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GLASS TRANSITION TEMPERATURE AND DIELECTRIC BEHAVIOUR IN VARIATION WITH SALT CONTENT OF MISCIBLE AND IMMISCIBLE POLY(ETHYLENE OXIDE)-BASED POLYMER ELECTROLYTES

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ABSTRACT

Glass transition temperature (T_g) of polymers has been studied in binary polymer-salt mixtures. Lithium perchlorate was dissolved in poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA) and several epoxidized natural rubbers (ENR). It turns out that T_g ascends with mass fraction of salt up to around W_s = 0.1. At higher concentration of salt, T_g might decrease owing to development of heterogeneities in polymer-salt systems. One observes linear increase of T_g in the range of low salt content. Depending on interactions between salt and polymer, (thermodynamic) activity of salt at higher concentration may cause negative or positive deviation of T_g from linearity. Composition dependence of T_g is discussed in thermodynamic terms. Adopting the approach of Gibbs and DiMarzio, partitioning of entropy of mixing in combinatorial and non-combinatorial part proves to be a prominent factor in ruling variation of T_g in those systems. Afterwards, universal dielectric behavior and impedance relaxation were investigated at room temperature over a wide range of salt concentration binary polymer-salt mixtures. Dielectric relaxations occur at extremely low salt concentrations in PEO and only at very high salt concentrations in ENR. Hence, conductivity of ENR-salt is one to two orders of magnitude lower as for PEO-salt. For ENR-salt mixtures, impedance spectroscopy reveals that the ENR with higher epoxy content displays macro-phase separation. It decays to a heterogeneous system characterized by one phase with the conductivity corresponding to maximal salt solubility and another phase with conductivity lower the former phase by one order of magnitude. Thus, above a critical salt content, we have a heterogeneous system. The influence of the ENR (immiscible) or PMMA (miscible) on the conductivity of PEO after addition of Li salt is discussed. PEO, ENR and PMMA possess oxygen in their respective chemical structures, which may be able to coordinate with the Li salt added. Nonuniforminity of Li salt concentration in different phases of the immiscible blends of PEO/ENR (60/40 wt/wt) enhances the conductivty of the mixtures as compared to that of the PEO-salt mixtures. The conductivity of PEO-salt mixtures is slightly higher than that of the miscible PEO/PMMA (75/25 wt/wt) with addition of salt. This may be due to reduced segmental motion cause by the increased T_g of the blend and a decrease in free ions in the amorphous phase of PEO as a small amount of the salt is solvated by PMMA in the blend. Therefore, the percolation path lies in the amorphous PEO rich phase of the blend.