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Dielectric relaxation analysis and Ac conductivity of polyvinyl alcohol/polyacrylonitrile film

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ABSTRACT

A film of 0.98 polyvinyl alcohol (PVA)/0.02 Polyacrylonitrile (PAN) has been prepared using casting method. The dielectric properties were measured as function of temperature and frequency. The dielectric permittivity of PVA is considerably enhanced by doping with PAN. Different relaxation processes have been recognized within the studied ranges of temperature and frequency. The frequency temperature superposition (FTS) is well verified. Frequency and temperature dependence of Ac conductivity, σ_{ac}, were studied. The conduction mechanism of pure PVA and PVA doped with PAN are discussed. The activation energy either for relaxation or conduction was calculated. Comparison with similar polymeric materials is discussed.

1. Introduction

Polyvinyl alcohol (PVA) is a semi-crystalline polymer, with a high solubility in water, low cost, non-toxicity, and flexible hydrophilic network. It has a high dielectric permittivity and good charge storage capacity. These properties make PVA is an important and interesting polymer [1,2]. On the other hand, polyacrylonitrile (PAN), a synthetic vinyl homopolymer, offers quite good resistance [3], thermal stability [4], and mechanical strength [5]. It is regarded as the most preferable precursor material for the production of high strength, and high modulus carbon fibers. PAN fibers exhibit a high degree of molecular orientation, and higher melting point ($T_m \sim 317$ to 330 °C) [6]. Moreover, PAN is completely non-toxic and suitable for biomedical applications [7–10].

Incorporation of conducting polymer into another forming a blend, composite, or inter penetrated bulk network may lead to combine electrical conductivity with desirable physical properties of both two polymers [11,12]. A treatment of polyaniline (PANI)/polyvinyl chloride (PVC) blend was examined [13]. The results of PANI/PVC blends showed an increase in conductivity at lower temperature.

knowing that the dielectric relaxation spectroscopy (DRS) is a useful method to throw light on the structure property relationships of polymers. Also, this method is sensitive to molecular fluctuation of dipoles within the dielectrics. These fluctuations are related to the molecular mobility of branched groups, segments or wholly polymer chains which show different relaxation processes. Moreover, the dipole motions within the amorphous and crystalline phases have an effect on the semi-crystalline polymers [14,15]. Structural transitions in polymers are generally accompanied by changes in their relaxation properties. So, the relaxation properties are important for studying polymeric materials [16].

When an oscillatory electric field is applied to a polymeric material, several types of polarization are operative such as; electronic, ionic, orientational, or space charge. Orientational and space charge polarizations are particularly important when structural transitions are concerned. We reported previously on PVA/carboxymethyl cellulose (CMC) blends [17] as well as on 0.98 PVA/0.02 PANI film [18]. It become clear that the physical properties depend on the blend ratio of PVA and CMC. The physical properties of PVA are considerably affected by doping with PANI. Based on our knowledge, there is no previous report on the dielectric relaxation of PVA/PAN mixture. Therefore, we aimed in this work to throw light on the dielectric properties of (0.98/0.02) PVA/PAN film.

2. Experimental

PVA powder of molecular weight ($M_w \sim 17000$ g/mol), and Polyacrylonitrile powder ($M_w \sim 150{,}000$ g/mol) were obtained

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from (Polymer Laboratories, Essex, UK). (0.98/0.02) PVA/PAN film was prepared as follows: 0.98 g of the PVA and 0.2 g of PAN were dissolved separately each of them in 25 mL distilled water under stirring until clear solutions were obtained. The solutions were added to each other under ultrasonic stirring at room temperature (RT) for 2 h. The obtained mixture was then cast into Petri dishes and left to dry in air at RT for 24 h. Finally, the films were peeled off from the Petri dishes and care was taken to obtain homogenous samples with thickness (≈ 0.1 mm). Dielectric spectroscopy measurements were accomplished using a Hioki (Ueda, Nagano, Japan) model 3532 High Tester LCR, with the accuracy of order ±0.08%. The dielectric permittivity (ϵ'), and dielectric loss (ϵ'') were recorded at frequency and temperature ranging from 100 Hz to 4.4 MHz and from RT to 428 K, respectively. Both ϵ' and ϵ'' were calculated as follows:

$$\epsilon' = \frac{Cd}{\epsilon_o A}, \quad \epsilon'' = \epsilon' \tan\delta \tag{1}$$

where C is the capacitance of the sample filled capacitor, d is the sample thickness, ε_o is the vacuum permittivity, and A is the electrode area. The temperature was measured with a T-type thermocouple having an accuracy of ±1 K.

3. Dielectric properties

3.1. Dielectric permittivity

Fig. 1 depicts the frequency dependence of ε' at different fixed temperatures. As seen, ε' decreases with increasing of frequencies. The decrease in ε' may be attributed to decreasing of the number of dipoles which contribute to polarization or the dipoles are no longer able to respond to the applied electric field. To emphasize the effect of PAN on the ε' PVA, the inset of Fig. 1 shows the variation of ε' of pure PVA and 0.98PVA/0.02PAN versus frequency at some selected temperatures. It is clear that ε' of PVA is considerably enhanced by doping with PAN. The pronounced increase of ε' of PVA can be explained based on the chemical nature of PAN that has strong polar nitrile groups [19].

Fig. 2 displays the temperature dependence of ε' for PVA/PAN film at some selected frequencies. It is shown that ε' of PVA increased by adding PAN similar to that of PVA/PANI film [18]. The behavior of ε' with temperature can be explained as follows: at lower temperatures, the thermal energy that is absorbed by the

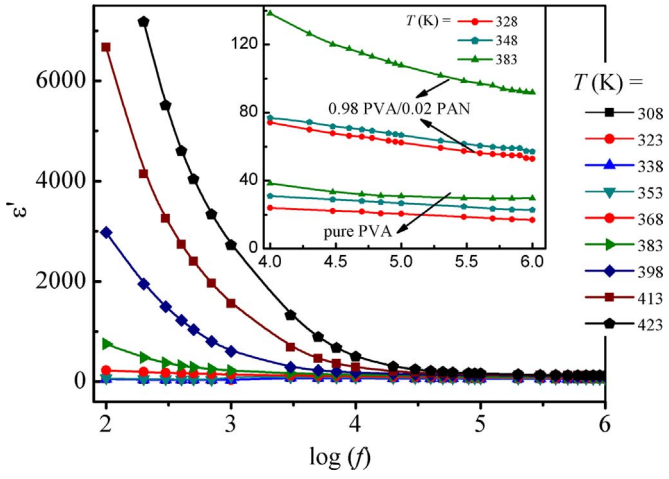

Fig. 1. The variation of dielectric permittivity, ε', as a function of frequency for 0.98 PVA/0.02 PAN film at different temperatures. The inset shows the variation of ε' versus frequency for pure PVA and 0.98 PVA/0.02 films at some selected temperatures. The arrows point to the data of each sample.

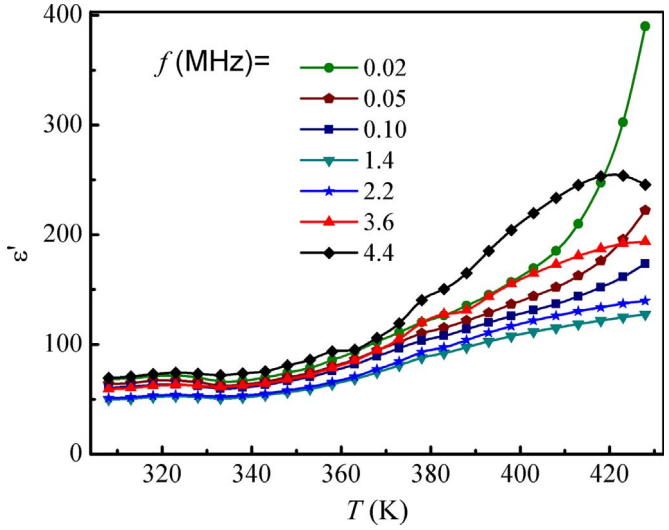

Fig. 2. The variation of dielectric permittivity as a function of temperature for 0.98PVA/0.02PAN film at different frequencies.

polymeric material, is small and then a small number of dipoles can rotate along with applied electric field [20]. As the temperature increased, the viscosity of polymeric films is decreased and the dipoles gain sufficient energy and can orient themselves easily in the direction of the applied electric field, thus ε' increased with increasing temperatures. In addition, the specific volume of the polymer increases with further an increase in temperature, and hence ε' increased [21,22].

3.2. Electric modulus

At low frequencies and high temperatures, the observed values of dielectric permittivity do not refer to the bulk of the material. This is related to the so called “interfacial polarizations” that are dominant in composite polymeric materials [23]. To avoid the contribution of the interfacial polarization or electrode polarization, the modulus formalism can be used to analyze the dielectric behavior of PVA/PAN film. In this section, the recorded dielectric data are expressed in terms of the complex electric modulus (M^*), which is defined as the inverse of the complex permittivity (ϵ^*):

$$M^* = M' + iM'' = \frac{1}{\epsilon^*} \tag{2}$$

$$M^* = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} + i\frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \tag{3}$$

where M' and M'' are the real and imaginary parts of the dielectric modulus, respectively.

The frequency dependence of the dielectric modulus M' at various temperatures is plotted in Fig. 3. It is clear that M' increases with increasing frequency and shows a peak around 1 MHz. The peak height decreases with increasing frequency and it can be attributed to ρ-relaxation [24]. Moreover, the values of M' tend to zero at low frequency indicating the removal of electrode polarization.

Fig. 4 shows the temperature dependence of M' for 0.98 PVA/0.02 PAN at different frequencies. It is observed that the values of M' decrease with increasing temperatures. A peak is observed around 340 K and it can be attributed to the glass transition, T_g, of the host polymeric material (PVA) [17]. It is called α_a- relaxation. Also, the values of M' decreased with the increase in temperature because of the thermally activated nature of the dielectric permittivity [23].