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Silicone-ionic liquid elastomer composite with keratin as reinforcing agent utilized as pressure sensor

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Abstract

Development of a flexible pressure sensor is crucial for the future improvement of the wearable electronic devices designed to detect dynamic human motion. In this study, a novel pressure sensor with remarkably improved force sensing characteristics is obtained through combined usage of polydimethylsiloxane (PDMS) and ionic liquid (IL). Keratin is dispersed homogeneously in the PDMS matrix to serve as a reinforcing filler. High conductivity IL is employed as sensitivity-enhancing constituent in the elastomer, and the effect of the amount of IL on elastomers' pressure-sensing performance is investigated. The elastomer with 70 parts per hundred rubber (phr) IL shows excellent pressure-sensing performance. This novel pressure sensor demonstrates high linear sensitivity (0.037 kPa^{-1}) in the large pressure region of 0-10 kPa. Response and recovery times are 8 ms and 11 ms, respectively, which are much shorter than previously reported. Moreover, the pressure sensor could distinguish different pressures via stable sensing signals in the pressure range of 0 to 50 kPa. The excellent performance of the novel pressure sensor has application potential in various fields, such as health monitoring and soft robotics.

Keywords: PDMS, ionic liquid, keratin, pressure sensor, fast response

Introduction

Flexible and soft pressure sensors have attracted significant attention for their applications in various fields, such as soft robotics,^[1] wearable electronic devices,^[2] and energy storage.^[3] The ability to sense low pressure (1-10 kPa), which is an important range covering intra-body pressure, is particularly important for pressure sensors.^[4] In recent years, vast efforts have been made to improve the performance of pressure sensors: e.g., via the integration of polymers with various nanomaterials including carbon nanotubes,^[5] gold/silver nanowires,^[6] graphene nanosheets,^[7] and metal nanoparticles.^[8] While the structures and materials of these novel pressure sensors are different, they all typically operate based on force-induced changes in piezoresistivity, capacitance, piezoelectricity and iontronic.^[4, 9] For example, Qin et al. prepared a pressure sensor by integrating hydrophobic carbon nanotubes into hydrophobically associated polyacrylamide hydrogel, reaching a sensitivity of 0.127 kPa^{-1} in the large-pressure region of 0-50 kPa.^[5] Lee et al. realized an ultra-robust, wide-range pressure sensor based on polyurethane foam coated with both conformal silicone rubber and CNT/TPU nanocomposite islands, the sensitivity of which was controlled from 0.013 kPa^{-1} to 0.032 kPa^{-1} .^[10]

Even though pressure sensors fabricated by incorporating nanomaterials into polymers show high sensitivity, they consequently display limited stretchability and long response times, thereby significantly limiting their applications. In order to produce an improved smart wearable sensor, it is therefore necessary to develop a highly stretchable and flexible sensor with short response and recovery times.

Silicone elastomers represent an excellent matrix for sensors due to their high stretchability and flexibility,^[11] as well as their inherent physical and chemical stability^[12] even at elevated temperatures.^[13] Ionic liquids (ILs), which have high conductivity, low viscosity and chemical stability, were also considered as excellent material candidates for the development of novel,

improved pressure sensors.^[14] However, the electromechanical instability of pure ILs limits their application as pressure sensors and require a mechanically robust matrix. Iontronic pressure sensors based on polymer-IL composites and possessing both the elasticity of the elastomer and the electrical conduction of the ILs have therefore received significant attention from researchers.^[15] For example, a flexible capacitive pressure sensor that incorporates micro-patterned pyramidal ionic gel was fabricated which showed excellent pressure sensitivity and a broad sensing range.^[16] Despite the great progress in the iontronic pressure sensor achieved so far, the development of iontronic pressure sensor is still limited due to the complicated fabrication process, high cost, and small linear response range.

Herein, a novel high-performance pressure sensor was fabricated by incorporating 1-butyl-3-methylimidazolium hexafluoroantimonate (BmimSbF₆) into polydimethylsiloxane (PDMS) elastomers. Wool keratin, which has high biodegradability, biocompatibility, and stability, was added as a reinforcing filler. In addition to improving the performance of the material as pressure sensor this method also provides a simplified preparation scheme with great potential for the large-scale production of ionic materials. Different loading amounts of BmimSbF₆ were tested in order to produce an optimized pressure sensor with excellent mechanical properties, high force sensing characteristics, and a wide linearity pressure range. More specifically, the optimized sensor demonstrated a sensitivity of 0.037 kPa⁻¹ at pressures below 10 kPa and a sensitivity of 0.003 kPa⁻¹ in the range between 10 kPa⁻¹ and 50 kPa⁻¹. Finally, the response time of the 70 phr BmimSbF₆-loaded pressure sensor showed a response time of 8 ms to a pressure input of 1.6 kPa (0.04 N) and a recovery time of 11 ms, which is much shorter than previously reported.

2. Results and discussion

2.1 Fabrication of IL-loaded pressure sensor.

Figure 1 illustrates the complete manufacturing process of the BmimSbF₆-loaded pressure

sensor. Vinyl-terminated DMS-V31, cross-linker HMS-30 and the catalyst (Pt 511) were mixed using a SpeedMixer. Wool keratin was used as a replacement for SiO₂ as reinforcing filler. BmimSbF₆ (volume fractions varied from 0 to 44%, see **supplementary information (SI Table S1)**) was then added as liquid filler, and the mixture was speed mixed again. Structures are shown in **SI Figure S1**. The system of ionic liquid and elastomer has been investigated in a previous study.^[17] The homogeneous mixture obtained was then coated as a film and cured in the oven at 80 °C for 2 h. Copper sheets were attached to the two surfaces of the film as electrodes, and specimens were investigated using a voltage response test as described in the experimental section in **SI**.

2.2 Properties of IL-loaded elastomer films.

FT-IR spectra were acquired in order to verify successful BmimSbF₆ loading into the silicone elastomer. For films into which BmimSbF₆ has been successfully incorporated, the FT-IR spectra display a characteristic imidazole ring peak at 1580 cm⁻¹ (**SI Figure S2**). Furthermore, the SEM images show that the ionic liquids (black dots) and keratin powders (white dots) are well-dispersed throughout the silicone network (**SI Figure S3**).

Gel fractions of the films were investigated in order to analyze the amount of bonded (gel fraction) and non-bonded (sol fraction) species in the elastomer network. The measured gel fractions of films with various BmimSbF₆ concentrations are shown in **Figure 2a**, demonstrating that the gel fractions of the films decreased with an increased loading amount of BmimSbF₆, which can be explained by the increased inhibiting effect of the IL at higher concentrations.

A comparison of the mechanical properties of pure PDMS film with SiO₂ and pure PDMS film with keratin is shown in **SI Figure S4**. Films with keratin as filler displayed similar mechanical properties to films with SiO₂ as filler which is an interesting finding since it indicates that keratin can replace SiO₂ as a solid filler to enhance the mechanical properties of

the film. This can potentially have great impact in making silicone elastomers more sustainable. However, this is not the scope of the current article.

The tensile stress–strain curves for PDMS-based films with various BmimSbF₆ amounts are presented in **SI Figure S5**, while the corresponding Young's modulus and tensile strengths are depicted in **Figure 2b** and **Figure 2c**, respectively. It is clear that the tensile strength and Young's modulus of the BmimSbF₆-loaded films are lower than those of the pure PDMS film, and that the tensile strength and Young's modulus decreased with increasing amount of BmimSbF₆. With an increase of BmimSbF₆ amount from 0 to 5 phr, both the tensile strain and Young's modulus decreased significantly, indicating that ionic liquid fillers act as softeners in the system, so that their addition effectively enhances the flexibility of the elastomer materials.

2.3 Pressure responses of IL-loaded sensors.

A dedicated test bench was designed to evaluate pressure sensor performance, as illustrated in **Figure 1**. The operation principle of the pressure sensor is analogue with the previously reported operational principle of iontronic pressure sensors,^[9] and a schematic illustration is shown in **SI Figure S6**. In order to describe the effect of BmimSbF₆ on the sensing performance of the investigated films, the voltage change curves for elastomers with different BmimSbF₆ amounts in response to an instantaneous pressure input of 40 kPa (1.0 N) are compared in **Figure 3a**. A tunable voltage change depending on the loading amount of BmimSbF₆ was observed, with the 70 phr BmimSbF₆-loaded sensor exhibiting the highest voltage change due to the increased charge density with increased IL loading.^[9] This behavior confirms that the amount of BmimSbF₆ is vital to improving pressure sensor sensitivity. As **Figure 3b** shows, the 70 phr BmimSbF₆-loaded pressure sensor has a high sensitivity of 0.037 kPa⁻¹ (1.56 N⁻¹) in the range of 0-10 kPa, while the sensitivity declines with increasing pressure in the high pressure range ($S_2=0.003$ kPa⁻¹, 0.12 N⁻¹), and the sensitivity is much higher than that of 50 phr BmimSbF₆-loaded pressure sensor (0.001 kPa⁻¹; **SI Figure S7**), further indicating that the

importance of BmimSbF₆ as critical to the sensitivity of the pressure sensor.

An additional advantage of the BmimSbF₆-loaded pressure sensor is that it responds quickly to applied pressure. As shown in **Figure 3c**, the 70 phr BmimSbF₆-loaded pressure sensor responds to a pressure input of 1.6 kPa (0.04 N) in 8 ms—much more quickly than most previously reported sensors. When external pressure was removed, the pressure sensor returned to its initial state in 11 ms—a shorter recovery time than that reported for any other sensor. This excellent response time is due to the liquid, and thus mobile, nature of the BmimSbF₆ in the network.

The stability of the 70 phr BmimSbF₆-loaded sensor was tested by multiple applications of a cyclic high pressure of 40 kPa (1.0 N). As depicted in **SI Figure S8**, the responsive signals were highly consistent under cyclic pressures. The voltage changes upon a step increase of pressure from 2.4 kPa (0.06 N) to 46.8 kPa (1.2 N) were measured to investigate the response over a relatively wide pressure range. As shown in **Figure 3d**, the voltage change dramatically increased with rising pressure, demonstrating the BmimSbF₆-loaded pressure sensor's capacity to distinguish various pressures via stable sensing signals. It also can be seen that the pressure sensor responds quickly to an applied pressure, and returns to the initial state in short time when the external pressure was removed.

An ideal pressure sensor with excellent performance should possess high sensitivity, wide linearity range, and short response time. The 3D chart presented in **Figure 4a** shows a sensing characteristics comparison of the pressure sensor developed within this study and pressure sensors with different fillers reported previously.^[5, 7, 10, 16, 18] By the overall evaluation of the sensitivity, response time and linearity range, the novel pressure sensor in this work is an overall better sensor. While it does not have the highest sensitivity, its response time is 75 times faster than that of a carbon nanotubes / hydrophobically associated hydrogel sensor,^[5a] 15 times faster than that of the graphene-paper pressure sensor,^[7b] and 3 times faster than that of the ionic gel

pressure sensor.^[16] Moreover, the BmimSbF₆-loaded sensor also has a wide linear pressure range. These results are also listed in **Figure 4b**.

Furthermore, not only can the 70 phr BmimSbF₆ loaded film be used as an iontronic pressure sensor, but it is also an excellent candidate for a capacitive pressure sensor. The dielectric permittivity, which is a critical parameter for the sensitivity of the capacitive pressure sensor, was also tested here. Unlike conventional PDMS elastomers, BmimSbF₆-loaded films exhibit high permittivity, as shown in **SI Figure S9**. The dielectric permittivity at 10⁶ Hz increased from 2.24 for the pure PDMS elastomer to 10.34 for the sample with 70 phr BmimSbF₆—i.e. almost 5-fold. Storage permittivities of BmimSbF₆-loaded films are also presented in **SI Table S2**.

3. Conclusion

In summary, a novel flexible pressure sensor was constructed by incorporating BmimSbF₆ into PDMS. The ionic pressure sensor thus produced exhibited outstanding mechanical properties, fast response, wide detection range, and high sensitivity. Furthermore, the 70 phr BmimSbF₆-loaded pressure sensor showed high pressurizing cycling stability under high applied pressure, as well as the ability to distinguish various pressures via stable sensing signals over the pressure range from 0 kPa to 50 kPa. Its response time of 8 ms to a pressure input of 1.6 kPa (0.04 N) is much shorter than that of most previously reported pressure sensors, and its recovery time of 11 ms is the shortest yet reported. This novel pressure sensor's excellent comprehensive performance and facile fabrication process mean that it has great potential for healthcare and smart wearable device applications.

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Supporting information

Supporting information is available.

Conflict of interest

The authors declare no conflicts of interest.

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Figure 1 Fabrication process and test setup of the BmimSbF₆-loaded pressure sensor.

Figure 2 a) Gel fractions, b) Young's moduli and c) tensile strains of films with different amounts of BmimSbF₆.

Figure 3 a) Voltage changes for films with different loadings of BmimSbF₆ in response to a pressure input of 40 kPa (1.0 N); b) Sensitivity of film with 70 phr BmimSbF₆ in response to varying pressures; c) Voltage change of 70 phr BmimSbF₆-loaded film after a sudden increase pressure from 0 kPa to 1.6 kPa (0.04 N); d) Applied force and relative voltage changes in response to a step-wise increase of pressure from 2.4 kPa (0.06 N) to 46.8 kPa (1.2 N).

Figure 4 a) 3D chart of a comparison of three key pressure sensor parameters: sensitivity, response time, and linear pressure range; b) Characteristics of reported pressure sensors.