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Printable Strain Sensors with Viscosity-Adjustable Ionic Liquids for Motion Monitoring

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Abstract— **Flexible strain sensors with ionic liquids have broad application prospects in various fields such as human-machine interaction, motion monitoring, and soft robots due to their conformability. The manufacture of strain sensors based on ionic liquids mainly relies on traditional molding methods and embedded 3D printing methods. However, these methods are complicated and involve lots of manual operations because of the strong fluidity of ionic liquids. In this paper, we propose the use of high conductivity ionic liquids composed of potassium iodide, glycerin, and polyethylene glycol (KI-Gly-PEG). All-in-one direct ink writing of ionic liquids is possible by adding functional materials into the KI-Gly system to change its rheological property and adjusting temperature during the process to assist in improving printing accuracy. We fabricated a flexible strain sensor with silicone rubber and KI-Gly-PEG solution by the all-in-one direct ink writing method. Further, we utilized the strain sensor to monitor the elbow bending angle by analyzing its resistance.**

I. Introduction

The recent development of wearable electronics, soft robots, and human-machine interaction have aroused interest in flexible electronics. As a key component of flexible electronics, flexible sensors have become prevalent for their biocompatibility, low weight, and high stretchability. They are widely used in physiological monitoring[1], sports rehabilitation[2] and human-machine interaction[3]. In these fields, the physical signal is the most intuitive reflection of the movement. While some signals such as body temperature and electrocardiograph (ECG) can be collected from the planar parts of the human body, other signals such as bending angles often need to be collected using a strain sensor placed on the shoulders, elbows, knees, or other joints. These parts are usually composed of irregular three-dimensional curved surfaces. Traditional rigid sensors are difficult to attach conformably to the skin and sometimes even fall off, which severely interferes with the signal. Therefore, flexible sensors with inherent qualities of stretchability and flexibility are necessary for achieving conformal attachment and reducing noise interference.

Strain sensors are mainly based on three principles: resistance[4], capacitance[5], and piezoelectricity[6]. Resistive flexible sensors are the most widely used strain sensors; they are based on the change in resistance corresponding to change in the geometry of conductive materials. Common conductor materials for strain sensors are liquid metal, organic solutions, hydrogel, carbon (carbon nanotubes, graphite), silver (silver nanowires, silver nanonets), and ionic liquids. However, each material has its limitations. For example, the fabrication route is complex due to the surface phenomenon of liquid metals. Conductors based on the doping principle generate a conductive network of metal or ion.

The existing methods of fabricating flexible sensors using ionic liquids are as follows: modeling, air-spray coating[8], multicore–shell fiber printing, embedded 3D printing, and direct ink writing[9] (DIW). Nevertheless, there are also restrictions hindering the performance of each technique when using ionic liquids as conductors. Modeling, as the most popular manufacturing method for strain sensors, has at least two challenges that limit their use. First, the modeling method is complicated, and much time is wasted in the processing of the model. Second, it requires a lot of manual operations, which not only reduces the repeatability of the experiment but also prevents large-scale manufacturing. The sensor structure fabricated by the multi-shell fiber printing method is too simple to be widely applied. As for air-spray coating, its accuracy cannot be further improved to meet the needs, which could substantially affect the stability of its conductive layer. Embedded 3D printing has constraints on the density range of the conductor and substrate solution, which reduces the scope of material selection. DIW is a general additive manufacturing method that supports layer-by-layer 3D printing, and offers a variety of materials for selection.

In this paper, to achieve the fabrication of strain sensors with ionic liquids using the DIW method, we propose the use of ionic liquids composed of potassium iodide, glycerin, and polyethylene glycol (KI-Gly-PEG) with a customizable viscosity. By adding different proportions of PEG to the KI-Gly conductive system, different rheological properties and conductivities can be obtained. Meanwhile, the rheological properties of the conductor depend upon the operating temperature and can be adjusted. Due to the higher melting point of glycerol, the viscosity of the solution decreases substantially when the temperature is lowered, thereby influencing the printing accuracy by reducing the lateral spreading of ionic liquid on the substrate. Based on this solution, we have developed a flexible strain sensor with large stretchability. By attaching the sensor to the elbow to monitor the degree of elbow bending, accurate physiological signals could be obtained, which is of great significance for long-term motion monitoring. It is found that the trend of the data collected by the sensor is positively correlated with the degree

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of elbow bending, which proves that our sensor can successfully track and recognize the motion of participants.

II. Results and Discussion

Conventional ionic liquids cannot be directly used for DIW due to their low viscosity. In order to meet the rheological property requirement of DIW, we added functional materials to the KI-Gly conductive system. A simple process was developed to convert commonly used ionic liquids into DIW inks with high performance. Finally, we used this method to manufacture a flexible strain sensor with superior elongation properties.

A. Adding functional materials to ionic liquids

As a low-toxic organic solvent, glycerin is generally regarded as an additive in medicines and cosmetics. Due to its high intermolecular force, its evaporation rate is much less than that of water, so it is often used as a solvent for ionic liquids. Compared with the previously used ionic liquids system, sodium chloride glycerin (NaCl-Gly), the potassium iodide glycerol (KI-Gly) system has a higher electrical conductivity. At the same time, the required configuration time of a KI-Gly system is shorter, and it has good electrical characteristics that make it more suitable as a sensor conductor [33]. But the original KI-Gly solution exhibits low viscosity, which makes it unsuitable to be used directly for DIW. The viscosity can however be adjusted by adding a thickener to change its rheological property, thereby improving the resolution of printing.

As a commonly used functional additive material, polyethylene glycol (PEG) has good biological safety and stability. It does not react easily with other substances and is easily miscible with water. Being an oligomer that can be produced with different molecular weights, PEG can have different physical states with distinct properties and functional uses. PEG-1500 appears as a white wax, which can be used as a thickener. Adding PEG-1500 to the ionic liquids in a KI-Gly system is a suitable solution for thickening. In this paper, we obtained ionic liquids with different viscosities by adding different mass fractions of PEG-1500 to the KI-Gly solution. The effect of viscosity of ionic liquids on DIW was studied. It was found that ionic liquids with low viscosity spread out laterally as they were being squeezed out from the needle during the printing process. However, ionic liquids with excess viscosity may block the needle, so they cannot be squeezed out.

Choosing a printing material with proper viscosity is particularly important. During viscosity measurement, a water bath was used to maintain the temperature of the KI-Gly-PEG solution at 25 ℃. The viscosity and conductivity of the KI-Gly-PEG solution with different concentrations of PEG are shown in Fig. 1a. The viscosity indicates a linear growth trend. Compared with the KI-Gly solution with a PEG concentration of 0%, the viscosity of KI-Gly-PEG solution with the PEG concentration of 30% increased from 525 mPa·s to 1137 mPa·s, and the conductivity decreased from 1181 μS·cm^{-1} to 540.51 μS·cm^{-1}. With the increase of PEG concentration, changes appear not only in viscosity but also in the volume of the entire solution system. The increase in these two parameters enlarges the dispersion of ions. Therefore, it results in the reduction in ion transfer speed and ultimately diminishes the conductivity of the solution. In contrast, the conductivity of the NaCl-Gly solution is about 352.1 μS·cm^{-1}. This proves the KI-Gly-PEG solution with 30% PEG concentration has both good conductivity and high viscosity.

By measuring the contact angle of the ionic liquid onto the PDMS (polydimethylsiloxane) membrane (Fig. 1b), we find that as the concentration of PEG increases, the contact angle decreases slightly. When the PEG concentration reaches 30%, the contact angle is 97°, and the ionic liquid is still in a non-wetting state. This proves the KI-Gly-PEG solution can still be used for DIW without affecting the subsequent procedure.

B. Ionic liquid printing under different temperatures

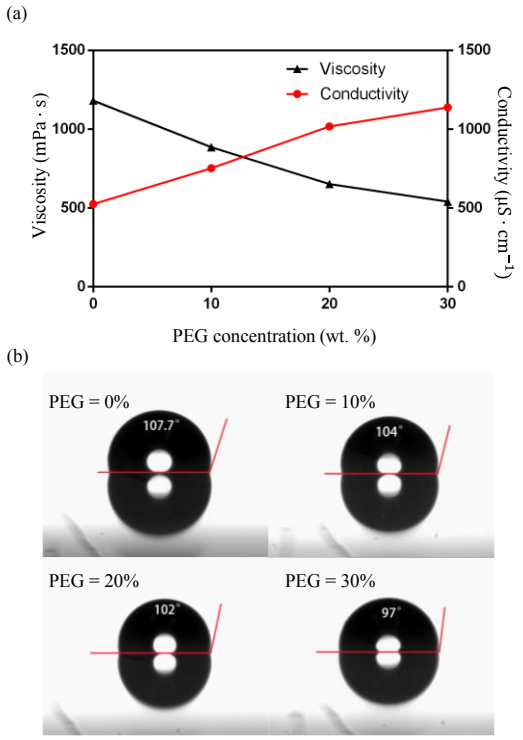

Figure 1. (a) Measurement results of contact angle between KI-Gly solution with different PEG mass fraction and PDMS membrane; (b) Viscosity and conductivity of KI-Gly solution with different PEG mass fractions.

Glycerol is one of the most used solvents for ionic liquids. The melting point of the glycerin solution is 20 ℃. As a result, its viscosity is greatly affected by temperature. The viscosity of the glycerin solution can be controlled by adjusting the temperature, thereby changing the printing accuracy. We used a KI-Gly-PEG solution with the PEG concentration of 30% and printed it at different temperatures (Fig. 2a). The temperature of the experimental environment of each group is 10 ℃, 20 ℃, 30 ℃, and 40 ℃. During printing, other parameters among different groups were controlled to be the same. The width of the line printed at different temperatures can reflect the effect of different temperatures on the printing accuracy. As the temperature rises, the print line width generally increases (Fig. 2b), however, ionic liquids printed at 10 ℃ do not comply with this rule. The reason is that when the printing temperature is 10 ℃ and the humidity is 50%, the moisture in the air condenses into frost, becomes liquid, and gathers on the printing substrate. Since glycerin and water are

highly miscible, the glycerin squeezed out, dissolves in the water that accumulates on the substrate, causing the printed line to spread around. In other words, it has a tremendous impact on printing accuracy. As can be seen from Fig. 2b, an environmental temperature of 20 ℃ can provide the highest printing accuracy. Therefore, 20 ℃ was finally selected as the printing temperature. Fortunately, the phenomenon of frost can be solved subsequently by using an enclosed chamber to provide a space with constant temperature and humidity.

We controlled the cooling stage at 20 ℃ and printed ionic liquids of different PEG concentrations on glass to select the most suitable ratio and temperature. The curve of the line width versus PEG concentration is shown in Fig. 3. When the PEG concentration is 0% and 10%, the printed ionic liquid spreads out. When PEG concentration is 30%, the printed ionic liquid maintains the line shape and width better.

C. Design and fabrication of flexible strain sensors

The strain sensor is composed of a substrate, an ion conductive layer, an electrode, and an encapsulation layer. Common polymer substrates for flexible electronics are PDMS, Ecoflex, and SEBS (styrene ethylene butylene styrene). In order to minimize the mechanical impedance of the strain sensor, the material chosen for use for the substrate and the encapsulation layer was silicone rubber (Ecoflex 00-30, Smooth-on).

The main part of the sensor is a micro-pipe. The overall structure of the micro-pipe is designed to be U-shaped, which is convenient for concentrating the electrodes on one side of the sensor. Electrodes can connect the conductive layer to the subsequent measuring circuit.

The entire strain sensor is manufactured by DIW. In the all-in-one process, the substrate, electrodes, ion conductive layer, and encapsulation layer are fabricated sequentially. In order to improve printing accuracy, the functional material THI-VEX (Smooth-on) is added to Ecoflex 00-30 to change its rheological property. After mixing with THI-VEX, the viscosity of Ecoflex 00-30 in the solution state improves greatly, while the physical properties are not changed.

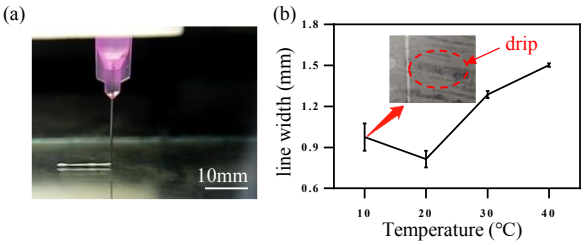

Figure 2. (a) Schematic diagram of ionic liquid printing; (b) Line width of ionic liquid printing at different temperatures.

During the process of encapsulation of the sensor, due to the lower temperature, the density of the KI-Gly-PEG solution with the PEG concentration of 30% is greater than the density of the silicone rubber encapsulation layer. Due to the variation in density between the two materials, the Ecoflex silicone rubber solution, which has a low density, always remains above the ionic liquid. The ionic liquid always remains on the substrate, which is critical for quality molding. The fabricated sensor has good stretchability and flexibility (Fig. 4). In addition, we tested the electrical performance of the sensor. In the fatigue test, the sensor showed good stability (Fig. 5).

The sensor can be attached to joints such as the elbow and to other body parts. The resistance change collected by the sensor reflects the physical variable, and enables the monitoring of the joint movement. In the demonstration of this study shown below in Fig. 6, the flexible strain sensor is attached to the elbow.

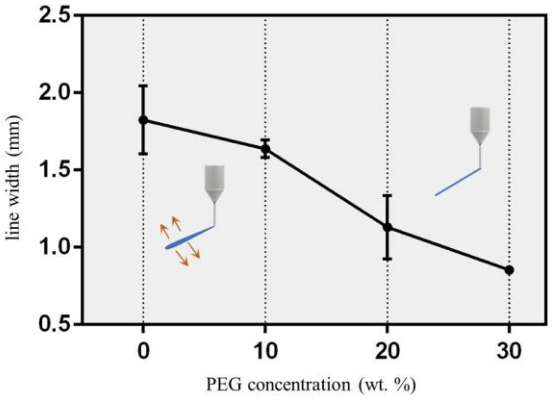

Figure 3. The line width of ionic liquids printed at 20 °C with different PEG concentration.

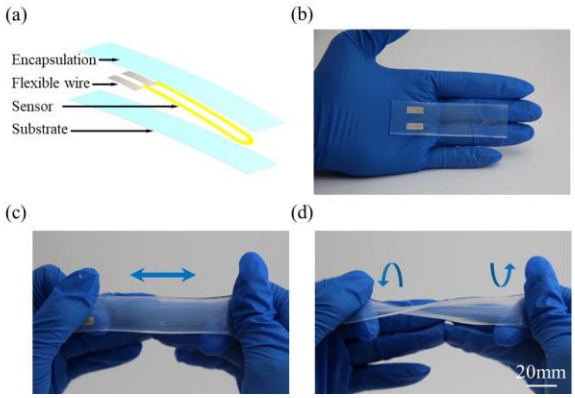

Figure 4. (a) Exploded view of sensor structure; (b) Schematic diagram of strain sensor; (c, d) Demonstration of the stretchability and flexibility of the soft strain sensor.

By bending the arm to different angles, specifically 45°, 90°, and 135°, the resistance value changes significantly. The bending action can be monitored in real time by sensors (see Video S1 in the Support information). In addition, the repeatability of multiple measurements at the same angle is appropriate. In fact, flexible strain sensors can also be used in conjunction with accelerometers, gyroscopes, temperature sensors, and other sensors to achieve comprehensive monitoring of sports activities. We envision that in future, flexible strain sensors will be applied in sports rehabilitation, movement monitoring, and other fields.

III. CONCLUSION

In this paper, we added functional materials to ionic conductive liquids to change the rheological properties of the ionic liquids. This method makes the ionic liquids perform well in the printing process. By adding PEG with different concentrations, ionic liquids with different viscosity and different conductivity can be obtained. The KI-Gly-PEG

solution with 30% PEG concentration has larger viscosity and proper conductivity, which contributes to printing accuracy.

In addition, we indirectly controlled the rheological property of ionic liquids during printing by adjusting the temperature of the forming platform. By decreasing the temperature, the viscosity of the ionic liquids can be further increased. Though temperature and humidity affect printing accuracy in this scheme, an enclosed chamber can be set up to control environmental factors, in the future.

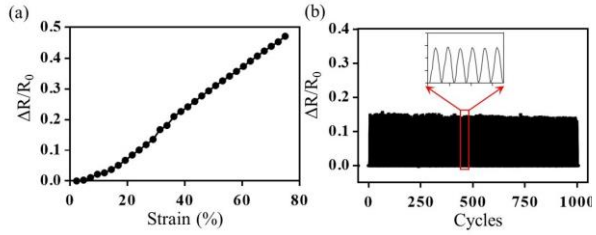

Figure 5. Sensitivity test and fatigue test of the sensor.

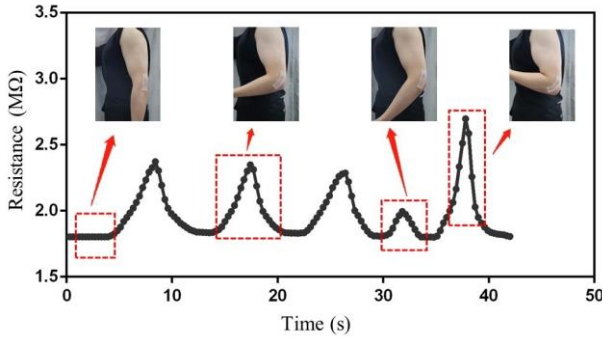

Figure 6. Position and readout of the flexible sensor for monitoring different elbow bending angles

To conclude, we combined ionic liquids, conductive silver paste, and silicone rubber to produce a flexible strain sensor with large stretchability by all-in-one DIW. The strain sensor can monitor mechanical signals in real time. We applied the flexible sensor to motion monitoring, and found that we can clearly distinguish the elbow bending angle. High conformability and stability make our flexible sensors not only promising for motion monitoring uses, but also for future development of devices meant for sports rehabilitation and human-machine interaction.

IV. Experimental Section

Preparation of ionic solution: The ionic liquids were prepared by mixing potassium iodide (KI) (5.5 g) (V900056, Sigma-Aldrich), glycerin (10 mL) (G810575, MACKLIN), and polyethylene glycol (PEG) (3.79 g) (81210, Mw = 1500, Sigma-Aldrich) with a planetary mixing machine (AR-100, Thinky Mixer) for one hour.

Contact angle measurement: We loaded the ionic liquids with different PEG mass fractions into a clean micro-syringe and installed them into a contact angle measuring instrument (OCA 15 PLUS, Dataphysics). The substrate is 150 μm thick PDMS film. After turning on the contact angle measuring instrument, we added 1 μL of liquid onto the PDMS film and recorded the results after stabilization.

Printing line width measurement: The ionic liquids with different PEG concentrations were loaded in 5 mL syringes with a needle having an inner diameter of 0.16 mm. The extrusion device is a syringe pump (PHD 2000, HARVARD APPARATUS) with extrusion rate of 100 mL/h.

Strain Sensor Fabrication Process: The sensor was fabricated using the all-in-one DIW technology. The major material of the sensor substrate and encapsulation layer is Ecoflex (00-30, Smooth-on). The printed silicone rubber substrate was processed by PLASMA treatment prior to use. The ionic liquids were then written using DIW onto the surface of the fabricated silicone rubber, and then encapsulated.

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