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Study of the electrical conduction in poly(ethylene oxide) doped with iodine

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ABSTRACT

Impedance measurements have been made in the frequency range 10 Hz–50 kHz and temperature range from 25 to 55 °C on poly(ethylene oxide) doped with iodine. The iodine concentration ranged from 0% up to 10% by weight. Impedance, dielectric constant, dielectric loss, AC conductivity and activation energy showed frequency and temperature dependence. It was found that impedance decreases with increasing frequency and temperature as well. The values of dielectric constant and dielectric loss decrease with increasing frequency, but increase with increasing temperature. For doped PEO composite films, the values of dielectric constant and dielectric loss vary anomalously in the low doping level of iodine. In addition, it was found that the AC conductivity of PEO composite films increases on increasing the frequency or the temperature. In general, the observed dependence of the dielectric constant, the electrical conductivity, the relaxation time and the thermal activation energy on the measuring conditions is attributed to the formation of molecular and charge-transfer complexes. This is in addition to other factors such as polarization and the electron hopping process.

1. Introduction

Recently, polymer electrolytes became on interesting area of research in view of their electronic and optical applications. The electrical conduction of these materials is mainly based on the charge transport which can be modified by the addition of small amounts of certain dopants. Many reported studies have shown that dopants and salts incorporated in a polymer could improve its electrical and other physical properties. Polymer electrolytes are ionically conducting polymers by dispersing a salt at the molecular level in a polymer such as polyethylene oxide (PEO). The high interest in these materials is due to technological applications as solid electrolytes in electrochemical devices such as batteries, display devices and sensors [1–6].

Iodine doped poly(ethylene oxide) is a successful material as it showed pronounced changes in the degree of the ionic conduction and the dielectric properties [7–11]. Poly(ethylene oxide) (PEO) is considered an exceptional polymer which can form electrolytic systems as it can dissolve metals and salt complexes easily. In addition, it posseses good processibility and outstanding mechanical properties. PEO contains amorphous and crystalline phases of low glass transition temperature, ($T_g \cong -57\,^{\circ}$C), and melting temperature of about 60 °C [12–15]. Iodine is one of the majority of dopants used to impact ionic conductivity to the polymer since its atom accepts an electron from the host atom and generates hole carriers. Iodine is known to form polymer–halogen complexes when doped into polymers, and affects their electrical and dielectric properties. When iodine is doped in polymers, it may reside at various sites, substitute into the polymer chains, or reside at the amorphous/crystalline boundaries and diffuse preferentially through the amorphous region forming charge transfer complexes. Moreover, it may exist in the form of molecular aggregates between the polymer chains [16–21]. Doping PEO with inorganic salts or iodine may generate complexes with cations coordinated by several oxygen atoms and electron/hole carriers that all can play an essential role in improving the electrical conductivity.

It well established that impedance spectroscopy is very powerful method normally used in characterization of solid state materials. The present paper is focused on the AC-electrical behavior of iodine thin films doped poly(ethylene oxide) as a function of dopant concentration, applied field frequency, and temperature.

2. Experimental

2.1. Composite films preparation

Poly(ethylene oxide) with average molecular weight of 300,000 g/mol was used to prepare composite films of PEO/I_2 by casting from solution made of PEO and iodine. Poly(ethylene oxide) powder and solid iodine were mixed together and dissolved in methanol as a suitable solvent. The solution was

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then stirred continuously by a rotary magnet at room temperature for a few hours. The stirring process lasted until the mixture reached a homogeneous viscous molten state. Then the mixture was immediately casted to thin films on a glass plate. After that, the methanol was allowed to evaporate completely at room temperature and under atmospheric pressure for a few days. The composite films were dried in an oven at 40 °C for 2 days. The final films thus obtained have thicknesses in the range starting from 50 to about 90 μm and iodine concentrations 0%, 0.03%, 1%, 3%, 5%, or 10% by weight.

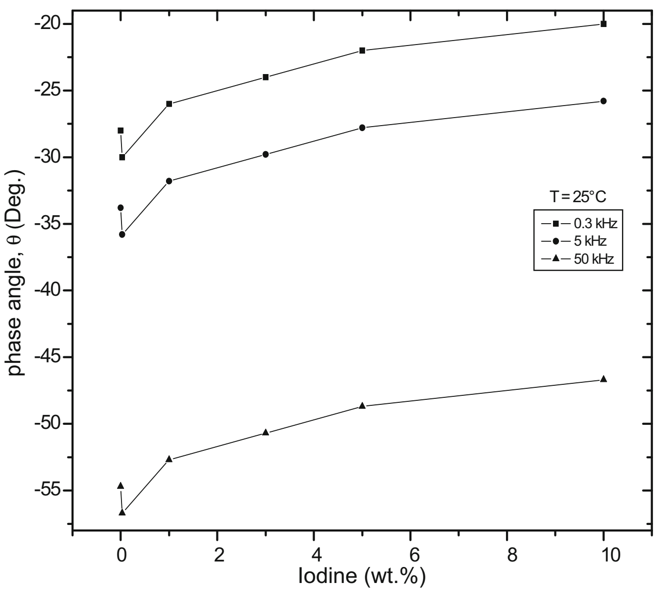

Fig. 1. Phase angle versus iodine content.

2.2. Impedance measurements

The phase angle and impedance of the prepared composite films were measured using LF Hewlett-Packard (HP) 4192A Impedance Analyzer. Disk-shape specimens were cut from the prepared composite films and placed between two copper plates (1 cm in diameter) of the test sample holder [22,24]. A thermocouple was kept in the closure for temperature measurements. Impedance measurements have been performed on the prepared films over a range of temperatures (25–55 °C) with steps of 10 °C, and a range of frequencies (10 Hz–50 kHz). Since the melting temperature (T_m) for PEO is about 55 °C, no higher temperature measurements were conducted.

3. Results and discussion

The AC conductivity and the dielectric constants of the doped poly(ethylene oxide) were measured at the following temperatures (25, 35, 45 and 55 °C) in the applied field frequency range from 10 to 50 kHz. The above casted films were of iodine concentrations of 0%, 0.03%, 1%, 3%, 5% and 10% by weight.

Complex impedance components (Z_r, Z_i), complex dielectric constant components (ε', ε''), AC conductivity, activation energy, and relaxation time were calculated using AC-equations as reported in literature [3,4,25–27]. Variation of phase angle with iodine concentration at different frequencies is shown in Fig. 1. It can be seen that the phase angle (ϕ) changed toward smaller negative values as a function of iodine concentration. However, the film of 0.03 wt% iodine showed reversal dependence of ϕ on I_2-concentration, i.e., it became more resistive and less capacitive. Fig. 2 shows increasing measured impedance values at room temperature for different I_2 concentrations 1%, 3%, 5% and 10 wt%. Also, it shows decreasing value for 0.03 wt% doped film. This

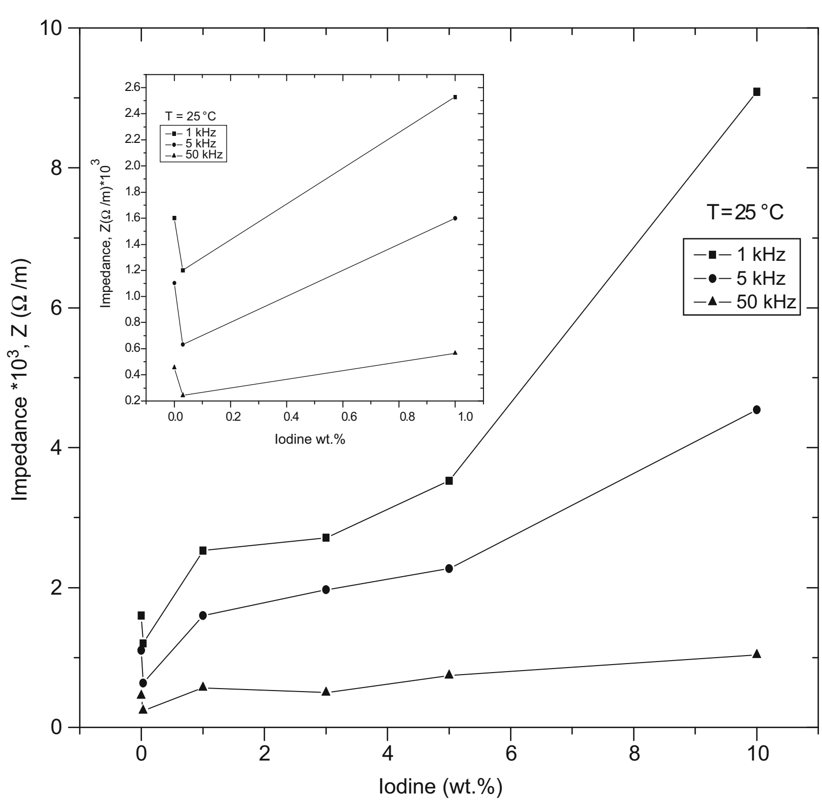

Fig. 2. Impedance variation with iodine content.