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Enhanced Dielectric Constant of Succinic Acid doped Polyvinyl Alcohol (PVA) Thin Film

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Abstract

The present paper reports the dielectric behaviour of high molecular weight water soluble polyvinyl alcohol (PVA) system doped with a dicarboxylic acid (succinic acid). Doped PVA samples were synthesized in the laboratory using solution casting method by keeping an optimum concentration of succinic acid (30 wt%) in PVA solution. These samples were characterised for their structural behaviour using FT-IR and XRD while frequency and temperature dependent dielectric properties were measured using Agilent LCR meter. It was observed that dielectric permittivity ($\in'$) of 30wt% acid doped PVA significantly increased compared to undoped PVA. This was attributed to the increase in the amorphous regions with acid doping that facilitated the orientations of dipoles. At all frequencies, room temperature dielectric properties ($\in'$ and $\in''$) of both undoped and doped samples showed a frequency dispersive behaviour. FT-IR and XRD analyses confirmed the increase in amorphous regions in doped samples compared to undoped semi-crystalline PVA.

Key words: PVA, dielectric behaviour, capacitance, succinic acid

1. Introduction

By virtue of being a versatile water-soluble polar polymer, polyvinyl alcohol (PVA) and PVA based composites/ nanocomposites have been rigorously explored for their potential applications in various industrial sectors including electronics and microelectronics packaging [1]. Numerous research works are being carried out on this polymer system since it is not only easy to process but it is cost effective and its mass production is equally promising [2]. Scores of research papers are available in the literature wherein their potential in memory devices, waveguides and in holographic recording using ion doped PVA, have been investigated [3]. Doped PVA is reported to have better mechanical, optical and electrical properties compared to undoped PVA [4-12]. Acid doped PVA electrolytes have been explored for use in electrochemical devices [13]. Being an insulator with very low conductivity (~10^{-12} S/cm), it has been identified as a passive layer in microelectronic packaging industry [12]. At the same time, its electrical conductivity can be improved by thermally generating charge carriers or by addition of suitable dopants or conductive fillers resulting which they can be used as electrical probes [3]. Other than these areas of potential applications, PVA has been investigated for applications as capacitors/supercapacitors and charge-storage/energy storage devices since their dielectric properties and capacitance can be increased by selective doping [2]. Temperature, frequency and field dependence of $\in'$ determine the dielectric relaxation behaviour [14]. PVA/PVA composites are flexible and their dielectric properties can be significantly modified which render them potentially viable as capacitors [15,16]. For instance, PVA/ cashew gum/ magnetite composites, [17] succinic acid doped PVA [18], Ag nanoparticles filled PVA [19] and $TiCl_2$ filled PVA have showed enhanced dielectric properties compared to pure PVA. It was attributed to the fact that addition of a suitable dopant causes (i) reduction in the impedance due to increased amorphous regions in the composites and (ii) slower relaxation time (τ) because charges (ions) can move freely in the polymeric matrix. The dopant effect of melanin on the dielectric behaviour of PVA polymer was confirmed indirectly by the conductivity measurement [21]. It has been reported that melanin doped PVA showed higher conductivity than undoped sample primarily due to a rise in the number of charge carriers that moved freely through the polymer. As an indirect inference, it was claimed that the increase in electrical conductivity was responsible for reduced values of dielectric constant in doped PVA. Similar results have been reported for succinic acid doped PVA which showed higher dc conductivity than undoped PVA [18]. It has also been reported that ferroelectric BZT powder filled PVA showed better dielectric behaviour than unfilled PVA [22]. As is evident from the exhaustive literature survey, only a few papers have addressed the structure-dielectric property correlation. Hence, in the present investigation, PVA system doped with succinic acid, which is an organic dicarboxylic acid, was prepared by solution casting method and characterised for their dielectric and structural behaviour and a correlation between them has been established. The main objective of this study was to enhance the dielectric properties and structural integrity of PVA for use (i) as a dielectric layer in devices or (ii) as an energy storage device.

2. Experimental Procedure

2.1. Materials and method: Pure PVA (Mw =1,25,000 g/mol) and succinic acid [$C_4H_6O_4$] were procured from CDH, (India) and Qualigen (India) respectively. In step I, PVA solution (8% w/v) was prepared by dissolving it in distilled water. In step II, various percentages of succinic acid (10, 20 30, 40 and 50 wt%) with respect to weight of PVA was mixed in the solution prepared in step 1. The resultant mixture was stirred continuously for 4 hrs at 80 deg C in a water bath to get a homogenous mixture. The stirred solution is cast onto a flat glass sheet and dried at room temperature. The films were stripped off from the glass sheet. The as-obtained crosslinked films were then kept in oven at 85°C for 20 hours for further crosslinking. Details of synthesis are available elsewhere [23]. Specimens of size (5mmx 5mm) were cut from these films for dielectric measurements.

3.0 Results and discussion

3.1 FT-IR analysis: Fourier transform infrared spectroscopy analysis was performed on the samples in the wavenumber range 400–4000 cm^{-1}. FTIR spectrographs of undoped and acid doped PVA are shown in Fig 1a.

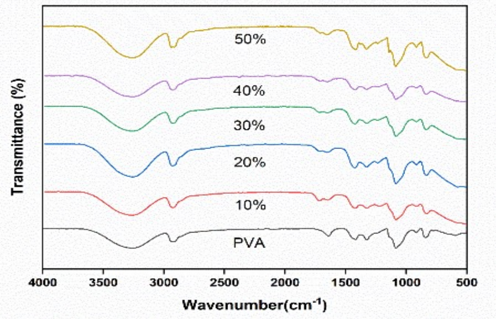

Figure 1a: FT-IR spectra of Succinic Acid doped PVA samples

Table 1: FT-IR peaks and their assignments for undoped and SA doped PVA

Assignments	Peaks (cm^{-1})	
	Undoped	SA Doped PVA
O-H stretching	3551-3114 cm^{-1}	3561-2892 cm^{-1}
C-H bond stretching of CH_2	2947 cm^{-1}	2980-2724 cm^{-1}
C-H bending of CH_2	1453 cm^{-1}	1461-1455 cm^{-1}
C-C stretching	948 cm^{-1}	942-929 cm^{-1}

The peaks and their assignments for pure PVA and acid doped PVA are shown in Table 1. The peaks for SA doped PVA are slightly shifted.

3.2 XRD analysis

The X-ray diffractograms of pure PVA and 30wt% SA doped PVA (size 10 mm x 10 mm) are shown in Fig.1b.

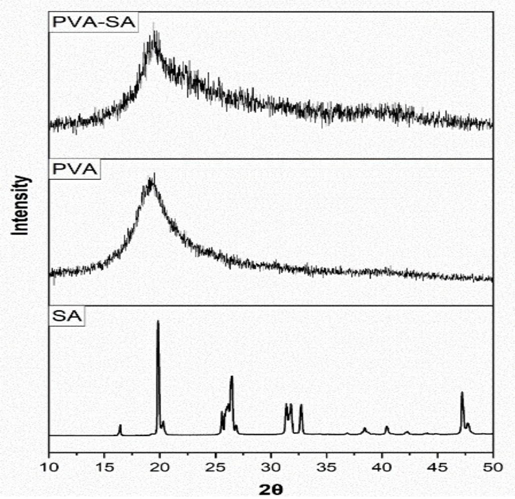

Figure 1b: XRD diifractograms of succinic acid, pure PVA and 30wt% SA doped PVA

The peak observed at 2θ = 20° in XRD pattern of pure PVA is indicative of its semi crystalline nature [24]. The intensity of the same peak reduced with SA doping primarily due to decrease in crystallinity and subsequent increase of amorphous regions in PVA [25-26]. All the sharp peaks shown in the XRD pattern of SA were missing in the XRD pattern of SA doped PVA which confirms that SA was completely dissolved.

3.3 Dielectric studies

Temperature and frequency dependent values of parallel capacitance (Cp) and loss tangent or dissipation factor (tan δ or D) of the samples were measured using Agilent 423B precision LCR meter at a frequency of 100 Hz, 120Hz, 1 kHz, 10kHz, 20kHz and 100 kHz from room temperature to 65°C. Test samples were electroded on both sides using conductive silver paste. The thickness of the samples was measured using a micrometer. Electroded samples were placed in a sample cell between two electrodes and voltage was applied. The sample cell was kept in a furnace which maintained a constant heating rate of 1°C per minute The parallel capacitance (Cp) and Dissipation factor (D or tan δ) were measured on the LCR meter and recorded through an online data acquisition system. The ratio between capacitances (Cp versus Co) gave a measure of the relative dielectric permittivity

$$\epsilon' = Cp/C_0 \qquad \ldots(1)$$

$$C_0 = \epsilon_o A/d \qquad \ldots(2)$$

is the capacitance with vacuum between parallel plates and $\epsilon_o = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum, A is the area of electrode, and d is the thickness of the sample. The thickness of the film was 0.26×10^{-3} m. Temperature and frequency dependent dielectric constant, dielectric loss and loss tangent (tan δ) of undoped PVA sample measured at various frequencies (100 Hz to 100 kHz) and temperature range (RT to 65°C) are shown in Fig 2 (a-d). Dopant concentration of 30 wt% SA is chosen since this concentration show optimum properties [23].

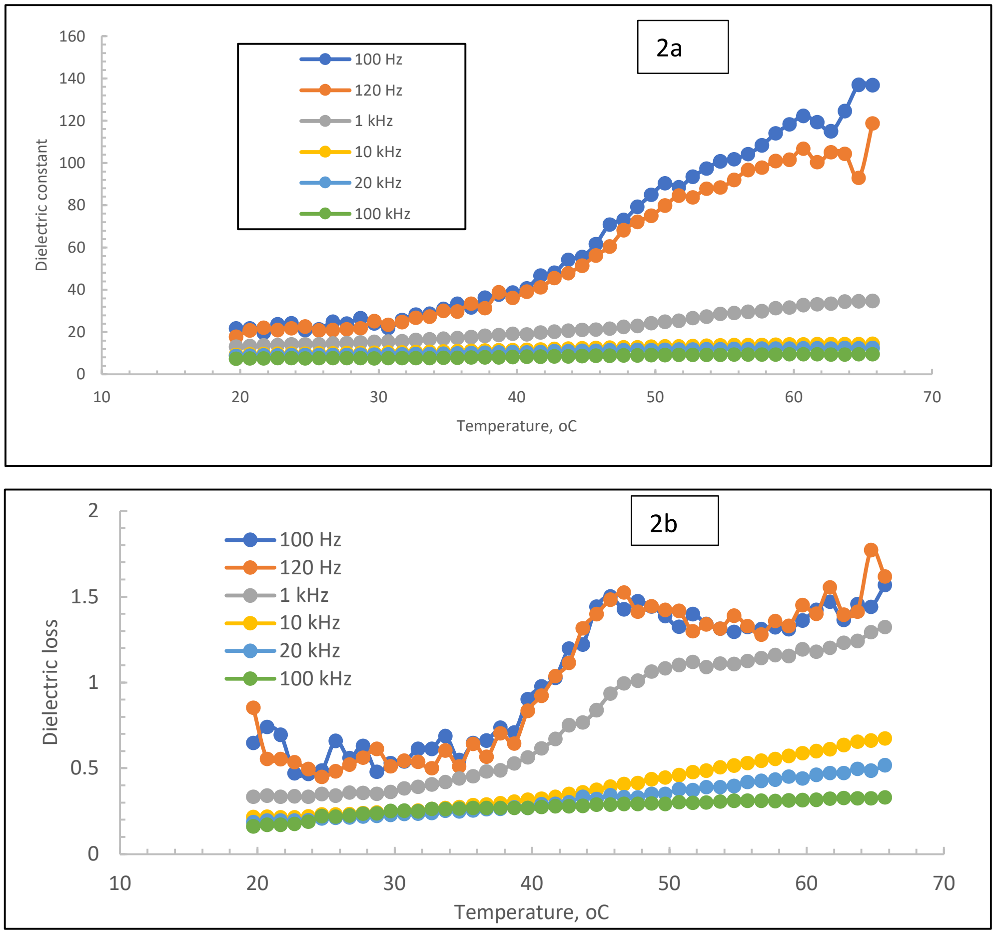

Figure 2: (a) Dielectric constant and (b) dielectric loss of undoped PVA as a function of frequency and temperature

The value of dielectric loss (ϵ") was quite low (<1) at all frequencies and temperature which indicates low dissipation of energy. As is evident from all these figures, both dielectric constant and dielectric loss decrease with increase in frequency at all temperatures. This is attributed to the fact that at low frequency dipoles have sufficient time to orient themselves in the direction of the applied electric field. However, as the frequency increases dipoles do not get sufficient time to orient leading to less contribution of charge carriers to dielectric constant. In other words, high and low values of dielectric constant at low and high frequency respectively is a direct consequence of charge accumulation at the electrode-dielectric interface (due to polarization) and their diffusion in the direction of the applied electric field. [11,27,28].

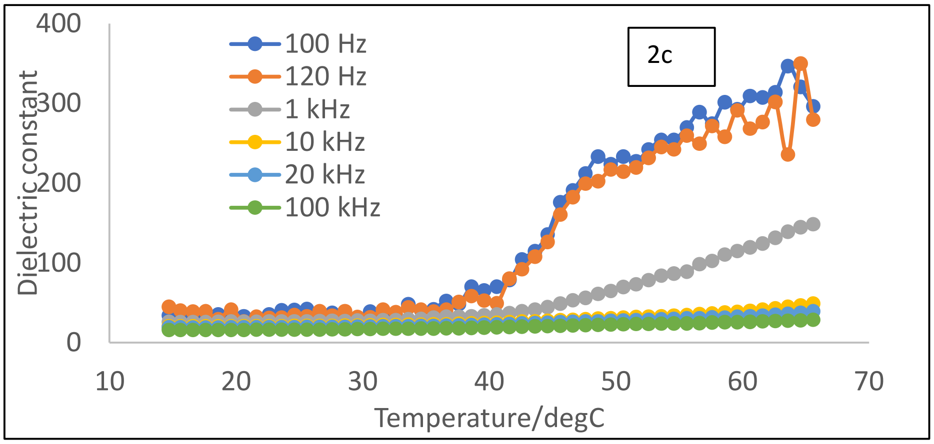

Figure 2c: Temperature and frequency dependent Dielectric constant of 30wt% SA doped PVA sample

The same concept has been explained mathematically for a free dipole oscillating in an ac field. The complex dielectric constant consists of a real and imaginary parts and is expressed as Eq. (3).

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}, \qquad (3)$$

where, ε_s and ε_∞ are the low and high frequency values of ε′. At low frequency, dipoles orient themselves with the applied field and $\varepsilon' \cong \varepsilon_s$. When the frequency increases ($\omega < 1/\tau$, where τ is relaxation time), there is a lag between dipole orientation and the applied field and ε′ starts decreasing. Finally, when $\omega = 1/\tau$, or at high frequency, the dielectric constant falls since dipoles cannot orient themselves according to the applied field and $\varepsilon' \cong \varepsilon_\infty$.

3.3.1 Structure-Dielectric property correlation

Figure 2 (c-d) shows the dielectric behaviour of 30wt% SA doped PVA. The influence of the acid dopant on PVA is complex. The dopant affects the dielectric properties firstly due to change in the semicrystalline nature of PVA and secondly due to increased cross-linking of PVA. The increase in the dielectric constant with an increase in the dopant concentration is primarily attributed to increase in charges (protons) and their polarization. The mobility or diffusion of these charges within the polymer matrix is supported by the motion of polymer chain segments. These polymer chain segment could move easily in amorphous regions compared to crystalline regions. SA doping not only provides more charges but also increases the amorphous regions (Fig 1b). The increase in the dielectric constant of doped PVA is thus attributed to reduced crystallinity and a more flexible polymeric backbone. At higher concentrations (>30 wt%), the dielectric constant would decrease because of higher charge accumulation that reduces overall polarization of charges. It has been reported

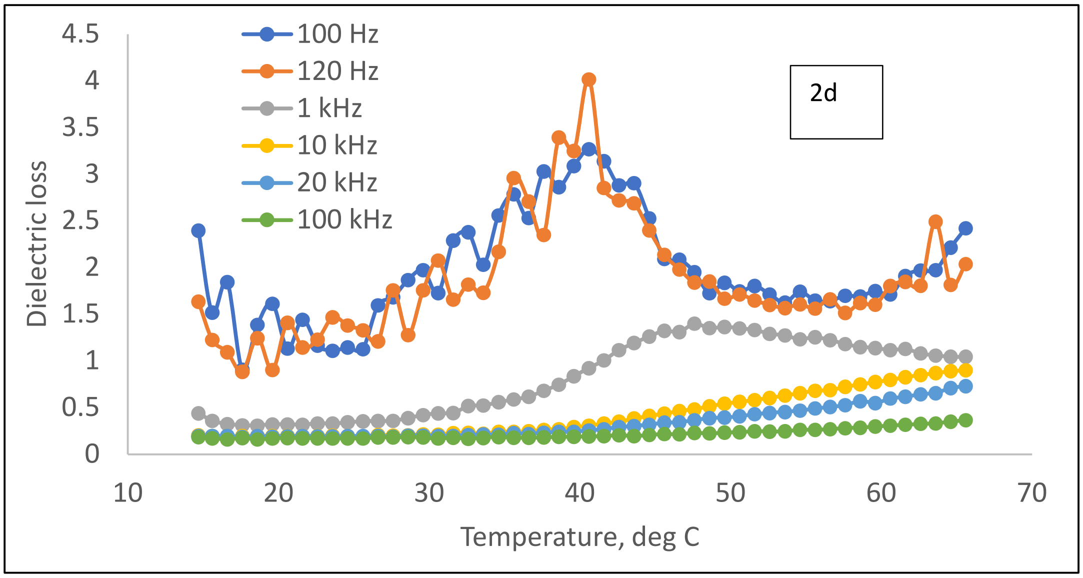

Figure 2d: Temperature and frequency dependent Dielectric loss of 30wt% SA doped PVA sample

that the amorphous nature results in greater ionic diffusivity with high ionic conductivity, which can be obtained in

Figure 2 (e) shows the comparison of dielectric constant of undoped PVA and 30wt% succinic acid doped PVA. As shown in Fig. 2(e), the dielectric constant increases with increasing temperature. The increase in dielectric constant of doped PVA may be attributed to the segmental motion of polymer chains which becomes faster with rise in temperature that eventually aids the polarization of charges.

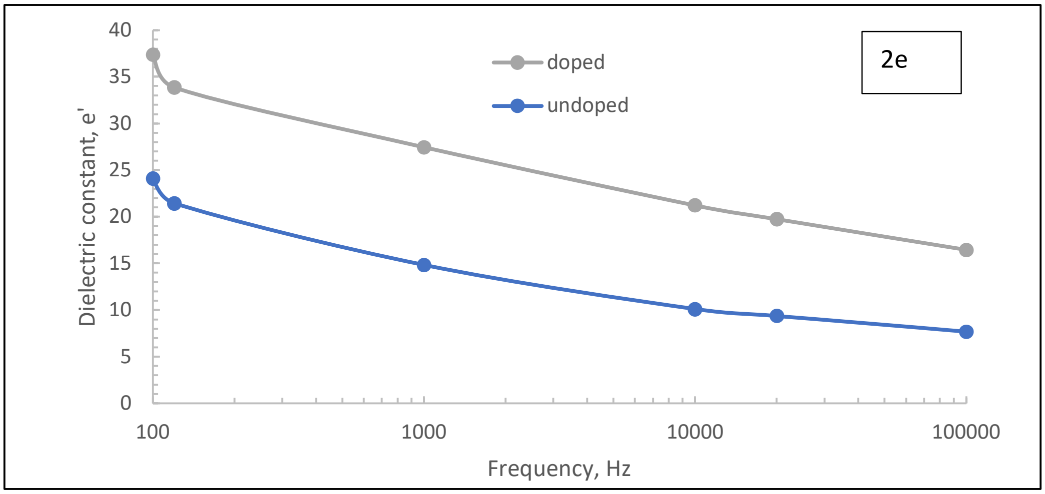

Figure 2e: Comparison of room temperature dielectric constant of undoped PVA and 30wt% SA doped PVA

4. Conclusions

The dielectric behaviour of succinic acid doped PVA is significantly improved compared to undoped PVA due to additional charges supplied by the dopant and their polarization through increased amorphous regions. It is found that at room temperature as well as at elevated temperature (upto 65°C) the maximum dielectric constant is obtained for PVA doped with 30 wt% Succinic acid.

Conflict of Interest

Authors declare No conflict of interest

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