Effect of Al_2O_3 Concentration on Conductivity and Relaxation Properties of Two Different PVA-PEO Blend Systems: A Comparative Study

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ABSTRACT: *Two PVA-PEO nano-composite blend systems, i.e. System-I: PVA-PEO-LiCF₃SO₃-EC and System-II: PVA-PEO-AgNO₃-PEG, are prepared using solution technique for different compositions of Al_2O_3 nano-filler (0-10wt%). Conductivity and relaxation properties of these systems are investigated using impedance spectroscopy. Relaxation dynamics for varying concentrations of nano-filler in these systems is investigated using modulus formalism wherein, variation of relaxation time values, calculated from M" vs. log f spectra are compared with conductivity variation at different Al_2O_3 concentration to closely inspect relationship between conductivity and relaxation properties. Scaling of modulus with nano-filler concentration is carried out to analyze time-composition superposition principle and dependency of relaxation dynamics on nano-filler concentration.*

Keywords: Conductivity, Modulus, Nano-composite Blend, Relaxation Time, Scaling

I. INTRODUCTION

"Blending" of polymers is one of cheap and easy techniques used nowadays for the preparation of polymer electrolytes, compared to systhesizing a new polymer; wherein, the polymers are mixed physically and the final blend electrolyte thus obtained consists of the desired properties of each of the host polymers and possesses enhanced conductivity and improved properties [1, 2]. Further, addition of plasticizers in the desired proportion also aids in improving the electrical properties of the electrolytes by increasing conductivity, but at times, these plasticizers may deteriorate the mechanical properties of the polymer electrolytes. In order to resolve this problem upto a certain extent, nano-fillers such as TiO_2, SiO_2, Al_2O_3, etc., consisting of nano-sized filler particles are incorporated into these electrolytes. This not only improves the mechanical properties but also enhances the conductivity and relaxation properties of the electrolyte by affecting the crystallinity of polymer matrix, free volume hole size distribution, crosslinking density of the matrix, mobility of polymer chain segments and chain packing [3-5], by favoring dissociation of salt to form free ions that contribute in conduction process and also by inhibiting crystallization and recrystallization processes [6]. Such formed polymer electrolytes consisting of nano-particles are called as *"polymer nano-composites"* [5]. In the view of this discussion, two new PVA-PEO nano-composite blend electrolyte systems given as System-I: PVA-PEO-LiCF₃SO₃-EC-$(Al_2O_3)_x$ and System-II: PVA-PEO-AgNO₃-PEG-$(Al_2O_3)_x$, (x=0 to 10wt%) are prepared and examined. The major aim of the present study is to investigate the effect of Al_2O_3 amount on conductivity and relaxation properties in these two systems. The variation in conductivity with nano-filler concentration of Systems-I and II are compared and correlated. Similarly, the comparison and correlation of the relaxation properties of these two systems is being done. The dependency of relaxation dynamics of both these systems on nano-filler concentration is also examined by carrying out Al_2O_3 composition-wise scaling of frequency dependent imaginary modulus (M").

II. EXPERIMENTAL PROCEDURE

The polymeric blend films for the two nano-composite systems; i.e., System-I: PVA-PEO-LiCF₃SO₃-EC and System-II: PVA-PEO-AgNO₃-PEG; consisting of different concentrations of Al_2O_3 nano-filler ranging from 0 to 10wt%; are prepared using solution cast technique wherein, required proportions of PVA, PEO, LiCF₃SO₃, EC, AgNO₃ and PEG for the respective systems, are allowed to dissolve in de-ionized water (solvent) using magnetic stirrer, for about 24 hours till the solution appeared completely homogeneous. Later, thus, obtained homogeneous solution, was poured in a teflon petridish and kept in a hot air oven at about 45°C for the complete evaporation of the solvent and to obtain perfectly dried blend films. The conductivity and relaxation studies of these perfectly dried blend films of both, Systems-I and II are carried out using SOLARTRON 1260 Impedance Gain/Phase Analyzer in the frequency range of 10Hz to 20MHz.

III. RESULTS AND DISCUSSION

DC conductivity is one of the most important parameters which throw light on the conduction properties of any system. Hence, for the present Systems-I and II, DC conductivity variation with Al_2O_3 concentrations is investigated thoroughly. As observed from Fig. 1, the conductivity of System-I drops initially with Al_2O_3 incorporation upto 6wt%. This may be due to the gradual formation of neutral aggregates of nano-filler particles at initial levels of filler concentrations, which in turn creates blockages in the conducting pathways, reduces the free volume, increases the crystallinity of the blend matrix and obstructs the movement of mobile ions and polymer segments through the matrix. Moreover, the formation of neutral aggregates also lower the number of mobile ions participating in conduction process. All these factors altogether reduce the ion and segmental mobility through the blend matrix and hence, lead to the drop in conductivity with increment in Al_2O_3 concentration upto 6wt% in the blend. This type of initial drop in conductivity with increasing amount of nano-filler is also observed by *J.E. Weston et. al.* [7] in $LiClO_4$-PEO-α-alumina system, by *D. Shanmukharaj et. al.* in PMMA-PEO:$LiClO_4$-EC/PC-Al_2O_3/TiO_2 [8] and PEO-$LiN(CF_3SO_2)_2$-SBT [9] systems and by *A. Sarnowska et. al.* in Al_2O_3 and TiO_2 doped (PVdF-HFP) [10] based system. However, in the present System-I, at higher concentrations of Al_2O_3 (>6wt%) the conductivity enhances systematically. At higher filler concentrations, the random distribution of filler particles may have initiated the process of formation of free volume in the blend matrix. This process of free volume formation gradually dominates the process of formation of neutral aggregates with filler addition, at higher filler amount (>6wt%), and this in turn facilitates amorphous phases in blend matrix, thus making the system flexible. This further avails the conducting pathways for ionic and segmental mobility and promotes the conduction process, which results in conductivity enhancement with Al_2O_3 concentration > 6wt%. On the contrary, as observed from Fig.1., System-II shows the reverse variation in conductivity with Al_2O_3 filler amount than that observed in System-I. Hence, the process of conduction is expected to occur differently in System-II from that taking place in System-I. In System-II, initial increment in the conductivity with the increasing Al_2O_3 filler concentration upto 6wt% suggests the formation of free volume and amorphous phases in the blend matrix due to enough separation between filler particles at low filler concentration. This further avails conducting pathways and provides flexibility to blend matrix which gradually promotes mobility of ions and polymer segments through matrix and leads to conductivity enhancement.
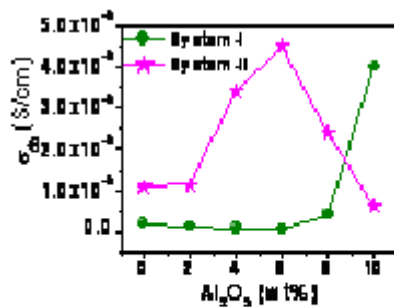

Fig. 1: variation in dc conductivity at various Al_2O_3 concentrations in Systems-I and II at 323K.
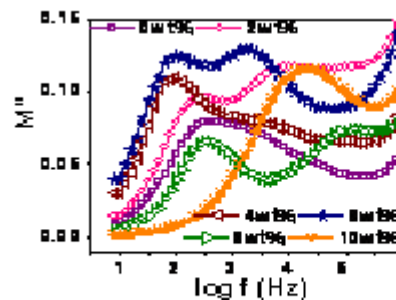

Fig. 2(a): Plot of Imaginary part of modulus (M") vs. log f of System-I for various Al_2O_3 concentrations at 313K.

However, beyond 6wt%, the conductivity gradually drops with increase in Al_2O_3 concentration. At higher filler concentrations, the filler particles are very close to each other and hence they form neutral aggregates. This blocks the conducting pathways, reduces the free volume and increases the crystalline phase in the blend matrix which in turn obstructs the movement of ions and polymer segments through the matrix. Moreover, the formation of neutral aggregates reduces the number of ions participating in conduction and further leads to fall in conductivity at Al_2O_3 concentration > 6wt% [3, 4, 11-13]. The similar behavior of conductivity with Al_2O_3 filler concentrations as observed in the present system is also observed by *M.R. Johan* in PEO-$LiCF_3SO_3$-EC-xwt% Al_2O_3 system [3], by *H.M.J.C Pitawala et. al.* in PEO_9-LiTf+xwt% Al_2O_3 system [4], by *M.A.K.L. Dissanayake et. al.* in their PEO_9-LiTf+xwt% Al_2O_3 system [11], by *P. Ekanayake et. al.* in PEO_9-$Mg(ClO_4)_2$-Al_2O_3 system [12] and in PE-supported P(AN-*co*-MMA)-Al_2O_3 system [13] by *M. M. Rao et. al.* The comparative study of DC conductivity of Systems-I and II indicate that upto 8wt% Al_2O_3, the System-II shows better conductivity than System-I but beyond 8wt%, the reverse is observed. The specimens consisting of 10wt% of Al_2O_3 of System-I and of 6wt% of Al_2O_3 of System-II show optimum values of conductivity. Additionally, relaxation dynamics of present Systems-I and II is investigated by using modulus formalism. The plots of frequency dependent imaginary part of modulus (M") for Systems-I and II are shown in Figs. (2a) and (2b), respectively. As observed from the modulus spectra, there exists a prominent peak in the low frequency

$(10^1-10^3 Hz)$ region for all blends of System-I and for all specimens of System-II, high frequency $(10^4-10^6 Hz)$ region shows the presence of such a prominent peak. These prominent peaks contribute to the "primary relaxation" process. For System-I, with initial increase in Al_2O_3 amount, frequency, 'f_{max}' associated with peak maxima shifts gradually towards lower frequency side, but beyond 6wt% of Al_2O_3, the peak maxima gradually shifts in the opposite direction. The reverse is observed for System-II, wherein, the maxima of the prominent high frequency peak shifts initially towards higher frequency region with Al_2O_3 upto 6wt% and beyond this amount the shift in peak maxima occurs towards lower frequency side. These 'f_{max}' values are further substituted in the equation, "$\tau = (1/2\pi f_{max})$" to calculate conductivity relaxation time (τ) and to analyze ionic conduction process to which relaxation time is associated [14, 15].
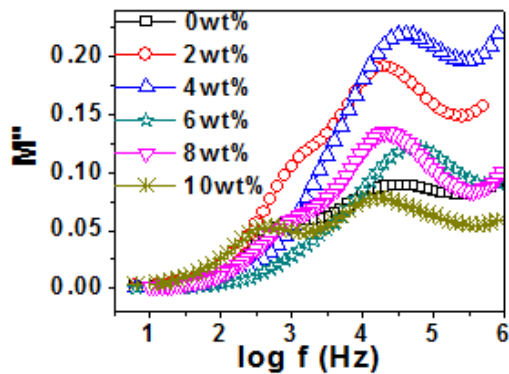

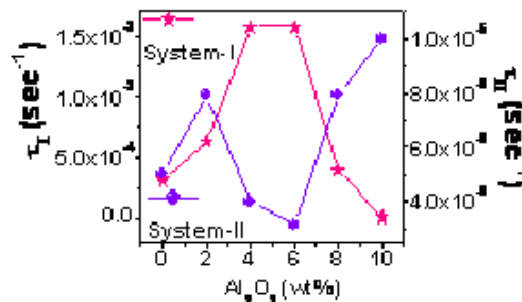Fig. 2(b): Plot of Imaginary part of modulus (M") vs. log f of System-II for various Al_2O_3 concentrations at 313K.

Fig. 3: Variation in Conductivity Relaxation Time (i) 'τ_I' for System-I and (ii) 'τ_{II}' for System-II, for various Al_2O_3 concentrations at 313K.

The variation in conductivity relaxation time, 'τ' with Al_2O_3 filler concentration in Systems-I and II is shown in Fig. 3. 'τ' values for System-I gradually increase with Al_2O_3 amount upto 6wt% and reduces with its further increment of nano-filler whereas, for System-II, the variation in 'τ' values with Al_2O_3 amount gets reversed to that observed for System-I. Hence, for both, Systems-I and II, with the increasing conductivity, the values of relaxation time are found to reduce and vice-versa. Reduction in 'τ' values indicates faster and easier mobility of ions and polymer segments through blend matrix which may be due to increment in the free volume and availability of conducting pathways for the movement of mobile constituents participating in the conduction process. This discussion is also supported by the description provided for nano-filler composition dependent conductivity variation. Secondly, in addition to the prominent peaks contributing in "primary relaxation" process, there also exist hump-like features in the modulus spectra for a few blend specimens of both Systems-I and II and these features correspond to "secondary relaxation". In System-I, initially, for the specimen with 0wt% of nano-filler, only low frequency relaxation peak is present in the M" vs log f spectra. However, beyond 0wt% filler concentration, a hump emerges in mid $(10^3-10^4 Hz)$ to high frequency region and gradually becomes prominent with increasing filler concentration. However, beyond 6wt% of Al_2O_3, the hump gradually loses its prominance and finally disappears in the specimen with 10wt% filler. Similarly, for System-II, blend polymer electrolyte with 0wt% Al_2O_3 shows the presence of a small relaxation hump at low frequency region which gradually vanishes with increasing filler concentration and finally disappears in the specimen with 6wt% of Al_2O_3. Beyond this Al_2O_3 amount, the hump reappears and becomes gradually prominent. This discussion clearly indicates that for both the Systems-I and II, the "secondary relaxation" gradually loses its existence with the increasing conductivity of the blends and finally gets suppressed in the specimens showing optimum conductivity. Hence, the respective lowest conducting specimens with 6wt% and 10wt% of Al_2O_3 of Systems-I and II show the presence of both primary as well as secondary relaxations, whereas, the optimum conducting specimens with 10wt% and 6wt% of Al_2O_3 of Systems-I and II, respectively, show a complete absence of secondary relaxation and thus, only primary relaxation is present for these specimens. This secondary relaxation may be due to polarization of ions in the polymer matrix. The gradual suppression of secondary relaxation with increasing conductivity suggests that polarization of ions reduces with conductivity enhancement and vice versa. Such multiple relaxations corresponding to multiple peaks in M" vs. log f spectra is also observed by *S. B. Aziz et. al.* in chitosan-silver triflate system [14], by *P. Sharma et. al.* in PEO-PMMA-$AgNO_3$-EC system [15], in PMMA-$LiCF_3SO_3$ system by *S. Ramesh et. al.* [16] in PVOH-CF_3COONH_4 system studied by *J. Castillo et. al.* [17] and also by *A. B. Afzal et. al.* in DBSA doped polyaniline/PVC composite system [18]. Also, the Al_2O_3 composition-wise scaling of modulus for Systems-I and II is carried out and shown in Figs. 4(a) and 4(b), respectively, at 313K. None of these figures depicts a perfectly superimposible single master curve. This suggests, the relaxation processes occurring in both the Systems-I and II depend upon the Al_2O_3 concentration.

IV. CONCLUSION

The variation in conductivity and relaxation time with Al_2O_3 concentration confirms that the electrical and relaxation properties get gradually deteriorated in System-I: $PVA-PEO-LiCF_3SO_3-EC$ but improves in System-II: $PVA-PEO-AgNO_3-PEG$, with increasing Al_2O_3 amount upto 6wt%. But at $Al_2O_3>6wt\%$, the reverse occurs wherein, these properties, get gradually better in System-I, but start deteriorating gradually in System-II. However, upto $Al_2O_3 \leq 8wt\%$, System-II shows better electrical and relaxation properties than System-I. But beyond 8wt% of Al_2O_3 concentration, the reverse occurs. Hence, at low Al_2O_3 amounts ($\leq 8wt\%$) System-II is more applicable than System-I, but at higher Al_2O_3 concentrations ($>8wt\%$), System-I is more advantageous than System-II. The specimens with 10wt% and 6wt% of Al_2O_3 of Systems-I and System-II, respectively, are best for applications as they show optimum conductivities and least relaxation time values. The time-Al_2O_3 composition modulus (M") scaling curves for Systems-I and II indicate the dependency of relaxation dynamics on Al_2O_3 concentration.

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