

Scanning Electron Microscope (SEM) was employed to examine the microstructures of both natural wood and WPBTS hydrogels. A noteworthy difference emerged when comparing the two: in the radial (R) direction of the wood within WPBTS, the honeycomb structure of the wood exhibited significant contraction as shown in the **Figure 2.3 (a) and (c)**. This phenomenon can be attributed to

the use of sodium hydroxide, which serves to soften the cellulose cell wall structure.^[152] Additionally, as shown in the **Figure 2.3 (c) and (g)**, the presence of hydrogel condensation both within and around the wood pores was observed in both the longitudinal (L) and radial (R) directions, indicating the successful adhesion of the hydrogel to wood cellulose. Furthermore, elemental maps revealed the presence of four elements: boron (B), carbon (C), sodium (Na), and oxygen (O). These elemental maps further confirmed the successful integration of the hydrogel with the wood structure.

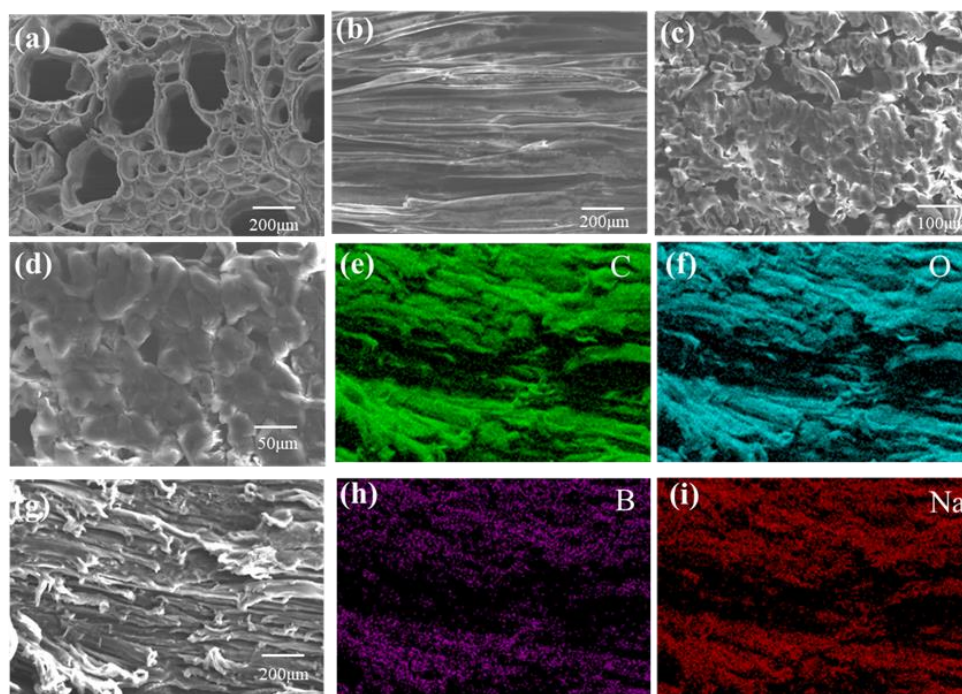


Figure 2.3 SEM image of natural wood and WPBTS. (a) SEM images of natural wood in R direction. (b) SEM images of natural wood in L direction. (c) SEM images of WPBTS in R direction. (d) Enlarged image of c. (g) SEM images of WPBTS in L direction. (e) The elemental maps of C for WPBTS hydrogel. (f) The elemental maps of O for WPBTS hydrogel. (h) The elemental maps of B for WPBTS hydrogel. (i) the elemental maps of Na for WPBTS hydrogel.

As depicted in **Figure 2.1** and **Figure 2.4 (a)**, after the removal of lignin, the color of natural wood undergoes a transformation from yellow to white, accompanied by a substantial mass loss of 60 wt.%. The mass ratios in the **Figure 2.4 (a)** imply the mass ratio of natural wood, delignified wood and WPBTS hydrogel wood to natural wood. This color change is attributed to the fact that the color-contributing elements in natural wood primarily stem from lignin^[155]. The elimination of lignin and

hemicellulose results in a softer "white wood" appearance. We conducted X-ray diffraction (**Figure 2.4(b)**) analysis on both natural wood and delignified wood. Our findings revealed the presence of two broad crystal reflections within the 2θ range of $10-40^\circ$, occurring at approximately 16.4° , 22.8° and 35.1° , corresponding to the (1 0 1), (0 0 2) and (0 4 0) crystal planes of cellulose.^[156] These reflections are indicative of the characteristic peaks associated with cellulose crystal structures. This XRD analysis underscores that the de-lignification process did not alter the crystal structure of cellulose. The intensity of these two diffraction peaks was higher in delignified wood compared to natural wood. This phenomenon is attributed to the increased relative cellulose concentration within the wood composition following the removal of hemicellulose and lignin, resulting in heightened diffraction intensity.

In addition, FTIR characterization of WPBTS was used to determine the successful binding of the hydrogel to the wood. In **Figure 2.4 (c)** for WPBST hydrogels, O-H stretches at 3315 cm^{-1} , which is a significant peak for PVA.^[178] C-H₃ bond stretches around 2960 cm^{-1} ^[179] and C-O bond of stretches at 1086 cm^{-1} ,^[180] both characteristic peaks for PVA. The spectral peak at 1705 cm^{-1} is due to C=O stretching vibrations in TA.^[181] The peaks at 1426 cm^{-1} and 1338 cm^{-1} are related to the asymmetric stretching vibration of B-O, which proves the presence of borax.^[157] These characteristic peaks successfully demonstrate the successful binding of PVA-Borax-TA hydrogels to wood.

Thermogravimetric Analysis (TGA) on both WPBTS and PBTS hydrogels are shown in **Figure 2.4 (d)** and **Figure 2.4 (e)**. Specifically, for the WPBTS hydrogel, we observed distinct thermal degradation patterns. The mass loss attributed to the evaporation of water occurred in the temperature range of $0-200^\circ\text{C}$ (**Figure 2.4 (d)**). Subsequently, between $200-300^\circ\text{C}$ (**Figure 2.4 (d)**), the primary degradation process was associated with polyvinyl alcohol (PVA).^[158] The most rapid degradation, occurring between $300-500^\circ\text{C}$ (**Figure 2.4 (d)**), was ascribed to cellulose within the hydrogel.^[159] For PBTS hydrogel, as shown in the **Figure 2.4 (e)**, Since water makes up the majority of the mass of the PBTS hydrogel (about 80%), the TGA curve decreases dramatically from 0 to 150°C , mainly due to the evaporation of water from the hydrogel. This process is mainly due to the volatilization of water from the hydrogel. After 150°C , the TGA curve decreases slowly and stabilizes. TGA analysis provides valuable information about the thermal stability and decomposition behavior of the hydrogel constituents.

Additionally, we investigated changes in the volume and mass of both hydrogels by immersing them in ultra-pure water. We observed that the mass and volume of both hydrogels increased as they soaked in the water as shown in **Figure 2.4 (f)** and **Figure 2.4 (g)**. Notably, the mass and volume of the PBTS hydrogel exhibited a greater increase compared to the WPBTS hydrogel. The mass and volume of PBTS hydrogels at swelling equilibrium in water were 3.5 and 4.1 times the initial mass and volume, whereas the mass and volume of WPBTS hydrogels at swelling equilibrium in water were 1.3 and 1.5 times the initial mass and volume. This discrepancy can be attributed to the inherent challenge of allowing moisture to penetrate the hydrogel due to the tightly interlinked cellulose structure of wood within the WPBTS hydrogel.^[161]

Subsequently, the water retention capacity of WPBTS and PBTS hydrogels was evaluated in **Figure 2.4 (h)**. The water retention of a hydrogel is the ability of a hydrogel material to absorb and retain water. A hydrogel with high water retention can absorb and retain large amounts of water without easily releasing this water due to changes in the external environment. The decrease in mass of hydrogels at room temperature is usually due to evaporation of water. The retention of water within the hydrogel is detected by placing the hydrogel at room temperature and measuring the change in its mass. Both hydrogels were subjected to the same temperature at 23°C, while we monitored changes in their mass every 12 hours (**Figure 2.4 (h)**). Throughout this experiment, we observed that the WPBTS hydrogel exhibited superior water retention compared to the PBTS hydrogel (**Figure 2.4 (h)**). This enhanced water retention capability can be attributed to the tightly interconnected cellulose structure of wood, which hinders the evaporation of water from the hydrogel into the surrounding air.^[160]

The WPBTS hydrogel also demonstrated excellent optical properties, as depicted in **Figure 2.4 (i)**. It exhibited an impressive transmittance of 40% across the wavelength range of 400 to 1000nm. This underscores the hydrogel's transparency and its ability to allow the passage of light, which makes it suitable for various optical applications. When the transmittance along the L direction and the R direction were examined separately, different results were observed due to the oriented structure of the cellulose backbone. WPBTS hydrogel has a slightly higher light transmission in the R direction than in the L direction.

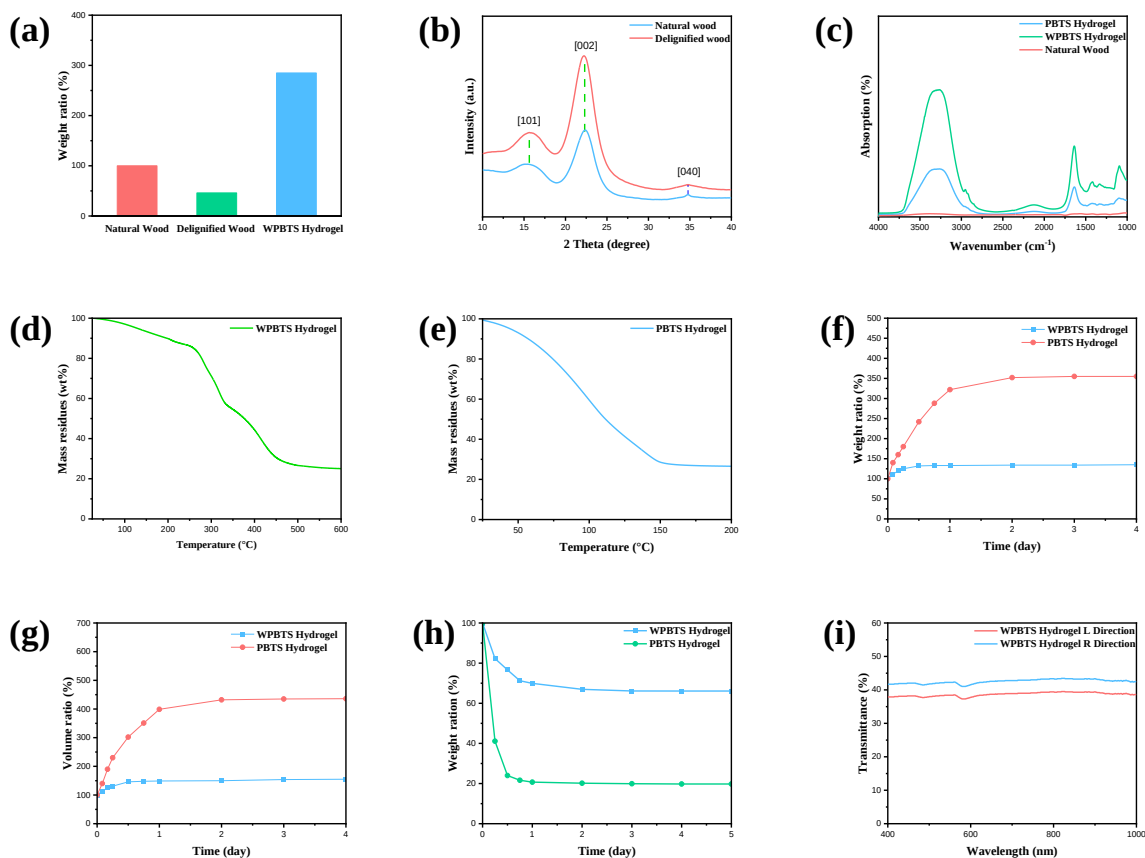


Figure 2.4 Structure properties of WPBTS and PBTS. (a) Weight ratio of natural wood, delignified wood and WPBTS. (b) XRD pattern of Natural wood and delignified wood. (c) FTIR of WPBTS and PBTS hydrogel. (d) TGA of WPBTS hydrogel. (e) TGA of PBTS hydrogel. (f) Changes in weight of WPBTS hydrogel and PBTS hydrogel mass in the swelling rate test. (g) Changes in weight of WPBTS hydrogel and PBTS hydrogel mass in the swelling rate test (h) Changes in the volume of WPBTS hydrogel and PBTS hydrogel in water retention tests. (i) Transmittance of WPBTS hydrogel in R direction and L direction.

As shown in **Figure 2.5(a)** and **Figure 2.5(b)**, the longitudinal (L) direction of wood is the direction along which the cellulose grows in a directional direction, and the radial (R) direction is the direction perpendicular to the cellulose growth. To illustrate the exceptional flexibility of the WPBTS hydrogel, it can be easily folded along the diagonal as shown in **Figure 2.5(c)**. It was folded in the L and R directions as shown in **Figure 2.5(d)** and **Figure 2.5(e)**. Upon returning the hydrogel to its original shape, no cracking or damage was observed. Furthermore, the WPBTS hydrogel displayed the ability

to be rolled up and recycled along either the L or R direction, and it could be folded from all sides without compromising its surface structure as shown in **Figure 2.5 (f)**. These demonstrations unequivocally highlight the outstanding flexibility and resilience of the WPBTS hydrogel, making it a robust and adaptable material for various applications. Whether in the rigid longitudinal (L) direction or the more pliable radial (R) direction, the WPBTS hydrogel demonstrates exceptional flexibility. It can be bent freely without incurring any damage to the hydrogel, displaying its robust and resilient nature in any directions.

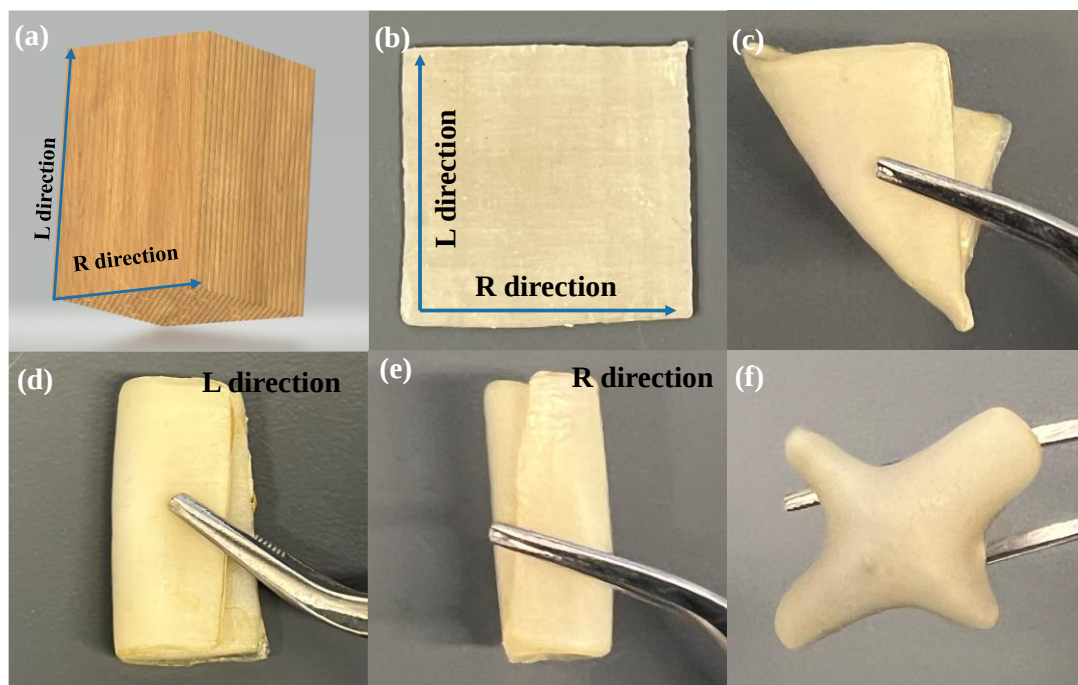


Figure 2.5 Physical picture of WPBTS hydrogel. (a) Schematic 3D model of WPBTS hydrogel in L and R directions (b) Optical image of WPBTS hydrogel in L and R directions (c) WPBTS hydrogel folded in half. (d) WPBTS hydrogel bends in L direction. (e) WPBTS hydrogel bends in R direction. (f) WPBTS hydrogel folds in four different directions simultaneously to the back.

SAXS (Small-Angle X-ray Scattering) testing was conducted on natural wood, de-lignified wood, and WPBTS, revealing that all three materials exhibited remarkable orientation. This orientation can be attributed to the stable structure of the cellulose skeleton inherent in wood. However, when lignin was removed and hydraulic condensation was introduced to create WPBTS, its orientation was found

to be weaker compared to that of natural wood and de-lignified wood. This disparity suggests that the modification process impacts the material's orientation.

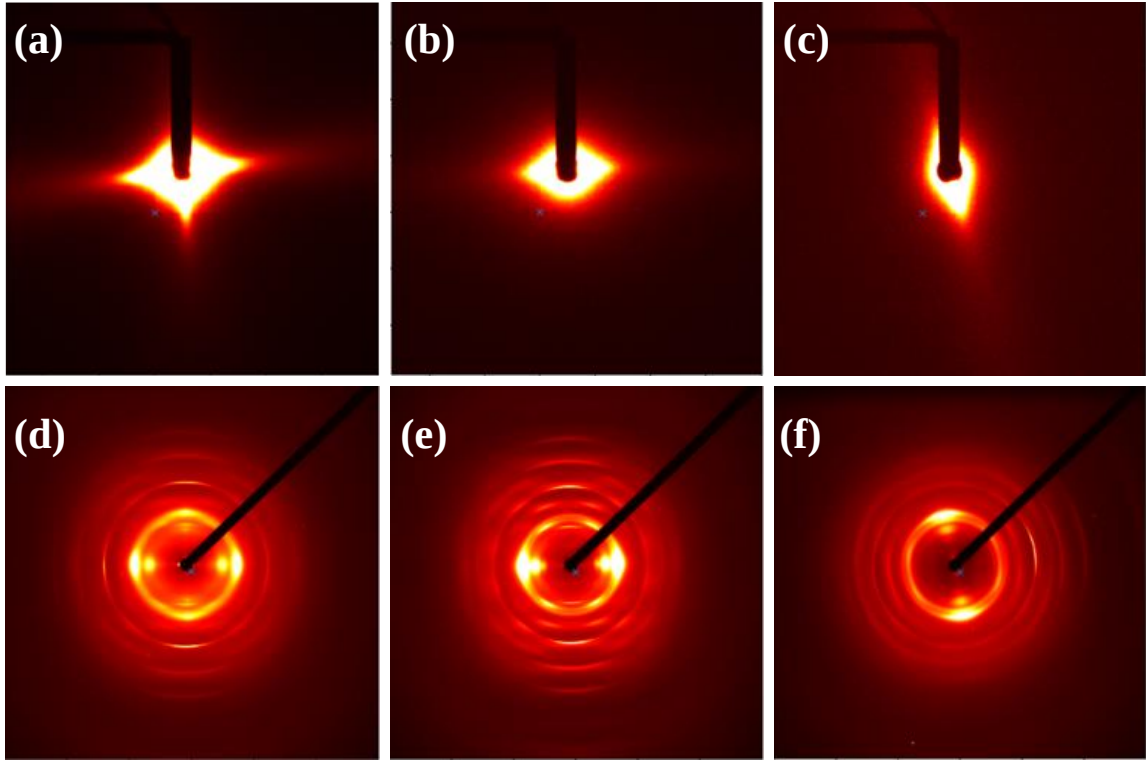


Figure 2.6 SAXS and WAXS of natural wood, delignified wood and WPBTS. (a) SAXS of natural wood, (d) WAXS of natural wood. (b) SAXS of delignified wood, (e) WAXS of delignified wood. (c) SAXS of WPBTS, (f) WAXS of WPBTS.

The tensile strength of WPBTS hydrogels with varying PVA concentrations (5wt%, 10wt%, and 15wt%) was assessed, as depicted in **Figure 2.7 (a)**. The concentration of polyvinyl alcohol (PVA) was found to have a significant impact on the mechanical properties of the hydrogel. In the case of WPBTS with 5wt% PVA, the low PVA concentration resulted in an inadequate solid content within the hydrogel, impairing the formation of effective crosslinking. Consequently, this hydrogel exhibited a relatively low breaking strength. Conversely, WPBTS with 10wt% PVA displayed remarkable mechanical characteristics. It demonstrated an elongation rate of 13%, coupled with an impressive breaking strength of 19.8 MPa (**Figure 2.7 (a)**). This represents a substantial improvement, as it is 45

times greater than that of the PBTS hydrogel (**Figure 2.7 (b)**). This combination of enhanced elongation and higher breaking strength showcases its exceptional mechanical properties. However, WPBTS with 15wt% PVA exhibited reduced elongation, registering only 7% (**Figure 2.7 (a)**). This can be attributed to the excessively high PVA concentration, which elevated the viscosity of the hydrogel solution, making it difficult to fully penetrate the wood structure. In summary, for WPBTS hydrogels, the optimal PVA concentration is 10wt%, as it strikes an excellent balance between elongation and breaking strength, outperforming PBTS hydrogels in terms of mechanical properties.

When comparing the breaking strength in the longitudinal (L) direction with that in the radial (R) direction, it is apparent that the breaking strength in the R direction is relatively weaker as shown in **Figure 2.7 (b)**. However, the R direction exhibits better elongation at the point of rupture as shown in **Figure 2.7 (b)**. This phenomenon can be attributed to the structural differences between the two directions. In the R direction, the hydrogel forms individual connections with the cellulose skeleton which can be seen in SEM. The exceptional stretchability of the hydrogel in this direction contributes to an overall higher fracture strain when it is stretched. Consequently, while the breaking strength may be weaker, the ability to elongate before rupture is notably enhanced (**Figure 2.7 (b)**). On the other hand, in the L direction, the cellulose backbone bears most of the load during stretching. While this direction may exhibit better breaking strength, it results in a lower strain before reaching the breaking point. In summary, the different mechanical properties between the L and R directions are due to the distinct roles played by the cellulose skeleton within the hydrogel. The R direction benefits from the hydrogel's stretchability, leading to improved elongation, while the L direction relies more on the strength of the cellulose backbone. This outcome demonstrates the hydrogel's remarkable stability and resilience, as it maintains its compressibility and structural integrity even under repetitive compression cycles. In addition to that, as shown in **Figure 2.7 (d)**, the WPBTS hydrogel possesses an elastic modulus of up to 204 MPa in the L-direction, which is much higher than its elastic modulus in the R-direction and PBTS hydrogel. Such stability is a promising characteristic for various practical applications where enduring and reliable performance is essential. Additionally, the corresponding material toughness can be obtained by calculating the integral area of the stress-strain curves of the WPBTS hydrogel in the L and R directions and of the PBTS hydrogel. This is due to the orientation of WPBTS hydrogels in the L-direction being much higher than that in the R-direction and PBTS hydrogels. The oriented structure allows stresses to be distributed more evenly within the

hydrogel, absorbing and dispersing energy more efficiently under tension or compression, which helps to prevent stress concentration and localized fracture, resulting in improved toughness.

Afterwards, *in situ* SAXS characterization (**Figure 2.7 (f)**) were conducted by stretching WPBTS on a customized tensile testing holder (**Figure 2.7 (g)**). The orientation of the WPBTS hydrogel gradually increased with the increase of strain. This is due to the better orientation of the cellulose backbone during *in situ* stretching. This enhancement is reflected in the increased longitudinal orientation of the material by stretching. These experiments provided valuable insights into the correlations between the mechanical behavior and structural changes of WPBTS under different stretching conditions.

The self-healing properties of WPBTS hydrogels were evaluated. In this examination, a complete piece of WPBTS hydrogel was deliberately cut in half, after which the two severed halves were firmly reconnected through the application of external force for ten minutes. Following the removal of the external force, the two previously separated halves successfully reverted to their original shape without exhibiting any surface scratches. This impressive self-healing ability can be attributed to the dynamic hydrogen bonds between cellulose and PVA, as well as the dynamic borate diester bonds between PVA and borax. These bonds continuously break and reform, enabling the hydrogel to effectively self-heal. Furthermore, we conducted tests on cuts made in both the longitudinal (L) and radial (R) directions. As shown in **Figure 2.7 (h)-(i)**, the self-healing fracture strength of WPBTS hydrogel in the R direction was determined to be 0.4 MPa, representing 30% of its initial fracture strength. In contrast, the self-healing performance in the L direction was less effective, with the self-healing fracture strength amounting to only 0.2 MPa, which is just 5% of its initial fracture strength. The variation in self-healing performance is attributed to the hydrogel's distribution around the cellulose backbone. When cutting in the L direction, it only affects a small portion of the cellulose, allowing the remaining hydrogel to successfully self-heal. Conversely, cutting in the R direction severs a substantial portion of the cellulose backbone, significantly compromising the mechanical properties of the self-healing hydrogel. After self-healing, the elastic modulus of WPBTS in the R direction recovers to 60% of its original state, while its toughness is restored to 35%. These results highlight the directional variation in self-healing performance and the remarkable recovery capacity of WPBTS hydrogels.

As shown in **Figure 2.7 (e)**, WPBTS hydrogels exhibit excellent mechanical properties compared to other hydrogels or natural tissue structures.^[182-191] Not only does it possess excellent fracture strength, but it also has a very high modulus of elasticity.

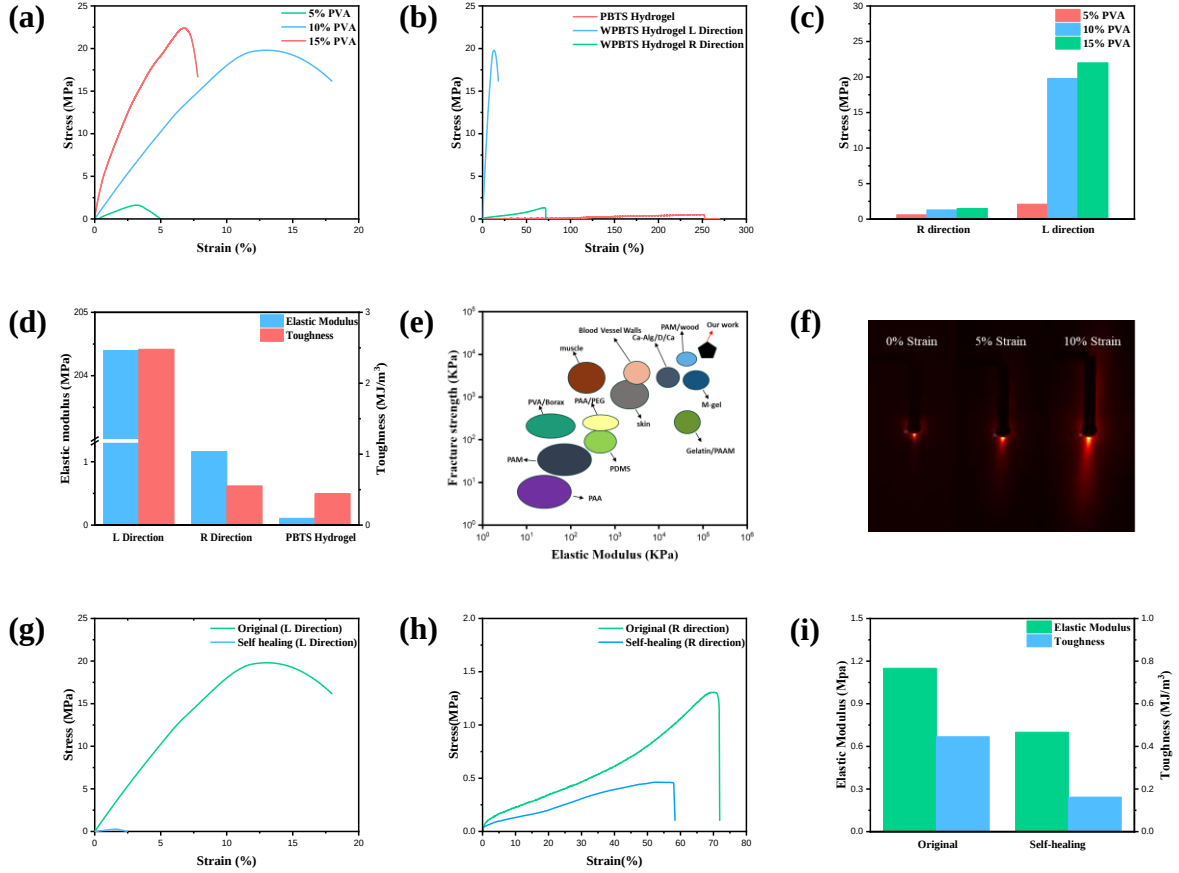


Figure 2.7 Mechanical properties of WPBTS and PBTS. (a) Tensile strain of 5wt%, 10wt%, 15wt% PVA WPBTS hydrogel in L direction. (b) Tensile strain of 10wt% WPBTS hydrogel in L direction, R direction and PBTS hydrogel. (c) Breaking strength of 5wt%, 10wt%, 15wt% PVA WPBTS in L direction and R direction. (d) Elastic modulus and toughness of WPBTS hydrogel in L direction and R direction and PBTS hydrogel. (e) Our work compares elastic modulus and fracture strength with other materials.^[182-191] (f) Changes in the orientation of WPBTS hydrogel during stretching. (g) Tensile strain of original and self-healing WPBTS in L direction. (h) Tensile strain of original and self-healing WPBTS in R direction. (i) Elastic modulus and toughness of original and self-healing WPBTS in R direction.

Furthermore, utilizing WPBTS hydrogels as flexible sensors to monitor changes in electrical signals during human movement. In the preparation of the hydrogel precursor solution, sodium sulphate was incorporated as an ion-conductive agent. We created sodium sulphate solutions with varying concentrations to measure the conductivity of WPBTS hydrogels. As the concentration of sodium sulphate increased, so did the hydrogel's conductivity (**Figure 2.8 (a)**). However, once the sodium sulfate content exceeded 0.9wt%, the hydrogel's conductivity remained stable and did not increase further with higher ion concentrations (**Figure 2.8 (a)**). To conduct real-time monitoring of human motion, we affixed WPBTS hydrogel to different joints of the human body using ordinary adhesive tape and recorded changes in electrical current through electrochemical work station (Gamry Instrument Inc.). The WPBTS hydrogel exhibited an impressive response time of only 20 milliseconds (**Figure 2.8 (b)**). We do regular finger bending when connecting the two ends of the WPBTS hydrogel in the L direction and the two ends of the WPBTS hydrogel in the R direction to the positive and negative electrodes of the electrochemical workstation, respectively as shown in **Figure 2.8(c)**. It was found that the magnitude of the initial current was different in the L direction and the R direction because the resistance of the WPBTS hydrogel in the L direction tended to be lower than that in the R direction. The salt ions in the hydrogel in the L direction move in an orderly manner along the direction of oriented cellulose growth. In contrast, in the R direction, salt ions need to be transported with relative difficulty across multiple cell wall structures with abundant pores. We observed that current fluctuations corresponded to movements such as bending the fingers, knuckles, elbows, or knees (**Figure 2.8 (d)-(e)**). This occurs because bodily motion compresses and deforms the hydrogel, altering the ion concentration per unit volume of the hydrogel, which in turn affects conductivity and current flow. These results indicate that WPBTS hydrogels can effectively and in real-time detect human motion. Furthermore, we discovered that WPBTS hydrogels could still detect stable signals during activities such as coughing and breathing (**Figure 2.8 (f)-(g)**), indicating their ability to perform reliably even under slight deformation. This versatility suggests that WPBTS hydrogels have potential applications in monitoring various human activities and physiological processes. To explore the limits of sensitivity in WPBTS hydrogels, we immersed the hydrogel in ultrapure water for varying durations to investigate changes in sensitivity. The hydrogel possesses swelling properties, causing its mass to increase as it absorbs water (**Figure 2.8 (h)**). The mass ratio is the ratio of the mass of the hydrogel after it has swollen in water to the initial mass not placed in water. This increase in water content enhances the rate of ion flow within the hydrogel, subsequently

influencing its sensitivity (**Figure 2.8(i)**). Notably, the highest sensitivity of WPBTS was achieved after a 4-hour immersion (**Figure 2.8(i)**). However, beyond this duration, the hydrogel's sensitivity began to decline due to the excessive water content, which resulted in a reduction in the relative ion concentration (**Figure 2.8(i)**). Subsequently, the hydrogel reached a state of swelling equilibrium, and its sensitivity remained stable. Throughout the process, the maximum sensitivity of the hydrogel increased to 1.52 times the initial sensitivity. (**Figure 2.8(i)**). This demonstrates the capability of adjusting the water content of the hydrogel as an effective means to enhance its sensitivity, offering potential applications where sensitivity adjustments are critical.

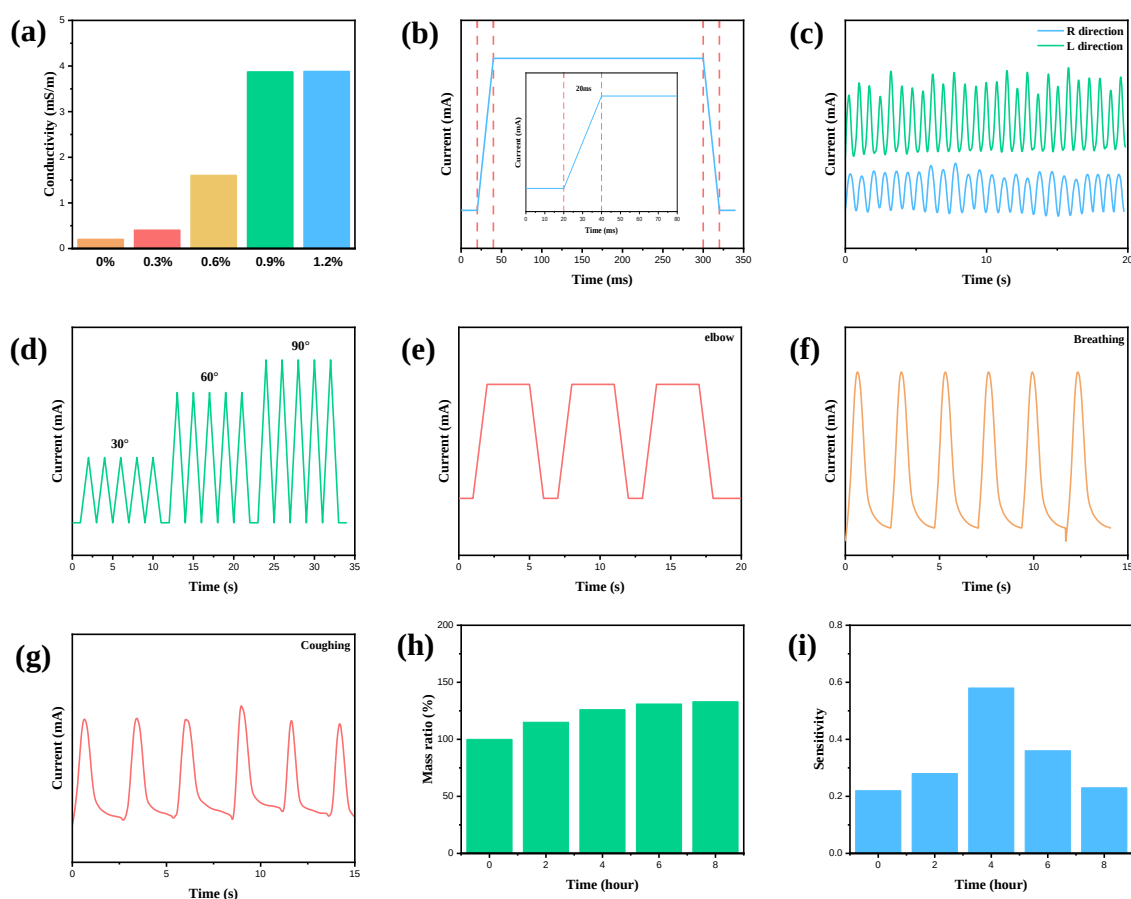


Figure 2.8 Sensing performance of WPBTS as flexible sensors. (a) Effect of different concentrations of Na_2SO_4 on conductivity. (b) Response time of WPBTS. (c) The change of current signal when folding in L direction and R direction. (d) Current signals of finger bending with different amplitudes. (e) Current signals of elbow bending. (f) Current signals of breathing. (g) Current signals of

coughing. (h) Changes of Mass WPBTS hydrogel Swelling. (i) Changes of sensitivity during WPBTS hydrogel Swelling.

2.5 Conclusion

Through the incorporation of hydrogels into the cellulose framework after delignification, we have achieved the successful synthesis of wood-based hydrogels. These hydrogels exhibit exceptional flexibility, impressive mechanical strength, high electrical conductivity, and rapid response times. Furthermore, they display remarkable sensitivity and self-healing capabilities while maintaining their functionality in high-saline environments over extended periods. This research breakthrough holds great promise for advancing the development of next-generation wearable devices and multifunctional sensors characterized by biomimetic properties. The synergistic combination of wood-based materials and hydrogels opens exciting possibilities for innovative applications in various fields, offering solutions that harness the best of both natural and synthetic materials.

Chapter 3 Study on the performance of flexible triboelectric nanogenerators using anion-mediated hydrogel.

3.1 Overview

To cope with the developing global energy shortage, the development of self-powered wearable devices has shown a significant growth in recent years. Hydrogel based triboelectric nanogenerator is a promising innovative technology for energy harvesting with significant potential advantages in the areas of eco-friendliness, sustainability, and adaptability. In this study, we have effectively synthesized a high-strength hydrogel based on gelatin, boasting a fracture strength of 1.5 MPa, a compression strength of 1.1 MPa, and exceptional compression cycling stability through the utilization of the anion-mediated effects and directional freezing methodologies. Moreover, the resultant hydrogel establishes a triboelectric nanogenerator when employed as an electrode, yielding an open-circuit voltage of up to 150V and a short-circuit current of 1 μ A. Remarkably, this device obviates the need for an external power supply to charge small electronic devices, offering an innovative solution to energy-related challenges.

3.2 Introduction

Human reliance on wearable sensors for monitoring physical and physiological conditions is increasing, contributing to an improved quality of life.^[162] Wearable and connectable devices, for instance, are capable of tracking parameters such as heart rate and electrocardiogram (ECG) signals, offering valuable data for diagnosing heart diseases. Flexible electronic devices can be used to measure skin temperature, which serves as a direct indicator of certain diseases linked to immune responses. Analyzing body movements can unveil health conditions related to orthopedic, muscular, or neurologic disorders.^[163] Moreover, adhesive electronic patches can keep tabs on sweat to provide insights into metabolic status. Sensing devices have been developed to monitor respiration, blood, and skin, delivering early warning signals for associated diseases.^[164]

While there have been substantial advancements in laboratory research over the past decade, the widespread adoption of flexible sensors in the market has been limited due to various bottlenecks, with flexible power source being a significant issue.^[165] More specifically, the inclusion of batteries in wearable sensor systems imposes constraints on their size, weight, and flexibility, which in turn restricts their potential applications. Furthermore, continuous monitoring is interrupted when the

battery is depleted, potentially impacting the accuracy of data collection, and reducing user engagement. Therefore, the development of wearable systems with innovative flexible power supply technologies is of utmost importance. The concept of triboelectric nanogenerators was initially introduced by Zhonglin Wang in 2008.^[166] This device is designed to convert mechanical motion into electrical energy, which can then be used to power various sensing processes, including data acquisition, processing, and transmission.

Hydrogel has significant advantages in triboelectric nanogenerators. Their high-water absorption capacity and flexibility enable them to conform to small mechanical movements and efficiently absorb ambient moisture, contributing to the overall system's stability.^[167] Additionally, the biocompatibility, malleability, and ample surface area of hydrogel materials make them suitable for applications in the biomedical field, particularly in implantable medical devices and biosensors. Furthermore, their environmental friendliness and adaptability to high humidity align with the sustainability and green technology requirements, making them a promising choice for various applications.^[168] In practice, hydrogels are often not used for long periods of time due to their weak mechanical properties and easily loses water in the air. The anion-mediated effect is a phenomenon that impacts hydrogels, leading to the development of a multiscale structure within the material. This effect occurs by altering the crystallinity and internal network structure of the polymer molecules.^[169] As a result, the mechanical properties of hydrogels are significantly enhanced, making them more durable and suitable for the triboelectric nanogenerators. Wu *et al.* successfully manipulated the aggregation state of PVA polymer chains by employing various ion pairs from the anion-mediated effect.^[170] This manipulation allowed them to achieve the creation of PVA hydrogels with dynamically tunable mechanical properties.

In this study, gelatin-based hydrogels with a Young's modulus as high as 2.2 MPa were successfully prepared by directed freezing to promote the growth of gelatin hydrogel ice crystals and the synergistic reaction of the anion-mediated effect on the polymer molecular chains inside the hydrogels. Evaluating the effects of various anions (lithium salts) on the output performance of the TENG, citrate showed the most improvement in mechanics, while acetate had a greater effect on the output efficiency, which was determined by the dual effects of its surface charge density and modulus.

3.3 Experimental Methods

3.3.1 Chemicals

Gelatin from porcine skin, Lithium acetate, Lithium sulfate, Lithium carbonate, Lithium chloride, and Lithium citrate are all bought from Sigma. Ecoflex 00-35 was purchased from Sigma. Liquid nitrogen was purchased from the University of Waterloo chemical store.

3.3.2 Material synthesis

10g of gelatin powder was added to 40 ml of UP water and stirred with 400 r/min for four hours at 55°C. The gelatin solution was then quickly poured into a circular model, after that it was frozen with liquid nitrogen. 20 mL of liquid nitrogen were used at a time and frozen for 30s, after all the liquid nitrogen had evaporated, liquid nitrogen was added again and continued for several times until all the gelatin solution was frozen. At this time the gelatin was frozen from liquid to solid. Subsequently, the gelatin hydrogel was taken out of the mold and immersed in prepared solutions. These solutions included lithium chloride, lithium carbonate, lithium sulfate, lithium acetate, and lithium citrate and each with a 15wt% concentration. Separately, these five salt solutions impregnated with hydrogels were kept in the refrigerator at 0 °C for 36 hours. Finally, the gelatin was removed from the salt solutions and its surface was washed separately using DI water to remove excess salt solutions from the surface.

3.3.3 Assembly of gelatin-based triboelectric nanogenerator

The prepared hydrogel was cut into thin slices of 1 mm thickness. Pour the Ecoflex solution into the rectangular model for 10 minutes to allow it to fully solidify into the silicone rubber. The cut hydrogel sheets were then placed on top of the thin silicone rubber (1 mm) and copper tape was placed on top of the hydrogel as friction layer (**Figure 3.1**). Finally, a new Ecoflex solution was prepared and poured on top of the hydrogel until the entire hydrogel was covered. Finally, the gelatin-based triboelectric nanogenerator was molded after waiting for the silicone rubber to solidify.

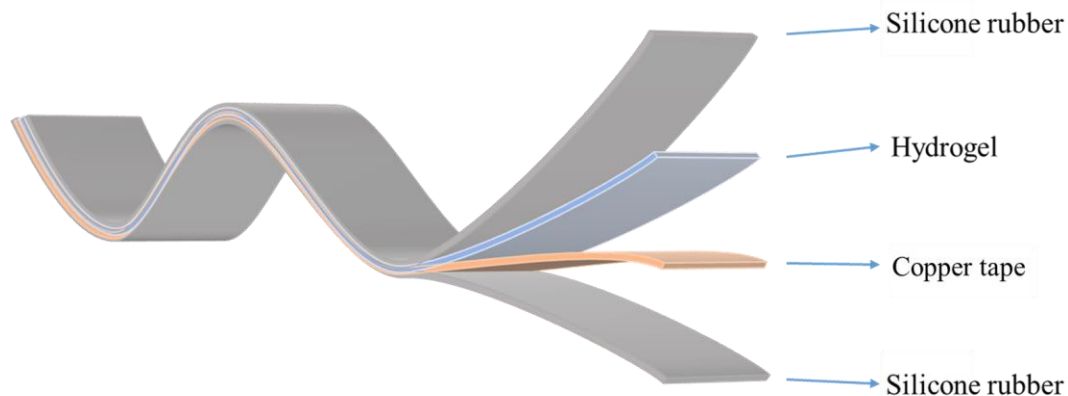


Figure 3.1 Structural diagram of gelatin based TENG device.

3.3.4 Characterization

The hydrogels were cut into strips of equal size (3x1x1mm) and clamped on an instron (ADMET Inc., USA) at a stretching rate of 20mm/min. Each hydrogel was measured three times to determine its tensile properties. The compression properties of the hydrogel were also measured by this instrument with the compressing rate of 10mm/min, where the hydrogel was cut into cylinders with a height of 0.5 mm and a radius of 1 cm. Open-circuit voltage and short-circuit current of triboelectric nanogenerators measured by SIBASS Three Phase Multi- Function Meter.

3.4 Results and discussion

The impact of different anions on gelatin hydrogels was assessed through a process that involved directed freezing followed by immersion. The effects of various anions on gelatin-based hydrogels were examined after involved directed freezing followed by immersion. The frozen samples were subsequently immersed in salt solutions that featured the same cation (Li^+) but had different anions. These salt solutions included LiCl , Li_2CO_3 , Li_2SO_4 , CH_3COOLi , and lithium citrate solutions. The anion-mediated effect is a phenomenon in which various ions in a solution influence the properties of biomolecules, colloids, and other substances within that solution. This effect is related to the nature of ion hydration in the solution. Ion hydration involves the formation of hydrated layers around ions when they are dissolved in water, and the characteristics of these hydrated layers are determined by the size, charge, and polarity of the ions. These hydration layers can interact with biological macromolecules and alter their structure and properties. As a result, the hydration properties of different ions can lead to different effects on biomolecules and colloids. Certain anions referred to as

leachates can disrupt the aggregation state and induce salinization. In contrast, other ions known as hydrophilic agents can enhance the aggregation state and, consequently, reduce solubility through a process known as salinization.^[171]

It has been demonstrated that salt dissolution of frozen samples occurs in solutions containing salts such as LiCl and CH₃COOLi. This phenomenon is attributed to the direct interaction of the anions with the polymer, which introduces an additional charge to the polymer molecular chain, increasing its solubility and thereby inhibiting the formation of hydrogels. Conversely, lithium citrate, Li₂CO₃, and Li₂SO₄ promote hydrogel formation during the salting-out process. This is achieved by the continuous expulsion of water molecules from between the polymer chains and the formation of new hydrogen bonds between the hydroxyl groups. These interactions lead to the aggregation of the polymer chains and an increase in crystalline regions, enhancing the formation of hydrogels. By leveraging both ice crystal growth and the anion-mediated effect, the hydrogel can form a three-dimensional, multi-scale network structure.

The mechanical properties of hydrogels under these five different salt precipitations were evaluated separately. Lithium citrate, Li₂CO₃, and Li₂SO₄ all showed enhanced fracture strength, compressive properties, and elastic modulus, with lithium citrate having the best mechanical performance, not only having a tensile strength of 1.5 MPa, but also a modulus of elasticity of 2.2 MPa, which is far more than the other salt solutions. The LiCl and CH₃COOLi, on the other hand, showed weak mechanical properties which is consistent with the analysis. The order in which anions affect mechanics is Li₃C₆H₅O₇ > Li₂CO₃ > Li₂SO₄ > CH₃COOLi > LiCl.

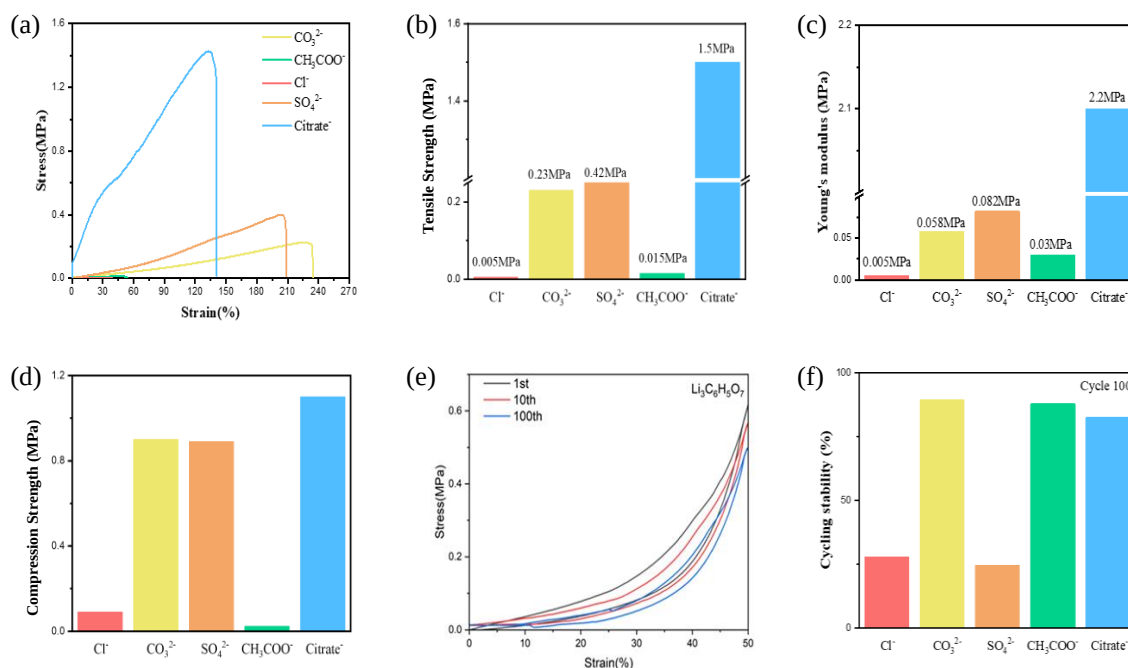


Figure 3.2 Mechanical properties of gelatin hydrogels. (a), Stress-Strain curve of five different anionic gelatin hydrogel. (b) The tensile strength of the five different anion gelatin hydrogels in (a). (c) Young's modulus of five different anionic hydrogels. (d) Compressive strength of hydrogels with five different anions. (e) 1, 10, 100 cycles of compression of lithium citrate. (f) Compression cycle stability of hydrogels with five different anions.

The principle of triboelectric nanogenerators involves a combination of contact initiation and electrostatic induction to convert mechanical motion into electrical output.^[172] In general, when two materials come into contact, electrons tend to transfer from the material with lower electron affinity to the one with higher electron affinity due to the differences in electron affinity. This transfer of electrons leads to a polarization effect at the interface between the two materials. Subsequently, as the two materials periodically separate or approach each other, the electric field at the interface changes, causing electrons to move back and forth between the two electrodes located behind the contacting materials through an external wire or circuit. This back-and-forth movement of electrons results in the generation of an alternating current (AC), which can be harnessed for various electrical applications.

[173]

Triboelectric nanogenerators have four basic modes of operation. (a) vertical contact-separation mode; (b) horizontal sliding mode; (c) single electrode mode; and (d) independent layer mode. ^[174-176]

The vertical contact-separation mode is the simplest structure of a Triboelectric Nanogenerator (TENG) (**Figure 3.3**). In this configuration, two dielectric films made of dissimilar materials are stacked face-to-face, and their respective back surfaces are coated with metal electrodes. These two dielectric films are in contact with each other, which results in the creation of surface charges of opposite signs on the two contacting surfaces. When these two surfaces separate due to an external force, a small air gap is formed in between, and this separation induces a potential difference between the two electrodes. If the two electrodes are connected through a load, electrons will flow through the load from one electrode to the other, creating a reverse potential difference to balance the electrostatic field. As the air gap between the two friction layers closes, the potential difference formed by the friction-induced charge disappears, and electrons flow back, completing the electrical circuit. This back-and-forth flow of electrons can be harnessed to generate electrical power.

The lateral sliding mode shares the initial structure with the vertical contact-separation mode (**Figure 3.3**). In this mode, when two dielectric films are in contact, they experience relative sliding along a horizontal direction parallel to their surfaces. This sliding motion generates frictional charges on both surfaces, resulting in polarization in the horizontal direction. This polarization drives electrons to flow between the upper and lower electrodes, balancing the electrostatic field created by the friction charge. The periodic sliding, separation, and closure of the materials lead to the generation of an AC output, which is the fundamental principle of a sliding TENG. Horizontal sliding can manifest in various forms, including planar sliding, cylindrical sliding, and disk sliding. By studying these different structures in relation to one another, researchers gain a deeper understanding of the sliding patterns and the more complex grid structures within them, allowing for improved design and performance optimization of sliding TENGs for various applications.

In the modes of operation described earlier, both involve two electrodes connected through a load. However, in some scenarios, such as when there are moving parts in the TENG (like a person walking on the floor), it might be inconvenient to electrically connect these parts to the electrodes through wires. To facilitate the collection of mechanical energy in such situations, a TENG in single electrode mode is introduced (**Figure 3.3**), which means having electrodes only at the bottom and grounding them. In the single-electrode mode, when the dimensions of the TENG are constrained, the approach

or departure of the upper charged object from the lower object alters the local electric field distribution. This change in the electric field distribution results in an exchange of electrons between the lower electrode and the Earth to equalize the change in potential at the electrode. This basic mode of operation can be employed in both contact-separation structures and sliding structures, offering a more convenient way to harness mechanical energy when physical wiring connections are challenging or impractical.

The freestanding triboelectric layer mode introduces a unique approach to harnessing electrical energy from moving objects (**Figure 3.3**). In nature, objects often become electrically charged upon contact with air or other materials, as exemplified when our shoes become charged as we walk on the floor. The charge density on the surface of a material can become saturated, and this electrostatic charge remains on the surface for an extended period, typically several hours. During this time, constant contact and friction are not required. In the Independent Layer Model (**Figure 3.3**), two discrete symmetrical electrodes are placed on the backside of the dielectric layer. The size and spacing of these electrodes are on the same order of magnitude as the dimensions of the moving object. When a charged object moves reciprocally between these two electrodes, it results in a change in the potential difference between the two electrodes. This potential difference drives electrons to flow back and forth between the electrodes through the load of an external circuit to equalize the change in potential difference. The reciprocating motion of the electrons between the pair of electrodes generates electrical power output. It is important to note that the moving charged object doesn't necessarily need to be in direct contact with the upper surface of the dielectric layer. For example, in the rotating mode, one of the discs is free to rotate and does not need to be in direct mechanical contact with the other portion. This reduces wear and tear on the material's surface, which is highly advantageous for improving the durability of TENGs.

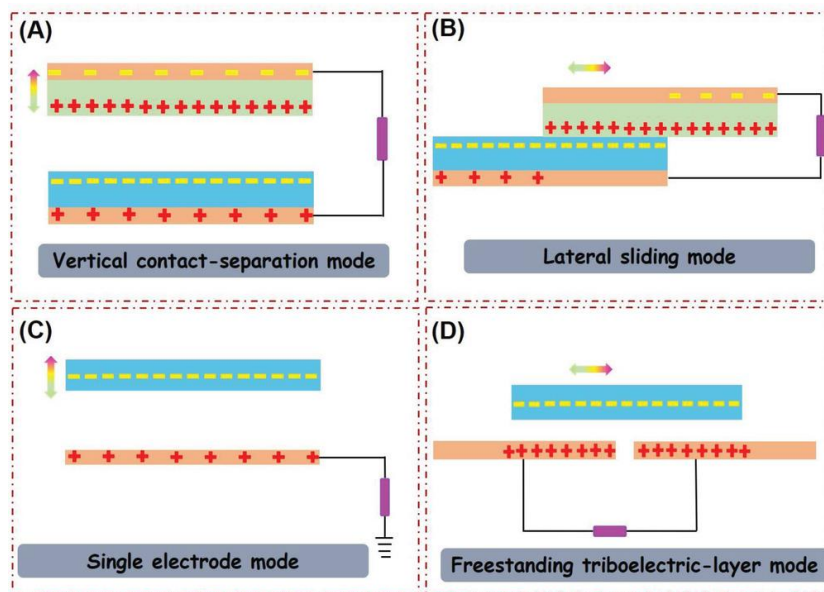


Figure 3.3 Working mechanism and 4 types working modes of triboelectric nanogenerator. Adapted from Advanced Energy Materials with permission.^[191] Copyright of Wiley publishing group and American chemical society.

The effect of hydrogel on the performance of the triboelectric nanogenerator when used as an electrode was subsequently measured. Different from the mechanical properties, the output performance of the triboelectric nanogenerator is related to the Young's modulus and surface charge density of the hydrogel. The Young's modulus of the hydrogel as a major factor affects the output efficiency when the device is separated from the friction layer contact. When the Young's modulus is small, the hydrogel tends to exhibit more deformation under the same force, which increases the contact area and the total amount of surface charge generated, resulting in greater voltage and current output. The **Figure 3.4(a)** and **Figure 3.4(b)** shows the open-circuit voltage of 15V and the short-circuit current of 0.23 μ A generated when CH₃COOLi-Gelatin based TENG separates from the PTFE contact at a frequency of 2 Hz. CH₃COOLi was tested and found to exhibit better output properties due to its smaller modulus (**Figure 3.4(c)** and **(d)**). Whereas lithium chloride, despite having a smaller Young's modulus, is too weak mechanically to produce good output properties (**Figure 3.4(c)** and **(d)**) due to its weaker mechanical properties that make it more susceptible to the destruction of the hydrogel structure when charges are generated. The difference in the output performance of the friction layer during contact separation at different frequencies was then evaluated separately (**Figure 3.4(e)** and **(f)**). At lower frequencies, the output performance of the TENG increases with increasing

frequency because higher frequencies at lower frequencies tend to cause greater deformation of the hydrogel (**Figure 3.4(e)**). At high frequencies, the output performance of the TENG shows a tendency to increase and then decrease with increasing frequency (**Figure 3.4(f)**), because when the frequency is too high, the contact and separation are too fast for the surface of the friction layer to effectively form enough charge. In the case of CH_3COOLi , the highest output voltage is produced at 7 Hz at low frequencies, while the highest output voltage at high frequencies is produced at 50 Hz (**Figure 3.4(f)**).

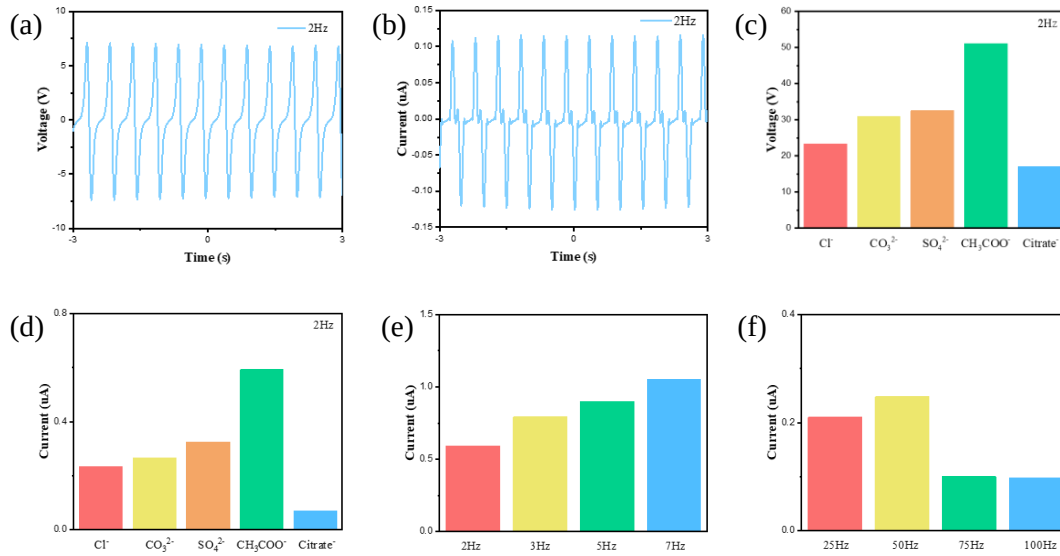


Figure 3.4 Output performance of gelatin-based triboelectric nanogenerators. (a) Open circuit voltage of pure gelatin hydrogel at 2Hz. (b) Short circuit current of pure gelatin hydrogel at 2Hz. (c) Open circuit voltage of gelatin hydrogel after regulating of different anions at 2Hz. (d) Short circuit current of gelatin hydrogel after regulating of different anions at 2Hz. (e) Short circuit current of gelatin hydrogel regulated by CH_3COOLi at low frequencies (2Hz, 3Hz, 5Hz, and 7Hz). (f) Short circuit current of gelatin hydrogel regulated by CH_3COOLi at high frequencies (10Hz, 25Hz, 50Hz, and 75Hz).

Next, capacitors with 1 μF , 2 μF , 3.3 μF , 4.7 μF , and 10 μF were charged using the triboelectric nanogenerator to evaluate the charging performance. The voltages across these different capacitors after 60s of charging at frequencies of 3 Hz and 25 Hz are illustrated in the **Figure 3.5(a)** and **(b)**. Notably, the 1 μF capacitors achieves a voltage of 2.4 V after charging for 60 seconds at 3 Hz, demonstrating the robust power supply capability of the device (**Figure 3.5(a)**). The TENG device's

output voltage was evaluated at a frequency of 3 Hz for various stretch lengths. It was observed that as the stretch length increased, the device's output voltage also increased (**Figure 3.5(c)**). This is because the stretched device has a larger surface area, resulting in the generation of a greater total amount of surface charge. When the device was stretched to 200% of its original length, its output voltage increased from 115V to 165V (**Figure 3.5(c)**). Importantly, when the stretching was halted, the output voltage promptly returned to its original value. This demonstrates the device's controllable stable output performance. The effect of different friction layer materials on output was also subsequently explored (**Figure 3.5(d)** and **(e)**). Dissimilar materials produce different amounts of charge when separated by contact. As shown in the **figure 3.4(d)** and **(e)**, the use of metals such as Cu and Al as the friction layer resulted in larger output voltages and currents due to the surface being more susceptible to generating more charges, while materials such as paper and PET resulted in smaller outputs. In the final phase of the study, the long-term stability of the devices was investigated (**Figure 3.5(f)**). One well-known disadvantage of hydrogels is their tendency to lose water and their inability to be stored in the air for extended periods. However, by employing silicone rubber as an encapsulation layer material, the hydrogel's capacity to retain water was significantly enhanced. After testing, even after being exposed to the air for a month, the device still retained more than 95% of its initial mass (**Figure 3.5(f)**). Furthermore, the device's output showed only a minor decrease (**Figure 3.5(f)**). These results indicate that the device has the potential for long-term usage, thanks to its improved water retention capabilities.

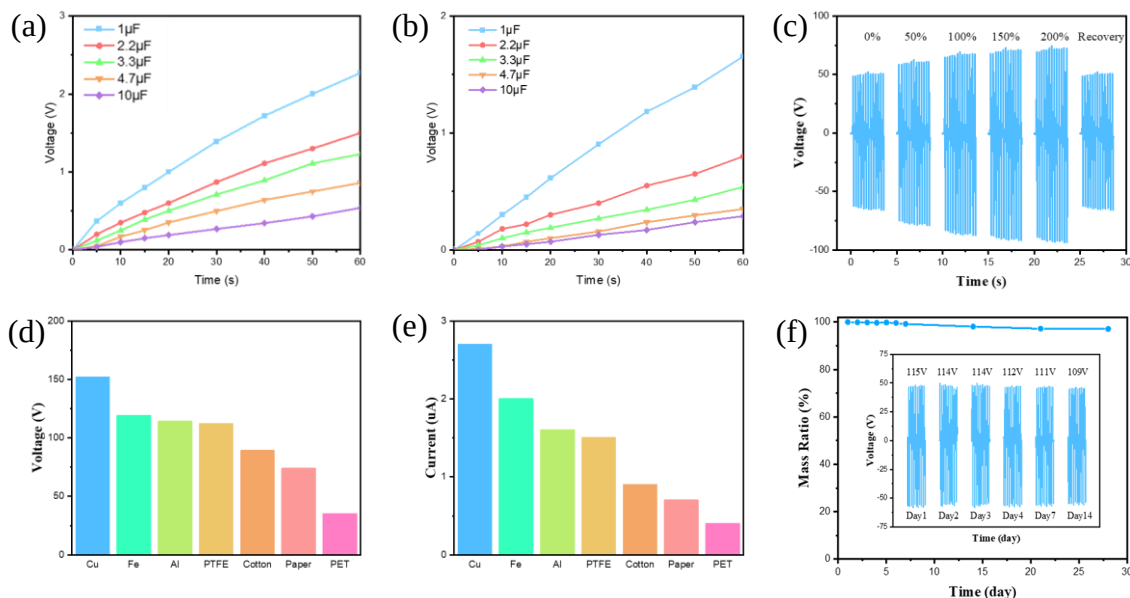


Figure 3.5 TENG output power under different conditions (a) Voltage characteristics of CH_3COOLi regulated gelatin hydrogel charging 1 μF , 2 μF , 3.3 μF , 4.7 μF , and 10 μF capacitors for 60 seconds at 3Hz. (b) Voltage characteristics of CH_3COOLi regulated gelatin hydrogel charging 1 μF , 2 μF , 3.3 μF , 4.7 μF , and 10 μF capacitors for 60 seconds at 25Hz (c) Open circuit voltage of TENG under different stretching lengths. (d) Effect of different friction layer materials on TENG open circuit voltage. (e) Effect of different friction layer materials on TENG Short circuit current. (f) Changes in device quality and output voltage after the TENG was placed at room temperature for four weeks.

3.5 Conclusion

In this chapter, gelatin-based hydrogels with significantly improved mechanical properties were successfully synthesized using directed freezing and the anion-mediated effect. These hydrogels exhibit a high fracture strength of 1.4 MPa and a Young's modulus of 2.2 MPa. When used as an electrode in a triboelectric nanogenerator, these hydrogels achieved an impressive output voltage of up to 150 V and an output current of 1 μA . Furthermore, their remarkable water retention and stability properties make them suitable for long-term use. The evaluation of the enhancement in the mechanical and electrical properties of the hydrogel based triboelectric nanogenerator using different anions (lithium salts) in the Hoffmeister series provides valuable insights for the rational utilization of

the anion-mediated effect. This research paves the way for the development of more effective and durable friction-based energy harvesting devices and related applications.

Chapter 4 Conclusion and future work

In this thesis, two types of hydrogel-based flexible electronic devices are introduced. The first involves the combination of natural wood with PVA-Borax-TA hydrogels. By introducing a cellulose backbone through this process, wood-based hydrogels with exceptional mechanical properties are achieved. It has a tensile breaking strength of up to 19.8 MPa, as well as a Young's modulus of up to 204 MPa. This wood-based hydrogel exhibits a high electrical conductivity 3.6 mS/m, a fast response time about 20ms, and remarkable self-healing ability, making it an excellent material for flexible motion sensors. The second was the successful synthesis of gelatin-based hydrogels with significantly improved mechanical properties using directed freezing and the anion-mediated effect. The breaking strength of these hydrogels is up to 1.4 MPa and Young's modulus is 2.2 MPa. When used as electrodes in a TENG, the output voltage of these hydrogels was up to 150 V and the output current was 1 μ A. In addition, it also has good stability, even if it is left at room temperature for 30 days, it can still maintain good condition and output power.

Future work should primarily focus on the combination of the two applications into a system. Presently, most flexible motion sensors still rely on external power sources for real-time signal transmission. By integrating a triboelectric nanogenerator with a high-performance hydrogel, it becomes possible to create a self-powered human motion sensor system. Mechanical energy generated during human movement can be efficiently converted into electrical energy, and the resulting electrical signals can be transmitted to a computer via Bluetooth for real-time detection. Specifically, a hydrogel with high electrical conductivity can first be prepared as an electrode, after which it is encapsulated into a hydrogel based TENG by encapsulation material. Finally, a Bluetooth device is connected to the TENG for wireless transmission of electrical signals. The device can be attached to the human body to accomplish wireless body sensing detection. When the human body moves, the TENG converts the mechanical energy generated by the movement into electrical energy, which is transmitted to the computer through the Bluetooth module. Depending on the amount of data obtained, different movement conditions of the human body can be determined. The device can also be effectively used in biomedicine as a self-powered implantable device to provide continuous power supply for medical devices and can effectively detect the power supply situation and the operating status of the device outside the body. This innovation holds great promise for the rational utilization

of energy and the advancement of clinical medicine in the future, offering new possibilities for self-powered, real-time monitoring of human motion and health.

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