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The effect of isothermal annealing on the AC conductivity of Polyvinyl Alcohol-based polymer as an energy storage system

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Abstract:

Polyvinyl Alcohol-based polymer was prepared using a casting technique. Impedance spectroscopy has been used to study the effect of isothermal heat treatment on the AC conductivity of doped polyvinyl alcohol (PVA) with silicon dioxide (SiO_2), magnesium triflate (MgTIF), and 2-Ethylhexylamine (EHA). The frequency dependence of the AC conductivity for the investigated samples has been studied according to Jonscher's power law at different annealing temperatures and annealing times. The frequency exponent (s) of Jonscher's law has been estimated by fitting the experimental data with this law. It has been found that (s) increases at low annealing time and temperature and then decreases at high annealing time and temperature, which could be interpreted in terms of NSPT and CHB models. The temperature dependence of the AC and DC conductivity at different annealing temperatures and different annealing times for the investigated samples according to the Arrhenius equation were studied, where the activation energies are E_g and E_a for the DC and the AC conductivity respectively were derived. It has been found that E_a and E_g increase with increasing annealing times.

Keywords: *Conductivity, Annealing time, Energy storage, Isothermal.*

1. Introduction

Communities are looking for sustainable and renewable energy due to resource scarcity and environmental concerns; this is essential for decarbonizing economic growth. Despite the development of green energy sources such as solar, wind, and geothermal energy, these sources generally suffer from discontinuity issues and must be logically combined. As we move away from our reliance on fossil fuels and toward clean energy sources, energy-storage devices are essential, secondary/rechargeable batteries (SBs) can reversibly transform electrical energy into chemical energy and are among the most promising technologies to use for this purpose [1, 2]. In comparison with inorganic solid-state electrolytes, polymer electrolytes have the benefit of being less expensive, lightweight, mechanical stability, corrosion resistance, and manipulating them more easily[3, 4]. They also exhibit superior mechanical, thermal, and possibly even electrochemical stability compared to liquid electrolytes [5]. Among all polymers, PVA is environmentally benign because it is harmless and biodegradable [6]. PVA is a well-known membrane material with exceptional properties such as dissolving easily in water, high dielectric constant, good thermal stability, chemical stability, hydrophilicity, and excellent film-forming capabilities [7, 8]. Various Models to explain AC conductivity mechanism, such as Quantum Mechanical Tunnelling (QMT), Overlapping Small and Large Polaron Tunneling (OLPT), Non_Small Polaron Tunneling (NSPT), and Correlated Barrier Hopping (CBH) [9, 10]. The QMT relies on electron tunneling facilitated by phonons, and it is temperature-independent but frequency-dependent, the frequency exponent (s) decreasing as frequency increases with a constant value around 0.8. In the OLPT model, (s) depends on both frequency and temperature decreasing with rising temperature to a minimum value before increasing as temperature rises. In the NSPT model, (s) is temperature dependent and increases as the temperature increase [11]. The CBH model predicts, (s) a temperature-dependent function that declines with increasing temperature.

2. Experimental Details:

The polymer was prepared by dissolving 2 gm of PVA (QualiKems Chemical Company, India) in 20 ml of deionized water and then adding 8 wt.% of SiO_2 to it (Aldrich Chemical Company). MgTIF was added to the mixture of PVA-SiO_2

combination at a rate of 28 wt.%. PVSM-$_{3000\mu L}$EHA composites were formed by adding 3000µL of EHA to the mixture and mixing it for 12 hours at 70°C. The composites were then put onto glass Petri plates and allowed to be cast. The samples' external surfaces were covered with silver paste to improve electrode contact. A spring-loaded sample holder held samples wedged between its two metal electrodes. The sample was placed in a temperature-controlled furnace. Electrical and dielectric measurements were performed at different annealing times (30, 40, 50, 60) min for each of the following annealing temperatures (75, 80, 90, 100) °C in the frequency ranges from 100 Hz to 1 MHz using a GW Instek LCR-8110G.

3. Results and Discussions

3.1. AC conductivity:

The ionic conductivity can be calculated by [12]:

$$\boldsymbol{\sigma = \frac{d}{RA}} \quad \textbf{(1)}$$

where d, R, and A represent the sample's thickness, resistance, and cross-sectional area, respectively. Jonscher's power law describes the dependence of the total conductivity σ(ω) on frequency, which includes AC and DC, given by [13, 14]:

$$\boldsymbol{\sigma(\omega) = \sigma_{dc}(0) + \sigma_{ac}(\omega) = \sigma_{dc} + A\,\omega^{s}} \quad \textbf{(2)}$$

where $\sigma_{dc}(0)$ is the DC conductivity independent of frequency(occurs due to free charges in the system), $\sigma_{ac}(\omega)$ is the AC conductivity dependent on frequency (occurs due to trapped charge), A is constant, and (s) is the frequency exponent (whose values are between 0 and 1), which reflects the level of contact between mobile ions and the lattice, and its fluctuation with frequency and temperature indicates the sort of conduction mechanism in the sample[14]. **Fig. 1(a: d)** show the effect of frequency on the AC conductivity of PVST-$_{3000\mu l}$EHA at various annealing times and temperatures. It can be noticed that the conductivity enhancement along the frequency range for all annealing times. The frequency exponent (s) in equation (2) was extracted from the slope of the plot of ln(σ) versus ln (ω) and it is listed in **Table. 1.**

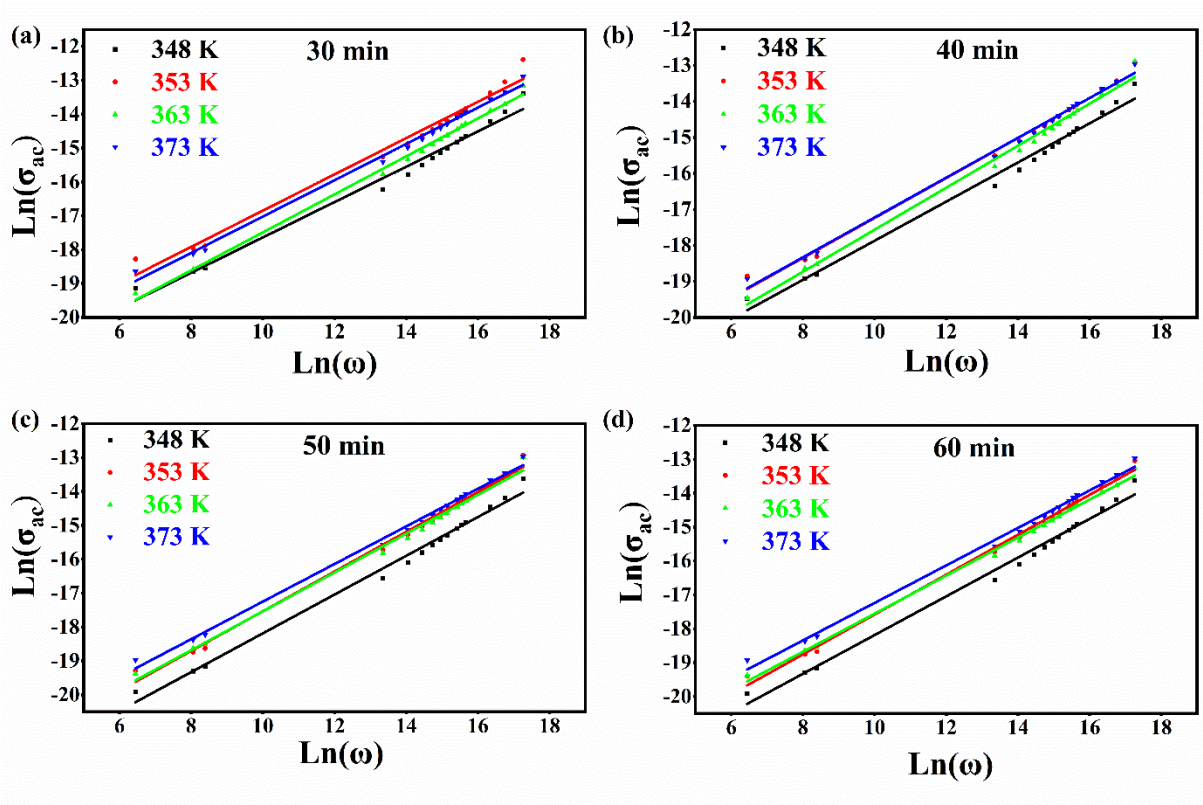

Figure 1(a: d) The effect of Angular frequency on AC conductivity (σ_{ac}) plot at various annealing times and temperatures (a) t=30 min; (b) t=40 min; (c) t=50 min; (d) t=60 min, for PVST-$_{3000\mu l}$EHA.

Table (1) The frequency exponent (s) values for PVST-$_{3000\mu l}$EHA at various annealing times and temperatures.

The exponent (s)				
Annealing temperature (K)	**Annealing time (min.)**			
	30	**40**	**50**	**60**
348	0.5214	0.5432	0.5718	0.5712
353	0.5347	0.5551	0.5859	0.5883
363	0.5603	0.5833	0.5729	0.5609
373	0.5356	0.5529	0.5546	0.5532

Table. 1 show the variation of (s) parameters with annealing times and annealing temperatures. It can be noticed that at low annealing times and temperatures on increasing behavior is observed up to a certain value which follows the NSPT model, while at high annealing times and temperatures, a decreasing behavior can be noticed which may be attributed to CBH model. Also, we can be noticed that the behavior for time=30 min as same as time=40 min, and the behavior for time=50 min as same as time=60 min. The change in reversal temperature with increasing time indicates that time is an influencing factor. **Fig. 2(a: d)** show the effect of temperature on AC conductivity for PVST-$_{3000\mu l}$EHA at various annealing times and constant frequencies according to Arrhenius equation (3) [16, 17]:

$$\boldsymbol{\sigma = \sigma_o \exp(\frac{-E_a}{KT})} \quad \textbf{(3)}$$

where σ, σ_o, K, E_a, and T are temperature dependence conductivity, pre-exponential factor, the Boltzmann constant, activation energy, and the temperature, respectively. It can be noticed that the conductivity increases with increasing temperature which may be due to the decreased viscosity and flexibility of the polymer matrix, which may boost charge carrier mobility and conductivity [14, 18]. The value of E_a for PVST-$_{3000\mu l}$EHA was calculated from the slope of the Arrhenius plot. It can be noticed that E_a increases with increasing annealing time and temperature. Also, as the frequency increases, the activation energy decreases, which may be attributed to the increased applied frequency enhancing the jumping of electrons between local states as shown in **Fig. 3.**

Fig. 4 shows the temperature dependence of the DC conductivity of PVST-$_{3000\mu l}$EHA at various annealing times. It can be observed that conductivity increases with increasing temperature. The activation energy (E_g) of DC conductivity was calculated according to equation (3) as observed in **Table. 2**. It shows that E_g increases with increasing annealing time**.**

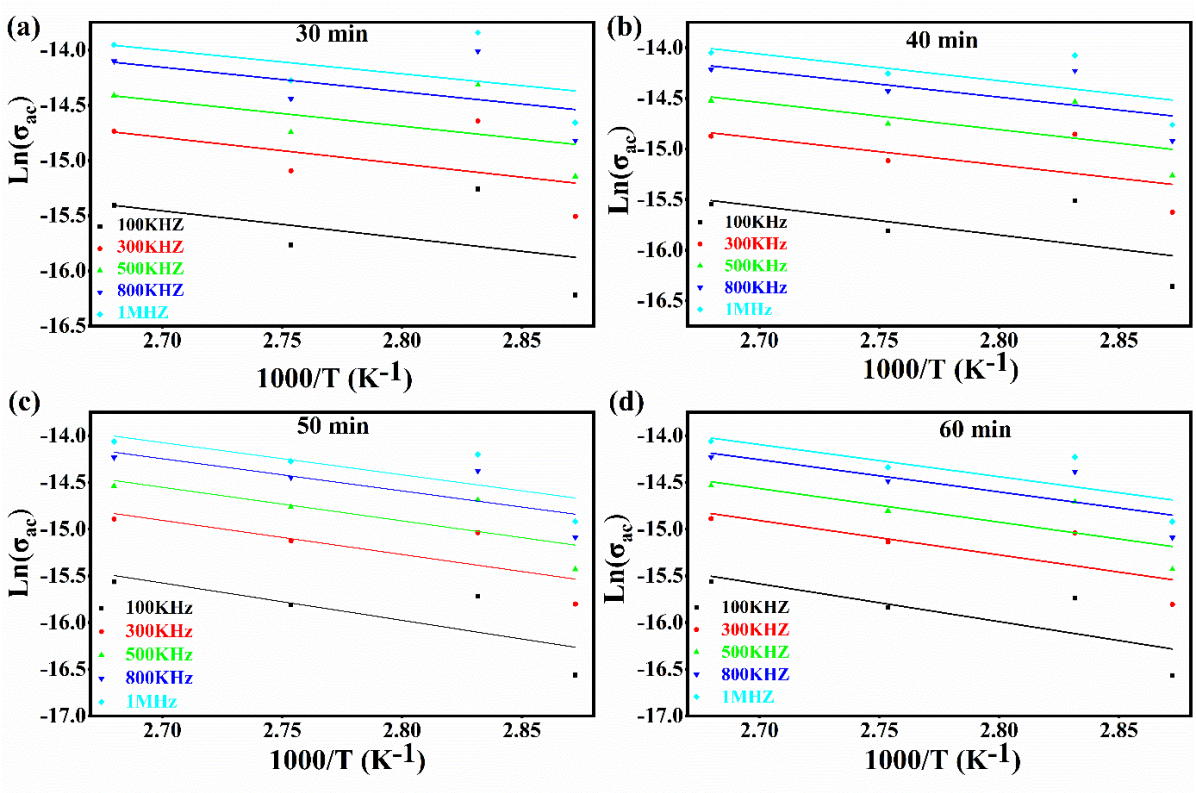

Figure 2 The effect of Temperature on AC conductivity (σ_{ac}) plot at various annealing times and constant frequencies; (a) t=30 min; (b) t=40 min; (c) t=50 min; (d) t=60 min, for PVST-$_{3000\mu l}$EHA.

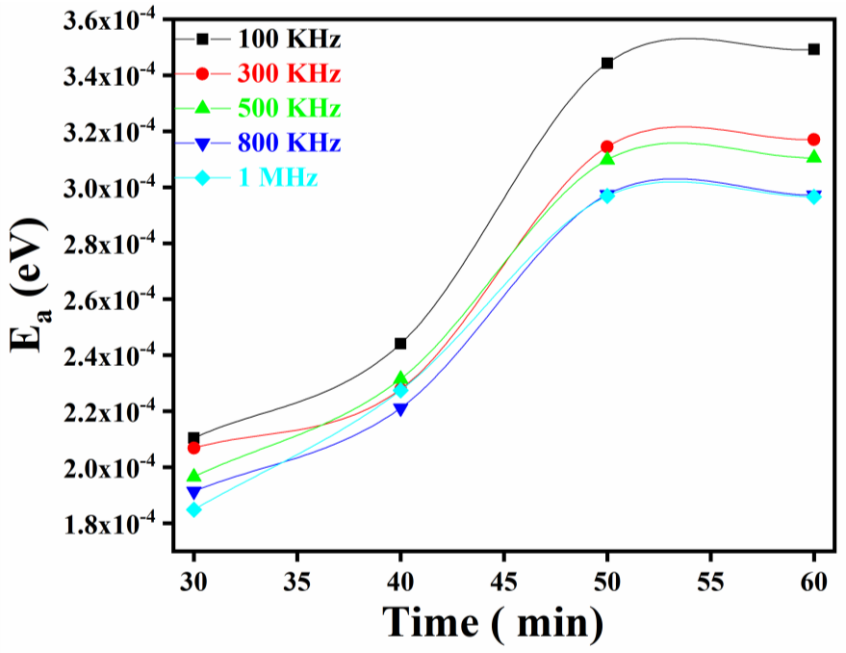

Figure 3 The variation of time with activation energy (E_a), for PVST-$_{3000\mu l}$EHA.

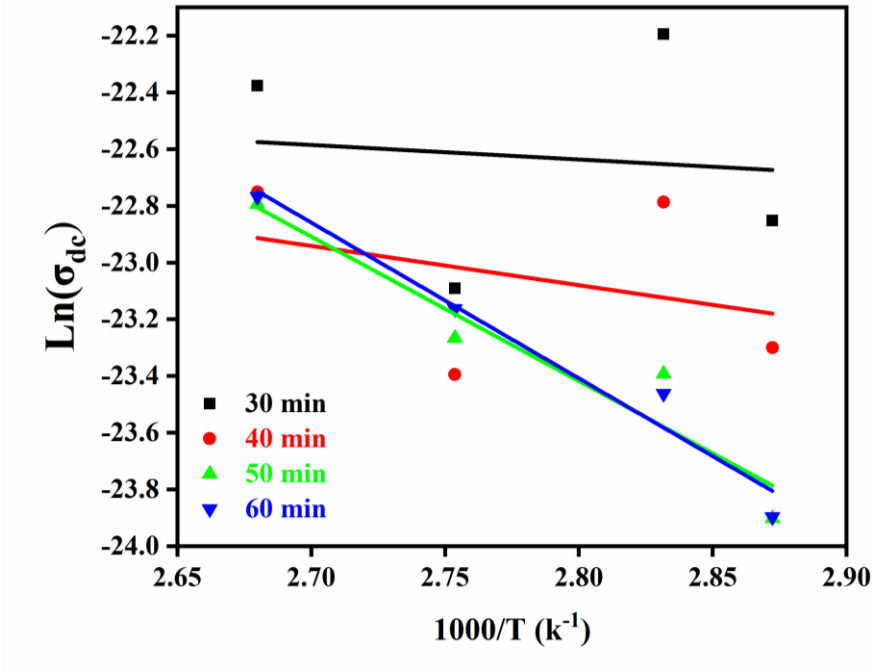

Figure 4 The effect of temperature on DC conductivity (σ_{dc}) plot at various annealing times.

Table 2 The values of activation energy ($E_{g)}$ of DC conductivity for PVSM-$_{3000\mu l}$EHA at various annealing times.

T (min)	E_g*10^{-5}(eV)
30	4.4126
40	11.928
50	43.889
60	47.3139

4. Conclusion:

AC conductivity of doped PVA with SiO_2, MgTIF, and EHA has been studied across a frequency range of 100Hz to 1MHz according to Jonscher's power law at various annealing temperatures and times. The frequency exponent (s) of Jonscher's law at low annealing times and temperatures on increasing behavior is observed up to a certain value which follows the NSPT model. In contrast, at high annealing times and temperatures, decreasing behavior can be noticed which may be attributed to the

CBH model. It has been found that E_a increases with increasing annealing time and temperature while decreasing with increased frequency. E_g increases with the time of annealing.

Ethical consideration:

The study was carried out according to the guidelines of the declaration of Benha University and approved by the Ethics Committee of the Faculty of Science, Benha University (Code: BUFS-REC-2024-262 Phy)

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