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Humido-sensitive conducting polymer films and applications to linear actuators

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ABSTRACT

Free-standing films made of poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS) with various PSS contents were newly prepared by casting water dispersion of the PEDOT/PSS colloidal particles in the presence of an extra PSS. Electrical conductivity, morphology, water vapor sorption, and electro-active polymer actuating behavior of the resulting films were investigated by means of four-point method, atomic force microscope (AFM), sorption isotherm, and electromechanical analyses. The maximum contraction of the film by application of an electric field increased with increasing both PSS content and relative humidity (RH), where the value attained 7% at 70% RH for the film with 93% of PSS. Since the isothermal sorption curve of the film was less dependent on the PSS content, the significant increase of the film contraction was explained by two mechanisms: (i) the extra PSS prevented from hydrogen bonding between adjacent PEDOT/PSS particles that suppressed dimensional changes of the film; and (ii) the higher the RH, the larger the degree of water vapor sorption, which led to the large film contraction by desorption of water vapor via Joule heating. On the basis of this phenomenon linear actuators utilizing PEDOT/PSS films were successfully developed and applied to leverage actuator and Braille cell.

1. Introduction

Polymers that undergo dimensional changes in response to various environmental stimuli are capable of transducing chemical or physical energy directly into mechanical work. Conducting polymers, such as polypyrrole, polythiophene, and polyaniline, have attracted considerable attention because dimensional changes resulting from electrochemical doping, characterized by transportation of solvated ions between inside of the polymer matrix and the surrounding electrolyte solution, electrostatic repulsion, and/or structural distortion through oxidation of π-conjugated polymers, can be applied to produce electro-active polymer (EAP) actuators or artificial muscles [1–3]. Most of them operate in an electrolyte solution or in a swollen state, while few reports have been investigated on solid-state polymers in a redox gas atmosphere or that employ a polyelectrolyte or ionic liquid [4–6].

Since the first observation of a curious phenomenon whereby electrochemically synthesized polypyrrole (PPy) films underwent rapid bending due to water vapor sorption [7], we devised polymer motors capable of transducing chemical free energy change of sorption directly into continuous rotation [8,9]. Furthermore, we found that the PPy film contracted in air under application of an electric field [10], which was explained by desorption of water vapor caused by Joule heating [11]. However, the PPy film exhibits contractile strain of ca. 1% [11] which is smaller compared with other EAP actuators [1–6]; besides the electrochemical synthesis is inefficient taking time compared with facile casting or printing process, which limits mass production and reduction in costs for practical applications.

Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT/PSS), commercially available in the form of water dispersion of colloidal particles, has attracted considerable attention because of its superior electrical and thermal stability especially in the conductive state, which provides potential applications to electrical and optical devices such as transparent electrodes for liquid crystal displays and touch panels [12], organic diodes [13], and organic field-effect transistors [14]. Previously, we reported that films made of PEDOT/PSS contracted in air under application of an electric field, the mechanism of which was explained by desorption of water vapor caused by Joule heating [15–17]. Unlike conducting polymer actuators driven by electrochemical doping and dedoping, this system operated in air without using an electrolyte solution and counter/reference electrodes. The contractile strain of the film was ca. 2%, which is still smaller than other EAP actuators [18,19]. Although the PSS, a typical hydrophilic polyelectrolyte bearing sulfonic acid groups, plays a predominant role for the water vapor sorption, little is known about changes in the electromechanical properties of the film. In this study, PEDOT/PSS films with various PSS contents were newly prepared by

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casting the water dispersion of PEDOT/PSS colloidal particles in the presence of an extra PSS. Electrical conductivity, morphology, water vapor sorption, and EAP actuating behavior of the resulting films have been investigated by means of four-point method, AFM, sorption isotherm, and electromechanical analyses. Furthermore, we have developed linear actuators utilizing PEDOT/PSS films and applied to leverage actuator and Braille cell.

2. Experimental

PEDOT/PSS was commercially available in the form of water dispersion as Clevios P AG (H.C. Starck). Free-standing films with different PSS contents were prepared by casting the PEDOT/PSS with an extra PSS (M_w = 75,000 g/mol, Aldrich) containing 10 wt.% of ethylene glycol in a Teflon dish and allowing it to solidify by evaporation of solvent at 60 °C for 6 h and subsequent annealing at 160 °C for 1 h in vacuum. Electrical conductivity of the PEDOT/PSS film was measured by a normal four-point method with a Lorester (MCP-T610, Dia Instruments). AFM measurements were carried out with a scanning probe microscope (SPM-9600, Shimadzu) equipped with a conductive probe, where height and current images were measured by tapping and contact modes (a bias of 0.5 V), respectively. Water vapor sorption of the film was measured by means of a volumetric method using a Belsorp-aqua3 (Bel Japan). Prior to the measurement, the film was cut into small pieces and dried at 160 °C for 6 h under a nitrogen stream until the weight reached a constant in order to remove sorbed water completely. Degree of sorption, defined as the weight percent between sorbed water and dry film, was measured at each water vapor pressure after reaching the equilibrium state. The EAP actuating behavior of the films (50 mm long, 2 mm wide, and 16 μm thick) was measured in air at 25 °C and various RHs with an electromechanical cell equipped with an inductive displacement sensor (EX-416V, Keyence) as shown in Fig. 1. Temperature at the film surface was measured with an infrared thermometer (THI-500S, Tasco) and RH in the vicinity of the film surface was measured with a hygrometer (THP-728, Shinyei).

3. Results and discussion

3.1. Electrical conductivity and morphology

PEDOT/PSS films with various PSS contents were prepared by addition of an extra PSS from 0% to 74% to the PEDOT/PSS colloidal dispersion as listed in Table 1. The PEDOT/PSS71 denotes the commercial product which contains 71% of PSS calculated from the weight ratio of PEDOT:PSS to be 1:2.5 [20]. It is found that the electrical conductivity linearly decreases with increasing the PSS content from 164 S/cm (PEDOT/PSS71) to 29 S/cm (PEDOT/PSS93), indicative of no percolation transition or phase segregation that may cause a discontinuous conductivity change.

Table 1
PEDOT/PSS films with various PSS contents.

Film	PEDOT/PSS (wt.%)	Extra PSS (wt.%)	Total PSS (wt.%)	Conductivity (S/cm)
PEDOT/PSS71	100	0	71.4	164
PEDOT/PSS76	84.8	15.2	75.8	124
PEDOT/PSS81	67.7	32.3	80.7	105
PEDOT/PSS86	51.7	48.3	86.2	73
PEDOT/PSS89	37.5	62.5	89.3	52
PEDOT/PSS93	25.9	74.1	92.6	29

In order to clarify the conductivity change in more detail, AFM measurements were carried out and results were shown in Fig. 2. Numerous particles with diameters of several-tens nm are randomly and densely packed forming the PEDOT/PSS71 film (a) with a surface roughness of 5.0 nm, which is in good agreement with an average diameter of PEDOT/PSS particles estimated by a dynamic light scattering (41 nm) [21]. The AFM current image reveals that the film surface is entirely covered with higher conductive regions, which favors current flowing through conducting paths, leading to the higher electrical conductivity [22]. On the other hand, the addition of PSS brings about a large morphological change: The PEDOT/PSS89 film (b) is composed of larger grains loosely aggregated with a higher surface roughness of 5.8 nm. The AFM current image clearly indicates that PEDOT-rich higher conductive regions (bright area) are sparsely distributed in the matrices of PSS-rich less conductive regions (dark area), where transport of charge carriers may take place by hopping between such higher conductive regions, thereby decreasing the electrical conductivity.

3.2. EAP actuating behavior

Fig. 3 shows time profiles of contractile strain, electric current, surface temperature of the PEDOT/PSS films with various PSS contents measured at 25 °C and 50% RH. Upon application of DC 10 V, the film (50 mm long, 2 mm wide, and 16 μm thick) exhibits significant contraction, which is explained by desorption of water vapor molecules sorbed in the film where electric current passes through the film and surface temperature of the film increases due to Joule

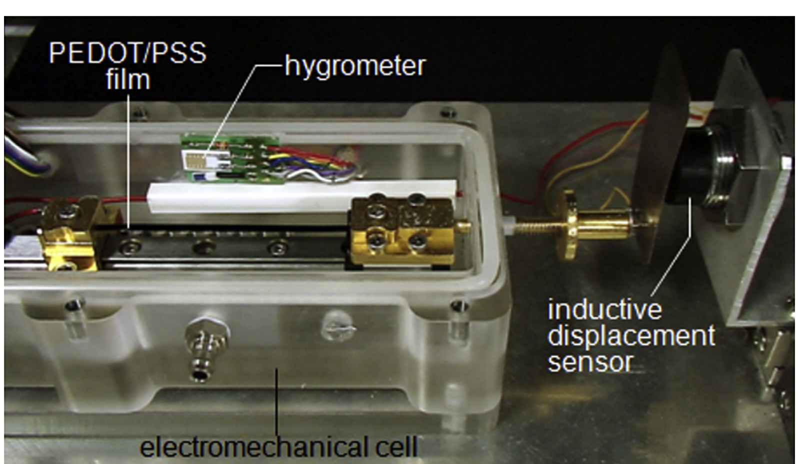

Fig. 1. Photograph of electromechanical cell for measurement of EAP actuating behavior of various PEDOT/PSS films.