Synthesis and characterization of PEO complexed with $NaClO_4$ soluble base salt and Nb_2O_5 Nano-filler

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Abstract— *Conducting solid phase polymer electrolyte (SPE) films were synthesized using solution casting method. The polyethylene oxide [PEO] complexed with an alkali salt sodium perchlorate [$NaClO_4$] and nano-filler Nb_2O_5 with varying weight percentile [5%-15%] ratios. The complexation of $NaClO_4$ salt with the polymer matrix PEO has been confirmed by XRD and surface morphology was understood by the SEM images and elemental composition was estimated by EDAX results. The AC conductivity measurements were done in the temperature range of 303K–343K using AC conductivity set up. The electrical conductivity shows an improvement and enhanced to fourth order. The conductivity in polymer electrolyte system is due to ions of alkaline salts and Nb_2O_5 nano-filler which are present in polymer matrix. Several electrical and dielectric characterizations were done for these films.*

Keywords— Activation Energy, Conductivity, Dielectric properties, Nanocomposite Polymer Electrolyte [NCPE], solution cast technique.

I. INTRODUCTION

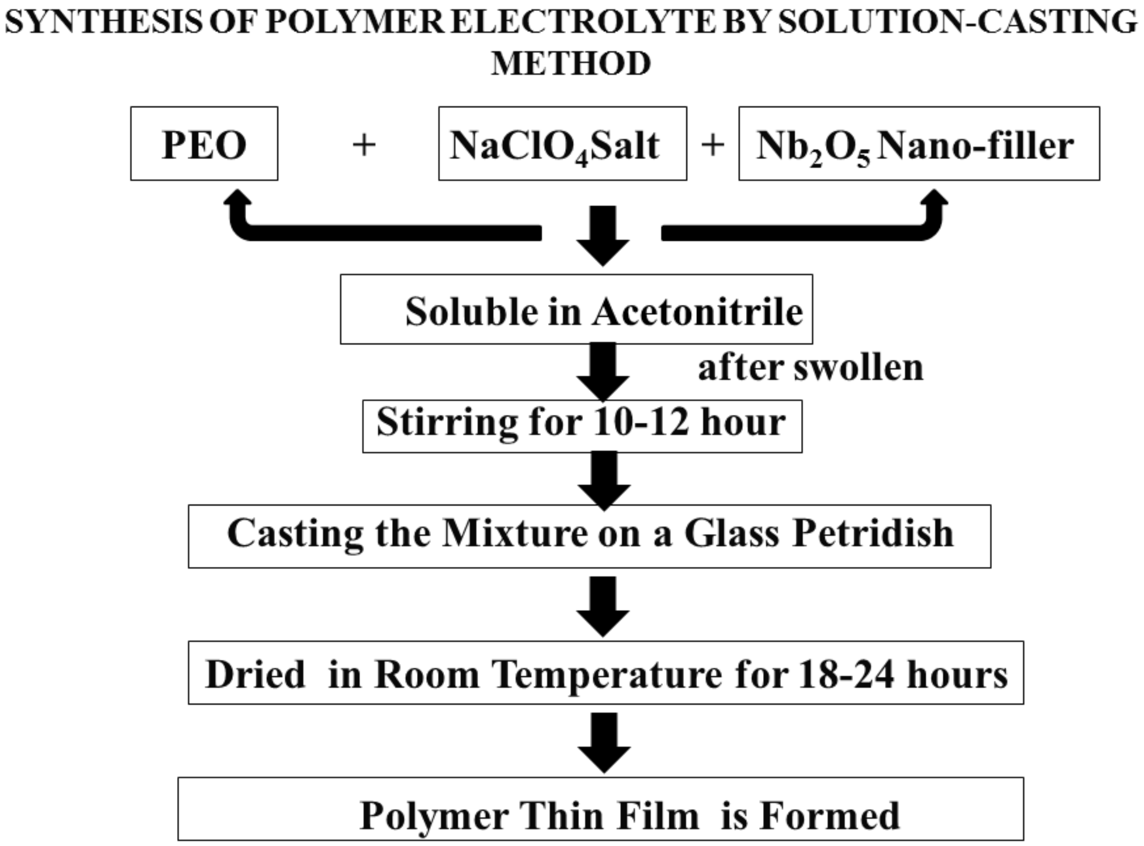
Solid polymer electrolytes [SPE], also named as ionic conductive polymers, make up of a new case of solid electrolytes, which have been intensively examined and developed since 1970s. In 1973, Wright [1,2] firstly described that polyethylene oxide (PEO)/salts complexes showed ionic conductivity concept. In 1979, Armand [3] claimed that the conductivity of PEO/salts complexes could achieve the order of 10^{-5} S cm^{-1} at 303K to 343K of temperature range. Most prominent alkali metal ions, for which polymer electrolytes have been originated, are Li^+ and Na^+ ions. In the present paper, we have discussed about PEO-$NaClO_4$ polymer-salt electrolyte complex where the conductivity is due to Na^+ion conduction. Earlier studies on Na^+ ion conducting polymeric electrolytes were on PEO complexes with $NaPF_6$[4], NaSCN, NaI and $NaCF_3SO_3$[5-7]. These electrolytes are utilized in solid state rechargeable sodium batteries [8,9]. It has been shown that PEO-$NaClO_4$ electrolyte is a Na^+ ion conducting polymer along with a partial contribution from anionic conduction. In order to improve the conductivity of PEO based electrolytes, at lower operating temperatures, researchers made many strategies to integrate a variety of nano-scale inorganic fillers such as SiO_2[10], Al_2O_3[11], TiO_2[12], ZnO[13], ZrO_2[14] and CeO_2[15] CuO[16] without affecting the other physical properties like mechanical stability, electrolyte reactivity towards electrode etc.,[17-20].

In the present study a systematic effort has been made to prepare and characterize the polymer electrolyte system (Consists of PEO as polymer) composed of sodium perchlorate ($NaClO_4$) as salt and Nb_2O_5 at 5, 10, 15Wt. % as nano-filler. The electrical conductivity of the polymer/salt complex films at 5 Wt.% of Nb_2O_5 concentration has been measured and found that the conductivity is maximum and also identified 5 wt% as an optimum conducting composition (OCC) of the Nb_2O_5 composite polymer electrolyte when compared to 10Wt.% and 15 Wt.% of Nb_2O_5. In this study, a systematic approach has been made to characterize by studying composition, structure, morphological, and electrical properties of the PEO-$NaClO_4$-Nb_2O_5 Nanocomposite polymer electrolyte (NCPE).

II. MATERIALS AND METHODS

PEO based polymer-salt electrolyte with nano-filler thin films were prepared by solution casting technique. PEO and $NaClO_4$ molar ratio 25:1 was taken from the optimized phase diagram of PEO-$NaClO_4$ system as a secondary host and PEO as primary host polymer matrix. The standard and simple technique solution casting method was used to prepare PEO-$NaClO_4$ composite polymer electrolyte films using acetonitrile as a common solvent. PEO (Aldrich) with molecular weight (MW) =106gr and $NaClO_4$ (sigma) with MW=122gr were dried in oven at 313K, for 1 hour prior to use. First, the weighted quantity of PEO and $NaClO_4$ were dissolved in acetonitrile solvent and stirred thoroughly for 4 hours at 308K temperature. The viscous solution was then put onto a teflon petridish and allowed to dry at room temperature for overnight. After that films were dried in oven at 318K for 18–24 hours to evaporate any residual solvent. Nb_2O_5 dispersed in composite polymer electrolytes in different weight percentages (i.e., 5, 10 and 15Wt.%) were also prepared by following the same subroutine process mentioned above. Thin films were preserved in a vacuum desiccator for the long term stability. Stable films from 5 Wt. %, 10 Wt. % and 15 Wt. % of Nb_2O_5 were prepared. Films are found very brittle beyond this concentration.

X-ray diffraction patterns of the pure Nb_2O_5 and the composite films were recorded by means of a high-resolution Rigaku X-ray diffractometer with Cu-Kα radiation over the Bragg angle (2θ) ranges from 10°–80°. The average size of the Nb_2O_5 polymer-salt composites was also estimated using XRD studies. Surface morphology and electrical properties of polymer-salt electrolyte samples were conventionally characterized by standard techniques. In this procedure, mobile ions were blocked at electrodes to generate space charge region. Electrical conductivity was determined by the movement of ionic space charge between blocking electrodes under the application of an AC field. AC conductivity of composite polymer electrolyte films was evaluated by Agilent LCR Precision Meter; model no 4980E which ranges from 20Hz-2MHz frequency. An external temperature setup was used in 303K–343K temperature range. In this set up nanocomposite electrolyte films were introduced between two polished copper blocking electrodes and temperature were monitored by Yudian PID temperature controller Model No.A1, with a thermocouple sensor. The process of synthesis of PEO/Salt with Nb_2O_5 nano-filler is explained clearly in the following flowchart 1.



III. RESULTS AND DISCUSSION

3.1 XRD ANALYSIS

XRD spectra of pure PEO, PEO-$NaClO_4$ with varying concentration of dispersed Nb_2O_5 filler composite polymers specimens were shown in the Fig.1. In Fig.1 peaks at 2θ=18.9° and 23°, corresponds to PEO crystallinity. When $NaClO_4$ was added to polymer matrix, decrease in crystallinity in $NaClO_4$ was observed and also confirmed by the intensity variation. It gives an idea that the crystalline state of PEO is disturbed by the Na^+ and O^- ions in polymer composite matrix. After the addition of Nb_2O_5 in PEO-$NaClO_4$ polymer-salt composite, the characteristic peaks of Nb_2O_5in composite which were due to incorporation?

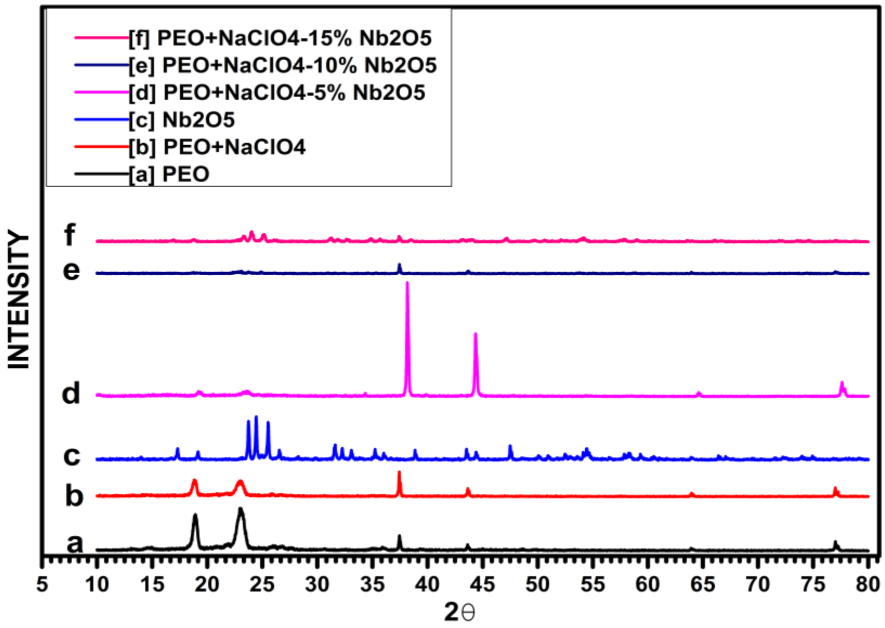


FIGURE 1: [a] PEO, [b] PEO-NaClO$_4$, [c]Nb$_2$O$_5$, [d]PEO-NaClO$_4$-5Wt.% Nb$_2$O$_5$, [e]PEO-NaClO$_4$ 10Wt.% Nb$_2$O$_5$,[f]PEO-NaClO$_4$-15 Wt.%Nb$_2$O$_5$.

The crystalline size of material was estimated using Scherer formula ($t = \frac{0.9}{\beta \cos(\theta)}$). The crystalline size of pure PEO, PEO-NaClO$_4$ is around 483.85 nm, 44.63 nm respectively. But when 5, 10, 15 Wt. % of Nb$_2$O$_5$ is added the crystalline size was varied as follows 52.67 nm, 46.68 nm, 46.06 nm respectively. It is noticed that due to the aggregation of PEO, NaClO$_4$ and Nb$_2$O$_5$ filler, the size of nano-composite decreases with increase in concentration of Nb$_2$O$_5$. The average size of the nano-composite is around 48.45 nm.

In Fig.1 [a] the peaks at 2θ = 19.1° and 23.5° are corresponded to (1 2 0) and (1 1 2) crystalline peaks of PEO[16]. The featured peaks of pure PEO in (PEO)$_{25}$:(NaClO$_4$)$_1$ complex (Fig.1[b]) shows variation in intensity suggesting that the ordering of the pure PEO is disturbed due to coordination interactions between the Na$^+$ ions and O$^-$ ions of PEO matrix polymeric chain. From Fig.1[c], it is also clears that, Nb$_2$O$_5$ particles are with 44.63 nm crystalline size. After the addition of Nb$_2$O$_5$ nano-filler in polymer electrolyte matrix, some fresh peaks were appearing. This corresponds to resembling the peaks of Nb$_2$O$_5$ presence as shown in Fig 1[d], [e] and [f]. This confirms the size of Nb$_2$O$_5$ nano-particles increases in 5Wt.% then decreases in 10 Wt.%, 15 Wt.% Nb$_2$O$_5$ concentrations. Due to aggregation in the composite with PEO matrix, NaClO$_4$ salt and Nb$_2$O$_5$, the crystalline size decreases in increasing concentrations.

3.2 SEM-EDAX

Surface morphology of electrolytes with 5Wt.%, 10Wt.% & 15Wt.% of Nb$_2$O$_5$ filler samples and their corresponding EDAX spectra were shown in Fig.2. Furthermore it is observed that PEO molecules are deposited on the surface of larger particles due to the interaction between PEO-NaClO$_4$ and Nb$_2$O$_5$.

The SEM image in Fig.2 shows the morphology of pure PEO compared with PEO-NaClO$_4$ and varying Wt.% of Nb$_2$O$_5$ substituted in PEO-NaClO$_4$ matrix. The SEM image in Fig.2[a] clearly shows that the morphology of pure PEO is very rough without any crystallites or particles on it and confirmed the elements present in PEO with EDAX result Fig.2[a$_1$]. In Fig.2[b] PEO-NaClO$_4$ show very smooth matrixes and clear surface morphology with rarely substituted grains on the surface and a respective EDAX result shown in Fig.2[b$_1$]. From the Fig.2[c], [d] and [e]which look like in flakes with rare presence and mostly sphere shaped granules on the polymer matrix.

Thus we conclude that there was a significant change in the morphology after the casting of NaClO$_4$ and Nb$_2$O$_5$ on PEO compared with pure PEO. From the EDAX results

<u>SEMEDAX</u>

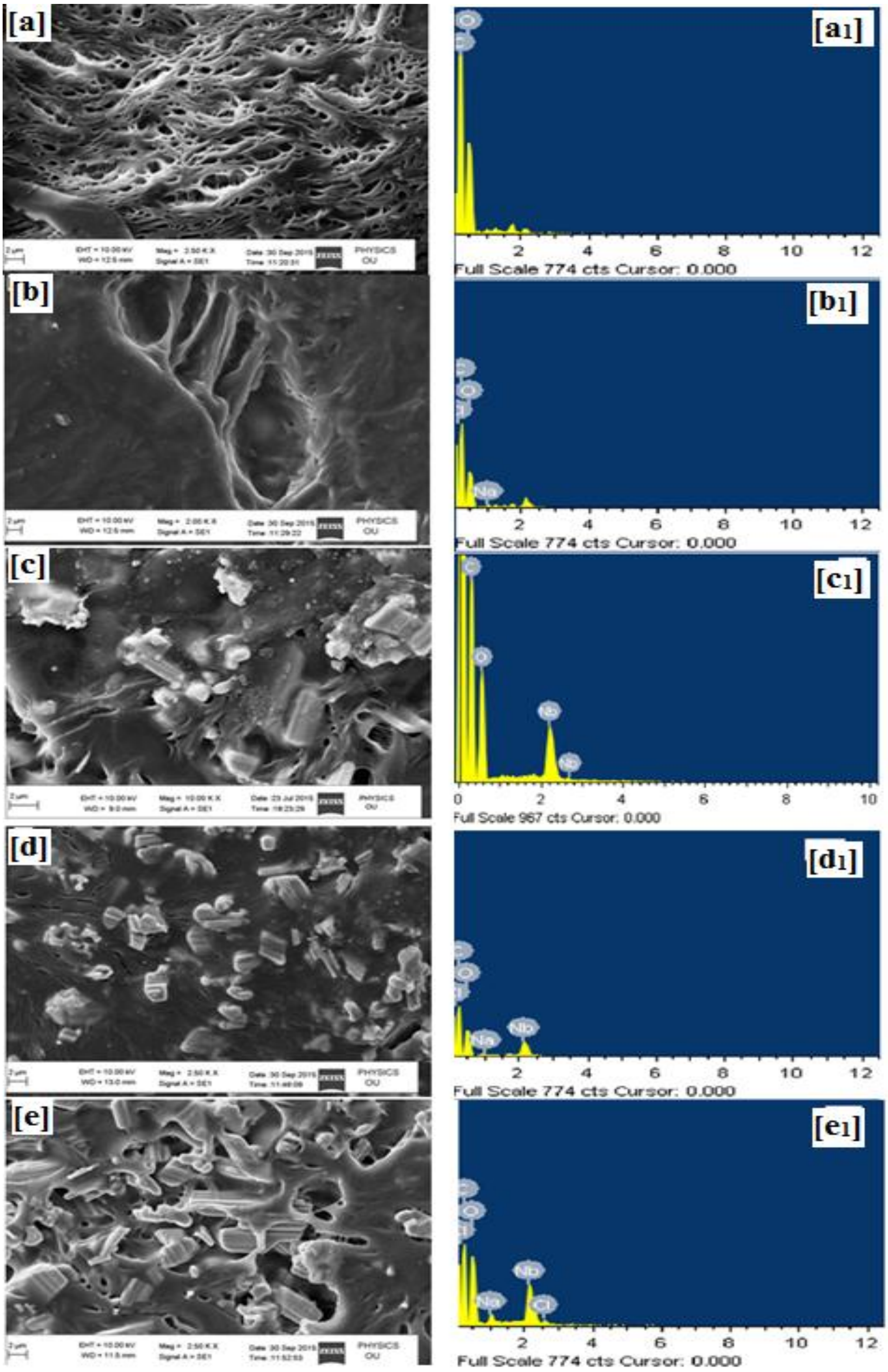


FIGURE.2: SEM Images [a]PEO, [b]PEO-NaClO$_4$, [c]Nb$_2$O$_5$,[d]PEO-NaClO$_4$,-5Wt.%Nb$_2$O$_5$, [e]PEO-NaClO$_4$-10Wt.%Nb$_2$O$_5$,[f]PEO-NaClO$_4$-15 Wt.% Nb$_2$O$_5$. and EDAX images[a$_1$]PEO,[b$_1$]PEO-NaClO$_4$,[c$_1$]Nb$_2$O$_5$,[d$_1$]PEO-NaClO$_4$-5Wt.%Nb$_2$O$_5$,[e$_1$]PEO-NaClO$_4$-10Wt.%Nb$_2$O$_5$,[f$_1$]PEO-NaClO$_4$-15 Wt.% Nb$_2$O$_5$.

Fig.2 [c_1],[d_1] and [e_1] represents the elements of PEO, $NaClO_4$ and Nb_2O_5 and the variation of the concentration of Nb_2O_5 fillers. Among the SEM images, when compared to Fig.2[d],[e] the Fig.2[c] has showed good results in electrical properties. This is due to 5Wt.% Nb_2O_5 granules werewell framing with mechanical strength and distributed of the granules in PEO-$NaClO_4$ polymer-salt matrix than other Nb_2O_5 concentrations.

3.3 Electrical studies:

The temperature dependence of AC conductivity of PEO, PEO-$NaClO_4$, PEO-$NaClO_4$ with (5, 10, 15Wt.% Nb_2O_5) is shown in Fig.3. It is observed that the conductivity plots have mostly positive temperature coefficients within the evaluated 303K-343K temperature range.

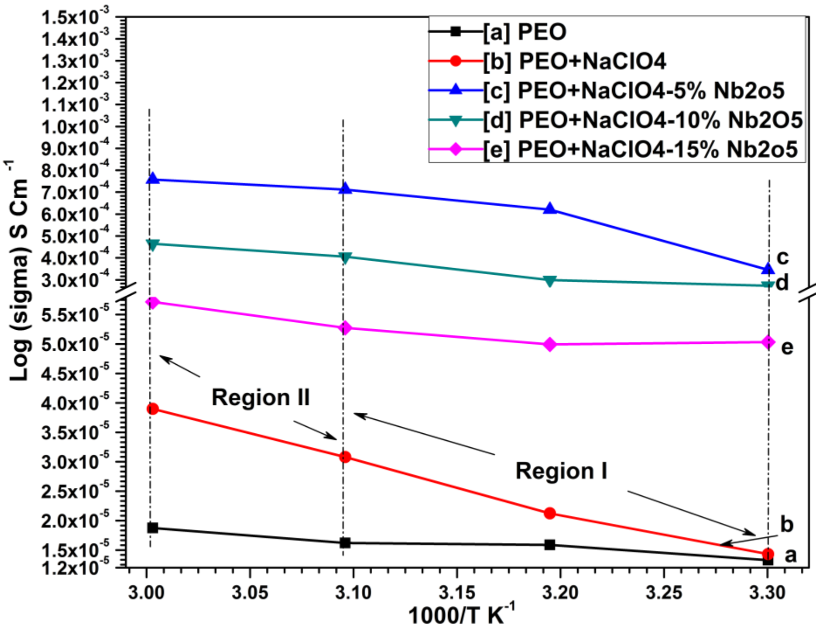


FIGURE.3: Arrhenius type Temperature dependent conductivity plots of [a]PEO, [b]PEO:$NaClO_4$::25:1, [c]PEO-$NaClO_4$-5 Wt.%Nb_2O_5; [d]PEO-$NaClO_4$-10 wt.% Nb_2O_5; [e]PEO-$NaClO_4$-5 Wt.% Nb_2O_5-15 wt.% Nb_2O_5.

Arrhenius type plot shows dissimilar linear behavior in two regions (above and below the melting point i.e., 323K) of PEO-$NaClO_4$-Nb_2O_5 polymer-salt nanocomposite electrolytes. Conductivity as a function of 5, 10, 15 Wt.% varying Nb_2O_5 concentrations with different temperature range (303K -333K) were shown in Fig.3. As the samples start melting from 323K so that the variation beyond 323k temperature can be observed in Fig.3.The AC conductivity at each temperature was measured and found that the conductivity reaches to an optimum value in 5wt.% of the Nb_2O_5 nano-filler than other Wt.%. At 303K and 333K temperatures the AC conductivity of 5wt% Nb_2O_5 reported as 3.4524×10^{-4} S cm^{-1} and 7.5754×10^{-4}S cm^{-1} respectively. Conductivity enhanced to third order range from fourth order was remarkable in this optimized 5wt% of Nb_2O_5 filler concentration. The enhancement of conductivity was achieved in this group of polymer-salt complex system with Nb_2O_5 nano-filler.

In addition of nanoparticles in polymer–salt complex creates an interface on surroundings of Nb_2O_5. Lewis acid–base interaction between the polar surface groups of Nb_2O_5 and the electrolyte ions prefers the dissolution of the $NaClO_4$ salt and produces to the greater extent of conducting pathways. Ion conduction mechanisms have been described before in the case of other nano-sized materials as fillers in polymer composite electrolytes [11,18,21]. As the Nb_2O_5 concentration is increased, fatherly a cut-down in conductivity was observed in Fig.3[d] with Nb_2O_5 10Wt.%. This drop of conductivity can be specified as blocking effect. These effects on the transport of charged carriers resulting from the collection of high concentrations of Nb^{2+}–Na^+ rich domains. Conductivity depends on the degree of crystallinity. Conductivity decreases with the decrease of crystallinity when filler are complexed with polymer-salt matrix, as the crystalline size of 15wt.% Nb_2O_5 has less when compared to other concentrations.

It is experimentally observed that the sample starts melting from 323K temperature in thermal furnace. It is also confirmed from Fig.3, a typical drop or raise at this temperature. These behaviors are ordered with Arrhenius type charge conduction in polymer-salt electrolyte complex with nano-fillers which can be expressed by equation (1).

$$\sigma = \sigma_0 \exp(-E_a / kT) \tag{1}$$

Whereas the σ_0 isa pre-exponential factor, E_a is the activation energy and 'k' is the Boltzmann's constant. The variation of activation energy (E_a) was above and below the melting temperatures reputed as Region I, Region II in Fig.3.

The variation of AC conductivity as a function, Nb_2O_5 concentrations is shown in Fig.4.

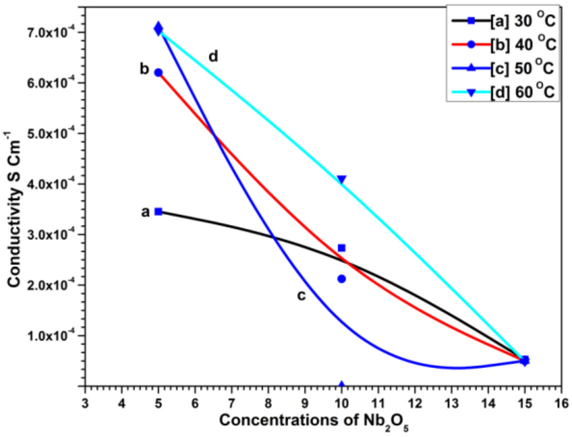


FIGURE.4: CONDUCTIVITY VARIATION WITH (POLYMER/SALT) WITH VARYING Nb_2O_5 CONCENTRATION AT DIFFERENT TEMPERATURES.

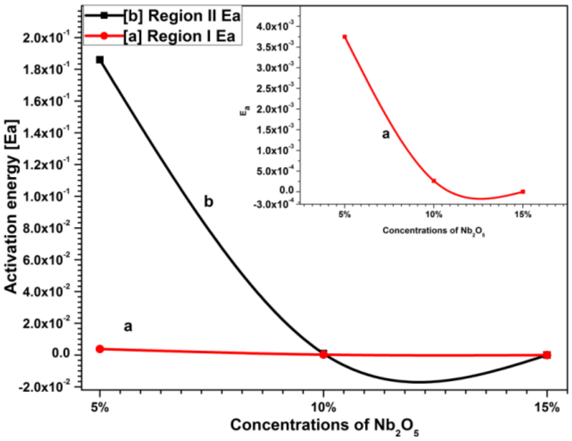


FIGURE.5: VARIATION OF ACTIVATION ENERGY (E_a) WITH DIFFER CONCENTRATIONS OF (A) ABOVE THE MELTING TEMPERATURE. (B) BELOW THE MELTING TEMPERATURE WITH Nb_2O_5 CONCENTRATION

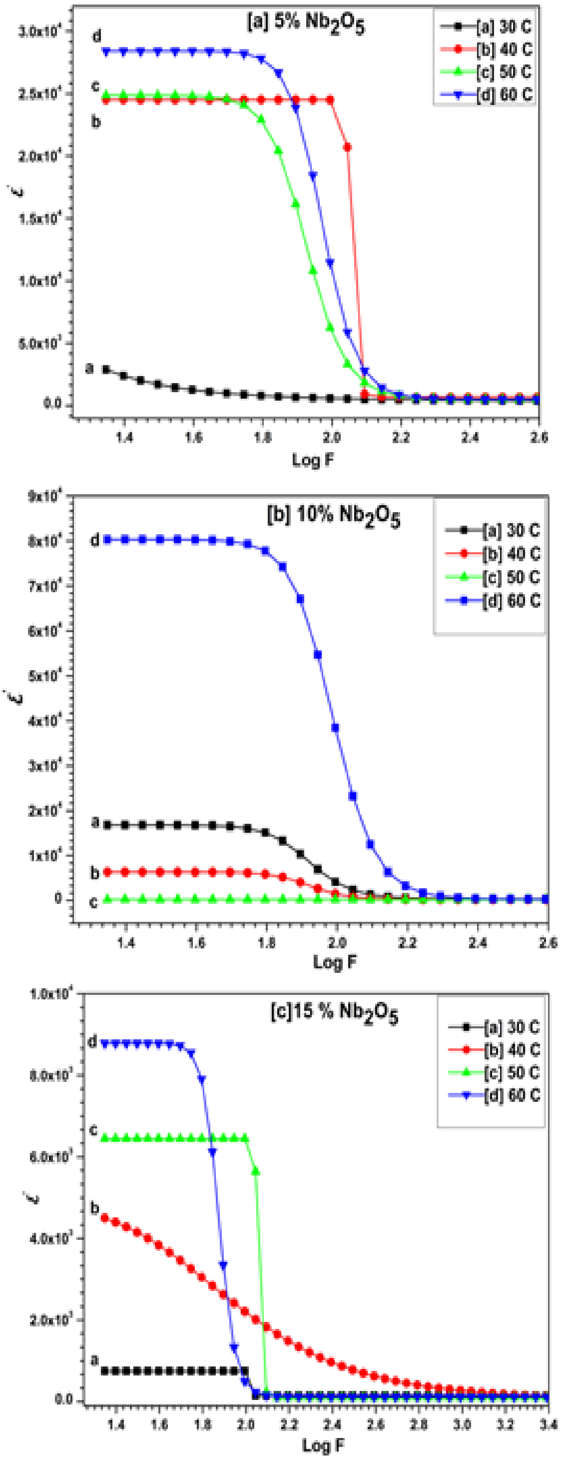
The filler deposited polymer composites has low conductivity in low temperature range as shown in Fig 4[a],[b]. In Fig.4[c],[d] shows the variation of conductivity, as the temperature reaching and crossing the melting temperature for 5 Wt.%, 10Wt.% and 15Wt.% concentrations of Nb_2O_5. When comparing them, the 5 Wt.% shows an increased conductivity than 10 Wt.% and 15 Wt.% Nb_2O_5 concentration.

Variation of E_a with varying concentration with Nb_2O_5 filler describes In Fig.5.It is evident from the plot, which shows two types of activation energies from the slope of the curve like Region-I and Region-II. The activation energy for both regions exists coherent with conductivity as shown in Fig.5.The plots [a],[b] in Fig.5 also indicate that the ionic conduction process depends on the Nb_2O_5 concentration.

3.4 Dielectric studies:

The real part of dielectric permittivity or dielectric constant (ε') and imaginary part of dielectric permittivity or dielectric loss (ε''), for the samples measured in the frequency range of 20Hz-2MHz with varying temperature from 303K-343K is shown in Fig.6[a],[b] and [c]. It is observed that ε' was decreased rapidly at lower frequencies and indicates nearly frequency independent behavior at higher frequency range[22].

The bulk polarization of sample results from presence of electrodes, which don't transfer the charge species into the external circuit. At higher temperatures, ε' is observed to be increased and it might be due to migration of the Na^+ and Nb^{2+} ions in polymer-salt complexes. At lower frequency range, the charge carriers will no longer be capable to revolve rapidly. So, their oscillation will begin to lay behind this field resulting in decrease of dielectric permittivity, ε'at low frequency region, the permanent dipoles align themselves along the field and add fully to the entire polarization of dielectric. At higher frequency range, the variation in the field is really rapid for dipoles to coordinate themselves, so their contribution to the polarization and hence, to dielectric permittivity can turn negligible. Consequently, the dielectric permittivity, ε' decreases with increasing frequency. The decrease of the dielectric constant ε' can also explain from interfacial polarization. The interfacial polarization develops as a result of conflict in conducting stage, but is interrupted at grain boundary due to lower conductivity. In general poly-crystalline materials, the grains shows semi conducting behavior while the grain boundary are insulators.



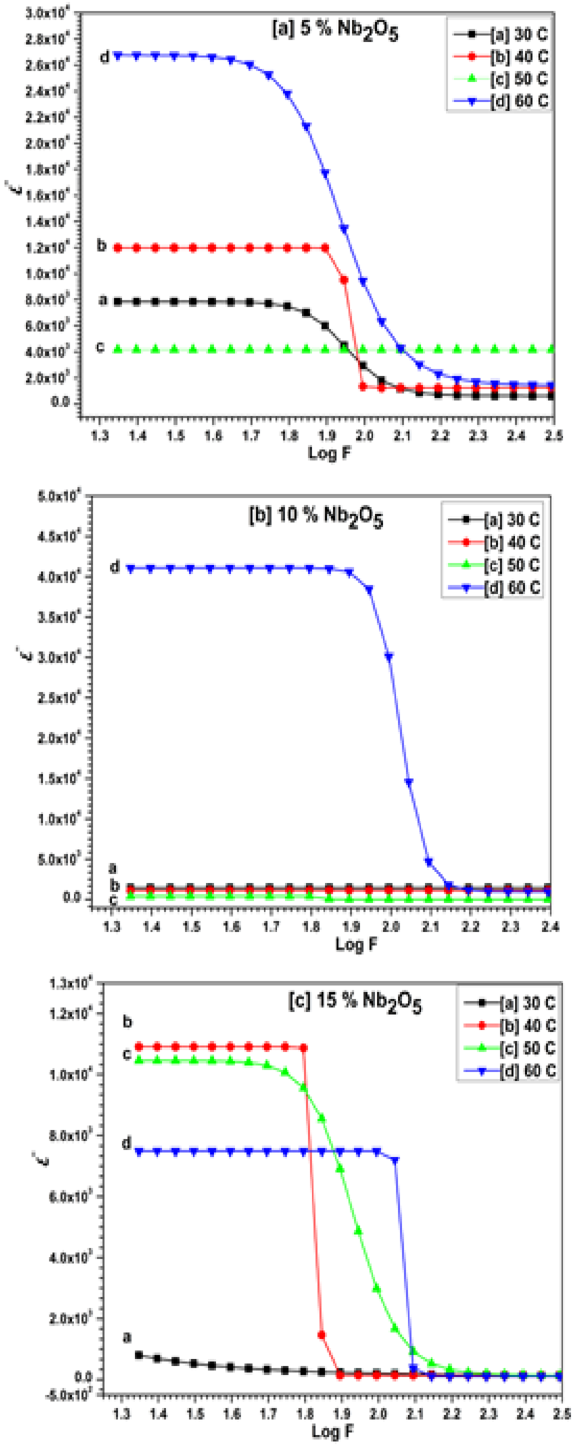


FIGURE.6.[A],[B]&[C] VARIATION OF DIELECTRIC CONSTANT (ε') WITH RESPECT TO FREQUENCY AT VARIOUS TEMPERATURES OF 5, 10, 15WT.% Nb_2O_5 RESPECTIVELY

FIGURE.7. [A],[B]&[C] VARIATION OF DIELECTRIC LOSS (ε'') WITH RESPECT TO FREQUENCY AT VARIOUS TEMPERATURES OF 5, 10, 15Wt.% Nb_2O_5 RESPECTIVELY.

The frequency dependence of dielectric loss, ε'' at different temperatures is shown in Fig.7[a],[b] and [c]. The maximum in dielectric loss ε'' peaks shifts towards lower frequency range as the temperature increase indicating a thermal activated behavior. Mostly, the dielectric losses (ε'') at low frequencies are much higher than those occurring at higher frequencies at specific temperature. This kind of dependence of ε'' on frequency is typically associated with losses by conduction.

IV. CONCLUSION

PEO-$NaClO_4$-Nb_2O_5 polymer-salt with nano-filler complex thin films were synthesized by solution-cast technique with three (5, 10, 15 wt.%) Nb_2O_5 varying concentrations. Structure and grain size of the films were studied and estimated as 46.06 nm, 46.63 nm and 52.67 nm respectively. Surface morphology was analyzed by SEM and elemental confirmation analysis was done by EDAX and found that all the films were nearly stoichiometric. As an application part the electrical conductivity and dielectric studies were done for the same respective samples. The plot of log conductivity against reciprocal temperature obeys Arrhenius rule. The ionic conductivity range of samples collection was found to be enhanced from 1.874×10^{-5} S/cm to 7.55754×10^{-4} S/cm by increase in temperature from room temperature to 343 K. Hence 5 Wt.% Nb_2O_5 nano-particles to polymer-salt composite can be treated as an optimized conducting composite (OCC). Calculated activation energy [E_a] from the Arrhenius plots was found to be 0.189 eV. The dielectric ε' constant and dielectric loss ε''were found to decrease with increase in frequency.

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