Intelligent Motion Detector: Compositing Reversibly-Crosslinkable Polymer Films with Encapsulated Electrodes and Cognitive Convolutional Neural Networks

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Research Article

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Abstract

This paper presents the design, fabrication, and implementation of a novel composite film, polybutadiene-based urethane (PBU)/AgNW/PBU sensor (PAPS), demonstrating remarkable mechanical stability and precision in motion detection. The sensor capitalizes on the integration of Ag nanowire (AgNW) electrodes into a neutral plane, embedded within a reversibly crosslinkable PBU polymer. The meticulous arrangement mitigates pore and interface formation, resulting in enhanced mechanical robustness, reproducibility, and long-term reliability. The PBU polymer underwent electrospinning and sequential Diels-Alder (DA) and retro-DA reactions, creating a planarized encapsulation layer. This encapsulation, matching the thickness of the pre-formed PBU film, effectively houses the AgNW electrodes. The PAPS outperforms conventional AgNW/PBU sensors (APS) in terms of mechanical stability and bending insensitivity. When affixed to various body parts, the PAPS generates distinctive signal curves, reflecting the specific body part and degree of motion involved. The PAPS sensor's utility is further magnified by the application of machine learning and deep learning algorithms for signal interpretation. K-means clustering algorithm authenticated the superior reproducibility and consistency of the signals derived from the PAPS over the APS. Deep learning algorithms, including a singular 1D Convolutional Neural Network (1D CNN), Long Short-Term Memory (LSTM) network, and dual-layered combinations of 1D CNN + LSTM and LSTM + 1D CNN, were deployed for signal classification. The singular 1D CNN model displayed a remarkable classification accuracy exceeding 98%. The PAPS sensor signifies a pivotal development in the domain of intelligent motion sensors.

1. Introduction

The movement of the human body offers more than just an indication of the physical capabilities of individual body parts of the wearer [1–3]. It also provides insights into the prognosis of an array of diseases, such as rheumatism, cardiovascular disorders, fractures, dementia, and Parkinson's disease, among others [4–6]. For harnessing human body movement as a diagnostic or prognostic tool for various diseases, certain critical factors must be taken into account. These include the ability to accurately detect repeated movements over an extended period of time (reproducibility), maintain detection capabilities even under strenuous movements (durability/reliability), detect changes in movement patterns, and possess a high degree of sensitivity for detailed detection [7–10]. Additionally, the incorporation of intelligence to infer motion through measured signals is paramount. To achieve high reproducibility, durability, and reliability of the motion sensor, the optimization of the sensor's constitutive material and structure is a prerequisite. A resistive motion sensor, in most cases, is realized by measuring the variation in electrical resistance that transpires when strain is applied to an electrically percolated conductor on a soft film [11–14]. Accordingly, the sensor must possess the capability to alter its structural or material form when subjected to mechanical stress, resulting in a change in electrical resistance. Upon the removal of the stress, it should be able to revert back to its original state.

The simplicity of the aforementioned sensor structure, though advantageous for fabrication, bears certain intrinsic shortcomings. Firstly, the exposure of the electrode on one surface of the film can compromise the long-term reliability and reproducibility of the sensor. For instance, when uniaxial strain is applied to the film, significant stress is exerted on the outer surface of the film, potentially leading to the detachment of the conductive material under repeated stress [15]. Secondly, the exposed state of the electrode can limit its functional longevity due to factors such as oxidation and corrosion [16]. Changes in material properties could also arise from contact with external materials. Thirdly, since electrodes are formed on a single surface of the polymer, a considerable disparity in mechanical properties between the conductors such as Ag nanowires (AgNWs) and the elastomer leads to asymmetry in film properties [17, 18]. This induces a complex stress environment in the presence of curvature-forming stress, obfuscating the origin of resistance changes. Thus, the optimal resistive motion sensor structure would entail the formation of electrodes between two identical films, with the contact area between the films chemically integrated. In this configuration, the electrode appears as if encapsulated within a singular polymer film. The electrode's interior positioning shields it from environmental factors and applied stress, ensuring long-term reliability and reproducibility by preventing its separation from the film.

However, realizing such a structure poses challenges given the properties of commonly used commercial polymers. Commercially available elastomeric polymers are often premised on high mechanical strength, excellent chemical resistance, and robust resistance to light and moisture, typically employing heat- or light-induced crosslinked materials [19–21]. In order to create a structure with an embedded electrode using such polymers, the polymer must first be cured to form a film. Following this, an electrode is formed on the film, which is then encapsulated with the same polymer as the initial film. Encapsulation can be achieved either by (1) coating conductors/polymer with the liquid polymer solution used initially [22, 23], or (2) lamination after creating a similar film [24, 25]. However, both these methods suffer from inherent drawbacks. Given that the typical crosslinking reaction is irreversible, there is a scarcity of functional groups available for chemical bonding with the subsequent film. This could lead to interfacial instability,
negatively impacting long-term reliability and reproducibility. Additionally, these methods often trap numerous pores at the interface between films or within the upper polymer. Hence, a novel approach is imperative to achieve a pore-free composite with a robust sandwich structure in which the upper and lower polymer films are completely integrated.

A significant challenge, however, lies in the fact that any strain, regardless of its type, if applied with identical magnitude, will produce a resistance change of the same degree. Consequently, although this sensor is capable of detecting almost all types of mechanical stress, it is unable to discern the specific type of stress that has led to the signal change. Recently, advancements in artificial intelligence (AI) offer potential solutions to this predicament. Typically, the methods based on AI emulate biological perception by employing cognitive processes learned from experiences to detect signal changes produced by stress applied to sensors. Much like humans discern stress types through past experiences and cognitively learned rehearsal processes, 1D Convolutional Neural Network (1D CNN), a deep learning algorithm, can discriminate various artificially formed measurement data. Consequently, they can potentially ascertain the magnitude or type of induced deformation and the body part where the sensor is applied.

In this paper, we present a novel pore-free sandwich-structured resistive mechanical sensor with superior structural stability, reproducibility, and long-term reliability. We employed a polybutadiene-based urethane (PBU) film, a reversibly crosslinkable polymer based on the Diels-Alder (DA) reaction, to implement a pore-free and interface-free film with impregnated AgNW electrodes inside the film. In pursuit of this objective, we meticulously executed a process involving the electrosprinning of a PBU solution, followed by a sequence of retro-DA reaction. This reaction allows the PBU fibers to spread fully to form a film, with the upper and lower films achieving complete integration through the subsequent DA reaction. Concurrently, the AgNWs maintain their conducting network while being recessed inside the integrated film. The strain sensor that we developed displayed remarkable stability and long-term reliability in the face of repeated stretching and bending tests, primarily due to its pore-free and interface-free encapsulation. This characteristic led to the generation of consistent data, which proved to be highly suitable for analysis through deep learning techniques. We applied unsupervised K-means clustering, a machine learning technique, to assess the uniformity of the electrical signals output by the sensor during stretching tests. K-means clustering partitions data into distinct clusters, where each data point belongs to the cluster with the nearest mean. In our case, we used this method to confirm that the unit graphs of these electrical signals demonstrated a high degree of similarity, reflecting the consistency and reliability of our sensor. Furthermore, we conducted an experiment where sensors were attached to various body joints to gather data for each distinct joint motion. The collected data was then processed through several deep learning models. Deep learning models, equipped with multiple layers of artificial neurons, are capable of learning abstract representations of data, making them highly effective in discerning complex patterns and relationships. Among the models we used, the 1D CNN model achieved a classification accuracy of 98.12%. CNNs are a category of neural networks that have proven extremely effective in areas such as image and signal processing. In our case, the 1D CNN was able to accurately classify the type and intensity of joint motions based on the sensor data.

2. Experimental section

2.1 Materials

Furfurylamine and glycerol 1,2-carbonate were procured from the Tokyo Chemical Industry, based in Japan. Methyl ethyl ketone (MEK), bis(3-ethyl-5-methyl-4-maleimidophenyl)methane (BMI), isophorone diisocyanate (IPDI), and dibutyltin dilaurate (tin) were obtained from Sigma-Aldrich, USA. HLBH-P 2000 was secured from Cray Valley, USA. A dispersion of AgNWs with a mean diameter of 21 nm and an average length of 21 µm was supplied by C3 Nano, USA, with the nanowires dispersed in isopropyl alcohol (IPA) at a concentration of 0.5 wt%. All these chemical reagents were utilized in their received state, with no further purification procedures. Precautionary measures and the usage of personal protective equipment were strictly adhered to during the manipulation of these chemical substances to mitigate any potential risks associated with their handling, particularly in the case of hazardous acids.

2.2 Synthesis of PBU

A mixture was prepared by combining HLBH-P 2000 (12.0 g, 6.0 mmol), IPDI (2.67 g, 12.0 mmol), diol 1 (1.29 g, 6.0 mmol), and MEK (15 g) in a vial. This mixture was stirred until it attained a homogenous consistency. Subsequently, the mixture was subjected to stirring in an oil bath for a duration of 2 h at a temperature of 60°C. The synthesis of diol 1 was carried out with glycerol 1,2-carbonate (6.0 g, 50.8 mmol) and furfurylamine (4.9 g, 50.8 mmol), and this reaction was conducted in an oil bath for a period of 3 h at a temperature of 60°C.

2.3 Fabrication of motion sensors
The procedure to construct a fully encapsulated PBU/AgNWs/PBU sensor, henceforth referred to as PAPS, is delineated in Fig. 1. Initially, a glass substrate was meticulously cleaned using water, isopropanol, and acetone. Post cleaning, it was thoroughly dried before a 0.5 wt.% AgNWs solution, dispersed in IPA, was applied using a spin-coating process at 1,000 rpm for 25 s. This was followed by a drying period at 110°C for 10 min. Subsequently, a spin-coating process was utilized to apply the synthesized PBU solution onto the AgNWs/glass substrate at 1,000 rpm for 25 s, after which the product was cured in an oven at 60°C overnight. The resulting PBU/AgNWs/glass substrate was then immersed in deionized water for an hour to instigate hygroscopic swelling of the PBU. Following this, the PBU film, with embedded AgNWs, was delicately peeled off the glass and allowed to dry at ambient temperature. The thickness of the resultant AgNWs/PBU film was approximately 40 µm. The PBU solution was then electrospun using a high-voltage electrospinning apparatus (ESR200R2, NanoNC, South Korea) onto the AgNWs/PBU at 12 kV, with the distance between the nozzle and the ground set at 150 mm, and a flow rate of 10 mL/h. The constructed PBU fibers/AgNWs/PBU was then allowed to dry at room temperature for 30 min and heated in an oven at 60°C overnight to stimulate a DA reaction for curing. Subsequently, the retro-DA and DA reactions were sequentially executed at 120°C for 2 h and at 60°C for 2 h, respectively. The final thickness of the encapsulated PAPS sensor was around 80 µm. For comparative purposes, an unencapsulated AgNWs/PBU sensor (APS) was fabricated, where PBU was spin-coated on the AgNWs/glass substrate at 700 rpm for 25 s, cured in an oven at 60°C overnight, immersed in deionized water for 1 h, and finally peeled from the glass. The thickness of the resultant APS was approximately 80 µm.

2.4 Characterization

Mechanical properties and wearable sensory data were obtained using a stretch-testing machine (Jaeil Optial System, South Korea). The sensor surface’s microstructure was thoroughly examined using a field-emission scanning electron microscope (FESEM; Carl zeiss, Germany) and an atomic force microscope (AFM; Multimode-8, Bruker, Germany). The electrode surface was observed using an optical microscope (Leica, DM2700m, Germany). A tensile testing apparatus (HZ-1007E, MMS TECH, South Korea) was employed to quantify stress variations induced by strain. Electrical characteristics were assessed using an LCR meter (LCR-6100, GwINSTEK, Taiwan) and a non-contact measurement tool (EC-80P, Napson Corp., Japan). Furthermore, optical properties were evaluated utilizing UV-visible spectroscopy (V-750, JASCO Corp., Japan).

3. Results and discussions

Figure 2 presents FESEM images, each corresponding to different stages in the fabrication of the strain sensor. Initially, the base electrode was constructed via an inverted-layer procedure [34]. This involved coating a glass substrate, already deposited with AgNWs, with a PBU solution. Subsequently, the AgNWs/PBU film was detached from the glass following the curing process. As shown in Fig. 2a, FESEM micrograph and an inset AFM image reveal the AgNWs/PBU electrode surface to be remarkably smooth, with a surface roughness value of around 1.89 nm. In the subsequent stage, PBU fibers were generated through electrospinning onto the electrode surface, resulting in the formation of an encapsulation layer. An FESEM image of this is depicted in Fig. 2b. These PBU fibers, with an average diameter of 6.2 µm, were observed to be stacked sequentially while simultaneously forming a network structure on the electrode surface. The DA reaction plays a pivotal role in the curing process of the PBU in this study. This reaction is a cycloaddition process wherein a diene, in this context represented by the furan ring, combines with a dienophile, represented by maleimide, under specific conditions to form a DA adduct. The DA reaction is characterized by its reversible nature, which is particularly important in this context. When the PBU undergoes the initial DA reaction, it facilitates crosslinking between the furan ring and maleimide. This crosslinking leads to a robust and stable structure that is necessary for the PBU to serve as an effective encapsulation layer. However, when the PBU is subjected to heat treatment at a temperature of 120°C, a retro-DA reaction is initiated. The retro-DA reaction causes the previously formed crosslinks to break, leading to the regeneration of the original furan ring and maleimide structures. This breaking of bonds and the reformulation of the original structures cause a portion of the PBU surface to fuse, which is a phenomenon uniquely enabled by the reversible crosslinking capabilities of the PBU. The second DA reaction is then triggered, which results in the formation of a new set of crosslinking bonds. These bonds form between the fully expanded PBU layer and the original PBU film in contact, allowing them to integrate into a single, cohesive entity. This intricate sequence of reactions showcases the versatility and adaptability of the DA reaction in creating and modifying polymeric materials.

Upon fabrication through an electrospinning process, the PBU fibers, influenced by the inexorable force of gravity, descend onto the surface of the foundational electrode positioned at ground level. The planar morphology of this embedded electrode, which exhibits an almost perfectly flat surface, facilitates the close adherence of these PBU fibers to the surface of the AgNWs/PBU electrode. This intimate interaction between the PBU fibers and the AgNWs/PBU electrode surface is visually represented in Figure S1a. However, a
contrast scenario is encountered when the AgNWs layer is established on a PBU film surface, which is distinguished by its considerable surface roughness (Figure S1b). The intricate geometric considerations of the AgNWs electrode pose a significant challenge in achieving intimate contact between the PBU fiber and the PBU substrate. This is starkly illustrated in Figure S1b, which shows the difficulty in establishing close contact due to the roughness of the surface and the unique geometry of the AgNWs electrode. An examination of Figure 2a reveals the unique network structure of the AgNW layer of the foundational electrode. This structure inherently provides ample vacant space that could be exclusively occupied by PBU. The presence of these vacancies opens up the possibility of inducing the integration and fusion among the PBU fibers themselves. Further, it also allows for the integration between the top and bottom PBU layers, thereby forming a more cohesive and robust structure. Remarkably, this process of integration and fusion relies solely on the inherent cross-linking capability of the PBU, thereby obviating the need for the application of any external physical pressure or force. This is a significant observation as it underscores the self-assembling capability of the PBU fibers under the given conditions. As this integration phase progresses, there is a gradual transformation in the form of the PBU fibers over time. Interestingly, this transformation does not exert any undue strain on the electrode, thus maintaining its structural integrity. Moreover, this process also does not promote the formation of pores, ensuring the continuity and uniformity of the material. This nuanced balance between transformation and stability is crucial for the overall performance and longevity of the developed structure.

For the PBU fibers to effectively serve their intended function as an encapsulant, it is absolutely crucial that they provide full coverage of the electrode's surface. This ensures that the electrode is completely shielded, thereby maximizing the protective qualities of the PBU fibers. Moreover, the thickness of the PBU fibers, once they have been fully fused into a film, should ideally be similar to that of the original, underlying PBU film. This requirement of maintaining a uniform thickness is significant as it aids in mitigating the intricacies of stress states that often arise due to the curvature of the film. By reducing these complexities, the operational mechanism of the sensor can be significantly simplified, which ultimately leads to an enhancement in the overall functionality of the sensor. The surface of the encapsulation layer, after the integration and fusion of the PBU fibers, was meticulously examined to verify the extent of surface coverage in accordance with the PBU electrospinning duration. This relationship is visually demonstrated in Figure S2. To provide a clear demarcation and thus confirm the presence of the electrospun fibers, the boundary was distinguished through a simple masking procedure using a kapton film. As the duration of the electrospinning process was extended, an increase in surface coverage was observed. This increase in coverage was coupled with a planarization of the encapsulation layer's surface, resulting in a more uniform and smooth layer. Following an electrospinning duration of 10 min, the integrated fibers had transformed into a film form that offered complete coverage of the electrode, effectively shielding it from external influences. Figure 2c presents a FESEM image of the surface of the encapsulated sensor. Upon examination, it is clear that the morphology of the encapsulated sensor's surface is distinctively different when compared with the image presented in Figure 2b. Following the encapsulation process, the DA, retro-DA, and subsequent DA reactions, as previously described, were sequentially carried out. These reactions, when executed systematically, allowed for a flat and thorough integration with the bottom PBU film. Notably, this process was accomplished without the formation of pores, thereby maintaining the integrity and continuity of the encapsulation layer, contributing to the overall robustness and efficiency of the sensor.

Figure S3 provides an in-depth analysis, offering both optical transmittance data and digital imagery of three configurations: the AgNWs/PBU, the PBU fibers/AgNWs/PBU, and the integrated PBU/AgNWs/PBU. The AgNWs/PBU configuration, consisting of AgNWs in combination with PBU, demonstrated impressive optical properties with a transmittance of 91% at a wavelength of 550 nm. This high transmittance signifies the superior optical characteristics inherent in both the AgNW and the PBU layers. In contrast, the PBU fibers/AgNWs/PBU configuration, which involves a layer of PBU fibers in addition to the AgNW and PBU, displayed a significantly lower transmittance of only 35%. This marked reduction in transmittance can be attributed to the scattering of light caused by uneven surfaces. These irregularities are a result of the unique physical shape and structure of the PBU fibers. However, the integration and subsequent planarization process led to an increase in transmittance for the PBU/AgNWs/PBU configuration, reaching a value of 85%. This substantial increase in transmittance suggests that the PBU fibers have successfully integrated and formed a singular, unified film.

In the context of the PBU fiber-based layer serving effectively as an encapsulation layer, it is of paramount importance that it also exhibits a high degree of integration with the bottom PBU layer. Figures 2d-f present cross-sectional images of the PBU/AgNWs/PBU configuration, providing valuable insights into the structural composition of the integrated layers. Specifically, Figures 2d and e feature FESEM images of samples subjected to the retro-DA reaction at 120°C for durations of 1 h and 2 h respectively. A comparison of these images reveals a distinct difference in the sharpness of the boundary between the two layers. This suggests that adequate thermal energy is a critical requirement for achieving robust integration between the layers. As such, it was determined that a retro-DA reaction duration of 2 h was necessary for complete integration. Figure 2f, displaying a high-resolution FESEM image of the cross-section of the encapsulated sample, confirms the integrity of the AgNWs layer. The layer showed no signs of deformation even after the integration of the top and bottom PBU films. This is particularly notable because the PBU fiber-based encapsulation process is designed to exploit
solely the unique properties of the polymer. It refrains from introducing any additional processes that might potentially result in deformation. Thus, the encapsulation process manages to maintain the structural integrity of the AgNWs layer, further attesting to the efficacy and gentleness of the integration process.

As elucidated in our preceding discussions, we have successfully pioneered a novel, straightforward encapsulation methodology based on the electrospinning of fibers. This methodology leverages the reversible crosslinking attributes of PBU. Simultaneously, we have probed into alternative methods capable of achieving integration by capitalizing on the inherent properties of PBU. Two such encapsulation strategies under examination were: the film lamination method and solution coating. In the preparation phase for both processes, an identical AgNWs/PBU film was meticulously fabricated to function as the bottom electrode. Following this, retro-DA and DA reactions were consistently performed under comparable conditions after the encapsulation processes. Figures S4 a-c provide a visual representation of the various stages involved in the lamination process, documented through digital imagery. An already cured PBU film was delicately arranged on the pre-prepared surface of the bottom electrode. Lamination was then achieved by the application of a pressure of 10 kPa for a duration of 10 min. Upon completion of the lamination, the top film and the bottom electrode gave the impression of being in seamless contact, with no discernible damage or porosity observed. Nevertheless, an intriguing observation was made post the heat treatment designed for integration. Pores, which were previously non-existent, began to appear. This phenomenon can likely be attributed to the expansion of air trapped during the film placement process. Despite best efforts, complete elimination of such trapped air is challenging due to process-induced defects that cannot be fully controlled or mitigated, leading to the formation of microscopic pores. Figures S4d and e depict the process of solution coating through digital images. This process, mirroring the lamination method, also generated pores during its execution. The emergence of these pores seems to be triggered by a combination of factors. Firstly, the partial dissolution of the bottom film and secondly, the formation of fine pores around the AgNWs that had permeated into the bottom film, both contributed to the pore formation.

We have also engaged in the empirical evaluation of resistance shifts prior to and subsequent to each encapsulation method. This was done in a bid to understand the potential alterations in the electrical properties of the electrode post encapsulation. The graph representing this data is illustrated in Figure S5. Upon the implementation of encapsulation facilitated by electrospun fibers, an intriguing observation was made. The resistance of the electrodes essentially mirrored the pristine level, indicating no discernable structural deviations in the AgNW electrode. This strongly suggests that the electrospinning-based encapsulation method effectively preserves the structural integrity of the AgNW electrode, thereby maintaining its original resistance level. Contrastingly, following the execution of the lamination or PBU coating processes, there was a notable surge in resistance. This escalation could likely be a consequence of the substantial plastic strain that was inadvertently inflicted upon the electrode layer during these procedures. The introduction of such strain could potentially distort the original structure of the electrode, consequently leading to an increase in resistance. More alarmingly, an even more severe increase in resistance was recorded post the solution coating process. This can be attributed to the dissolution of the bottom PBU substrate incited by the solvent, which was present in high concentrations in the PBU solutions that were deposited on the electrode. This dissolution process, coupled with the subsequent recovery of the PBU, can cause displacement of the AgNW strands that were initially in contact. This, in turn, can lead to the disruption or severing of certain conductive pathways, thereby accounting for the drastic increase in resistance. These observations collectively underscore the inherent advantages of the PBU fiber-based encapsulation method over alternative encapsulation strategies. Notably, this method demonstrates a complete immunity to pore generation and effectively suppresses the deterioration of electrical properties, thereby making it a highly promising approach for the encapsulation of AgNW electrodes.

Figure 3 meticulously delineates the outcomes of comprehensive sensor characteristic evaluations, and it juxtaposes the mechanical and electrical characteristics of two distinct sensor types. These types include the unencapsulated AgNWs/PBU-based sensor, referred to as APS, and the encapsulated PBU/AgNWs/PBU-based sensor, denoted as PAPS. The objective behind this comparison is to shed light on the tangible impact of the encapsulation process on the performance and characteristics of the sensor. To ensure an accurate and fair comparison and to mitigate any potential influence of extraneous variables during the process of characteristic evaluations, both APS and PAPS were meticulously fabricated to closely match each other in terms of their thickness. Both sensors were engineered to achieve a similar thickness that is approximately 80 µm. As a preliminary step, we embarked on ascertaining the mechanical properties of the two sensor types through a well-established tensile test, the results of which are illustrated in Figure S6. This step is of paramount importance, as the parameters of tensile strength and break elongation are critical elements that determine the suitability and performance of a material when applied to strain sensors. Intriguingly, owing to the inherent stretchability of the PBU film, both sensor types, APS and PAPS, exhibited a break elongation that reached up to nearly 350% as shown in Fig. 3a. In addition to the impressive elongation, the tensile strengths of the two sensors were found to be remarkably similar, both registering a value of approximately 3.5 MPa. This similarity suggests that the two distinct PBU layers that constitute the PAPS were effectively integrated...
with each other, thereby exhibiting mechanical behavior that closely resembles that of a singular PBU film. Figure 3b presents the result of an experiment designed to measure changes in resistance while the two sensor types were subjected to increasing levels of strain until fracture occurred. This experiment provided valuable insights into the electrical stability of the sensors. Following the application of a specific level of strain, both APS and PAPS underwent complete damage, culminating in a sharp rise in resistance to the mega-ohm level. However, when subjected to identical levels of strain, the PAPS demonstrated a considerably more stable behavior compared to the APS. This improved stability indicates that the encapsulation process serves to enhance the electrical stability of the sensor. To further illustrate the outcomes of the experiments, digital photographs of each sensor post-test are provided in Figure S7. The fracture in the APS was observed predominantly in the midsection, whereas the fracture in the PAPS occurred in the unencapsulated area that was in direct contact with the jig of the LCR meter. This discrepancy in fracture locations can likely be attributed to the variation in thickness between the encapsulated and unencapsulated parts of the sensor. A noteworthy observation is that the top PBU layer in the PAPS remained firmly adhered to the sensor until the moment of fracture.

In our pursuit of evaluating the long-term stability of the APS and PAPS, we conducted meticulous measurements of resistance change across 5,000 cycles of repetitive stretch-and-release tests under varying strain conditions. As illustrated in Figs. 3c and d, we observed an increase in resistance when the sensors were subjected to stretching, which subsequently recovered upon release. Moreover, the rate of resistance change also escalated in correlation with the increase in applied strain and the cycle number. Nevertheless, the PAPS demonstrated remarkably superior stability compared to the APS. Particularly noticeable was the significant divergence in the shape of the graph when a strain of 30% was applied. This distinct behavior strongly suggests that encapsulation significantly enhances the long-term reliability of the strain sensor. Figures S8a-d present the FESEM images of the APS surface following the application of 5%, 10%, 20%, and 30% stretching strain up to 10 cycles respectively. All samples were analyzed after a release period of 24 h. As corroborated in the tensile test, the PBU film exhibits sufficient elasticity to withstand a strain of 30%, hence no tearing or discernible deformation was observed after the tests under all conditions. However, AgNWs possess ductility of less than 10% [35], thus when a strain exceeding 10% was applied, certain AgNWs exhibited breakage. In addition, when subjected to a strain of more than 20%, the AgNW strands began to protrude through the surface of the PBU film, a phenomenon that adversely affects the degradation of electrical properties more than the severing of the AgNWs. While broken AgNWs impregnated on the PBU surface can re-establish contact to restore the electrical pathway, this recovery is considerably more challenging when the AgNW is exfoliated. This underscores the importance of preventing AgNW peeling in order to ensure the long-term reliability of stretchable strain sensors. In the case of PAPS, the PBU fibers, formed through the process of electrospinning, establish a robust encapsulation layer on the electrode surface. This allows for the manifestation of stable mechanical and electrical behavior even during repeated stretch-and-release testing. The PAPS adopts a sandwich structure, with two PBU layers of equivalent thickness formed above and below the AgNWs layer. Given that the electrode layer occupies the neutral plane, it is theoretically immune to stress induced by bending. We charted the resistance change of both PAPS and APS across 5,000 cycles of repetitive bending tests with varying radii of curvature, the results of which are displayed in Fig. 3e. In the bending test with a curvature radius of 300 μm, the resistance change rate of the APS escalated to 54.59%, whereas the resistance change rate of the PAPS remained a mere 0.08%, even after 5,000 cycles. Figure 3f illustrates the dynamic resistance response of both PAPS and APS over 5,000 bending cycles with a curvature radius of 300 μm. During the bending test, the highest and lowest resistance peaks of the APS gradually increased, but the PAPS demonstrated a negligible resistance change. This indicates that the PAPS sensor, due to the stable location of the AgNW electrode on the neutral plane between the two PBU layers, exhibits a marked insensitivity to bending. These findings suggest that the PAPS is a highly reliable and durable strain sensor.

The stresses exerted upon the joints of the human body throughout daily activities are characteristically multifaceted, varying in both form and magnitude over time. Consequently, by employing an appropriate deep learning algorithm, it is conceivable to discern the type and size of the deformation that contribute to the sensor signal alterations. In this study, we endeavored to enhance the intelligence of our developed sensor through the application of several deep learning models. Before introducing the APS and PAPS to deep learning, we undertook an investigation into the similarity of unit data points derived from the two sensors. To achieve this, we utilized the K-means clustering algorithm, a renowned unsupervised machine learning technique, and collected 400 data points for each condition from the results of the stretching tests conducted on the APS and PAPS. The K-means clustering technique involves the formation of a cluster by establishing a centroid for each dataset and allocating data points based on this centroid. Being unsupervised learning, the labels of the datasets were removed prior to clustering [36, 37]. Given that the stretching tests of the APS and PAPS were performed under four distinct conditions (5, 10, 20, and 30% stretching strain), four centroids were selected, data points allocated and subsequently clustered. The visual representation of these results is provided in Figure S9. Figures S9a and c depict the extent to which data points with comparable characteristics are effectively clustered in scatterplot images of the APS and PAPS, respectively. A total of 1600 data points were allocated, with 127, 630, 713, and 130 data points of the APS distributed across the four clusters. In contrast, the
data points of the PAPS were distributed as follows: 404, 400, 451, and 345, thereby indicating a significantly lesser deviation. The heightened similarity among data points obtained under each identical PAPS condition implies that fewer data points are grouped into disparate groups. Figures S9b and d present the results of the silhouette coefficient analysis that quantitatively express the quality of clustering in the APS and PAPS, derived through the computation of distance between each cluster and surrounding clusters. The final silhouette coefficient, which is the average of all distances calculated on the basis of each cluster, is expressed as a value ranging between −1 and 1. A value closer to 1 signifies a greater distance from the cluster adjacent to the data cluster, thus indicating a high-quality cluster [38]. The silhouette coefficients of the APS and PAPS were determined to be 0.5039 and 0.6063, respectively, thereby confirming the superior quality of the PAPS clustering. This outcome implies a high degree of similarity in data points, attributable to the enhanced stability and long-term reliability of the encapsulated PAPS. As a result, we were able to ascertain that the collection of high-quality data, suitable for deep learning application, was indeed achievable.

We undertook the task of accumulating electrical signals, represented as resistance changes, for the purpose of monitoring the movements of various human body joints such as the elbow, finger, knee, and wrist. To do so, we affixed the PAPS to multiple locations on a healthy volunteer. As depicted in Figure S10, we established a connection between the copper tapes and the fabricated PAPS in order to detect the output electrical signal, after which we sealed it with polydimethylsiloxane (PDMS) to bolster the safety precautions for the volunteer. The sealed PAPS was subsequently attached to the elbows (at 45° and 90°), wrists (at 30°, 60° and 90°), fingers (at 30°, 60° and 90°), and knees (at 45° and 90°). The electrical signals generated during this procedure were gathered, amassing a total of 4,500 data points. Figure 4 provides a graphical representation of the resistance change when each joint is flexed at various angles. The resistance of the affixed PAPS demonstrated an increase and recovery when the joint was bent and subsequently straightened, respectively. In the machine test, the stress induced by bending was the primary factor in the sensor, while in the wearable test, the stress caused by both bending and stretching occurred concurrently. Nevertheless, given that the PAPS was fabricated to be insensitive to bending, it experienced less stress and could thus be tested reliably under harsh conditions. As can be observed from the figure, the graph shapes corresponding to specific positions and angles displayed similarities, with noticeable differences in the extent to which they could be differentiated from other conditions.

Building upon the data pertaining to the rate of resistance change, which was amassed during the prior wearable test, we further deployed it for deep learning applications. Through the use of deep learning algorithms, computers are capable of learning data, thereby facilitating the faster and more precise recognition of graphical shapes, as well as the classification and prediction of behavior compared to human abilities. In order to enhance the learnability of the gathered data for computers, the first step we undertook was to categorize the resistance change data into individual cycles. Given that the initial value of the data varies for each classified cycle, we carried out the min-max normalization process to simplify the learning of graph shapes by computers. The calculation method for min-max normalization is delineated in Eq. 1 below [39]. The signals that were collected underwent a preprocessing stage, wherein normalization was performed such that the minimum value was set to 0 and the maximum value was set to 1.

\[
x_{\text{scaled}} = \frac{x - x_{\text{min}}}{x_{\text{max}} - x_{\text{min}}} 
\]

1

Subsequent to data normalization, we partitioned the data into three sets: training, validation, and testing, adhering to a ratio of 6:2:2 respectively. Thereafter, we structured a variety of deep learning models with the intention of efficiently classifying and predicting the amassed data. While both 1D CNN and Long Short-Term Memory (LSTM) models excel in the analysis of time-series data, their methods of data evaluation differ somewhat. The 1D CNN model tends to be more attuned to local features, whereas the LSTM model is adept at assessing overarching patterns within the data [40]. In our research, we put forth four deep learning models: a singular 1D CNN, an LSTM, and dual-layered combinations of 1D CNN + LSTM and LSTM + 1D CNN. Figure S11 illustrates the accuracy of the training, validation, and testing data for each of these models. The LSTM, 1D CNN + LSTM, and LSTM + 1D CNN models demonstrated an accuracy below approximately 92%, while the singular 1D CNN model achieved a classification accuracy surpassing 98%. We undertook the evaluation of the deep learning models utilizing precision, recall, and F1 score - critical metrics for classification. These metrics are calculated on the basis of True Positives (TP), True Negatives (TN), False Positives (FP), and False Negatives (FN). Table 1 displays the precision, recall, and F1-score values for each model. The 1D CNN model garnered high values of 90% or more across all metrics in comparison to the other models. Elevating model complexity augment the number of parameters to be computed, thereby facilitating the model's ability to learn more intricate patterns. Nonetheless, a complex model might only perform optimally on the
training data and exhibit reduced accuracy with new data. Moreover, considering that the complexity of the data collected in this study is not high, a single 1D CNN model structure proves to be suitable.

\[
\text{accuracy} = \frac{TP + TN}{TN + TP + FN + FP}
\]

\[
\text{precision} = \frac{TP}{TP + FP}
\]

\[
\text{recall} = \frac{TP}{TP + FN}
\]

\[
\text{f1score} = 2 \cdot \frac{\text{precision} \cdot \text{recall}}{\text{precision} + \text{recall}}
\]

Table 1
Classification report according to the joint motion angle.

<table>
<thead>
<tr>
<th>Class</th>
<th>1D CNN</th>
<th>LSTM</th>
<th>1D CNN + LSTM</th>
<th>LSTM + 1D CNN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Precision</td>
<td>Recall</td>
<td>F1-score</td>
<td>Precision</td>
</tr>
<tr>
<td>Finger 30°</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.93</td>
</tr>
<tr>
<td>Finger 60°</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.99</td>
</tr>
<tr>
<td>Finger 90°</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.99</td>
</tr>
<tr>
<td>Wrist 30°</td>
<td>0.92</td>
<td>1</td>
<td>0.96</td>
<td>0.87</td>
</tr>
<tr>
<td>Wrist 60°</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.82</td>
</tr>
<tr>
<td>Wrist 90°</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.99</td>
</tr>
<tr>
<td>Knee 45°</td>
<td>0.98</td>
<td>1</td>
<td>0.99</td>
<td>0.86</td>
</tr>
<tr>
<td>Knee 90°</td>
<td>0.92</td>
<td>1</td>
<td>0.91</td>
<td>0.81</td>
</tr>
<tr>
<td>Elbow 45°</td>
<td>0.99</td>
<td>1</td>
<td>0.95</td>
<td>0.99</td>
</tr>
<tr>
<td>Elbow 90°</td>
<td>1</td>
<td>1</td>
<td>0.99</td>
<td>0.83</td>
</tr>
<tr>
<td>Average</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
<td>0.91</td>
</tr>
</tbody>
</table>

The schematic representation of the 1D CNN model, which showcased superior performance in categorizing and predicting the collected data, is delineated in Fig. 5a. Initially, data that has been subjected to a pre-processing stage is introduced to the convolutional layer via the input layer. The convolutional layer serves as a filter, effectively highlighting specific features in the data while simultaneously reducing its dimensionality. This is subsequently followed by the max-pooling layer, which is a down-sampling...
technique designed to extract the most prominent features, thus further reducing data dimensions without losing the essential characteristics of the data set. After undergoing these stages, the data is relayed to the fully connected layer, where all neurons are interconnected, thus facilitating communication between different neurons and allowing for a more integrated analysis of the data. Ten distinct classifications of joint movements are eventually conducted at the output layer, thus providing a comprehensive categorization of the various types of movements that were captured by the sensor.

Figures 5b-c present visualizations of the accuracy and loss function graphs for the training and validation data during the learning phase. These graphs elucidate the direct correlation between the number of epochs, or learning iterations through the dataset, and the model's performance; as the number of epochs increases, the accuracy of the model improves while the loss concurrently decreases. This indicates that the model's ability to accurately predict and categorize data improves with each additional pass through the dataset. Furthermore, a comparative analysis of the accuracy/loss values of the training and validation data during the learning process revealed a high degree of similarity in their graphs. This similarity is indicative of a well-balanced model, as it mitigates the risk of overfitting and underfitting, common pitfalls in machine learning that lead to a decrease in prediction accuracy. Figure 5d presents a confusion matrix, which offers a visual representation of the model's performance in terms of its ability to correctly classify joint movement data. The matrix revealed that the wrist joint at 30°, knee joint at 90°, and elbow joint at 45° were classified with respective accuracies of 95%, 96%, and 92%. Other joint movements were classified with an impressively high accuracy of 100%. The proposed model's performance in classifying the training, validation, and testing data was commendable, with respective accuracies of 98.04%, 97.23%, and 98.12%. This high level of accuracy attests to the robustness and reliability of the model in classifying joint movements. Finally, the integration of the fabricated PAPS and deep learning resulted in the creation of a smart wearable sensor. This achievement underscores the potential of the PAPS as an intelligent sensor that can be applied to advanced technological fields in the future, particularly those requiring detailed and accurate analysis of human body movements.

4. Conclusion

In the present study, we have successfully developed a composite film demonstrating superlative long-term reliability, reproducibility, and mechanical stability by strategically integrating Ag nanowire (AgNW) electrodes into a neutral plane, thereby precluding the formation of pores and interfaces. Our methodology was rooted in synthesizing a reversibly crosslinkable polybutadiene-based urethane (PBU) polymer. This polymer was then processed into fibrous form through the technique of electrospinning, which allowed us to create a highly porous and interconnected network of PBU fibers. This fibrous network served as the host for our AgNW electrodes, which were subsequently integrated into the structure. The encapsulation of the prepared AgNWs/PBU electrode film was accomplished through a series of Diels-Alder (DA) and retro-DA reactions. The DA reaction, a classic method in organic chemistry for the construction of cyclic structures, allowed for reversible crosslinking. This crosslinking was essential for the integration process, while the retro-DA reaction facilitated the dissolution of the crosslinks, permitting the adjustment of the material's properties. This process allowed us to form an encapsulation planarized layer that matched the thickness of the pre-formed PBU film. Our novel planarized PBU/AgNW/PBU sensor (PAPS) exhibited superior mechanical stability and insensitivity to bending when compared to the AgNW/PBU sensor (APS). Furthermore, when the PAPS was affixed to various bodily segments, it generated distinctive signal curves, each corresponding to the specific body part and the degree of movement involved. We deployed a machine learning algorithm, specifically K-means clustering, to substantiate the reproducibility and consistency of the signals derived from the PAPS. This data analysis demonstrated that the performance of the PAPS far surpassed that of the APS. In the final stage of our research, we sought to classify signals detected from the PAPS sensors attached to various body parts. This classification was accomplished through the application of four distinct deep learning algorithms: a singular 1D Convolutional Neural Network (1D CNN), a Long Short-Term Memory (LSTM) network, and dual-layered combinations of 1D CNN + LSTM and LSTM + 1D CNN. In our findings, the singular 1D CNN model outperformed the other three, demonstrating a classification accuracy exceeding 98%. This achievement exemplifies the successful realization of an intelligent motion sensor of exceedingly high reliability. Such an accomplishment not only represents a significant advancement in the field of intelligent sensor technology but also sets the stage for future explorations and improvements.

Abbreviations

PBU
polybutadiene-based urethane
PAPS
PBU/AgNW/PBU sensor
Declarations

Supplementary Information

The online version contains supplementary material available at...

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Competing interests

The authors declare no competing interests.

Authors’ Contribution
Jong-Woong Kim supervised the whole research process and contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Su Bin Choi. Machine learning and deep learning were performed by Hyun Sik Shin. The manuscript was written by all authors. All authors read and approved the final manuscript.

References


Figures

1. Cleaning of glass

2. Deposition of AgNWs

3. Deposition of PBU

4. Curing, peel-off and flip-over

5. Electrospinning of PBU

6. DA, retro-DA and DA reaction

Figure 1

Fabrication process of the PBU/AgNWs/PBU sensor (PAPS).
Figure 2

(a) FESEM and AFM images of AgNWs/PBU. The AgNWs are embedded beneath the surface of the PBU. FESEM micrographs of electrospun PBU fibers on the AgNWs/PBU: Electrospinning duration was (b) 3 min and (c) 10 min. Cross-sectional views of (d) half-integrated PBU/AgNWs/PBU following a retro-DA reaction for 1 h and (e) fully-integrated PBU/AgNWs/PBU after a retro-DA reaction for 2 h. (f) High-resolution image of the area denoted by the red square in (e).

Figure 3

Influence of encapsulation on the mechanical behavior of motion sensors. (a) Stress-strain curves and (b) electrical resistance in relation to applied stretching strain for APS and PAPS. (c) and (d) depict resistance changes in APS and PAPS with cyclic stretching, respectively, across various stretching strains. (e) Resistance change for APS and PAPS as a function of different curvature radii after
5,000 bending cycles. (f) Dynamic resistance response of APS and PAPS during repeated bending tests with a 300 µm curvature radii for 5,000 cycles. The bending test was conducted outward based on the AgNW electrode of the APS.

Figure 4
Resistance changes for various joints utilizing wearable PAPS: (a) Elbow joint bending at angles of 45° and 90°, (b) wrist joint bending at angles of 30°, 60°, and 90°, (c) finger joint bending at angles of 30°, 60°, and 90°, and (d) knee joint bending at angles of 45° and 90°.

Figure 5
Deep learning process and result indicators for joint motion classification. (a) Schematic diagram of the 1D CNN deep learning algorithm. (b) Accuracy learning curve of training and validation data with increasing epoch. (c) Loss learning curve of training and validation data with increasing epoch. (d) Confusion matrix for various joint bending motions.
Supplementary Files

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- SIACHMFinal.docx