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Structural and Piezoelectric Characterization of P(VDF-TrFE)/Ionic Liquid Gels

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Abstract

Poly(vinylidene fluoride-trifluoroethylene)(P(VDF-TrFE)) gels were prepared by the permeating ionic liquid [1-Ethyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide] from the surface. The prepared P(VDF-TrFE)/IL gels were structurally and electrically investigated. The XRD patterns and FT-IR spectra implied that the most part of the P(VDF-TrFE) formed with the ferroelectric Form I crystal phase, however, a part of P(VDF-TrFE) showed the new composited structure with ILs in the P(VDF-TrFE) permeated gels. The polarization switching and piezoelectric response of P(VDF-TrFE)/IL permeated gel films were measured. The piezoelectric constant d_{33} of P(VDF-TrFE)/IL gel films increased.

1. Introduction

Recently, soft robotic device have attracted much attention for wearable and implantable device directly contacted with the human body, and the electroactive materials with physically flexible, soft, stretchable feature are required for the soft actuators and sensors. Poly(vinilidene fluoride) (PVDF) and its copolymers with trifluoroethylene [P(VDF-TrFE)] are well known to be the ferroelectric and piezoelectric polymers with large electric dipole moments.[1-3] They are recognized as one of potential candidates for soft actuation and sensing devices utilizing their piezoeletric characteristiscs. However, the responsible displacement of the conventional piezoelectric materials has been not enough to practical use. To achieve the large displacement for piezoelectric actuator, materials need to the high flexibility of piezoelectric. In our previous work, P(VDF-TrFE) composite gel mixed with gelator showed high piezoelectric performance, because of their superior softness.[4] However, the solvent DMF volatilized with time and gels lost their softness. In this study, new P(VDF-TrFE) gels were fabricated using ionic liquid which is used for preparation of polymer gel and has low-volatility. We preparted the P(VDf-TrFE)/IL gel by IL permeating method and investigated the ferroelectric and piezoelectric properties.

2. Experimental method

P(VDF-TrFE) powder was dissolved in methyl ethyl ketone (MEK) and spincoated on a substrate. After annealing at 130 °C for 1.5 hours, a ionic liquid (IL) [Emim][TFSI] was dropped on the P(VDF-TrFE) thin films. The IL covered films were heated at 90 °C to permeate IL into the films and gelate.

The gelation and structure of IL permeation films were evaluated by X-ray diffraction (XRD) and fourier transform infrared spectroscopy(FT-IR) measurement.

For electrical characterization, substrate/Al/P(VDF-TrFE)/Al was fabricated. After poling the P(VDF-TrFE), IL was permeated into the P(VDF-TrFE) layer. The *J-E* curves and the piezoelectric displacement of P(VDF-TrFE)/IL gel films were measured.

3. Results and Discussion

Figure 1 shows XRD pattern of the P(VDF-TrFE)/IL permeation gel, mixture gel, and original P(VDF-TrFE) thin film. P(VDF-TrFE) thin film permeated mixed and IL mixture gel. Here, P(VDF-TrFE)/IL mixture gels were prepared by mixing P(VDF-TrFE) and IL. In IL permeated film, the characteristic peak at 12.5 ° was slightly showed which observed in P(VDF-TrFE)/IL mixture gels. Thus, it was suggested that the IL permeation film was gelated. The

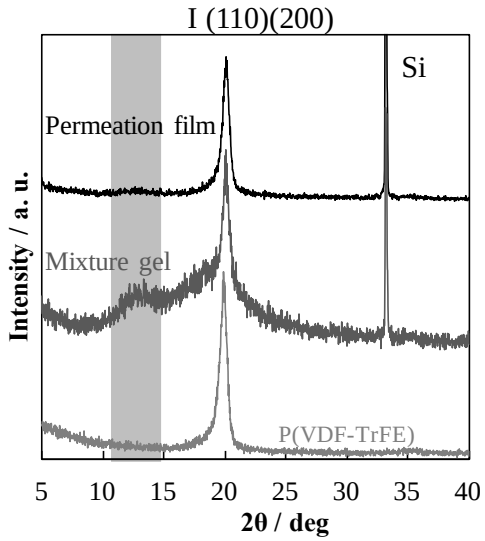

Fig. 1. XRD patterns of P(VDF-TrFE)/IL permeation gel, mixture gel, and P(VDF-TrFE) thin film.

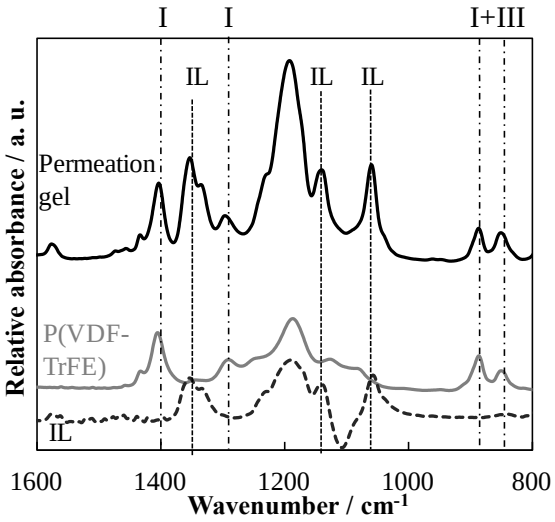

Fig. 2. FT-IR spectra of P(VDF-TrFE)/IL permeation gel, P(VDF-TrFE) thin film and IL.

strong characteristic peak at 19.9 ° corresponds to the (110) and (200) reflections of the Form I of P(VDF-TrFE) in all samples.

Figure 2 shows the FT-IR spectrum of IL permeation gel, P(VDF- TrFE) thin film, and IL. The absorption peaks at 1054, 1132 and 1347 cm^{-1} correspond to the IL. Thus, the IL permeated enough to P(VDF-TrFE) films. The absorption peaks at 840, 880, 1270 and 1428 cm^{-1} correspond to the Form I of the P(VDF-TrFE). Hence, from the results of XRD patterns and FT-IR spectra, the P(VDF-TrFE) molecules formed ferroelectric crystal phase Form I even in gel state, and the P(VDF-TrFE)/IL gels exhibited the new structure.

Figure 3 shows the *J-E* curves of the P(VDF- TrFE)/IL permeation gel film and pristine P(VDF-TrFE) films. In the IL permeated gel film, the current peaks related to the polarization switching of P(VDF-TrFE) were observed in both positive and negative electrical field, however the leak current was also observed. This leakage of current was considered to be caused by conductive properties of IL. The coercive electric field (E_c) of P(VDF- TrFE)/IL gel films were estimated to be approximately 52 MV/m, and the remnant polarization (P_r) were 58 mC/m^2. These results

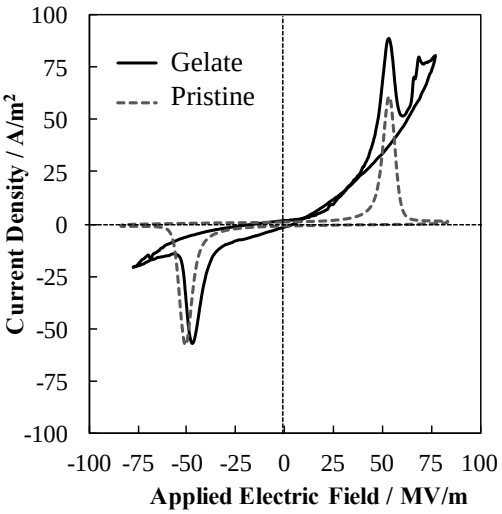

Fig. 3. *J-E* curves of P(VDF-TrFE) films before and after gelation.

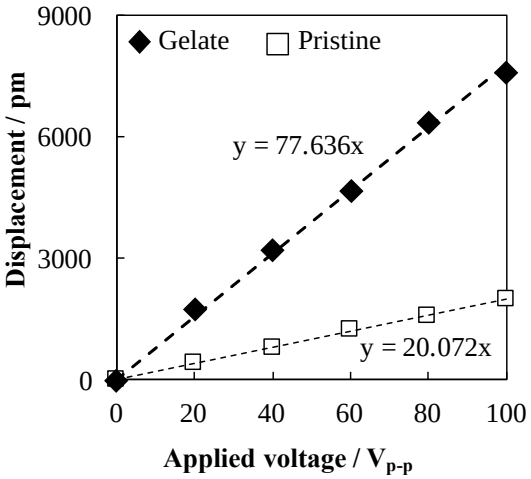

Fig. 4. Piezoelectric displacements of the P(VDF-TrFE) thin films before and after gelation.

suggested that P(VDF-TrFE)/IL gels exhibit ferroelectric properties sufficiently.

Figure 4 shows the relationships between the piezoelectric displacement and applied voltage to P(VDF-TrFE)/IL gel films. The displacement is proportional to applying voltage. The liner relationship indicated the piezoelectric properties of P(VDF-TrFE)/IL gel films. The piezoelectric constant d_{33} in P(VDF-TrFE)/IL gel films was estimated to be 78 pm/V, whereas 10 ~ 20 pm/V for typical P(VDF-TrFE) films. The increase of d_{33} in P(VDF-TrFE)/IL gels was considered due to enhance of softness by gelating.

4. Conclusions

P(VDF-TrFE) gels were prepared by permeating the ionic liquid. The gelation of P(VDF-TrFE) was confirmed from the XRD patterns. The structure of P(VDF-TrFE)/IL gels were measured by using FT-IR. From XRD patterns and FT-IR spectra; and the P(VDF-TrFE) gels have ferroelectric crystals. The polarization switching of P(VDF-TrFE)/IL gels were observed and obtained enough remnant polarization. Furthermore, P(VDF-TrFE)/IL gels showed the piezoelectric properties, and the piezoelectric constant d_{33} was estimated to be 78 pm/V. This value was higher than those observed for pristine P(VDF-TrFE) films. The P(VDF-TrFE)/IL gels indicate potential as an electroactive material for soft robots.

Acknowledgement

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References

[1] S. Miyata, ferroelectric polymer (1988) 278.

[2] K. Koga and H. Ohigashi, J. Appl. Phys., 59, (1986) 2 142

[3] T. Furukawa, M. date, E. Fukuda, J. Appl. Phys. 51, 1135 (1980)

[4] M. Fukagawa, Y. Koshiba, M. Morimoto, K. Ishida, Jpn. J. Appl. Phys. 56 (2017) 04CL03