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High-performance transparent hybrid (ionic and dielectric) gel actuator system based on poly(vinyl chloride)/dibutyl adipate/ionic liquid gels operating at a low applied voltage†

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This study presents a transparent hybrid (ionic and dielectric) gel actuator system based on polyvinyl chloride (PVC) and ionic liquid (IL) gels with dibutyl adipate (DBA) as the plasticiser. The system operates at a low applied voltage (10–20 V), and the total transmittance at visible wavelengths (450–700 nm) is >85.5–88.5% for all IL species. The ionic conductivity of the gel depends on the IL species. The electrochemical and electromechanical properties are also investigated. The PVC/DBA/IL gel actuator is a hybrid (ionic and dielectric) gel actuator system, wherein the ionic gel actuator mechanism is dominant, while the PVC/DBA gel actuator is a dielectric gel actuator system. The maximum strain of the PVC/DBA/IL gel actuator under an applied square-wave voltage (±10 V) is 0.39% at 0.005 Hz, thus indicating that the PVC/DBA/IL gel actuators can generate sufficient strain for practical applications. These transparent, flexible, and robust gels have significant potential as actuator materials in wearable and transparent electronic and energy-conversion devices.

Introduction

Actuator materials that can convert various types of energy to mechanical energy have been widely studied owing to their potential in various applications, such as optical switches, artificial muscles, sensors, and micropumps.[1–5] Recently, transparent actuators have emerged as an important category of actuators;[6–8] transparent actuators with large deformations could be used in transparent soft robots. However, reports on transparent actuators with low driving voltages (10–20 V) remain limited.

Electroactive polymer (EAP) actuators, comprising soft, flexible, and low-density materials that exhibit mechanical responses to electric stimuli, have attracted considerable interest owing to their potential as muscle-like actuators for bio-medical and human affinity applications.[9,10] Among existing EAP actuators, dielectric elastomers have been considered for application as power actuators, such as those required for wearable robotics, owing to their remarkable properties, including large deformation capabilities, high energy densities, and strong responses.[11,12]

Unlike dielectric elastomers, dielectric gels such as polyvinyl chloride (PVC) gels (PVC with a plasticiser) have relatively low driving voltages (200–600 V).[13,14] Moreover, they can undergo large deformations and generate powers equivalent to those generated by dielectric elastomers. Hashimoto *et al.* applied stacked dielectric gel actuators to wearable robots, developed a contraction-and-expansion-type artificial muscle based on a PVC gel, and studied its properties.[15,16] Previously,[17,18] based on existing studies on PVC gel actuators,[19–23] we conducted a detailed investigation of the electromechanical responses and electrochemical properties of PVC gels and proposed an electromechanical model for PVC gel actuators. However, for dielectric gel actuators to be utilised in wearable robots, the driving voltage must be reduced significantly. Therefore, high stresses and strains must be generated at low driving voltages.

Ionic gel actuators are lightweight, highly flexible, and biocompatible EAP actuators that require low operating voltages, making them suitable for a wide variety of applications, particularly in the development of devices such as artificial muscles, sensors, and actuators.[24,25] Ionic gels contain polymer networks that swell in electrolyte solutions or ionic liquids (ILs) and are conductive in their solid form. IL/polymer composites for actuator applications have garnered interest as a means to improve the electrochemical stability window, actuation force, and frequency at low voltages.[26–28]

Few studies have investigated transparent hybrid actuators with both dielectric and ionic gels at low driving voltages (10–20 V). Transparent actuators can be combined with other transparent materials to develop devices such as wearable

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transparent electronics. PVC/IL gels with dibutyl adipate (DBA) as the plasticiser are expected to form transparent hybrid dielectric and ionic gel actuator systems. The DBA molecules move towards the anode side owing to the anion current (dielectric gel actuator mechanism), while ionic motion causes the anode side of the gel layer to shrink and the cathode side to expand (ionic gel actuator mechanism), leading to bending of the actuator toward the anode. Moreover, this IL cation and anion movement occurs under a low applied voltage (10–20 V);[17,18,26–28] hence, large deformations (mainly by the ionic gel actuator mechanism) are expected at low voltages.

To this end, we propose a hybrid actuator system and develop a new transparent actuator that can operate at low applied voltages (10–20 V) based on PVC/IL gels with DBA as the plasticiser. The electrochemical and electromechanical properties of the prepared transparent PVC/DBA/IL gel actuators are investigated.

Experimental

Materials

PVC (M_W: ~233 000; Aldrich) and DBA (FUJIFILM Wako Pure Chemical Corporation) were used as received without further purification. The ILs selected were 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMI[TFSI], IoLiTec), 1-ethyl-3-methylimidazolium bis(fluoromethylsulfonyl)imide (EMI[FSI], Kanto Chemical Co., Inc.), trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide (THTDP[TFSI]; IoLiTec), and trihexyltetradecylphosphonium chloride (THTDP[Cl]; IoLiTec); these ILs were used as received without further purification. Scheme 1 shows the chemical structures of these compounds. Tetrahydrofuran (THF, FUJIFILM Wako Pure Chemical Corporation) was used as received without further purification.

Preparation of the actuator gel

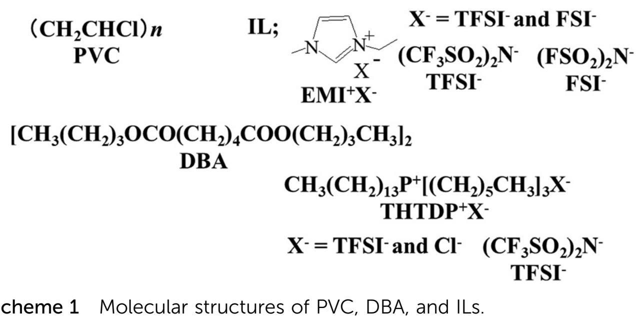
To prepare the transparent PVC/DBA/IL gel actuators, 300 mg of PVC, 900 mg of DBA, and 200 mg of IL in 6 mL of THF were combined and stirred for over 5 h. Then, the solution was cast in a Teflon mould (2.5 × 2.5 cm^2), and the solvent was allowed to evaporate. The resulting gels were approximately 350 μm thick.

Displacement measurement[29]

The actuator experiments were conducted by applying a square-wave voltage to a 15 mm × 2 mm actuator strip clipped by two gold electrodes. The displacement between one side of the gel actuator and a location at a free length of 10 mm was measured using a laser-based displacement metre (Keyence, LC2100/2220). The actuator was activated using a waveform generator (Yokogawa Electric, FC 200) in conjunction with a potentio/galvanostat (Hokuto Denko, HA-501G), and its electrical parameters were measured. The resulting displacement parameter δ was used to compute the difference between the strains ε of the PVC/DBA/IL and PVC/DBA gel layers by assuming planar (*i.e.*, undistorted) cross-sections along the actuator based on the equation

$$\varepsilon = 2d\delta/(L^2 + \delta^2), \quad (1)$$

where d is the actuator thickness and L is the free length.[30]



Scheme 1 Molecular structures of PVC, DBA, and ILs.

Characterisation of the gel

Stress–strain curves were obtained using a thermal stress–strain instrument (TMA/SS 6000, Seiko) and then used to estimate the Young's moduli of the gels. The total transmittance was measured at wavelengths of 300–700 nm using a UV-visible spectrometer (UV-3600, Shimadzu Co., Ltd). The morphology was observed by ultra-high resolution scanning electron microscopy (S-5500, Hitachi). The conductivity was determined *via* impedance measurements using an impedance analyser (Solartron 1250).

Results and discussion

The Young's moduli (MPa) of the PVC/DBA/IL and PVC/DBA gels are summarised in Table S1 (ESI†). The Young's moduli of the PVC/DBA/IL and PVC/DBA gels are of the same order, with values of 0.25–0.36 MPa for the PVC/DBA/IL gels depending on the IL species and 0.18 MPa for the PVC/DBA gel with no IL.

The total transmittances of the PVC/DBA/TFSI and PVC/DBA gels at wavelengths of 300–700 nm are shown in Fig. 1. The total transmittance of the PVC/DBA/TFSI gel at visible wavelengths (450–700 nm) is >88.5%. Similar results are observed for the other ILs; the total transmittances at visible wavelengths (450–700 nm) are >85.5–88.5% for all species. By contrast, the total transmittance of the PVC/DBA gel at visible wavelengths (450–700 nm) is >83.1%.

The total transmittances of the PVC/DBA/IL gels at 550 nm are listed in Table 1. For all the PVC/DBA/IL gels, the total transmittances are >87.7%. Therefore, in the prepared transparent gels, the transmittance losses at visible wavelengths are caused by surface reflection rather than light absorption inside the gel. By contrast, for the PVC/DBA gel, the total transmittance at 550 nm is 84.8%. Thus, the total transmittances of the PVC/DBA/IL gels are higher than that of the PVC/DBA gel. The differences in total transmittance are related to the components and composition ratios of the actuator gel and IL species.

The morphologies of the PVC/DBA/IL and PVC/DBA gels were examined by planar and cross-sectional scanning electron microscopy (Fig. S1, ESI†). The gels have similar morphologies with uniform structures, no networks of highly entangled nanofibers, and no domains. Next, we examined the ionic

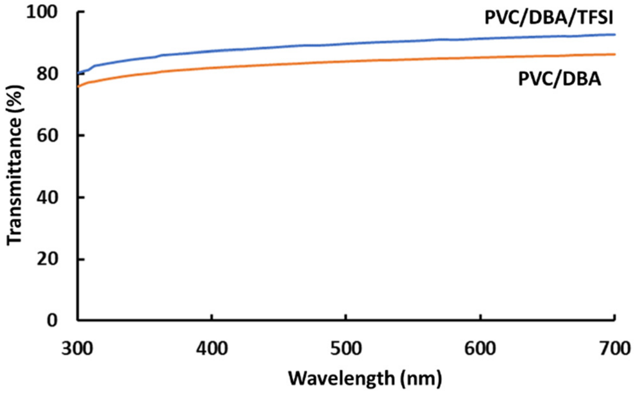


Fig. 1 Total transmittance of the PVC/DBA/TFSI and PVC/DBA gels.

Table 1 Total transmittance (%) of the PVC/DBA/IL gels at 550 nm

IL	Transmittance (%)
EMI[TFSI]	90.5
EMI[FSI]	87.7
THTDP[TFSI]	90.4
THTDP[CI]	89.8
None	84.8

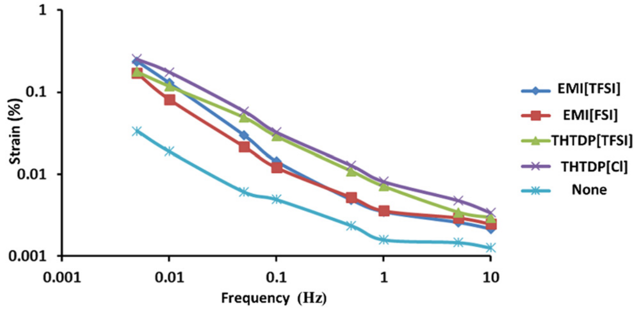


Fig. 2 Strain calculated from the peak-to-peak displacements of the transparent PVC/DBA/IL and PVC/DBA gel actuators at different applied square-wave voltage (±5 V) frequencies.

conductivity κ (= thickness/($R \times$ area)) of the PVC/DBA/IL gels. As shown in Table 2, the ionic conductivities range from 0.040 to 0.287 mS cm^{-1}, with minimal correlation between the ionic conductivities of the gels and the corresponding pure ILs. The ionic conductivities of the gels depend on the IL species. For example, the ionic conductivity of the PVC/DBA/EMI[TFSI] gel is higher than that of the PVC/DBA/THTDP[TFSI] gel, indicating that the ionic conductivities of the PVC/DBA/IL gel layers are dependent on the cation species in the IL. Moreover, the ionic conductivities of the PVC/DBA/EMI[TFSI] and PVC/DBA/EMI[FSI] gels are higher than those of the PVC/DBA/THTDP[TFSI] and PVC/DBA/THTDP[Cl] gels, leading to the assumption that THTDP[TFSI] and THTDP[Cl] are more easily trapped by PVC than EMI[TFSI] and EMI[FSI].

The time-dependent voltages, currents, and displacements for the transparent PVC/DBA/TFSI and PVC/DBA gel actuators were measured under an applied square-wave voltage (±5 V) at different frequencies; the results at a frequency of 0.005 Hz are shown in Fig. S2 and S3 (ESI†). The strains[30] calculated from the peak-to-peak displacements of the transparent PVC/DBA/IL and PVC/DBA gel actuators are shown in Fig. 2 as a function of the frequency of the applied square-wave voltage (±5 V). The strains are dependent on the measurement frequency. For all frequency ranges, the strains observed for the PVC/DBA/IL gel actuators are higher than that observed for the PVC/DBA gel actuator. From the time-dependent current curves in Fig. S2(b) and S3(b) (ESI†), the PVC/DBA/IL gel actuators are hybrid (dielectric and ionic) gel actuators, whereas the PVC/DBA gel actuator is a dielectric gel actuator. From the time-dependent displacement curves in Fig. S2(c) and S3(c) (ESI†), there is a creep. It is considered that the creep deformation of solvent-rich (S-R) layer on the surface of the anode is caused by Maxwell stress.[17] Table 3 shows the maximum strain values of the PVC/DBA/IL and PVC/DBA gel actuators. The maximum strains of the PVC/DBA/IL gel actuators are 0.17–0.25%, whereas the maximum strain of the PVC/DBA gel actuator is 0.03%. The maximum strains of the PVC/DBA/IL gel actuators are dependent on the IL species and higher than that of the PVC/DBA gel actuator. Therefore, the PVC/DBA/IL gel actuators are hybrid (dielectric and ionic) gel actuators, wherein the ionic gel actuator mechanism is dominant, while the PVC/DBA gel actuator is a dielectric gel actuator. In addition, the maximum strain of the PVC/DBA/TFSI gel actuator under an applied square-wave voltage (±10 V) is 0.39% at a frequency of 0.005 Hz. To investigate the durability of the PVC/DBA/TFSI gel actuator, the displacement was measured under an applied square-wave voltage (±10 V, 0.05 Hz) for an extended time. Similar actuation was sustained for 3 h. Therefore, the PVC/DBA/IL gel actuators generate sufficient strain, making them suitable for practical applications (such as tactile displays).

Table 2 Ionic conductivity κ (mS cm^{-1}) of the PVC/DBA/IL gels and ILs

IL	Gel	Neat	Ref.
EMI[TFSI]	0.187	6.6	31
EMI[FSI]	0.287	17.7	32
THTDP[TFSI]	0.061	0.14	33
THTDP[CI]	0.040	4.63	34

In this study, the actuator curves toward the anode because the ionic motion causes the anode side of the gel layer to shrink and the cathode side to expand (ionic gel actuator mechanism), as reported in a previous paper on the operational mechanisms of a poly(dimethylsiloxane)/IL gel actuator with poly(3,4-ethylenedioxythiophene) (PEDOT) electrodes.[35] In addition, the DBA

Table 3 Maximum strains (%) of the transparent PVC/DBA/IL and PVC/DBA gel actuators under an applied square-wave voltage (±5 V)

IL	Maximum strain (%)
EMI[TFSI]	0.24
EMI[FSI]	0.17
THTDP[TFSI]	0.19
THTDP[CI]	0.25
None	0.03

molecules used as plasticisers in the PVC/DBA/IL gel actuator move towards the anode side owing to the anion current (dielectric gel actuator mechanism), similar to the results of a study that developed an electromechanical model of the electric bending response of a PVC gel based on the electrochemical formation of the solvent-rich (S–R) layer and its creep deformation by Maxwell stress.[17] Our data demonstrate that the actuator functionality is based on a combination of ionic and dielectric gel actuator mechanisms and that the ionic gel actuator mechanism is predominant (time-dependent current curves in Fig. S2(b) and S3(b), ESI†).

Conclusions

In this study, novel transparent PVC/DBA/IL gel actuators were developed, and their electrochemical and electromechanical properties were investigated. The total transmittances at visible wavelengths (450–700 nm) were >85.5–88.5% for all IL species, with the ionic conductivities of the gels dependent on the IL species. The PVC/DBA/IL gel actuators were hybrid (ionic and dielectric) gel actuators, wherein the ionic gel actuator mechanism was predominant, while the PVC/DBA gel actuator was a dielectric gel actuator. Furthermore, the maximum strain of the PVC/DBA/TFSI gel actuator under an applied square-wave voltage (± 10 V) was 0.39% at 0.005 Hz, indicating that the PVC/DBA/IL gel actuators can generate sufficient strain for practical applications (such as tactile displays). The results obtained in this study show that transparent, flexible, and robust gels are promising materials for wearable transparent electronic and energy-conversion devices. Moreover, the proposed approach can be used with other PVC-containing electrochemical materials to develop wearable transparent electronic devices to increase the range of potential applications.

Author contributions

Naohiro Terasawa: conceptualisation, validation, formal analysis, investigation, data curation, writing – original draft, writing – review & editing, visualisation, supervision, project administration; Hirosato Monobe: conceptualisation, supervision.

Conflicts of interest

There are no conflicts to declare.

References

1 R. H. Baughman, C. X. Cui, A. A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. De Rossi, A. G. Rinzler, O. Jaschinski, S. Roth and M. Kertesz, *Science*, 1999, **284**, 1340.
2 L. Yang, K. Setyowati, A. Li, S. Gong and J. Chen, *Adv. Mater.*, 2008, **20**, 2271.
3 M. D. Lima, N. Li, M. J. Jung de Andrade, S. Fang, J. Oh, G. M. Spinks, M. E. Kozlov, C. S. Haines, D. Suh, J. Foroughi, S. J. Kim, Y. Chen, T. Ware, M. K. Shin, L. D. Machado, A. F. Fonseca, J. D. W. Madden, W. E. Voit, D. S. Galvão and R. H. Baughman, *Science*, 2012, **338**, 928.
4 R. R. Kohlmeyer and J. Chen, *Angew. Chem., Int. Ed.*, 2013, **52**, 9234.
5 K. Liu, C. Cheng, J. Suh, R. Tang-Kong, D. Fu, S. Lee, J. Zhou, L. O. Chua and J. Wu, *Adv. Mater.*, 2014, **26**, 1746.
6 T. Hwang, H. Kwon, J. Oh, J. Hong, S. Hong, Y. Lee, H. Ryeol Choi, K. Jin Kim, M. Hossain Bhuiya and J. Nam, *Appl. Phys. Lett.*, 2013, **103**, 023106.
7 C. Wu, J. Feng, L. Peng, Y. Ni, H. Liang, L. He and Y. Xie, *J. Mater. Chem.*, 2011, **21**, 18584.
8 S. E. Zhu, R. Shabani, J. Rho, Y. Kim, B. H. Hong, J. H. Ahn and H. J. Cho, *Nano Lett.*, 2011, **11**, 977.
9 K. Asaka and H. Okuzaki, *Soft Actuators: Materials, Modeling, Applications, and Future Perspectives*, Springer, Berlin, 2014.
10 F. Capari, *Electromechanically Active Polymers: A Concise Reference*, Springer, Berlin, 2016.
11 F. Carpi, D. de Rossi, R. Kornbluh, R. E. Pelrine and P. Sommer-Larsen, *Dielectric Elastomers as Electromechanical Transducers*, Elsevier, Amsterdam, 2008.
12 R. Pelrine and R. Kornbluh, in *Electromechanically Active Polymers*, ed. F. Carpi, Springer, Berlin, 2016, pp. 671–686.
13 T. Hirai, in *Soft Actuators: Materials, Modeling, Applications, and Future Perspectives*, ed. K. Asaka and H. Okuzaki, Springer, Berlin, 2014, pp. 169–182.
14 Y. Li, Y. Li and M. Hashimoto, *Sens. Actuators, B*, 2019, **282**, 482.
15 Y. Li and M. Hashimoto, *Sens. Actuators, A*, 2015, **233**, 246.
16 Y. Li and M. Hashimoto, *Sens. Actuators, A*, 2016, **239**, 26.
17 K. Asaka and M. Hashimoto, *Sens. Actuators, B*, 2018, **273**, 1246.
18 K. Asaka and M. Hashimoto, *Smart Mater. Struct.*, 2020, **29**, 025003.
19 H. Xia, T. Ueki and T. Hirai, *Adv. Mater. Res.*, 2009, **79–82**, 2063.
20 H. Xia, M. Takasaki and T. Hirai, *Sens. Actuators, A*, 2010, **157**, 307.
21 H. Xia and T. Hirai, *J. Phys. Chem. B*, 2010, **114**, 10756.
22 M. Ali and T. Hirai, *J. Mater. Sci.*, 2011, **46**, 7681.
23 H. Xia, T. Ueki and T. Hirai, *Langmuir*, 2011, **27**, 1207.
24 Y. Bar-Cohen and Q. Zhang, *MRS Bull.*, 2008, **33**, 173.
25 F. Carpi and E. Smela, *Biomedical Applications of Electroactive Polymer Actuators*, Wiley, 2009.
26 R. Mejri, J. C. Dias, S. Besbes Hentati, G. Botelho, J. M. S. S. Esperança, C. M. Costa and S. Lanceros-Mendez, *Eur. Polym. J.*, 2016, **85**, 445.
27 D. M. Correia, L. C. Fernandes, P. M. Martins, C. García-Astrain, C. M. Costa, J. Reguera and S. Lanceros-Méndez, *Adv. Funct. Mater.*, 2020, **30**, 1909736.
28 D. M. Correia, J. C. Barbosa, J. P. Serra, R. S. Pinto, L. C. Fernandes, C. R. Tubio, S. Lanceros-Mendez and C. M. Costa, *Adv. Eng. Mater.*, 2021, **23**, 211004111.
29 N. Terasawa and I. Takeuchi, *Sens. Actuators, B*, 2010, **145**, 775.
30 Q. Pei and O. Inganaes, *J. Phys. Chem.*, 1992, **96**, 10507.

31 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, https://iolitec.de/en/node/455 (accessed 9 February 2024).

32 1-Ethyl-3-methylimidazolium bis(fluorosulfonyl)imide, https://en.solvionic.com/products/1-ethyl-3-methylimidazolium-bisfluorosulfonylimide-99.9 (accessed 9 February 2024).

33 Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide, https://iolitec.de/en/node/328 (accessed 9 February 2024).

34 Trihexyltetradecylphosphonium chloride, https://iolitec.de/en/node/132 (accessed 9 February 2024).

35 N. Terasawa, *Sens. Actuators, B*, 2018, **257**, 815.