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Research Article

INTRINSICALLY SOFT BIOELECTRONICS BASED ON ELASTOMERIC NANOCOMPOSITE

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Abstract

Stretchable electronics has gained global attention due to its potential applications in various fields, including wearable electronics, biomedical engineering, healthcare monitoring, soft robotics, and human-machine interfaces. Stretchable electronics have the unique ability to seamlessly integrate with the constantly deforming human body, known as "biointegration," leading to significant advancements in wearable and implantable biomedical devices. Meanwhile, nanomaterials and nanofabrication technologies have played a crucial role in their development, enabling the integration of electronic materials onto stretchable matrix that can withstand mechanical deformations. Elastomeric materials such as polydimethylsiloxane (PDMS), styrene-butadiene-styrene (SBS), and polyurethane (PU) are commonly used as stretchable substrates, while conducting nanomaterials are incorporated as conductive fillers. These materials address the challenges posed by the mechanical mismatch between traditional rigid electronics and biological tissues, offering improved flexibility, enhanced device-tissue interface, and reduced immunological reactions. By incorporating appropriate fillers into elastomers, researchers aim to develop intrinsically soft bio-integrated electronics that monitor electrophysiological as well as physical signals coming from biological tissues without hindrance from mechanical mismatch between electronics and soft tissues. This comprehensive review explores the materials and functionalization techniques of elastomers, as well as the development of functionalized elastomer-based bio-integrated devices such as sensors and stimulators. Future research directions and challenges in the field of stretchable electronics and bio-integrated devices are also discussed.

Keywords: Bioelectronics, Nanomaterials, Biointegration.

INTRODUCTION

In recent years, there has been a growing interest among researchers worldwide in the development of stretchable electronic devices. These devices hold great promise for a wide range of applications in fields such as epidermal electronics, biomedical engineering, healthcare monitoring, soft robotics, electronic skins, and human-machine interfaces. The unique characteristic of stretchable electronics lies in their ability to conformally integrate with the constantly deforming human body, a phenomenon known as "biointegration".[1] This feature has led to significant advancements in wearable or implanted biomedical devices, which can now benefit from the flexibility and adaptability provided by stretchable electronics.[2] The remarkable progress achieved in the field of nanomaterials and nanofabrication technologies over the past few decades has played a pivotal role in the development of stretchable electronics.[3] These devices are considered the next generation of electronic devices that can augment traditional silicon-based electronics for seamless integration with the human skin or curved, deformable interfaces. Stretchable electronics can be broadly defined as devices that integrate electronic materials and/or circuits onto stretchable substrates, enabling them to withstand mechanical deformations such as bending, twisting, compression, and stretching. This mechanical flexibility is made possible by the use of elastomeric flexible substrate materials, in contrast to rigid printed circuit boards.[4] These conductors need to possess high mechanical strain tolerance (> 50 percent) and exhibit high electrical conductivity to fulfill the functionalities of next-generation devices.[5] However, many of the electronic components used in these applications are traditionally fabricated from rigid materials such as metal and silicon, which have elastic moduli significantly greater than those of human body tissues (Figure 1). This mechanical mismatch can lead to various challenges, including high contact impedance, low signal-to-noise ratio, localized strain on tissues, poor device-tissue adhesion, immunological reactions, and scar development.[6]To address these challenges, considerable efforts have been made to develop inherently soft and poseable electronic devices, necessitating the use of electronic materials that are intrinsically soft and stretchable. Among the promising candidates for such materials are functionalized elastomers.[7]

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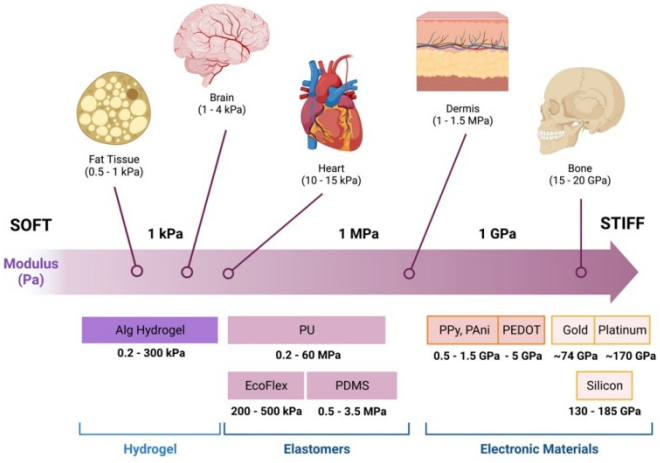

Figure 1. Comparison of the moduli of various elastomers and the moduli of biological tissues from soft to stiff.

The choice of materials plays a critical role in the development of stretchable conductors with the desired mechanical and electrical properties. Elastomeric materials, such as PDMS, Ecoflex, and PU, are commonly employed as substrates or matrices for integrating stretchable electronics with other

system components, as they offer high stretchability.[8] However, achieving high electrical conductivity necessitates the incorporation of traditional metallic conductors or dispersed conductive nanomaterials, such as metallic nanowires and carbon nanotubes (CNT), as conductive fillers. Numerous studies have explored the interplay between these conductive additives and matrices with distinct mechanical properties, presenting both challenges and opportunities in integrating materials with contrasting mechanical characteristics. The soft mechanical properties of elastomers enable their conformal integration with biological tissues, making them particularly suitable for applications in soft bio-integrated electronics. Elastomer structures consist of entangled polymer chains that are crosslinked, allowing for easy stretching as the chains unwind. The elasticity of the elastomeric materials and devices is essential for their seamless integration with dynamically malleable biological tissues. In terms of elastic modulus, conventional electrical materials such as metal and silicon exhibit moduli that are more than ten times higher than that of bone (>100 GPa).[9]

In contrast, elastomer moduli vary depending on factors such as the type of elastomer and the degree of crosslinking, making them more comparable to tissue moduli. To further enhance the functionality of elastomers for use in soft and bio-integrated electronics, they can be functionalized with appropriate fillers, such as nanoscale materials or polymers. This review aims to provide an in-depth exploration of cutting-edge technologies for functionalizing elastomers to create intrinsically soft and bio-integrated electronics. The classification and synthetic principles of elastomers, including the various types of polymer chains that constitute these materials, will be discussed. Additionally, the article will examine different functional fillers, such as nanoscale materials with percolated networks and functional polymer chains, that can be combined with elastomer chains to confer specific functionalities to the elastomer. Furthermore, the demonstration of functionalized elastomer-fabricated devices, including sensors and stimulators will be discussed. Finally, this analysis will conclude with a summary of the key findings, a discussion of the remaining challenges, and recommendations for future research in the field of stretchable electronics and bio-integrated devices.

ELASTOMERIC NANOCOMPOSITE

Intrinsic conductive material synthesis is one of the first strategies for producing stretchable conductors. Most frequently, nanomaterial fillers are dispersed in an elastomeric matrix, combining the electrical conductivity of the fillers with the mechanical stretchability of the matrix material. (Figure 2) Maintaining a balance between stretchability and conductivity is necessary to accomplish high mechanical and electrical performance. This is because incorporating more additives into the elastomeric substrate increases electrical conductivity while making the composite material stiffer as a whole. In addition, the majority of elastomeric materials used to create stretchable components are solution-based, and solution processing of multi-stacked layers in functional devices must address issues involving dissolution, mixing, or fracture of the underlying elastomeric layer. Therefore, methods of adding fillers and their dispersion, as well as adhesive bonding compounds such as surfactants, play crucial roles in enhancing the overall composite's quality.

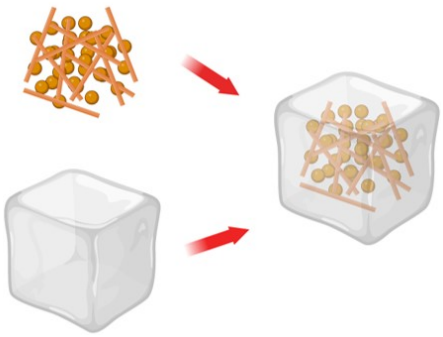

Figure 2. Schematic illustration of elastomeric nanocomposite by combining conductive nanofillers and elastomer matrix.

Elastomers

Elastomers consist of polymer chains that are interconnected through crosslinking, forming a network structure. Due to the entangled nature of the long polymer chains and the presence of sparse crosslinking along these chains, elastomers can undergo deformation when the entanglements are untangled and the chains are stretched. The crosslinking between polymer chains plays a crucial role in maintaining the integrity of the entire polymer network, making the deformation, such as stretching, non-permanent.[10]Additionally, elastomers exhibit the ability to return to their original shape after the external force is removed. The mechanical properties of elastomers, including Young's modulus and stretchability, are determined by the degree of crosslinking in the backbone chains of the elastomer. Higher crosslinking strength and/or density result in increased stiffness and toughness of the elastomer. Conversely, weaker crosslinking and/or lower density lead to softening of the elastomer and increased susceptibility to puncturing. There are two types of crosslinking: physical crosslinking and chemical crosslinking, as illustrated in Figure 3.

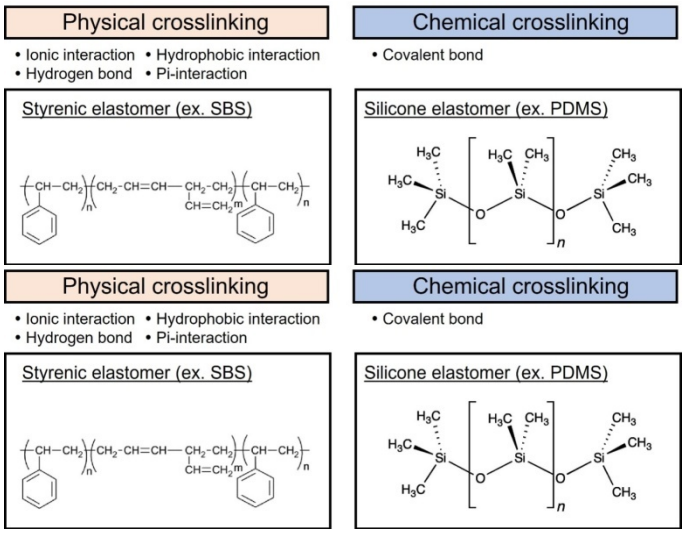

Figure 3. Types of crosslinking and the representative examples of each type of elastomers.

In physically crosslinked elastomers, the polymer chains are connected through relatively weak interactions, such as ionic contacts, hydrogen bonds, hydrophobic interactions, or π-interactions.[11] These interactions, which can involve electrostatic attraction between ions, dipole-dipole attraction, aggregation of nonpolar molecules in aqueous solutions, or molecular interactions, serve as driving forces for crosslink formation. Unlike chemical crosslinking, physical crosslinking

involves noncovalent bonding, which is weaker and less stable. Consequently, these physical contacts between polymer chains can be easily broken. However, physically crosslinked elastomers offer certain advantages, such as improved processability and the ability to be reprocessed using solvents, heat, or pressure.

Controlling the composition of blocks in the elastomer polymer chain can be used to adjust the mechanical properties of physically crosslinked elastomers. The polymer chains in physically crosslinked elastomers can be separated into two sorts of blocks: regions with/without physical interactions. The blocks where physical crosslinking occurs are equivalent to hard regions in the elastomer, whereas the remaining blocks are soft regions. As a result, the density of crosslinking in an elastomer can be regulated by adjusting the ratio of these two segments in the elastomer chain.[12]

Chemical crosslinking is commonly accomplished by inducing crosslinking reactions with crosslinking agents or accelerators. As a result, the mechanical properties of chemically crosslinked elastomers can be adjusted by varying reaction parameters such as crosslinking agent concentration, reaction temperature, and so on. Furthermore, several chemical crosslinking reactions, such as click chemistry, enzyme-mediated, and UV-mediated reactions, can be used. The sort of initiating mechanism used to establish the covalent bonds influences these reactions.

Polymer chains in chemically crosslinked elastomers are more tightly linked to one another than in physical crosslinking due to the development of covalent bonds. Chemically crosslinked elastomers are more mechanically stable than physically crosslinked elastomers because the elastomer chains are tightly connected. In terms of chemical stability, polar solvents such as water or alcohol have no effect on chemically crosslinked elastomers; however, a variety of organic solvents can penetrate into the elastomer matrix, producing swelling. For example, in organic solvents such as pentane, chloroform, and tetrahydrofuran, a representative chemically crosslinked elastomer PDMS swells. When filler materials are added into chemically crosslinked elastomers to provide additional functionality, excessive volumes of the filler in comparison to the elastomer might reduce the crosslinking density of the elastomer. Excess filler can potentially disrupt the crosslinking reaction or impede the mass transfer of the polymer chains in the reaction fluid. Because of the lower crosslinking probability, mechanical characteristics like as toughness suffer. In the case of physically crosslinked elastomers, the number of filler components has no effect on the crosslinking interactions. As a result, more filler materials can be added to physically crosslinked elastomers than to chemically crosslinked elastomers.

The following are some examples of representative elastomers. Styrenic elastomers are one type of physically crosslinked elastomer. Poly(SBS) and poly(styrene-co-ethylene-butylene-co-styrene) (SEBS) are two examples that are crosslinked *via*π-interactions. A chemically crosslinked elastomer is the silicone elastomer PDMS, which is one of the most extensively used elastomers. Covalent linkages crosslink silicone elastomers, and the reactions are mediated by platinum-containing catalysts.

PU-based elastomers exhibit both physical and chemical crosslinking. Similar to physically crosslinked elastomers, PU-based elastomers consist of long soft blocks comprising polyol chains, as well as hard blocks composed of urethane groups that form hydrogen bonds. The urethane groups, which consist of interconnected isocyanate and diol groups, have the ability to create chemical crosslinks with other isocyanate groups through allophanate bonding. This means that PU-based elastomers possess both physical and chemical crosslinking. By adjusting the ratio of constituent groups within the polymer chain, the properties of PU-based elastomers can be modified. This offers advantages such as excellent processability, along with enhanced mechanical and chemical stability.

The biocompatibility and anti-toxicity of the elastomers must be ensured for applications to bio-integrated electronics. Although polymeric elastomers have been shown to be chemically non-toxic, the monomers that make them up can still be harmful. As a result, chemical stability is a critical issue for long-term applications of bio-integrated devices. Some elastomers, such as silicone-based elastomers (PDMS or Ecoflex) and thermoplastic PU, have been reported to be chemically compatible with the body and suitable for medical use over long periods of time. It is also necessary to ensure the biocompatibility and anti toxicity of functional filler materials blended with elastomers.

Conductive fillers

The mechanical properties of elastomers can be controlled by controlling crosslinking or customized by including chemical functional groups into the polymer chain. Other approaches, however, are necessary to improve the performance of elastomers, notably their electrical characteristics, for use in bio-integrated electronics. One extensively used method is to incorporate functional fillers into the elastomer. Elastomers with conducting or semiconducting characteristics can be created by adding functional fillers into the elastomer matrix. In such circumstances, the fillers are principally responsible for the increased electrical properties, and the elastomers serve as an elastic and solid matrix that physically maintains the 3D configuration of fillers.Nanoscale conducting materials are the most frequent sort of filler. These nanoparticles are categorized according to their dimensions, with 0D, 1D, and 2D nanomaterials (Figure 4).

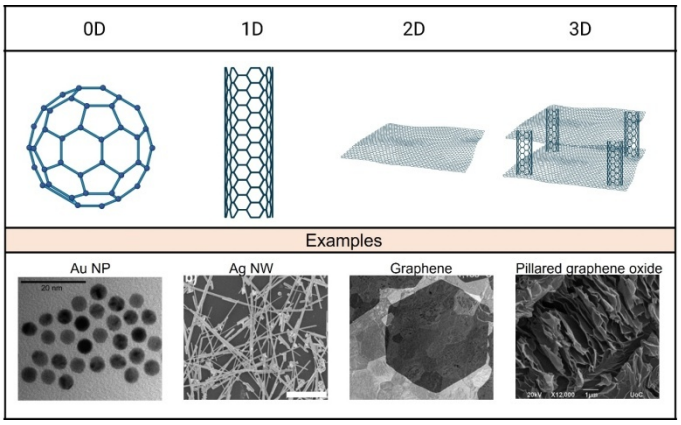

Figure 4. Representative examples of nanomaterials classified into their dimensions. Copyright 2017, 2019, 2015 Nature Publishing Group; 2021 Royal Society of Chemistry.

Carbon-based fillers

Conductive carbon nanomaterials have garnered significant attention for the development of stretchable conductive nanocomposites due to their impressive electrical conductivity, exceptional mechanical fatigue resistance, good chemical and thermal stability, and relatively low cost.[13]Among the various carbon-based conductive nanofillers used in these nanocomposites, CNTs, carbon nanofibers (CNFs), carbon blacks (CBs), and graphene are the most widely utilized. Carbon blacks (CBs) have long been utilized as additives in commercial conductive composites for energy-storage devices. They possess exceptional mechanical strength, high electrical conductivity, excellent chemical stability, and are cost-effective. On the other hand, CNTs are characterized by their lattice-like tubular structure composed of a periodic honeycomb graphene network with covalently bonded carbon atoms. CNTs exist in two primary forms: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). MWCNTs consist of multiple concentric cylindrical layers of graphene, while SWCNTs are composed of a single graphene layer rolled into a cylinder. CNTs exhibit outstanding electrical conductivity, high aspect ratio, and mechanical strength, making them promising candidates for stretchable conductors. In terms of achieving high electrical conductivity, CNTs are more effective than zero-dimensional CBs at relatively lower filler concentrations due to their one-dimensional structure and high aspect ratio. Notably, stretchable conductors based on well-aligned CNTs have demonstrated remarkable electrical conductivity of 2200 S cm^{-1}under 150% strain.[14] These conductors have been successfully employed as stretchable electrodes in highly sensitive capacitive pressure sensors with excellent optical transparency. Carbon nanofibers (CNFs) share a similar cylindrical nanostructure with CNTs but possess larger diameters and lengths arranged as cones, cups, or plates. CNFs have a comparatively less oriented nanostructure, resulting in a higher number of defects, which can adversely affect their electrical and mechanical properties. Nevertheless, CNFs remain excellent candidates for tough nanocomposites and soft strain sensors, offering a compromised yet still impressive combination of electrical conductivity, mechanical strength, and cost-effectiveness. 2D carbon nanosheets, including graphene and its derivatives, have gained significant attention as conductive fillers in the fabrication of stretchable composite materials for soft and flexible electronics. These nanosheets are highly sought after due to their excellent electrical properties, high surface area, good optical transparency, and outstanding mechanical characteristics. Over the past decade, there has been significant progress in the large-scale, cost-effective production of high-quality graphene using methods such as chemical vapor deposition (CVD) and chemical exfoliation.[15] This has enabled the continued use of graphene in the field of flexible and stretchable electronics. Specifically, for applications such as flexible strain sensors and supercapacitors, polymer matrices have been developed to incorporate three-dimensional (3D) porous conductive networks of graphene. Examples include graphene aerogels and graphene foams, which possess large surface areas and exceptional electrical conductivity, enhancing the performance of these devices.

Metal-based fillers

Despite the excellent chemical stability and fatigue resistance of carbon-based conductive nanofillers, their inherently low electrical conductivity poses a significant challenge for stretchable electronics that demand high conductivity.[16] To address this issue, metal-based nanofillers such as silver, gold, and copper nanowires have emerged as promising alternatives due to their intrinsic high electrical conductivity. These metal-based nanofillers come in various geometries, including nanoparticles (NP), nanowires (NW), nanosheets, and nanoflakes. Among them, silver is the most popular choice due to its lower cost compared to gold and greater stability than copper. The relatively low fusion temperature of silver nanowires (AgNWs) is advantageous as it can potentially reduce electrical resistance. Consequently, significant advancements have been made in the development of stretchable conductors based on silver.

In the context of soft bioelectronic devices, stretchable conductors with high electrical conductivity are essential. Lee and colleagues have made noteworthy contributions by designing and synthesizing ultralong AgNWs measuring around 500 μm.[17]This new form of highly stretchable and highly conducting metal electrode exhibits very low sheet resistance and can stretch up to 460%. It outperforms other stretchable conductors based on carbon-based nanomaterials such as CNTs and graphene, thanks to its superior electrical conductivity and high aspect ratio. The combination of excellent electrical conductivity and good mechanical compliance is crucial, and the intrinsic ductility of silver, along with the enhanced percolation network achieved through long AgNWs under strain, contributes to the electrode's exceptional stretchability and conductivity. While 1D nanowires are commonly regarded as highly effective additives, gold nanoparticles (AuNPs) have demonstrated exceptional performance as highly stretchable and conductive materials due to their unique behavior. By depositing AuNPs on PU films, these films exhibit remarkable electrical conductivity. Under unstrained conditions, the conductivity reaches 11,000 S $cm^{-1}$and 1800 S cm^{-1}, with maximum strains of 115% and 486%, respectively. Even when the films are stretched to strains of 60% and 110%, the conductivity remains relatively high, at 3500 S cm^{-1} and 210 S cm^{-1}, and 2400 S cm^{-1} and 94 S cm^{-1}, respectively.[18] This is in contrast to other carbon-based conductors where the conductivity values tend to decrease significantly after straining, despite their higher aspect ratio morphology.

The exceptional conductivity retention of AuNPs under strain can be attributed to their self-assembly behavior induced by stretching tension. When a tensile strain is applied, the AuNPs undergo reorganization and alignment along the direction of the tensile force. This reorganization and the formation of a conduction band facilitate the creation of a conductivity pathway in the direction of the strain, contributing to the sustained high conductivity. This unique behavior of AuNPs enables them to maintain their conductivity even in the presence of strain, despite their relatively low aspect ratio morphology. Among conducting metal fillers, silver nanowires (AgNWs) are widely used, but copper has gained significant interest as a promising alternative due to its superior cost-effectiveness and abundance.[19] However, copper's susceptibility to oxidation, which reduces its conductivity, poses a significant limitation for its use as a filler material. To fully utilize the benefits of copper, various anti-oxidation strategies have been developed to maintain its conductivity without compromising its electrical properties. These strategies include coating copper with graphene oxide, nickel, chitosan,

or ligands, as well as reducing the oxide layer to metallic copper using acid solutions and embedding copper in elastomers. Nanofillers play a crucial role in creating conductive pathways, which determine electrical conductivity. Modifying post-treatment techniques for nanofillers can aid in optimizing the formation of conductive pathways. Typically, synthesized nanofillers are coated with stabilizing ligands that hinder the conductivity pathway. To reduce contact resistance, ligand washing processes can be employed to remove the dense ligand layer, or ligand exchange can be performed using shorter chain length ligands. Additionally, techniques such as soldering with additives and welding have been utilized to facilitate electron transfer at the junctions between nanofillers, further enhancing the overall conductivity of the composite materials.

Conductive polymer-based fillers

The development of flexible electronics has focused on incorporating conducting polymer fillers in combination with carbon and metal fillers. Conducting polymer fillers offer the advantage of tunable electrical and mechanical properties through molecular engineering or the formation of block copolymers with rigid electronic blocks and flexible blocks.[20] Among the conducting polymers studied, PPy, polyaniline (PANi), polyindole, and polythiophene (PTh) are commonly used examples. However, their low solubility can limit their applicability in certain contexts.

On the other hand, a water-soluble conducting polymer called poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) has been developed. PEDOT:PSS exhibits solution-processability, high conductivity, tunability of electrical and mechanical properties, transparency, and is commercially available, making it an ideal material for driving innovation in stretchable conductors. Its processability also enables mass production of flexible electronics. Although the fracture strain of PEDOT:PSS is relatively low (around 5%) and its Young's modulus is less than 2 GPa, it possesses high electrical conductivity (>1000 S cm^{-1}) and excellent transparency.[21] To enhance its mechanical compliance, plasticizers like glycerol, Triton X-100, and ionic liquids can be added to reduce the elastic modulus. Another approach is the formation of polymeric blends with water-soluble polymers such as poly(ethylene glycol) (PEG) or poly(ethylene oxide) (PEO). Additionally, elastomers incorporating PEDOT:PSS, one of the most widely used stretchable conductive nanocomposites based on conducting polymers, have gained attention for soft bioelectronic interfaces used in sensing and stimulation. These elastomers exhibit tissue-like mechanical properties, good biocompatibility, and a water-rich nature. For example, PEDOT:PSS hydrogels can provide both ionic and electronic conductivity, making them promising for emerging soft bioelectronic devices.[22] Zhang et al. demonstrated a novel method for obtaining injectable conductive PEDOT:PSS hydrogels by cross-linking PEDOT:PSS suspension at room temperature, opening possibilities for fabricating injectable conductors within human tissue and expanding biomedical applications.

Percolation network

The percolation threshold refers to the minimum volume fraction of conductive nanofillers required to form a continuous conductive pathway within an insulating elastic matrix. For spherical nanofillers like carbon blacks, the percolation threshold is typically around 10-20 vol%, which aligns with predictions from classical percolation theory.[5]Loading the composite with a high concentration of rigid nanofillers can lead to challenges in processability due to high viscosities and compromised mechanical performance due to nanofiller aggregation. To produce high-performance conductive nanocomposite materials, it is important to effectively reduce the percolation threshold without compromising the electrical properties. Several parameters of the conductive nanofillers can be adjusted to customize the electrical properties and enhance performance. These parameters include the aspect ratio, dimensional size, surface wettability, size distribution, and contact resistance between individual nanofillers. Percolation networks are formed by interconnecting the conductive fillers dispersed within the elastomer matrix. Charges can flow through these networks, and when the elastomer undergoes deformation, the percolation networks also deform. Some connections between filler elements may be disrupted, while others remain intact or new connections can be formed. The electrical pathways through the networks are maintained even when the elastomer composite is mechanically deformed.

The shape of the fillers plays a critical role in the formation of the percolation network (Figure 5). For instance, when 0D microscale fillers (such as aluminum oxide microparticles) are dispersed in an elastomer matrix, the particles tend to remain separated. On the other hand, the same volume percentage of 1D fillers like carbon fibers can create a percolation network.[23] While adding more 0D fillers can eventually result in a percolation network, an excessive amount can compromise the soft mechanical nature of the elastomer. Generally, 1D materials are more likely to establish percolation networks while preserving the elastomer's desired soft mechanical properties.

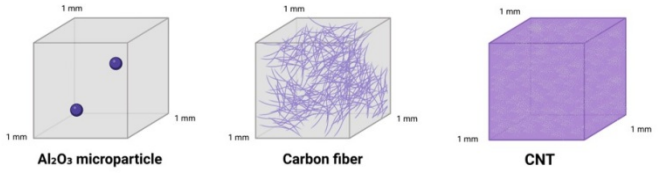

Figure 5. Schematic illustration of functionalizing elastomers showing the degree of percolation network formed within the same volume percent of each type of conductive fillers.

The size of the fillers is also crucial. Nanometer-sized fillers, such asCNTshave the ability to form denser and more stable percolation networks compared to micrometer-sized fillers like aluminum oxide particles or carbon fibers. This is because the number of nanoscale fillers is significantly higher, even if the volume percentage or weight percentage in the elastomer matrix is the same. With a higher number of fillers, the likelihood of interparticle contacts and connections increases. Consequently, nanoscale materials are commonly used as functional fillers in the fabrication of elastomer composites to achieve desired electrical and mechanical properties.

APPLICATIONS

Stretchable conductive nanocomposite materials with exceptional electrical and mechanical properties have numerous applications in bioelectronic sensors and stimulators (Figure 6). In order for physical sensors such as strain sensors

and pressure sensors to attain high sensitivity, their electric responses, such as impedance, capacitance, and electrical voltage, must exhibit significant changes when subjected to external deformations/forces. In contrast, stretchable conductors of bio-integrated sensors must maintain high electrical conductivity under mechanical deformations such as stretching, shearing, and bending in order toobtain stable electrophysiological signals. To accommodate the different electrical behaviors of sensors and conductors when subjected to external mechanical forces, it is necessary to employ distinct designs of conductive networks within stretchable nanocomposites.

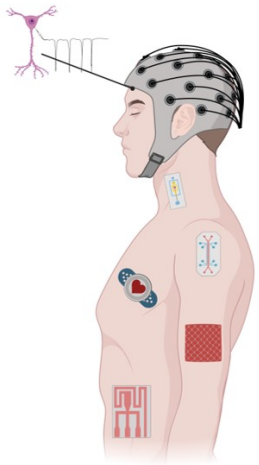

Figure 6. Demonstration of functionalized elastomers applied as intrinsically soft bioelectronic devices.

Sensors

Electrophysiological sensors

The major activities of organs are controlled by electrophysiological (EP) signals. By measuring EP signals, the condition of the body and/or aberrant pathological cues can be analyzed and detected. Electroencephalograms (EEGs, from the brain and nerves)[24], electrocardiograms (ECGs, from the heart)[25], and electromyograms (EMGs, from the muscles) are representative EP signals. Electrodes affixed to the organ of interest can record EP signals. Due to their high conductivities and resolutions, metal-based electrodes are the most employed for EP recording. However, the comparatively poor contact between metal-based rigid EP sensors and the target tissue is a critical issue.[26]Thick and rigid electrodes cannot adhere to soft tissue with a high degree of curvature, which results in a high contact impedance, a large capacitance, and a low signal-to-noise ratio (SNR). Although electrolytic lubricants can be used to decrease the interfacial impedance, they are incompatible with permanent or implantable applications. As an alternative to rigid metal electrodes, functionalized conductive elastomers-based electrodes have received considerable attention in recent years. Soft, stretchable, elastomer-based electrodes can make highly conformal interfacial contact with curved and soft biological tissues under arid conditions, which is advantageous for long-term, high-quality EEG, ECG, and EMG signal recording. Noninvasive surface EEG (sEEG) and invasive intracranial EEG (iEEG) are two types of techniques used to monitor EEG signals. EEG sensors, especially those used for iEEG, need to be non-toxic and mechanically flexible. To meet these requirements, various medical-grade functionalized elastomers can be utilized. In a study conducted by Tybrandt et al., a stretchable conductive polymer was developed for recording neural signals in EEG.[27] This conductive polymer consisted of gold-coated titanium dioxide nanowires (Au-TiO2 NWs) embedded in a PDMS material. The Au-TiO_2 NWs were patterned on a partially cured PDMS substrate and then coated with a PDMS encapsulation layer. The initial conductivity of the resulting Au-TiO2 NW/PDMS sheet, which had a thickness of 3 μm, was measured to be 16,000 S cm^{-1}. However, its resistance increased by a factor of 10 when subjected to 100% strain. In experiments involving rodents, 32-channel neural grid electrodes were implanted in the somatosensory cortex to record somatosensory evoked potentials (SSEPs). The implanted neural grid expanded spontaneously on the brain's pial surface, conforming to its shape. The neural electrodes exhibited low impedance (10 kΩ at 1 kHz in saline), enabling high signal-to-noise ratio (SNR) SSEP recording, which remained effective even after 3 months.

EP signals are responsible for coordinating the contraction and relaxation of the myocardium, enabling the circulation of blood throughout the body in rhythmic patterns. These patterns can be represented as the vector sum of the EP potentials of the local myocardium, which are recorded as electrocardiogram (ECG) signals. ECG signals provide valuable information about various cardiac disorders. Traditional metal electrodes, commonly used with gels for ECG sensing on the skin, degrade quickly during movement and when the gel dries out. To address this issue, a conductive dry adhesive (CDA) has been developed, taking inspiration from the hierarchical structure of geckos.[28] The CDA is composed of a carbon-based PDMS nanocomposite. Within the elastomeric matrix of the CDA, carbon nanomaterials such as one-dimensional CNTs and two-dimensional graphene particles are codoped to create a conductive percolation network. Additionally, graphite and graphene nanopowders are added to enhance the electrical conductivity of the CNT-based composite, achieving a value of 0.01 Scm^{-1}. The CDA-based sensor demonstrates the capability to record ECG signals of comparable quality to those obtained with commercial skin electrodes. Moreover, the CDA-based device exhibits effective performance even underwater and during dynamic motions, while commercial electrodes tend to detach under such conditions.

Choi et al. developed a functionalized elastomer known as the Au@AgNWs/SBS nanocomposite, which incorporates metal nanomaterials.[29] Their study demonstrated an implantable device capable of recording spatiotemporal ECG signals from the surface of a pig's heart. The device utilized electrodes made of an electroconductive mesh wrapped around the heart, composed of Au@AgNWs (gold-coated silver nanowires) embedded within an SBS matrix. The gold coating on the silver nanowires improved biocompatibility and protected against oxidation. By employing this nanocomposite, a stretchable cardiac mesh was created, enabling simultaneous ECG recording at 34 locations on the porcine heart. Combining multiple ECGs allowed for the generation of a spatial-temporal voltage map of the cardiac surface. The mapping results, compared to an acutely ischemic porcine model, revealed heightened local voltages at the ischemic lesion, indicating the potential of the device for detecting cardiac abnormalities. EMGs play a crucial role in detecting abnormalities in muscular function. Traditional EMG systems have been developed for rehabilitation and brain-machine interfaces. However, the insufficient contact between the skin and

electrodes often leads to high impedance and low signal-to-noise ratio (SNR). To address this issue, functional elastomers have been utilized to establish conformal contact with the skin, enabling the recording of EMG signals with a high SNR. One example is the stretchable graphene-based electronic tattoo (GET) that offers great potential for soft and wearable EMG sensors.[30] The GET, with a thickness of only 463 nm, is fabricated by transferring and cutting graphene produced through chemical vapor deposition onto an elastomeric substrate using a mechanical cutter plotter. The patterned GET is then applied to the skin to measure EMG signals from the forearm. The quality of the EMG signals recorded by the GET is comparable to that of conventional gel electrodes based on Ag–AgCl.

Strain sensors

Stretchable conductive nanocomposite materials have been widely used to fabricate high-performance physical sensors for detecting various mechanical deformations/forces, such as strain, pressure, and shear force, due to their excellent electrical and mechanical properties in addition to their low cost and good processability. When subjected to mechanical deformation, the conductive network within the elastic matrix endures geometrical changes (stretching, separation of conductive particles, microcracking, etc.), resulting in electrical resistance variations that can be correlated with the external mechanical forces.[31]This is because the strains within the matrix phase and the conductive additives are vastly different. Wearable physical sensors can detect both small strains (such as pulse and heartbeat) and large deformations (such as joint movements), which are closely related to physiological conditions of individuals. As a result, ubiquitous physical sensors are promising for human health monitoring, rehabilitation, sports performance training, and COVID-19 monitoring applications. Stretchable conductive nanocomposites-based wearable sensors have demonstrated the ability and feasibility to detect mechanical strain, pressure, and temperature indicating various physiological signals related to a person's health conditions, such as respiration rates, heart rates, muscle tension, and joint movements.

Conductive elastomers can perform strain sensing thanks to the Poisson effect and the percolation network. Resistance is proportional to the length of a conductor and inversely proportional to its thickness. Elastomers are deformed by tensile stress, causing their length to increase while their thickness decreases. Consequently, the resistance of a conductive elastomer rises with increasing tensile force. The rearrangement of conductive percolation networks is an additional crucial factor to take into account. Through the conductive percolation network of a conductive elastomeric matrix, the electrical current flows. When an elastomer is stretched, conductive additives are typically rearranged and percolation network junctions are typically severed. Therefore, the resistance of the conductive elastomer increases as it is extended. Using the change in resistance upon stretching, the tensile strain imparted to the conductive elastomer may be calculated. For instance, You et al. presented an apexcardiogram (ACG) sensor that detected variations in the heart's temporal volume.[32] The apexcardiogram sensor comprised a layer of Au particles embedded within a PDMS matrix. Due to the fact that the small Au particles were assembled as a monolayer that served as a percolation network, the resistance change of the Au particles was extremely sensitive to a small strain (2%), which was sufficient for recording myocardial strain. Mounted on the chest of an adult subject, the fabricated ACG sensor effectively recorded the mechanical movements of the cardiac apex, as confirmed by the simultaneous recording of ECG signals using conventional Ag/AgCl electrodes.

Pressure sensors

Sensing pressures, such as blood pressure, cardiac ventricular pressure, and cerebral pressure, is essential in the healthcare industry. Pressure sensors can also be incorporated into synthetic epidermis. Three of the most prevalent sensing techniques are capacitive, resistive, and piezoelectric pressure sensing. A capacitive pressure sensor consists of an elastomeric insulative layer positioned between two conductive layers. The amount of capacitance is inversely correlated to the distance between the two conductive layers. For instance, a microporous dielectric elastomer-based wearable capacitive pressure sensor was developed.[33] The porous dielectric elastomer sandwiched between CNT/Ecoflex electrode layers exhibited highly sensitive pressure detection over a broad pressure range (0.1–130 kPa). The high sensitivity was obtained by increasing the compressibility by a factor of 20 by introducing a 62.8% porosity (pore size 288 μm) into the dielectric layer. At the same applied pressure, the change in capacitance increased as the compressibility increased. Additionally, a wearable pulse-sensing device was demonstrated. The pressure sensor effectively recorded pulses from a human wrist.

Special designs and/or materials are used to induce a pressure-dependent change in resistance in resistive pressure sensors. A pressure sensor was constructed with a thin, elastomeric insulative layer (which can be replaced by empty space) sandwiched between two conductive layers.[34] As pressure was applied externally, the insulating layer deformed and the contact area between the two conductive layers grew. Consequently, as the pressure was increased, the resistance decreased.Jung et al. developed a pressure sensor using a porous pressure-sensitive rubber. After being sonicated, a solution of MWC-NTs, PDMS, and reverse micelles became homogeneous and gel-like, and was then printed. A wearable pressure sensor was created through nozzle jet printing of the mixture. Due to the evaporation of solvents trapped within the micelles, micropores emerged following the solidification of the printed conductive rubber. The fabricated four-channel pressure sensor was placed on a wrist and used as a wearable human-machine interface to wirelessly control the motion of a robot (*e.g.*, forward, backward, counter-clockwise, and clockwise rotational movements).

Using piezoresistive composite elastomers, a novel pressure sensor was presented.[35] A mixture of CNTsand PDMS was poured into a microdome-shaped silicone mold with a height and diameter of 3 and 4 μm, respectively. The patterned surfaces of two microdome-structured CNT/PDMS composite films were fixed to face each other. When external pressure was applied, the flexible microdomes deformed, resulting in an increase in current and a reduction in resistance. To analyze the effect of microdome structure on sensitivity, various varieties of pressure sensors, including planar, single, and interlocked microdomes, were compared; and the pressure sensor with an interlocked microdome structure was 24 times more sensitive than the planar sensor (0.6 kPa^{-1}). The

interlocked microdome structure pressure sensor also demonstrated a low detection limit of 0.2 Pa.

Stimulators

The functionalized elastomers not only can be used in a variety of sensor types, but they are also highly effective stimulators. Electrical stimulations can modulate the electrophysiological activity of tissue. As medical treatments, electrical stimulations like deep brain stimulation, cardiac resynchronization therapy, and spinal cord stimulation have been utilized. However, the mechanical mismatch between conventional rigid electrodes and tissue has resulted in a number of complications. Therefore, the use of conductive elastomers for electrical stimulation has gained increasing interest. Minev et al. developed a microelectrode array (MEA) using a composite material consisting of platinum (Pt) and PDMS.[36] They combined PDMS with platinum granules to create the composite, with platinum particles ranging in diameter from 0.5 to 1.2 μm selected to enable the rapid formation of an electrical percolation network. The MEA was fabricated by screen-printing the Pt/PDMS composite onto a micropatterned gold electrode. The electrochemical properties of the MEA were suitable for neural stimulation, with a charge storage capacity of 47 ± 3 $mCcm^2$, which was two orders of magnitude higher than that of a flat platinum film. The researchers implanted the MEA with seven contact patches on the epidural surface of a rat's spinal cord. By electrically stimulating the dorsal aspect of the spinal cord, they were able to induce locomotor-like leg movement. Optimal stimulation was achieved by increasing the stimulation amplitude from 10 to 250 A. The Pt/PDMS MEA exhibited softness (tensile modulus of 10 MPa), allowing for successful spinal stimulations *in vivo* without any adverse effects. To address the inflammatory responses caused by rigid implantable cardiac stimulators, researchers have proposed the use of flexible, implantable cardiac stimulators made from functional elastomers. Park et al. introduced electromechanical cardio plasticity by utilizing epicardial mesh electrodes that can apply pressure and electrical stimulation to the heart simultaneously.[37] The epicardial mesh electrodes were composed of a composite material consisting of ligand-exchanged silver nanowires (LE-AgNWs) uniformly dispersed in a SBS elastomeric matrix, which exhibited a high electrical conductivity of 11,210 S cm^{-1}. These composite electrodes had a low elastic modulus of 44.71 ± 7.54 kPa, similar to that of 2 mm thick epicardial tissue sheets (34.67 ± 6.2 kPa). The epicardial mesh provided mechanical support for cardiac contraction, while the electrical stimulation helped synchronize the cardiac contraction process.

In orthopedic clinics, thermotherapy has proved to be an effective treatment method, particularly for relieving joint pain. Thermal stimulation expands vascular systems and surrounding collagen tissue, thereby facilitating tissue regeneration and pain management. However, conventional heaters cannot be incorporated conformally into joints that deform and bend dynamically. In thermotherapy, conformal contact between the device and the epidermis enables an efficient heat transfer. Thermotherapy also requires precise temperature control to prevent low-temperature skin injuries, which can be achieved through conformal contact of the temperature sensor with the skin and precise temperature feedback. Therefore, thermo-therapies have utilized wearable warmers.

In thermal therapies, instead of using heavy and cumbersome heat packs, portable wearable heaters can be used to accomplish conformal contact between the device and the skin, efficient heat transfer, and precise temperature control. Such applications have been made possible by the high electrical conductivity, mechanical suppleness, and thermal stability of conductive elastomers. Choi et al. developed a stretchable heater for articular thermotherapy using LE-AgNWs and SBS composite.[38] The large-area stretchable mesh-type heater, measuring 14 cm x 6.5 cm, was successfully applied to the wrist of a subject, maintaining conformal contact and sustained thermal stimulation for 12 hours of dynamic motion without causing irritation. To enhance long-term biocompatibility, Choi et al. coated theAgNWs with a thick gold shell (Au@AgNW) in subsequent studies. The wearable thermal stimulator exhibited excellent Joule heating performance at a strain of 50%, while retaining its electrical conductivity. The heater maintained superb conformal contact with the skin, ensuring reliable heating even during wrist flexion or extension.

Conclusions and perspectives

The functionalized elastomeric nanocomposites have emerged as a promising option for intrinsically flexible and bio-integrated electronics. Their ability to form conformal interfaces with the human body makes them well-suited for various applications in this field. While blending elastomers with functional additives, such as conducting or semiconducting materials, is a common method for functionalization, technical challenges remain. The performance of functionalized elastomers is lower than that of conventional electronic materials, and their functionality can be compromised by mechanical deformations and stress. Biocompatibility and toxicity concerns associated with certain infill materials also need to be addressed. Despite these obstacles, functionalized elastomers offer great potential for sensors, stimulators, power supply devices, and displays in bio-integrated electronics. Further research is required to improve material performance, develop customized processing techniques, and enhance integration capabilities. High-resolution patterning techniques are crucial for the advancement of functionalized elastomers. Ultimately, the future of soft and bio-integrated electronics based on functionalized elastomers appears promising. Conductive nanocomposites have shown significant promise in terms of material design and application. The availability of diverse conductive nanomaterials and the ease of fabrication make them appealing for the development of stretchable and flexible electronic devices. Incorporating conductive nanofillers, such as carbon and metal-based nanomaterials, into stretchable matrices has enabled the creation of high-performance conductive nanocomposites for sensors and stimulators. Carbon-based nanofillers offer excellent mechanical properties and stability, while metal nanowires possess high conductivity and transparency. The combination of different nanofillers enhances the stretchability and conductivity of the nanocomposites. However, challenges persist in the field of conductive nanocomposites for stretchable electronics. Achieving stable interconnections with other electronic components and commercial devices remains a crucial aspect for practical implementations. Robust integration strategies are needed to ensure reliable performance under various mechanical deformations. Furthermore, advanced fabrication techniques like 3D printing hold promise for creating complex

and multifunctional flexible electronics. The impact of conductive nanocomposites on the future of stretchable electronic devices lies in the integration of novel structures, new functionalities, and advanced fabrication methods. In conclusion, the potential of functionalized elastomers and conductive nanocomposites in the domains of intrinsically flexible and stretchable electronics, respectively, is significant. Continued research and development efforts are necessary to improve material performance, address biocompatibility and device-tissue interface concerns, enhance integration capabilities, and explore advanced fabrication techniques. By doing so, we can unlock the full potential of these materials and pave the way for innovative and transformative applications in the field of bio-integrated and stretchable electronics.

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