

Preparation and Characterization of Elastomeric Solid Electrolyte Based on PEO-EDA-LiClO₄ Blends

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PEO-EDA-LiClO₄ 블렌드계 탄성체 전해질의 제조와 특성

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ABSTRACT : Solid polymer electrolytes were prepared by UV irradiation of the blends consisting of poly(ethylene oxide)(PEO), epoxy diacrylate(EDA) and LiClO₄. Conductivities of the electrolyte films were measured as a function of blend composition, salt concentration and temperature. The electrolyte having the composition of poly(ethylene oxide) (70% by weight)/epoxy diacrylate (30% by weight) with mole ratio of 10 of ethylene oxide/Li⁺ exhibited a high ionic conductivity of 1.2×10^{-5} S/cm at 25°C. This blend is transparent and shows elastomeric properties. Morphological studies by means of differential scanning calorimetry, X-ray diffraction and polarized optical microscopy indicated that the cured epoxy chains in the blends inhibit the crystallization of poly(ethylene oxide) and thereby induce the blend systems to be completely amorphous in certain compositions.

요 약 : Poly(ethylene oxide)(PEO)와 epoxy diacrylate(EDA) 및 금속염인 LiClO₄를 블렌드하고 자외선 가교시킴으로써 이온전도특성을 나타내는 고체 전해질을 제조하고, 제조된 전해질의 이온전도도를 블렌드조성, 염농도 및 온도 변화에 따라 측정하였다. PEO/EDA의 조성비가 70/30 wt%이고 ethylene oxide/Li⁺의 몰비가 10인 전해질이 25°C에서 1.2×10^{-5} S/cm 에 달하는 높은 이온전도도를 나타내었다. 제조된 전해질 필름은 투명하였으며 고무와 같은 탄성을 나타내었다. DSC, XRD 및 편광현미경을 이용한 모폴로지 분석으로부터 에폭시 사슬이 PEO의 결정화를 억제함으로써 완전히 무정형인 블렌드를 제조할 수 있음을 확인할 수 있었다.

Keywords : poly(ethylene oxide), blend, solid polymer electrolyte, ionic conductivity, morphology

I. Introduction

Since Wright et al. discovered a solvating ability of a polymer toward alkali salt, there have been considerable interests in solid polymer electrolytes due to their wide applicability to solid-state re-

chargeable batteries, smart windows, electrochromic devices, and sensors as well as the easy processibility of plastic materials.¹⁻⁴ For the solid polymer electrolyte to be applicable in practice, it is required that they have reasonably high conductivity as well as mechanical, thermal and electrochemical stability under service conditions.

Poly(ethylene oxide) (PEO) has been the most extensively studied as a matrix polymer for the

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polymer electrolytes because it has a backbone structure which is able to be coordinated with alkali cation very well. However, PEO/salt systems have poor mechanical properties and low ionic conductivity at room temperature due to high crystallinity of PEO. One approach to overcome the problems is the blending of PEO with other polymers. Some blend systems, such as PEO/poly(2-vinylpyridine) or poly(4-vinylpyridine)/LiClO₄,^{5,6} PEO/poly(propylene oxide)/NaI,⁷ PEO/poly(vinyl acetate)/LiClO₄⁸ and PEO/poly(propylene oxide)/LiCF₃SO₃⁹ were reported to exhibit ionic conductivities of up to 10⁻⁴ S/cm at room temperature and good mechanical properties. In the blends, it is generally accepted that amorphous portions of PEO provide ionic conductive pathways, whereas the other polymers provide mechanical strength and prevent the crystallization of PEO.

In this paper, we synthesized solid polymer electrolytes by blending of PEO with UV curable epoxy diacrylate(EDA) and lithium perchlorate (LiClO₄). Ionic conductivities and microstructure of the electrolyte films prepared by UV-irradiation were analyzed in terms of the blend compositions and ethylene oxide/Li⁺ mole ratios.

II. Experimental

1. Materials

Poly(ethylene oxide) (PEO, M_n=1,000,000) and lithium perchlorate(LiClO₄) were purchased from Aldrich. UV-curable epoxy diacrylate resin (EDA), which is the diacrylate ester of bisphenol A was kindly donated from Samwha Chem. They were carefully dried under vacuum before use. Dichloromethane and THF, used as solvents, were distilled. Benzoin ethyl ether, used as a photoinitiator, was purchased from Aldrich.

2. Preparation of Blends

PEO, EDA, and LiClO₄ were separately dissolved in 1:1 mixture of dichloromethane/THF as a solvent.

Appropriate quantities of the solutions were mixed with constant stirring and then photoinitiator was added to the system. The mixture was poured onto a Teflon-coated mold and the casted films were irradiated using a 500 W high-pressure mercury lamp as the irradiation source. An irradiation time was 20s. Residual solvent of the cured films was removed in the vacuum oven at 50°C. The prepared films, nearly 100 μm thick, were stored in a desiccator.

3. Measurement of Ionic Conductivity

Complex plane impedance and inductance analyses were conducted on an Impedance Analyzer in the frequency range from 10 Hz to 5 MHz and temperature range 20-100°C using a Solartron impedance/gain analyzer. The sample was sandwiched between two stainless-steel plates. The electrochemical cells were assembled in a dry glove box. Bulk resistance was determined by plotting the real versus the imaginary part of the impedance. Bulk resistance was derived from such a plot where the imaginary impedance is zero. Conductivity was calculated from the bulk resistance according to following equation:

$$\sigma = D / (A \times R_b)$$

where σ is conductivity, D is the thickness of the sample, A is sectional area of the sample, and R_b is bulk resistance.

4. Thermal and Morphological Analysis

The DSC thermograms were recorded from -100 to +250°C at a heating rate of 10°C/min using a Shimadzu thermal analysis system. The calorimeter was flushed with dry nitrogen. The T_g values were determined as the midpoints of the heat capacity change during the relaxation temperature.

X-ray diffractograms of the samples were recorded using a Phillips 180 X-ray diffractometer in the 2θ range from 10 to 60.

Crystalline morphology was investigated by using Leica polarizing optical microscope equipped with a Mettler FP90 hot stage. The polymer film sealed between glass plates was melted at 200 °C for 5 min, then allowed to crystallize until it cools to room temperature.

III. Results and Discussion

Figures 1 and 2 illustrate the temperature dependence of the ionic conductivity for the blends of PEO(90)/EDA(10)/LiClO₄ and PEO(70)/EDA(30)/LiClO₄ with different salt contents. One can observe that the conductivity increases with temperature, which is due to the increase in segmental motion of the host polymer with temperature. And it is also seen that there is an abrupt change in the conductivity curve around 50 °C for PEO(90)/EDA(10)/LiClO₄ with ethylene oxide/Li⁺ mole ratio of 13 and 16. The sudden change in conductivity of the electrolytes with the compositions is related to a melting transition of crystalline portion of PEO. (Table 1) The increase in amorphous portion, which is only phase responsible for ion transport, of the system at the temperature range facilitates the motion of the cation between complexation sites.¹⁰

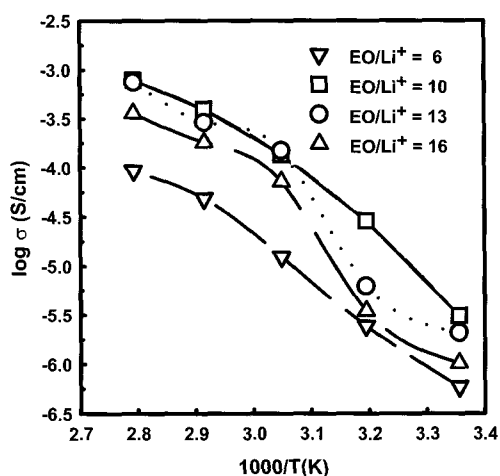


Figure 1. Arrhenius conductivity plots of PEO(90)/EDA(10)/LiClO₄ blends.

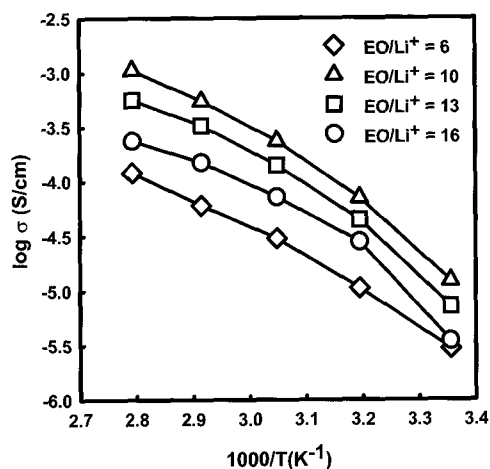


Figure 2. Arrhenius conductivity plots of PEO(70)/EDA(30)/LiClO₄ blends.

Table 1. Glass Transition (T_g), Melting Temperature (T_m), Heat of Melting (ΔH_m), and Ionic Conductivity of PEO/LiClO₄ and PEO/EDA/LiClO₄ Complexes

PEO/EDA (wt %)	EO/Li ⁺ (mole ratio)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	σ at 25 °C (S/cm)
100/0	No salt	-	70.3	179.0	-
	20	-47.8	60.0	106.6	-
	16	-42.7	59.5	89.3	3.3110^{-7}
	13	-39.8	52.4	60.5	4.7810^{-7}
	10	-35.0	48.0	26.8	1.1810^{-6}
	6	-31.0	-	-	1.2910^{-7}
70/30	No salt	-56.8	64.4	178.0	-
	20	-44.4	53.7	107.3	7.5810^{-7}
	16	-42.0	50.7	87.4	1.0210^{-6}
	13	-36.0	47.7	57.2	2.0910^{-6}
	10	-33.0	30.7	18.9	3.0910^{-6}
	6	-30.0	-	-	5.8910^{-7}
90/10	No salt	-51.2	49.7	127.9	-
	20	-46.6	39.8	63.7	1.7810^{-6}
	16	-44.8	38.2	25.3	3.4710^{-6}
	13	-43.9	27.0	11.6	7.2210^{-6}
	10	-39.1	-	-	1.2310^{-5}
	6	-34.4	-	-	1.3210^{-6}
50/50	No salt	-51.9	44.5	95.0	-
	20	-40.0	44.8	59.4	1.4710^{-7}
	16	-36.0	43.0	24.2	2.3810^{-7}
	13	-36.2	31.2	6.90	3.2410^{-7}
	10	-32.4	-	-	4.4110^{-7}
	6	-28.5	-	-	1.4010^{-7}

And, it may be noted that the ionic conductivity increases as the salt content is increased; it reaches a maximum value at the EO/Li⁺ mole ratio of 10 and decreases as the salt content is further increased. The maximum in the ionic conductivity with salt content is generally observed behavior of polymer/salt complexes.¹¹ Ionic conductivity increases initially due to the increase in the number of charge carriers. But, at higher salt content, the conductivity falls as a consequence of a decrease in flexibility of the polymer chain accompanied by the formation of larger ionic aggregates.

Figure 3 shows the variation of room temperature ionic conductivity as a function of ethylene oxide/Li⁺ mole ratio for PEO/LiClO₄ and PEO/EDA/LiClO₄ blends. For all cases, the ionic conductivity shows a maximum value at the ethylene oxide/Li⁺ mole ratio of 10. It is to be noted that the ionic conductivity of the PEO(70)/EDA(30)/LiClO₄ blend at an ethylene oxide/Li⁺ mole ratio of 10 is 1.2×10^{-5} S/cm at room temperature, which is nearly one order of magnitude higher than that obtained here for PEO/LiClO₄ system. The blend at the composition shows transparent and elastomeric properties with dimensional stability. But, when the EDA content reaches 50 % by weight in the blend, the conductivity values become lower than those of PEO/LiClO₄ system. This should be because epoxy chains cannot solvate the salt and PEO phase cannot form the continuous phase at the composition.

Figure 4 illustrates DSC thermograms of PEO/salt and PEO(70)/EDA(30)/salt at different salt concentrations. It can be seen that endothermic peak corresponding to melting of crystalline PEO decreases in size and position as the salt content increases. This indicates that crystallinity of PEO is reduced in the presence of salt. The effect of salt content on the melting behavior of PEO is observed to be similar in PEO(70)/EDA(30)/LiClO₄ system. But, at a same value of ethylene oxide/Li⁺ mole ratio, melting temperature and the endotherm peak area of the PEO/EDA/LiClO₄ system are lower compared to PEO/LiClO₄ system. Also, less salt is

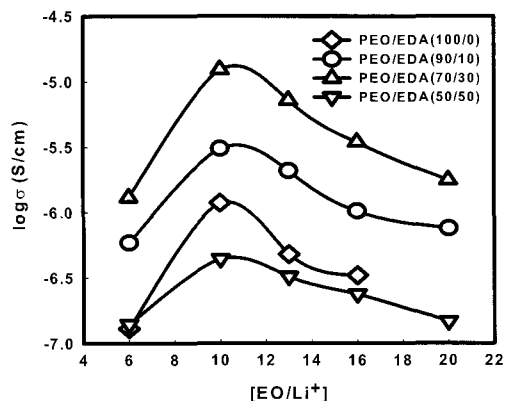


Figure 3. Variation of ionic conductivity as a function of EO/Li⁺ mole ratio for PEO/LiClO₄ and PEO/EDA/LiClO₄ blends at 25°C.

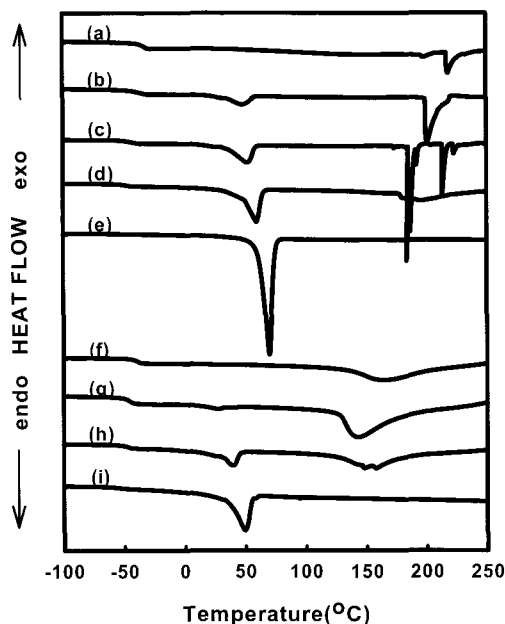


Figure 4. DSC thermograms of PEO/LiClO₄ and PEO(70)/EDA(30)/LiClO₄ complexes: (a) EO/Li=6; (b) EO/Li=10; (c) EO/Li=13; (d) EO/Li=20; for PEO/LiClO₄ (e) pure PEO; (f) EO/Li=10; (g) EO/Li=13; (h) EO/Li=6; for PEO(70)/EDA(30)/LiClO₄ (i) PEO(70)/EDA(30).

required to disrupt the crystallinity of PEO in the PEO/EDA/LiClO₄ system than that needed in PEO/LiClO₄ system. The value of ethylene oxide/Li⁺ mole ratio at which the endotherm peak dis-

appeared is 6 for PEO/LiClO₄ system while it is 10 for PEO(70)/EDA(30)/LiClO₄ system.

Table 1 demonstrates the glass transition temperatures and melting parameters for the PEO/EDA/LiClO₄ blend system of different compositions. It was noted that increase in salt content leads to an increase in glass transition temperature of PEO for all systems, indicating a reduction in segmental motion of the polymer due to the formation of ionic aggregates. It can be seen that, at the same salt content, the glass transition temperature for the electrolyte system is not much affected by EDA content. The melting behavior in PEO, on the other hand, is affected by EDA content as well as the salt content. As EDA content increases, melting temperature and the area of endotherm peak corresponding to melting of crystalline PEO decreases. This indicates that the epoxy network formed by UV irradiation impedes the crystallization of PEO in the ternary system.

Disruption of the crystal in PEO/EDA/LiClO₄ at certain compositions was confirmed by X-ray

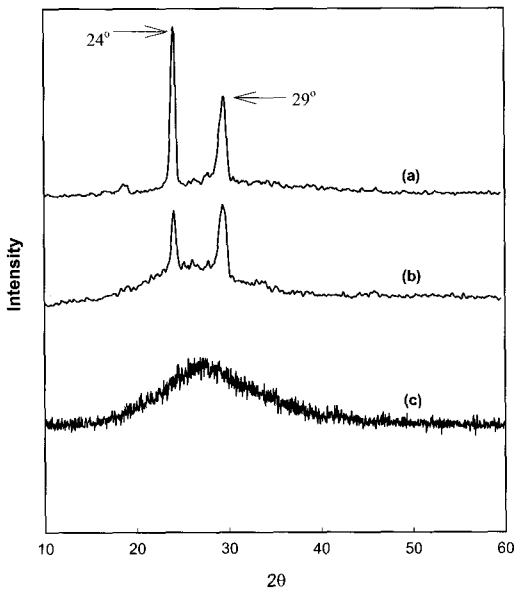
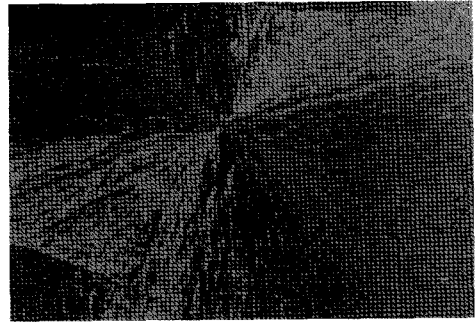


Figure 5. X-ray diffraction patterns for polymer electrolyte samples. (a) PEO (b) PEO(70)/EDA(30) (c) PEO(70)/EDA(30)/LiClO₄ (EO/Li = 10).

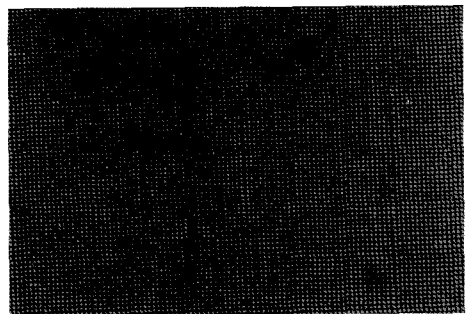
diffraction and polarized optical microscopy. Figure 5 demonstrates the X-ray diffractograms of PEO, PEO(70)/EDA(30) and PEO(70)/EDA(30)/LiClO₄ with ethylene oxide/Li⁺ mole ratio of 10. Pure PEO, as seen in Figure 5(a), shows a sharp peaks with



(a) PEO



(b) PEO(70)/EDA(30)



(c) PEO(70)/EDA(30)/LiClO₄(EO/Li⁺ = 10)

Figure 6. Polarized optical micrographs of the samples crystallized from the melt.

broad underlying hump, reflecting its semicrystalline structure. PEO(70)/EDA(30) shows diffraction peaks similar to PEO but the intensity and the area under the peak decreases. [Figure 5(b)] For PEO(70)/EDA(30)/LiClO₄ system at an ethylene oxide/Li⁺ mole ratio of 10, however, as seen in Figure 5(c), the sharp diffraction peaks disappear completely and background, typical of amorphous polymers, is only observed. Figure 6 shows the polarizing optical micrographs of the PEO and PEO/LiClO₄ complexes crystallized from the melt. Pure PEO, as seen in Figure 6(a), grows as almost perfect crystalline forms and shows the typical Maltese cross structure. Figure 6(b) indicates that regularity of the PEO spherulite is somewhat disrupted by the action of cured epoxy network. And, in the PEO/EDA blend complexed with LiClO₄, any clear crystals can not be observed. It confirms that the presence of cured epoxy network enhances the disruption of the long-range crystalline order of the PEO in the ternary system.

IV. Conclusion

Solid electrolyte films were prepared by UV-irradiation of PEO/epoxy diacrylate/LiClO₄ blend system. The PEO(70 weight %)/EDA(30 weight %)/LiClO₄ at an ethylene oxide/Li⁺ mole ratio of 10 exhibited ionic conductivity value of 1.2×10^{-5} S/cm at 25 °C. The value is one order of magnitude higher than the maximum conductivity value for PEO/LiClO₄ complexes considered here. Additionally, the electrolyte film at the composition shows transparent and elastomeric properties with dimensional stability.

References

1. D. E. Fenton, J. M. Parker, P. V. Wright, "Complexes of alkali metal ions with poly(ethylene oxide)", *Polymer*, **14**, 589 (1973).
2. M. B. Armand, "Polymer solid electrolytes - an overview", *Solid State Ionics*, **9&10**, 745 (1983).
3. N. Kobayashi, M. Uchiyama, K. Shigehara, E. Tsuchida, "Ionically high conductive solid polymer electrolytes composed of graft copolymer-lithium salt hybrids", *J. Phys. Chem.*, **89**, 987 (1985).
4. M. B. Armand, "The history of polymer electrolytes", *Solid State Ionics*, **69**, 309 (1994).
5. J. Li, I. M. Khan, "Highly conductive solid polymer electrolytes prepared by blending high molecular weight poly(ethylene oxide), poly(2- or 4-vinylpyridine), and lithium perchlorate", *Macromolecules*, **26**, 4544 (1993).
6. J. Li, E. A. Mintz, I. M. Khan, "Poly(ethylene oxide)/poly(2-vinylpyridine), and lithium perchlorate", *Chem. Mater.*, **4**, 1131 (1992).
7. R. D. A. Paulmer, A. R. Kulkarni, "Synthesis and characterization of ternary polymer electrolytes with enhanced miscibility and high conductivity", *Polym. Inter.*, **38**, 165 (1995).
8. I. E. Animitsa, A. L. Kruglyashov, O. V. Bushkova, V. M. Zhukovsky, "Morphology and ionic conductivity of poly(ethylene oxide)-poly(vinyl acetate)-LiClO₄ polymer electrolytes", *Solid State Ionics*, **106**, 321 (1998).
9. J. L. Acosta and E. Morales, "Structural, morphological and electrical characterization of polymer electrolytes based on PEO/PPO blends", *Solid State Ionics*, **85**, 85 (1996).
10. C. Berthier, W. Gorecki, M. Minier, M. B. Armand, J. M. Chabagno, P. Rigaud, "Microscopic investigation of ionic conductivity in alkali metal salts-poly(ethylene oxide)", *Solid State Ionics*, **11**, 91 (1983).
11. M. A. Ratner, D. F. Shriver, "Ion transport in solvent-free polymers", *Chem. Rev.*, **88**, 109 (1988).