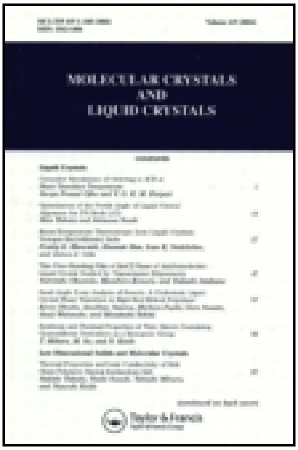

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Characteristics of PEDOT/NBR/PEDOT Solid Actuator Depending on the NBR Polarity

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A dry type conducting polymer actuator PEDOT/NBR/PEDOT is prepared. Nitrile rubber (NBR) containing room temperature ionic liquid, 1-butyl-3-methyl imidazoliumbis (trifluoromethylsulfonyl) imide (BMITFSI), have been utilized as a new type of solid polymer electrolytes. Various types of NBR having different amounts of acylonitrile (ACN), viz. 23, 35, and 40 mol.%, are synthesized in order to examine the effect of polarity of NBR on the actuation behavior. A conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), was synthesized on the surface of the SPEs by using a chemical oxidative polymerization technique. The electrical potential was applied on PEDOT layer which caused volume change to result in actuation behavior. The characteristics of the PEDOT/NBR/PEDOT actuator were carefully examined.

Keywords: electroactive polymer; ionic liquid; NBR; PEDOT

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INTRODUCTION

Conducting polymers (CPs) exhibit expansion and shrinkage behavior depending on doping and dedoping process by applying electrochemical potential, respectively. Several conducting polymers soft actuators have been studied extensively [1,2]. Most of the actuators have a bilayer or a trilayer configuration [3–5]. These layers consist of insulating polymer support and an electroactive CP layer. The physical adhesion between these two layers can be encountered by delaminating problems initiated by repeated volume alternation at the interface [6,7]. One possible resolution to this problem is the use of single layer actuator. Vidal *et al.* fabricated a solid type conducting polymer actuator using polybutadiene-co-poly(ethylene oxide) as a base resin coated with PEDOT as a electroactive layer in which two polymers were interpenetrated each other at the interface [8]. Sansinena *et al.* reported monolithic type polyaniline electrochemical actuators [9]. Recently, we introduced a solid type PEDOT/NBR/PEDOT actuator system based on a PEDOT, nitrile rubber (NBR) and room temperature ionic liquid (RTIL) as an electroactive polymer, insulating polymer support and a liquid electrolyte, respectively [10–12]. In this actuator, it was observed that the anion size of the electrolyte had an influence on the actuation mode [12].

In this study, we examined the actuation behavior depending on the nature of NBR by changing the concentrations of the acrylonitrile (ACN). In the preparation of the actuator system, we have synthesized three different grades of NBR resin as polymer substrates which consisted of different amounts of ACN, viz. 23, 35, and 40 mol.%. Thin NBR films ($150 \sim 200\,\mu m$) were prepared by using a compression molding process.

A conducting polymer, poly (3,4-ethylenedioxythiophene)(PEDOT), was synthesized on the surface of the NBR by using a chemical oxidation polymerization technique. The PEDOT/NBR film was immersed in an ionic liquid, e.g., 1-buthyl-3 methylimidazolium bis(trifluoromethylsulfonyl) imide (BMITFSI) in order to produce a solid polymer actuator. The physical properties of NBR/BMITFSI solid polymer electrolyte were characterized by the measurement of dielectric constant and ionic conductivity. The effects of the ACN-concentration in NBR film on the displacement of PEDOT/NBR/PEDOT actuator were investigated and discussed.

EXPERIMENTAL SECTION

Material

3,4-Ethylenedioxythiophene (EDOT) was purchased from Aldrich Chemical Co. and was purified by passing it through an activated neutral aluminum oxide column. $FeCl_3$ was purchased from Aldrich Chemical Co. and was used as received.

Synthesis of the Room Temperature Ionic Liquid (RTIL)

The synthesis of 1-butyl-3-methyl imidazoliumbis(trifluoromethylsulfonyl)imide (BMITFSI) was carried out according to the procedure described by Bonhote *et al.* [13].

Preparation of NBR Film

The three different grades of NBR resin, containing different amounts of ACN, viz. 23, 35, and 40 mol.% were prepared. The preparation scheme and the structure of NBR were represented in Figure 1. The virgin NBR resin was mixed with proper amounts of ZnO, S, and stearic acid in a Haake mixer at 90°C for 5 min and then in a two roll mixer at 100°C for 2 min. The resulting NBR compound was pressed into a mold at 160°C for 20 min under a pressure of 100 kg_f/cm^2 to complete the vulcanization process. The resulting films were 150 ~ 200 μm in thickness.

Preparation of PEDOT/NBR/BMITFSI Composite Film

The PEDOT/NBR/BMITFSI composite film was carried out according to the procedure described by Vidal *et al.* [8]. As shown in Figure 2, the NBR films were soaked in pure EDOT for 10 min, and then their surface was wiped off with filter paper. The oxidative polymerization of swollen films was induced by immersing in a 1 M $FeCl_3$ solution for 6 h. The films were then washed several times with methanol. The resulting PEDOT-NBR films were dried in a vacuum at 25°C for 24 h. After the edges were cut off, the PEDOT-NBR films were

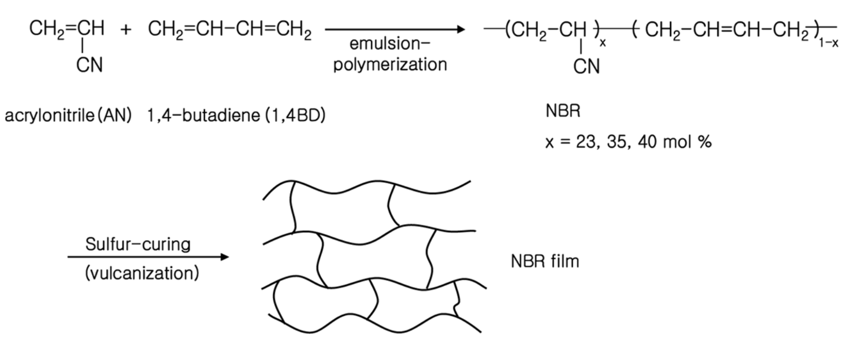

FIGURE 1 Preparation scheme and general structure of NBR.

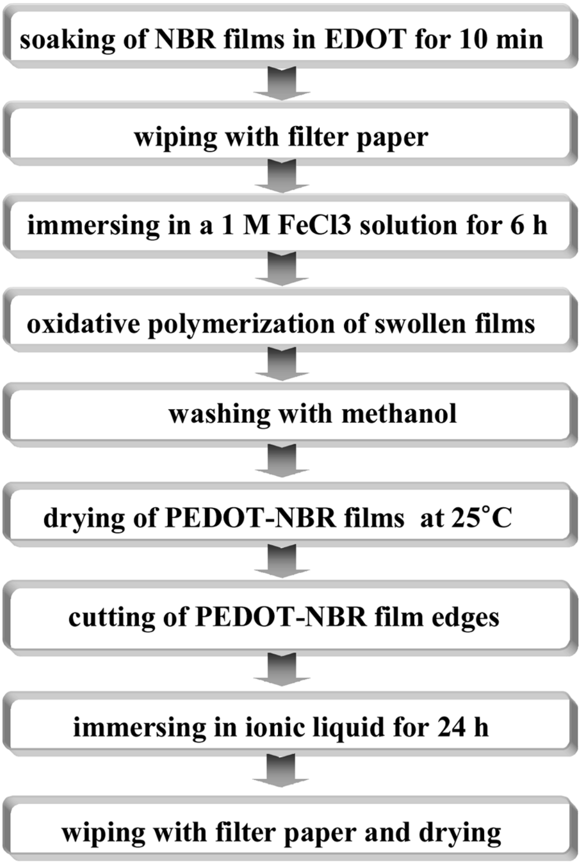

FIGURE 2 Schematic diagram of the fabrication of PEDOT/NBR/PEDOT actuator.

immersed in a 50/50 CH_2Cl_2/BMITFSI solution for 24 h at room temperature. After evaporating the CH_2Cl_2, the incorporated BMITFSI produced a 10～15% increase in weight. The composite films were stored in air.

Instrumentation

The ionic conductivity of the BMITFSI swollen NBR film was determined by AC impedance spectroscopy. Cells equipped with two blocking stainless steel electrodes were used to hold the film. A Teflon spacer was included to fix the dimension of the sample. The impedance tests

TABLE 1 Results of Physical Properties of NBR or NBR/Ionic Liquid

Sample	Acylonitrile (mol.%)	Dielectric constant (10^5 HZ)	Ionic conductivity in RTIL at 20°C ($\times 10^{-4}$ S/cm)	Tg (°C)	Tg (°C) NBR/ RTIL	Uptake of RTIL (wt.%)	Actuation displacement (mm)
NBR-1	23	7.6	0.54	−20.87	−28.52	40	3
NBR-2	35	9.6	1.3	−14.32	−30.01	60.3	8
NBR-3	40	10	2	−4.42	−33.94	67.8	12

were carried out in the frequency range of 10 MHz ~ 100 kHz using a Solatron SI model 1260 Impedance/Gain phase analyzer. Tg value was obtained by differential scanning calorimetry (DSC) between −80 and 100°C (Celsius) using Seiko Exstar 6000 (DSC 6100) scanning calorimeter equipped with a liquid nitrogen auto-cooling accessory. A sample was cooled to −80°C, held at that temperature for 5 min, heated to 100°C, held for 5 min, cooled, and the cycle repeated. All heating and cooling rates were 10°C/min.

The displacement of the actuator was measured by laser beam radiation using a Keyence LK-081 (Keyence Co., Japan). The point of the laser radiation was focused on 5 mm from the bottom of the film which was 30 mm long, 3 mm wide and 200 μm thick. Cyclic voltammetry (CV) was performed by the cyclic scanning of the potential between −5 and +5 V with a sweep rate of 500 mV s^{-1} in the solid electrode.

RESULTS AND DISCUSSION

The three different grades of the NBR film were successfully prepared and their physical properties were measured and summarized in Table 1. It was observed that the dielectric constant was increased as the acrylonitrile content increased, and the resulting ionic conductivity was also increased. The strong dipole effect of nitrile group affects the polarity of NBR. The characteristic of the solid electrolyte films produced by the impregnation of an ionic liquid, BMITFSI into the NBR matrix films was determined by measuring the ionic conductivity, dielectric constant and uptake of BMITFSI. The dielectric constant and the uptake of BMITFSI of the NBR films increased with increasing ACN content. The increase in the ionic conductivity of the NBR/RTIL film was observed in the sample having higher acrylonitrile content. The uptake appeared to be affected by the ACN content, which determines the polarity of the NBR film. The NBR-3 film containing 40% of ACN showed the highest BMITFSI uptake (70 wt.%). Sufficient weight uptake might indicate good affinity between the BMITFSI and NBR. As expected, the weight uptake of the ionic liquid and the dielectric constant of the NBR film increased with increasing acrylonitrile content. After impregnation of the RTIL, the Tg values of the NBR-1, NBR-2 and NBR-3 films were 7.65°C, 15.69°C and 29.52°C lower than those of the original films,

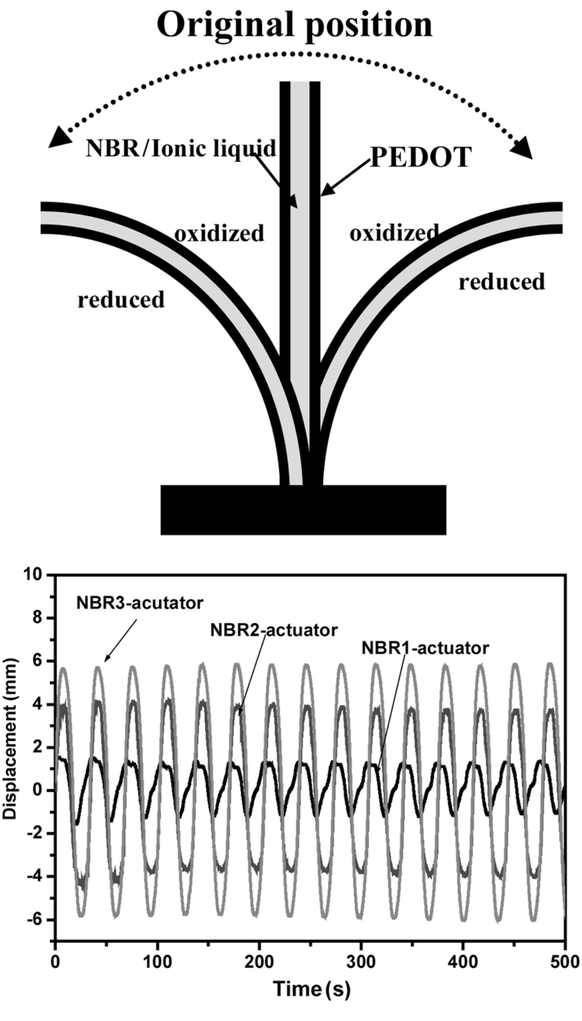

FIGURE 3 Bending motion and displacements of the PEDOT/NBR-1, NBR-2, or NBR-3 actuators activated in the ionic liquid BMITFSI and monitored by laser radiation: −5 and +5 V. Scan rate: 500 mV s^{-1}.

respectively. This indicates that the incorporated BMITFSI acts as an efficient plasticizer of NBR polymer. The original Tg value is dependent on the nitrile content. The presence of polar nitrile group allowed higher degree of dipole interaction between polymer chains to yield the restriction of polymer mobility. However, the polar nitrile groups also helped the incorporation of polar ionic liquid. The decrease in the Tg value afforded by the increase in the BMITFSI uptake resulted in the increase in the ionic conductivity as well as the enhancement of the deformation mobility by the applied potential.

Figure 3 shows a bending motion of PEDOT/NBR/PEDOT solid actuator by applied potential. A larger displacement was clearly observed in the sample having higher amount of nitrile groups. If the potential was applied on the actuator film, the liquid electrolyte started to move to oxidized PEDOT side to cause volume expansion. In the actuation mode, the insulating polymer support should have enough flexibility to allow facile displacement and NBR rubber containing higher amount of RTIL exhibited more flexibility. So a sufficient amount of electrolyte is the key factors for controlling actuation mode. The ranges of displacement of actuators based on NBR-1, 2, 3 were 3, 8, and 12 mm, respectively. There were approximately 2.5 and 4 fold increases in the displacement in the NBR-3 actuator, compared with those of the NBR-1 and NBR-2 actuators. The NBR-3 film containing 40% of ACN exhibited a higher dielectric constant compared with NBR-1 and NBR-2. The enhanced absorption of a polar liquid electrolyte was also due to the high polarity of ACN. In this way, the high polarity of ACN in NBR-3 film caused enhanced BMITFSI uptake, which meant that a high displacement was relatively easy to achieve.

CONCLUSION

Solid state electroactive polymer actuators were described which were based on the three different grades of NBR and an ionic liquid. The dielectric constant and the uptake of ionic liquid of the NBR films increased with increasing ACN content. At 40 mol.% ACN in NBR-3 film, an enhancement in displacement, to $\sim$12 mm was observed as compared to the NBR-1 and NBR-2.

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