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Contractile behavior of polypyrrole films in air under ac voltages

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Abstract

The polypyrrole films doped with tetrafluoroborate were electrochemically synthesized and contractile behavior was measured in air under ac voltages. It was found that the film did not respond at MHz frequencies but underwent gradual contraction where the changes in the strain, electric current, and temperature of the film were independent on the frequency in a range from dc to 1 MHz under the same effective value of the electric field. The resistance of the film was constant about 35 Ω but the capacitance decreased with the frequency, indicating that the electrically induced contraction of the film under ac voltage could be explained by the same mechanism under dc voltage where the dehydration of polymer chains and/or dopant ions due to the Joule heating.

Keywords: Electrochemical polymerization; Semiconducting films; Polypyrrole and derivatives

1. Introduction

Conducting polymers have attracted considerable attention because dimensional changes resulting from electrochemical or chemical doping can be applied to produce polymeric actuators or artificial muscles [1-4]. The combination of electrical and hygroscopic nature of conducting polymers provides an insight into the development of a new class of electro-driven actuators or artificial muscle systems that work in ambient air [5]. We have previously found that electrochemically synthesized polypyrrole (PPy) films exhibit contraction in air but elongation in a vacuum under application of an electric field [6]. The apparent dimensional change of the film under the electric field can be expressed by two processes: one is the contraction due to the desorption of water vapor and another is the thermal expansion of polymer chains both caused by Joule heating [7,8], which is different from electrochemical or chemical doping in an electrolyte solution or redox gas atmosphere. Under isotonic conditions, the film can lift a load in the course of the contraction where the power density increases with the load applied and the value attains 0.78 W kg^{-1} (6 μW) under the load of 60 g corresponding to the tension of 4 MPa [9]. On the other hand, under isometric conditions, the film can generate a contractile stress of 6 MPa under 2 V [10], which is four orders of magnitude larger than its own weight and 20 times that of skeletal muscle in animals [11]. Upon stretching the film by 1%, the stress increases to about 9 MPa, which is explained by the increase of Young's modulus due to the desorption of water vapor molecules that plasticize polymer chains. The work capacity of the film increases as the applied voltage becomes higher and reaches 48 kJ m^{-3} at 3 V, while the energy efficiency, defined as the ratio of work capacity to the electric energy, is on the order of 10^{-3}%. This system is of interest not only for proposing a new class of electro-responsive conducting polymers but also for understanding the electromechanical properties of humido-responsive conducting polymers. In this study, we have made investigations of electro-responsive behavior of the PPy film in air under ac voltages.

2. Experimental

2.1. Preparation and properties of PPy film

Pyrrole and propylene carbonate were purified by distillation before use. Tetraethylammonium tetrafluoroborate as an electrolyte was commercially available and used without further purification. Polypyrrole (PPy) films doped with tetrafluoroborate were electrochemically synthesized by anodic oxidation of pyrrole. The pyrrole monomer and tetraethylammonium tetrafluoroborate were

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dissolved in propylene carbonate containing 1% of water in concentrations of 0.06 and 0.05 mol l^{-1}, respectively. A constant current (0.125 mA cm^{-2}) was applied through a platinum plate (50 x 20 mm) as an anode and aluminum foil as a cathode with a potentiostat (HA-301, Hokutodenko Co. Ltd.) at –20°C for 14 h. After polymerization, the PPy film was peeled from the platinum electrode, soaked in a large amount of propylene carbonate and dried overnight in a vacuum. The film had a thickness of about 30 µm with a doping ratio evaluated by elemental analysis was 0.33, indicating the molar ratio between pyrrole unit and dopant ion was about 3:1. The electrical conductivity measured by a normal four-probe method with a digital multimeter (VOAC-7512, Iwatsu Co. Ltd.) was 67 S cm^{-1} at 25°C. Tensile properties were measured with a tensile tester (Tensilon II, Orientec Co. Ltd.) at a constant strain rate of 10% min^{-1} (chuck distance 20 mm, head speed 2 mm min^{-1}) under the thermostatic conditions (25°C, 50% RH). Young's modulus and tensile strength were calculated from the stress-strain curves to be 780 MPa and 37 MPa, respectively.

2.2. Measurement

The contractile behavior of the PPy film (35 mm long, 1 mm wide, and 30 µm thick) was measured using a laser displacementometer (LB-080, Keyence), where an electric field was applied with an LCR meter (3532-50, Hioki Co. Ltd.) through copper wires attached to both ends of the film with silver paste (Fig. 1). The temperature at the film surface was measured with an infrared thermometer (THI-500S, Tasco Co. Ltd.) and relative humidity (RH) in the vicinity of the film was measured with a hygrometer (MC-P, Panametrics Co. Ltd.), the probe of which was located 1 mm from the film surface.

3. Results and discussion

3.1. Contractile behavior under ac voltages

Fig. 2 shows changes in the strain, electric current, surface temperature of the film, and RH in the vicinity of the film surface under ac voltages at a frequency of 1 MHz. When an ac voltage is applied to the film under thermostatic conditions (25°C, 50% RH), the film undergoes contraction repeatedly in response to the electric field. The degree of contraction increases with the applied voltage and attains about 1% under 2 V. The electric current passing the through the film is in proportion to the applied voltage, while the temperature at the film surface rises with the square of voltage, indicative of Joule heating. It is noted that RH in the vicinity of the film surface increases by the electric field, demonstrating that the water vapor sorbed in the film desorbs and scatters into ambient air, while a gradual decrease of RH will be due to the temperature rise near the film because the saturated water vapor pressure increases with the temperature [6]. On the other hand, a drop of the RH when the electric field is removed can be explained as the resorption of water vapor from the air surrounding the film. Since the dimensional change of the film coincides with that in RH, the contraction is associated with the desorption of water vapor. The contractile behavior of the PPy film measured in a frequency range from dc to 1 MHz is shown in Fig. 3. One

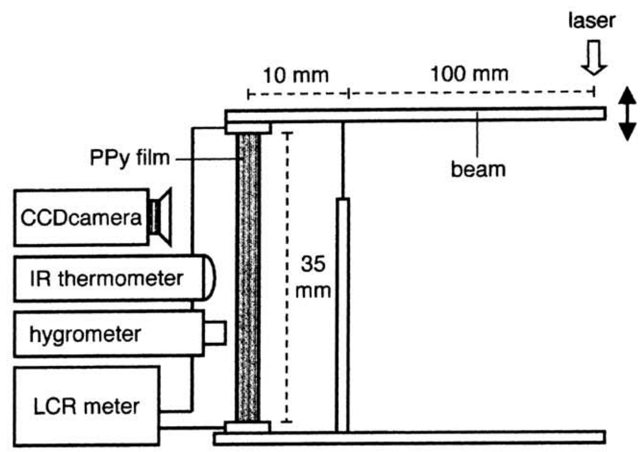

Fig. 1. Apparatus for measurement of contractile behavior of the PPy film under dc and ac voltages.

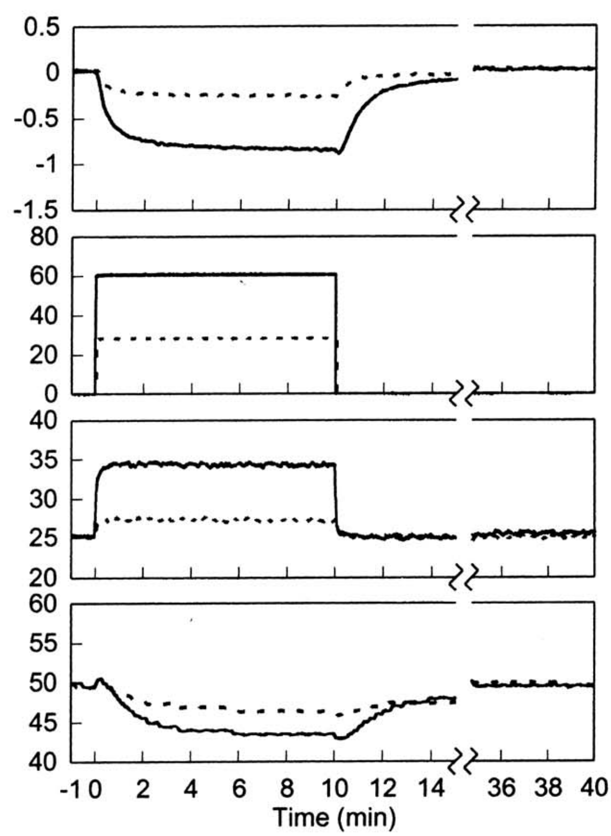

Fig. 2. Time profiles of strain, electric current, surface temperature of the PPy film, and RH in the vicinity of the film surface under ac 1 V (broken lines) and ac 2 V (solid lines) at 1 MHz measured at 25°C under 50% RH.