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Morphology and dielectric investigations of hydrated-halt P(VDF-HFP) membranes

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Abstract

This study focuses on a preparation and characterization of hydrated-salt membranes based on the blend of poly(vinylidene fluoride-hexafluoropropylene) [P(VDF-HFP)] and magnesium chloride ($MgCl_2{\cdot}6H_2O$). The membranes with $MgCl_2{\cdot}6H_2O$ concentration of 0-4 wt% were prepared by solution casting technique. An elemental composition of the prepared samples was analyzed using energy dispersive x-ray spectroscopy (EDS). The surface morphology and pore size of these membranes were investigated by scanning electron microscopy (SEM). Surface roughness of the as-received membranes was evaluated by atomic force microscopy (AFM). The degree of the crystallinity and phase structures of the P(VDF-HFP) membranes were analyzed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The dielectric and the electrical conductivity of all samples were measured in a range of 1-10^5 Hz. The SEM and AFM images revealed that the formation of the microporous P(VDF-HFP) membranes was controllable by the adjustment of $MgCl_2{\cdot}6H_2O$ content. The surface roughness, pore size and ionic conductivity of the as-received membranes increased with $MgCl_2{\cdot}6H_2O$ concentration. The dielectric constant reached its maximum value of about 25 at 3.5 wt% of $MgCl_2{\cdot}6H_2O$. The XRD results showed that the mixture of $MgCl_2{\cdot}6H_2O$ salt led to a decrease in the degree of crystallinity. However, the salt-loaded P(VDF-HFP) enhanced the fraction of an electroactive β-phase up to 84 % and this was confirmed by the FTIR results. This pointed out that the hydrated-salt P(VDF-HFP) membranes had a potential in new applications such as energy harvesting area.

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*Keywords:*Poly(vinylidenefluoride-hexafluoropropylene); microporous membrane; morphology; magnesium chloride; dielectric property

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1. Introduction

Electroactive polymers (EAPs) are soft multi-functional materials exhibiting piezoelectric, pyroelectric and ferroelectric properties [1,2]. Nowadays, the EAPs have been extensively used in a variety of applications such as actuators, transducers, microelectromechanical systems, storage memory devices, energy harvesting gadgets, and biomedical sensors because of their stability in high electric field, no toxicity, light weight and chemical resistance. In addition they are of high flexibility and an ease of manufacture of complex shapes [1,3,4].

Poly(vinylidenefluoride) (PVDF) and its copolymers, i.e., poly(vinylidenefluoride-trifluoroethylene) [P(VDF-TrFE] and poly(vinylidene fluoride-hexafluoropropylene) [P(VDF-HFP)] have been promoted as a family of the interesting semi-crystalline polymer consisting of the commonly crystalline phases of α, β, γ, δ and ε polymorphs. The existence of these crystalline phases is dependent on the preparation processes and the molecular chain conformations. The non-polar α- and δ-phases have the trans-gauche-trans-gauche' (TGTG') conformation, while the γ- and ε-phases are the trans-gauche-trans-gauche-trans-gauche-trans-gauche' (TTTGTTTG') conformation [5-7]. The polar β-phase with the chain conformation of all trans (TTTT) has been predominantly responsible for the piezoelectric, pyroelectric and ferroelectric properties thanks to the largest spontaneous polarization per unit cell related to a dielectric property [8-10]. Nevertheless, thermodynamic stability of the α crystal is preferable to the desirable β crystal. It is too difficult to prepare the polar phase in the polymers without particular techniques. Therefore, numerous worldwide researchers have significantly paid attention to the reliable methods of the α-to β-phase transformation such as mechanical stretching [5], combination of stretching and electrical poling [11], dip-coating [12], electrospinning [13], low temperature polar solvent crystallization [14] and addition of nucleating agents [1,4,15]. Among these, the most common method to enhance the electroactive β-phase is to utilize the drawing process followed by poling in oil at a high electric field due to low cost and simplicity. However, the main drawbacks of the manner is a long time process and low film quality [11]. In the case of the electrospinning, there are not only the advantages (i.e., ease of usage, reproducibility, low cost, high efficiency) but also the restrictions on a large-scale manufacture and safety of research workers [16]. Recent researches on the electroactive polymers have focused on the incorporation of the hydrate salts (i.e., cerium (III) nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$], yttrium (III) nitrate hexahydrate [$Y(NO_3)_3 \cdot 6H_2O$)], lanthanum (III) chloride heptahydrate ($LaCl_3 \cdot 7H_2O$) and magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$)) [6,10,17]. This technique is able to increase the β-phase fraction of the electroactive polymers without the electrical poling and the stretching procedure. Although the $MgCl_2 \cdot 6H_2O$ filler has been already researched in the P(VDF-HFP), the correlation between morphology and the salt concentration has rarely been studied.

In this work, we aims to investigate experimentally on the preparation process of P(VDF-HFP) membranes doped with the $MgCl_2 \cdot 6H_2O$ salt using a conventional solution casting. The as-prepared membranes were systematically and sequentially characterized according to the preferred properties, i.e., chemical composition, morphology, phase of crystalline structure and electrical behavior. The mathematical relationships based on the observation data of pore size and surface roughness were analyzed. Moreover, the optimal process for the film preparation was reasonably discussed in accordance with the experimental results.

2. Experimental

2.1. Materials

The available P(VDF-HFP) in pellet form (M_W=450,000 g/mol, 427179, Sigma-Aldrich) was dried at 80 °C for 12 h prior to use. The solvent dimethlyformamide (DMF, D158550, Sigma-Aldrich) and the magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, M2393, Sigma-Aldrich) was an analytical grade.