

The DC bias function of electrical characterization of PVA induced nickel chloride composite film

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Abstract The synthesis of *nickel chloride* (NiCl_2)-mixed with *polyvinyl alcohol* films of 15–20 μm in thickness has been carried by solution blending technique. The dielectric properties of the films have been measured in the frequency range of 20 Hz to 1 MHz under a positive bias potential in the range from 0 to 40 V. Improved electric characterization was demonstrated due to ionic incorporation of NiCl_2 . The low-frequency polarization was based on the Maxwell–Wagner interfacial model. Hence, this composite film may suggest as suitable electronic polar medium for versatile low-frequency applications.

Keywords Polymers · Dielectric properties · Electrical properties

Introduction

Polyvinyl alcohol has important applications in the field of medical and surgical devices, pharmacy, as well as in the industry of packaging, adhesion, and in agriculture [1, 2]. Recently, chemical cross-links in polyvinyl alcohol (PVA) have been simulated using an atomistic model by Bermejo et al. to predict the exact modular form of PVA [3]. The influence of the molecular weight-dependent electrical properties in pure PVA has been previously reported [4]. Our current contribution confirms a variation of electrical response in PVA related to its molecular weight. Several authors have reported an

improvement of electrical properties of polymer in its pure PVA or composite by the role of segmental mobility of polymer PVA [5–9]. Abd El-Kader et al. [10] have experimental evidence of an improved electrical property of NiCl_2 -doped PVA, following gamma irradiation. The results were attributed to irradiation-induced morphological change of the polymer, which could be controlled by the percentage of dopant. Impedance analysis provides a valuable method to study the correlation between the molecular motion in polymers and their electrical response. Previous studies have demonstrated that the incorporation of metallic salts in organic polar polymers can induce pronounced changes in their performance [11, 12]. These ions of alkyl halide become entangled with the polymer chains, inducing ionic polarization at low frequencies. An addition of NiCl_2 to PVA seems to retard the process of conjugated polymer formation along the polymer chain by thermal degradation confirmed with structural change [13]. The real-time holographic grating modulation with voltage by different film thicknesses proved by PVA induced NiCl_2 composition by diffraction efficiency [14].

In the present work, properties of nickel chloride-doped PVA have been studied, focusing particular attention to understanding the role of alkyl halide in the electrical response and the mechanisms that are most significant when the films are subjected to an external DC bias potential.

Material experimental

Low molecular weight polymer PVA and NiCl_2 in the granular form were supplied by SD Fine Chem, Mumbai. The PVA was completely dissolved in distilled water at 60 °C with consistent stirring. NiCl_2 was added to the PVA solution (the ratio of host polymer and NiCl_2 was taken as 90:10 for casting the film by weight percent), which was then kept consistent by stirring for 60 min. The resulting solution was poured into a

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Petri dish and kept at room temperature (30 °C) for 40 h. In this way, greenish thin NiCl₂-doped PVA films were obtained. These films were dried in a thermally enclosed oven at 45 °C for 24 h; moisture-free samples were obtained by a slow heating rate. Then, the film was silver pasted on both sides and used for the electrical characterization.

Electrical characterization

An impedance analyzer (Agilent 4282A precision inductance–capacitance–resistance (LCR) meter), equipped with the 16451B test fixture for dielectric measurements, was used for the measurement of dielectric constant and losses. The guard electrode contact method was adopted with a PVA film sample size of 40 mm in diameter, silver pasted from both sides. The relative dielectric constant value was also confirmed by measuring the out-of-plane capacitance (C_p) with the formula of relative dielectric constant [11]

$$\varepsilon = C_p \times 9.96 \times 10^9.$$

All data were recorded at an ambient condition within the frequency range of 20 Hz to 1 MHz, and the sample was subjected to various DC bias ranging from 0 to 40 V. The Agilent 4282A precision LCR meter provides inbuilt DC bias potential variation facilities, enabling the simultaneous application of DC bias potential along with the AC signal required for the measurement of the electrical parameters.

Role of NiCl₂ as dopant

Nickel chloride belongs to the alkyl halide group with a chemical structure similar to CdCl₂. The Ni-Cl bonds are of ionic nature [15]. In its crystalline form, each Ni²⁺ is sixfold coordinated to Cl²⁻ ions, and each chloride is bound with three Ni²⁺ ions. The compound is soluble in water and exhibits a greenish color. The reason for choosing NiCl₂ is that it blends very easily in solution. However, NiCl₂ is inducted in polymers for several technical reasons such as cost reduction, improvised processing, density control, optical effect, thermal conductivity, controlled thermal expansion, improved electric and magnetic properties, flame retardation, and improved hardness to which have merits over several transition metals. The exact ionic bonding scheme of PVA moiety with NiCl₂ is represented as follows:

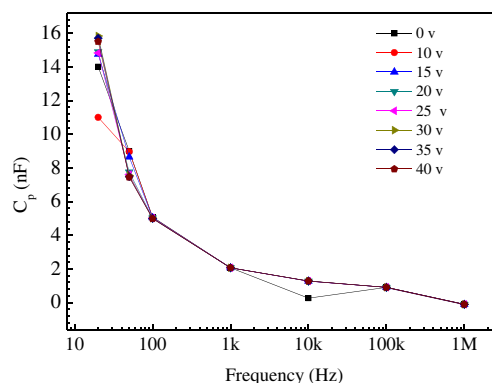
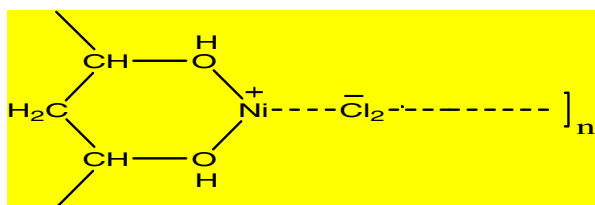


Fig. 1 Parallel capacitance (C_p) versus frequency of NiCl₂-doped PVA film

Results and discussion

Ionic dopant with polymer improves structural properties. Several ionic agencies like CuCl₂, NiCl₂, and FeCl₂ demonstrate the improved electrical conductivity as a function of temperature by suppressing the activation energy [16]. The low frequencies in NiCl₂-doped PVA are attributed to the presence of the ionic dopant. Figure 1 shows the parallel capacitance (C_p) as a function of frequency in NiCl₂-doped PVA film. Maximum C_p values are obtained at lower frequencies and higher DC bias. A value of $C_p=15.49$ nF is measured at 20 Hz with 40 V of positive DC bias. The trend indicates an increase in C_p that is directly proportional to the applied DC bias at low frequencies. As the frequency is increased, the magnitude of C_p decreases. The series capacitance (C_s) as a function of frequency is plotted in Fig. 2. The highest magnitude value observed is $C_s=140$ nF at a lower frequency to the applied bias potential. Figure 3 indicates the dielectric constant as a function of frequency on NiCl₂-doped film. It can be appreciated in Fig. 3 that the magnitude of the dielectric constant at a low frequencies, and hence that of

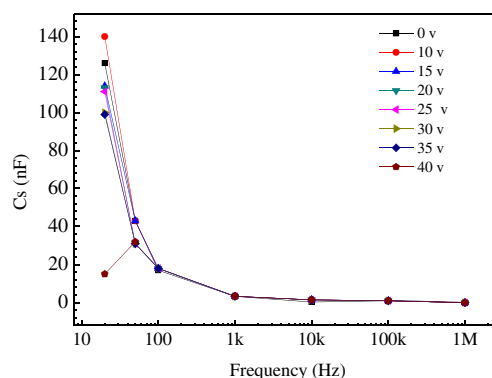


Fig. 2 Perpendicular capacitance (C_s) versus frequency of NiCl₂-doped PVA film

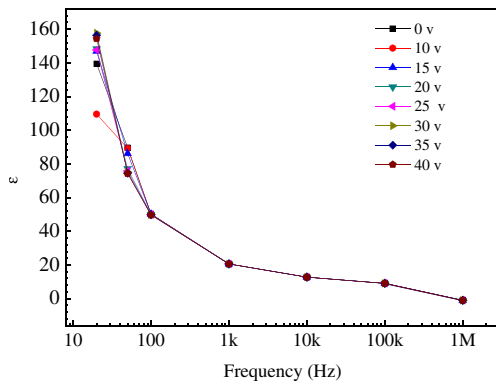


Fig. 3 Dielectric constant (ϵ) versus frequency of NiCl_2 -doped PVA film

polarization, is directly proportional to applied DC bias. In dielectric spectroscopy, large frequency-dependent contributions to the dielectric response, at low frequencies, typically come from built-up charge. According to the Maxwell–Wagner–Sillars (or often just Maxwell–Wagner) model, polarization occurs either at inner dielectric boundary layers on a microscopic scale or at the external electrode–sample interface on a macroscopic scale. In both cases, this polarization leads to a separation of charges through a depletion layer. The charges are often separated over a considerable distance (on the atomic and molecular sizes), and their contribution to the dielectric loss can be orders of magnitude larger than the contributions to the dielectric response of charge variations due to molecular fluctuations. Figure 4 displays the data of dielectric loss as a function of frequency in NiCl_2 -doped PVA film. A maximum loss value of 3.35 was observed at 20 Hz of frequency at 40 V of applied positive DC bias. The dielectric losses increase as the applied DC bias is increased. Impedances versus frequency curves are shown in Fig. 5. The maximum impedance is observed at low frequencies and at higher DC bias; the trend indicates an increase of impedance proportional to the applied bias at lower

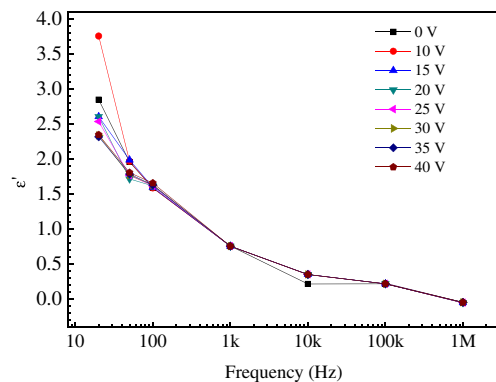


Fig. 4 Dielectric loss (ϵ') versus frequency of NiCl_2 -doped PVA film

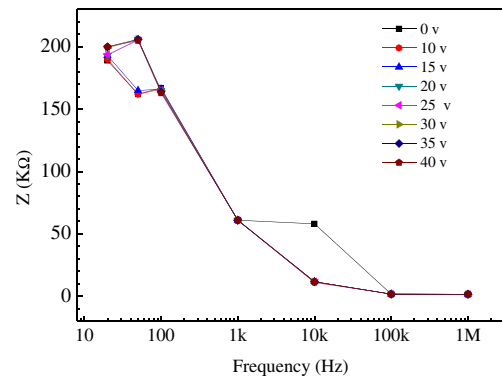


Fig. 5 Impedance (Z) versus frequency of NiCl_2 -doped PVA film

frequencies (below ≈ 100 kHz). The measured impedance of the composite film with a value of $Z=200$ k Ω at 40 V is observed. Figure 6 displays the *quality* (Q)-factor as a function of frequency of NiCl_2 -doped PVA film. Basically, the Q -factor is a measure of a resonant system. It is a system that responds to frequencies close to its natural frequency much more strongly than to any other frequencies. The Q -factor indicates the resistance of the system to resonate. According to Fig. 6 (shown in the upper inset), the Q -factor in our films is positive and directly proportional to the applied DC bias potential at 100 MHz. At 1 MHz, the quality factor exhibit negative magnitude, which can be due to the increase in damping [17]. It may be due to ionic dopant. The phase angle (θ) versus the frequency curves are shown in the lower inset of Fig. 6. The increase in magnitude of admittance is directly proportional to the applied bias potential at high frequencies (1 MHz) as demonstrated in Fig. 6. The phase angle also varies directly proportional to the applied bias potential, yielding negative magnitudes up to a 100-kHz frequency and positive magnitude at higher frequencies of about 1 MHz. The overall variation of electrical performance is dominated by additional DC biasing with AC signal.

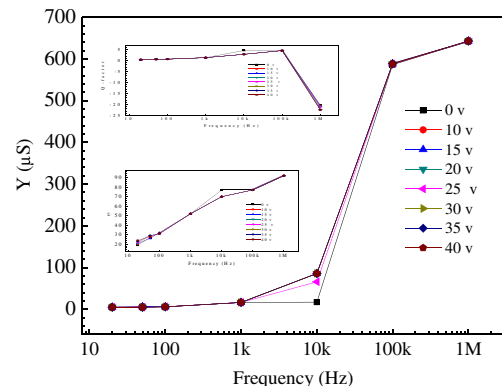


Fig. 6 Admittance (Y) versus frequency of NiCl_2 -doped PVA film. The upper inset is the Q -factor and lower inset is the phase angle

Conclusions

In the present study on LCR measurement, the NiCl₂ (alkyl halide) incorporation with polymer PVA is crucial for electrical properties. The electrical characterization correlated with respect to applied DC bias potential. The results obtained at the lower-frequency polarization are based on the Maxwell–Wagner model. The dielectric constant (ϵ) loss (ϵ'') and impedance (Z) are directly proportional to the applied bias potential. Q-factor has a positive magnitude at 100 MHz frequency. At 1 MHz frequency, the trend was found with negative magnitude; it may be due to the increase in the damping factor of the NiCl₂ dopant. As result, Q-factor is directly proportional to applied DC bias potential. The admittance (Y) of the film is directly proportional to the applied bias potential at higher frequencies. The phase angle (θ) of the film is directly proportional to applied bias potential at higher frequency. The dependence of the dielectric response on the applied DC bias voltage on NiCl₂-doped PVA film may be used for several versatile applications including good dielectric polar medium and conduction [18, 19].

References

1. Finch CA (1992) Polyvinyl alcohol—developments. Wiley, New York, p 282
2. Garel DR, Gaudreau P, Zhong LM (1991) *J Surg. Res* 51:297
3. Javier SB, Ugarte CM (2009) *Macromol. Theory Simul* 18:259–267
4. Girish J, Pade SM (2006) *J Appl Polym Sci* 102:1014–1016
5. Sengwa R J, Kaur, K (2003) *Indian J Eng Mater Sci*, 492
6. Abed Al-Kedar FH (2001) *J Appl Polym Sci* 39:1471
7. Zone CD, Lopez AA, Carmen MJ (2001) *Polym Sci Part B: Polym Phys* 39:1968
8. Hodge RH, Dastow TJ, Edward GH, Simon GP, Hill AJ (1996) *Macromolecules* 29:8137
9. Khalaed MA, Elwy A, Hussein AM, Abdullah K (2003) *Egypt J Sol* 26:83
10. Shehap A, Abd Allah RA, Basha AF, Abd El-K FH (1998) *J Appl Polym Sci* 68:687–698
11. Riande E, Diaz-Calleja R (2004) *Electrical properties of polymers*. Marcel Dekker, New York
12. Hanafy TA (2008) *J Appl Polym Sci* 108:2540–2549
13. El-Shahawy MA (1994) *Polym Degrad Stab* 43(1):75–79
14. Fontanilla-Urdaneta RC, Arturo OP, Israel FT (2011) Real-time holographic gratings modulate with voltage by different thickness film. *Opt Eng* 50:045801. doi:10.1117/1.3569623
15. Pray AP, Tyree SY, Martin DF, Martin Dean F (1990) Anhydrous metal chlorides. *Inorg Synth* 28:321–2. doi:10.1002/9780470132401.ch36
16. Abdallah M, Bakir E, Yousif E (2011) Study the electrical conductivity of crosslinked polyester doped with different metal salts. *J Saudi Chemical Society*. doi:10.1016/j.jscs.2011.08.001
17. XinHua D, NianHua L, LiPing A (2009) *Chinese Sci Bull* 54(12):1861–9541
18. Ragab HM (2011) Spectroscopic investigations and electrical properties of PVA/PVP blend filled with different concentrations of nickel chloride. *Physica B* 406:3759–3767
19. Girish J, Khatake SM, kalemulla S, Rao NM, Cuberes T (2011) Effect of dopant and DC bias on polymer pervoskite composite films. *Curr Appl Phys* 11:1322–1325