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# DIELECTRIC DISPERSION AND RELAXATION BEHAVIOUR OF SYNTHESIZED POLYMER ELECTROLYTE MEMBRANE FOR ELECTROCHEMICAL APPLICATIONS

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**Abstract -** *Sulfonated poly ether ether ketone (SPEEK) based polymer electrolyte membrane has been prepared by solution casting technique. The dielectric and proton conductivity of the blend membrane have been investigated by means of impedance spectroscopy which shows the existence of bulk and material-electrode interface properties of the membranes. The dielectric constant (ε' & ε") decreases with increase of frequency in the low frequency region due to the presence of space charge polarization whereas frequency independent behavior is observed in the high frequency region due to the dynamics of cations coordinated polymer chain segments. Moreover the electrical modulus formalism (M' & M") predicts a non Debye type relaxation. The scaling behavior of the membrane shows that the dynamical relaxation process is temperature as well as composition independent. The obtained results demonstrate that the developed composite membrane could be utilized for electrochemical applications.*

## 1. INTRODUCTION

The growing awareness on environmental issues and energy crisis due to depletion of fossil fuels pressing researchers in finding alternative source of energy with almost zero emissions. The development of polymer electrolyte membrane (PEM) with higher ionic conductivity is the main objective in recent research. PEM have been studied for their application in batteries, fuel cells and sensors. Fuel cells are excellent electrochemical energy conversion devices that directly convert the chemical energy of the fuel into electric energy with almost zero emission of unwanted gas [1]. PEEK is a highly thermoplastic polymer with excellent mechanical, chemical and thermal properties. Sulfonation of PEEK introduces hydrophilic properties to polymer. Polyethersulfone (PES) has high glass transition temperature, good mechanical, thermal and chemical stability. Blending of one polymer with another is an effective way of achieving good qualities of both the polymers [2]. It becomes important to understand the ion transport mechanism along with polymer segmental relaxation processes in polymer electrolytes. The main objective of this current work is to investigate the conductivity and dielectric properties of the prepared polymer electrolyte membrane. In this approach, both frequency and temperature are varied for dielectric spectroscopy, so that a wide range of molecular mobility can be examined.

## 2. Materials and Methods

Poly (oxy – 1, 4 – Phenyleneoxy – 1, 4 – Phenylene carbonyl – 1, 4 Phenylene) (PEEK; MW= 20800) (Sigma Aldrich, USA) Poly (oxy-1, 4- phenylene sulfonyl- 1, 4 – phenylene) (PES; MW=35000) (Sigma Aldrich, USA). N, N – Dimethyl sulfoxide (DMSO), Sulfuric acid ($H_2SO_4$) (98%) (Merck, Germany). The polymer electrolyte membranes were prepared by solution casting technique.

PEEK was sulfonated using sulfuric acid and the sulfonation of PEEK was carried out as reported earlier [3]. Appropriate weight ratio of SPEEK and PES polymer were dissolved separately in DMSO and the solutions were mixed together and casted in Petri dish then dried to form a blend membrane. Impedance analysis of the samples was carried out using frequency response analyzer from the impedance data Dielectric, Modulus and scaling parameters of the samples are studied.

### 3. Result and Discussion

The proton conductivity of SPEEK and their blend membranes is shown in Fig.1 (a). The conductivity of the blend membrane is less than the Pristine SPEEK membrane due to hydrophobicity of PES polymer. From the Arrhenius plot it is observed that as temperature increases conductivity also increases.

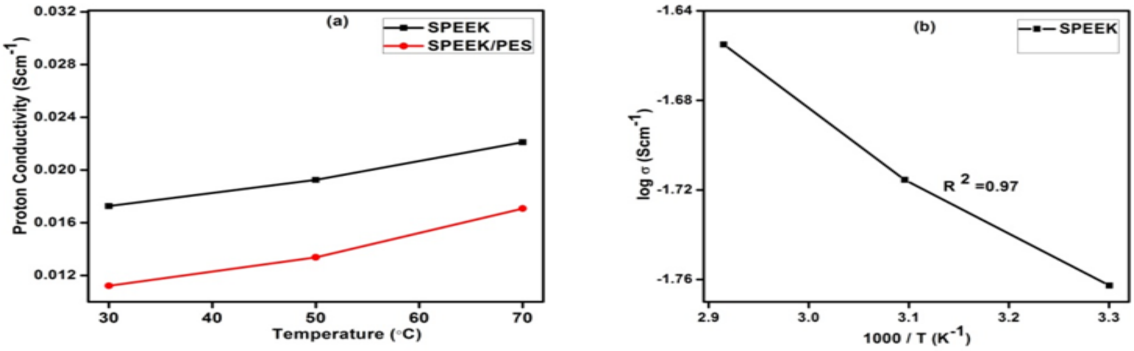


**Fig-1** (a) Proton Conductivity of SPEEK and Blend Membrane (b) Arrhenius plot of SPEEK membrane

The real (ε') and imaginary (ε") part of dielectric spectra of the membranes are shown in Fig. 2. There is a large increase in ε' and ε" values at lower frequencies due to the significant contribution of electrode polarization (EP) effect which mostly occurs in electrolytes as a result of an accumulation of ions near the electrode surfaces. Further, the ε" peak has a shift towards higher frequency side with increase of temperature which confirms the thermally activated dynamical behavior of the polymer electrolytes [4]. This increase in ε" is due to increase of ion concentration and mobility of ions with the increase of temperature.

The Electrical modulus is used to investigate conductivity and its associated relaxation in ionic conductors and polymers.

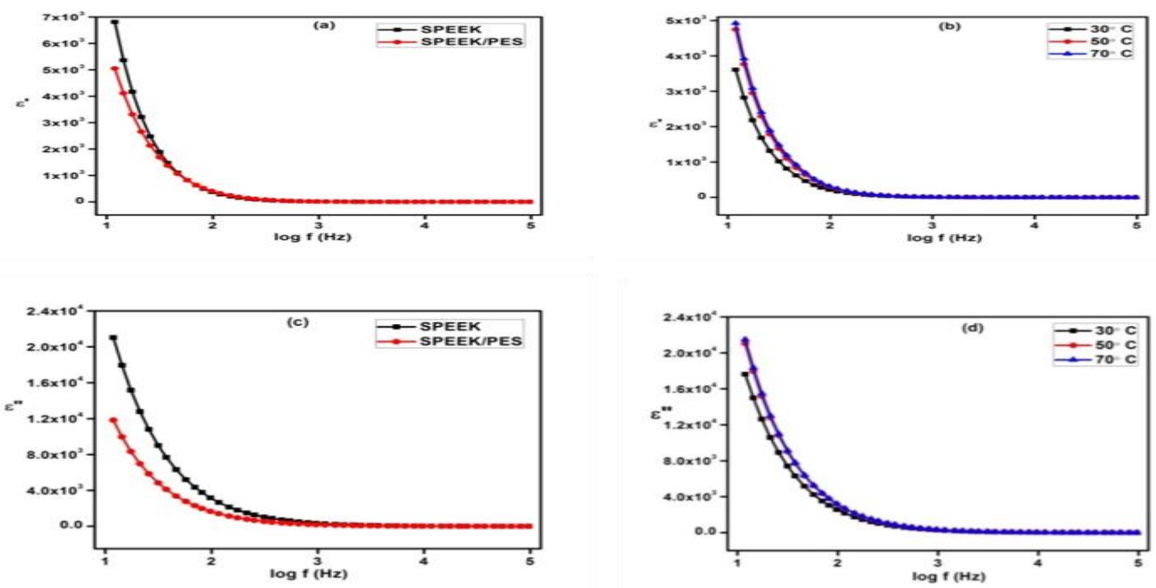


**Fig-2:** Dielectric spectra (ε' & ε") of SPEEK and Blend Membranes

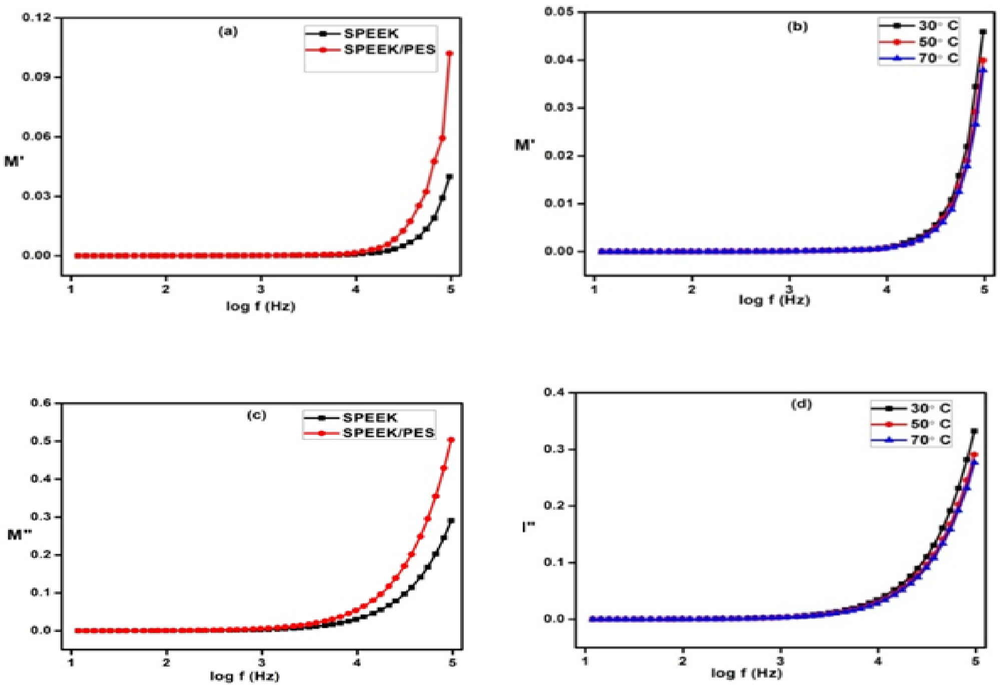


**Fig-3:** Modulus Spectra (M' & M") of SPEEK and Blend Membrane

Fig.3. shows the frequency and temperature dependence of modulus (M' & M") spectra for the membrane. At lower frequencies *M'* & M" values are very small, tend to be zero indicating the removal of electrode polarization, while the increase of modulus with increasing frequency is due to the distribution of relaxation processes over a range of frequencies. The reduction in the values of modulus at higher temperature results from the increase in the mobility of the polymer segment and charge carriers [5]. It is known that the maximum *M''* peak spectra for the highest conducting sample shifts to higher frequency compared to other sample indicating that the relaxation time decreases as conductivity increases.

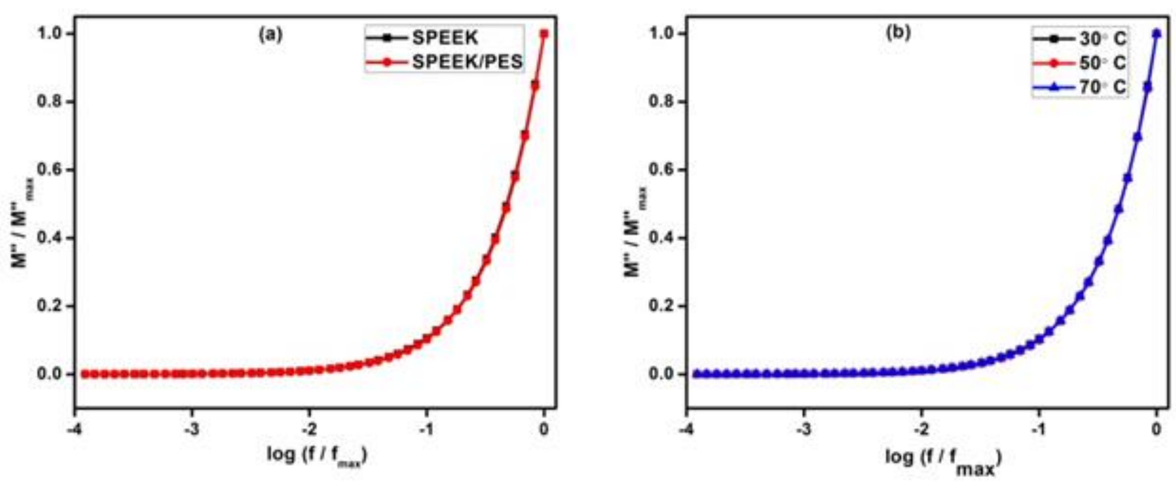


**Fig-4:** scaling behavior of (a) SPEEK and Blend Membranes (b) Temperature dependence of Membranes

The scaling of modulus data (M") provides information about relaxation dynamics with charge carrier concentration and temperature. From the Fig.4 it is obvious that all the spectra at different temperatures overlap on a single master curve indicating that the dynamical process occurring at different frequencies has the same thermal activation energy [5]. The occurrence of perfect spectral overlapping suggests a common relaxation mechanism in both the electrolytes.

## 4. CONCLUSION

The conductivity and dielectric behavior of polymer membranes were investigated in the 10 Hz to 1 MHz frequency range. The sample having higher conductivity has higher dielectric property. From the modulus spectra it is suggested that the ionic and polymer segmental motion are strongly coupled. The scaling behavior indicates the dynamical relaxation processes is temperature and composition independent for the prepared membrane.

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