

Ionic Conductivity of New Dual-Phase Polymer Electrolyte Composed of Poly(epichlorohydrin-*co*-oxirane) and NBR

JIN-LAN JU, QING-CHAO GU, HAI-SHENG XU, CHANG-ZHENG YANG

Department of Polymer Science and Engineering, Nanjing University, Nanjing 210093, People's Republic of China

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ABSTRACT: A new type of dual-phase polymer electrolyte (DPE) film was prepared by mechanical mixing of a poly(epichlorohydrin-*co*-oxirane) (ECO) and poly(acrylonitrile-*co*-butadiene) rubber (NBR) binary solution and then by solution casting. Both of the polymers are commercially available. The casting films were swollen with a LiClO₄/propylene carbonate (PC) solution to obtain DPE films. The ionic conductivity of the DPE films was calculated on the basis of alternating current impedance measurements. The results showed that the ionic conductivity is dependent on the content of the LiClO₄/PC solution and the ECO/NBR blend ratio. High ionic conductivity ($>10^{-3}$ S/cm at 298 K) was achieved when the ECO content in the matrix is 90% (w/w), the concentration of LiClO₄/PC solution is at 3 mol/L, and the weight percent of LiClO₄/PC is 40. The impedance spectrum provided evidence that a dual-phase structure was created, in which the ECO phase provided an ion-conductive pathway and the NBR phase acted as a supportive matrix. A new ionic conductivity mechanism was proposed. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 353–357, 1998

Key words: polymer electrolyte; poly(epichlorohydrin-*co*-oxirane); NBR; impedance spectrum

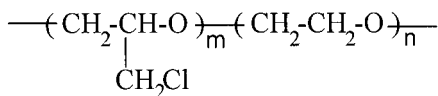
INTRODUCTION

Ever since the discovery of ionic conductivity in alkali metal salt complexes of solid polymers such as poly(ethylene oxide)^{1,2} and the recognition of their technological importance for the construction of solid-state rechargeable batteries, electrochromic devices, and sensors, creation of solid polymer electrolytes having a conductivity of about 10^{-3} S/cm at room temperature has remained an ambitious goal.³ However, the typical ion conductivity values of solid polymer electrolytes are of the order of 10^{-5} S/cm at room temperature. Therefore, in recent years, considerable attention has been dedicated to the development

and the characterization of polymer gel electrolytes because of their liquidlike ionic conductivity.^{4–6} This system includes a polymer, an ionic salt, and a small molecule organic solvent and can be easily prepared by swelling the polar polymer film with a lithium salt solution. Unfortunately, the swelling process often degraded the mechanical properties, so the application of this electrolyte to devices is far from satisfactory. To solve the problem, Matsumoto et al. proposed a new concept: a dual-phase polymer electrolyte (DPE),^{7–9} in which a highly polar polymer impregnated with a lithium salt solution forms continuous ion-conductive channels and a nonpolar polymer produces good mechanical strength. They obtained a rubbery film composed of NBR and SBR with good tensile strength and high conductivity at room temperature. So far, no other DPE was reported.

Correspondence to: Q.-C. Gu.

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Scheme 1 Structure of ECO.

In the present work, we extended Matsumoto's concept to a novel dual-phase system prepared from poly(epichlorohydrin-*co*-Oxirane) (ECO), nitrile butadiene rubber (NBR), and lithium perchlorate (LiClO_4) in propylene carbonate (PC). In this system, the ECO was chosen as a highly polar matrix. The ionic conductivity of the novel dual-phase system is 1.3×10^{-3} S/cm, while that of the DPE system reported earlier by Matsumoto is 7.2×10^{-4} S/cm.² The two systems are a dual-phase system and typically differ from one another only through the absence or presence of coordination between the Li^+ ion with the polymer matrix. The structure of the ECO is shown in Scheme 1.

Here, it is recognized that the $\text{---}(\text{CH}_2\text{---CH}_2\text{---O---})_n$ segment of the ECO has the ability to solvate alkali-metal salt and can form the complex with alkali-metal ion. Thus, the ECO not only produces an ion-conductive channel, but also can coordinate with Li^+ ions after swelling with a lithium salt solution. NBR in the novel dual-phase system can maintain good mechanical strength and especially can redeem strength compromised by the ECO on account of its aging and softening. Dynamic mechanical analysis showed that there was an intermediate zone between the two phases, which assured the DPE films to have good strength. Consequently, a new DPE film with ionic conductivity of 1.3×10^{-3} S/cm at 298 K and good mechanical properties was obtained.

EXPERIMENTAL

Both ECO and NBR are commercial products. The former was obtained from the Nanxiang Rubber Product Factory (Shanghai, China) and purified before use. The XPS result showed that the epichlorohydrin content was 41% (mol/mol) in purified ECO. NBR was used as received from the Lanzhou Chemical Co. (Lanzhou, China) and the acrylonitrile content was 29.4% determined by elemental analyses. $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (A.R., Shanghai Reagent Factory II, China) was applied after being dehydrated completely.

Weighted amounts of ECO, NBR, and THF were mixed and heated (with stirring) until the mixture became homogeneous. Films were prepared by evaporating the solvent completely. The resultant films were immersed in a solution of LiClO_4/PC to obtain a blend polymer electrolyte film.

Ionic conductivity was measured using the standard a.c. impedance method in the frequency of 5 Hz to 100 kHz with an EG&G Princeton Applied Research Electrochemical Impedance System at 298 K. Two parallel stainless-steel discs (16 mm in diameter) were used as electrodes, and the a.c. amplitude was 5 mV.

RESULTS AND DISCUSSION

Miscibility of ECO and NBR

Figure 1 shows the dynamic mechanical analysis curve for the ECO/NBR blend polymer. The two phases are immiscible. Between the glass transition temperature (T_g) of ECO (-42.7°C) and that of NBR (-19°C), there is a shoulder, which implies that there was an intermediate zone between the two phases. The intermediate zone keeps the blend from easily breaking owing to phase separation; thus, the system has long-time stability.

For LiClO_4/PC , the maximum solution content of ECO and NBR were 40 and 19%, respectively. This phenomenon can be explained in terms of the solubility effect, that is, the affinity between the matrix polymer and the absorbed solution. PC

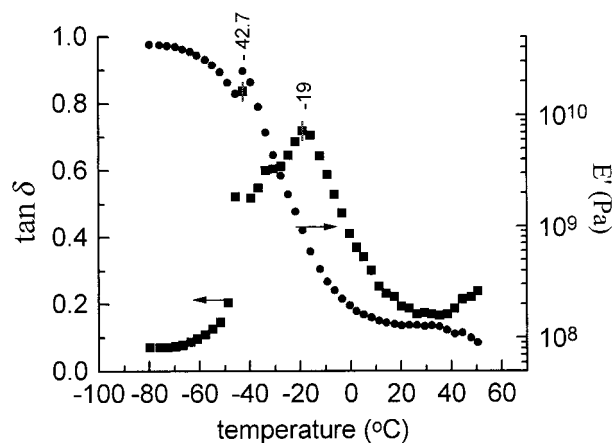


Figure 1 Dynamic mechanical analysis of ECO/NBR = 90/10.

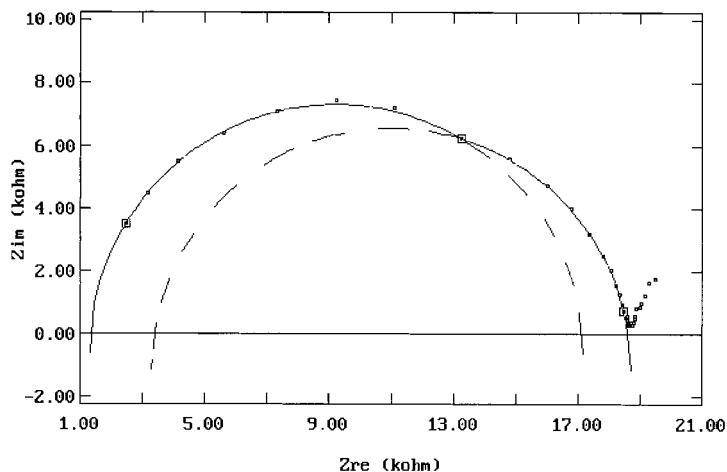


Figure 2 Typical impedance spectrum for the DPE film, made from ECO/NBR = 50/50 and 0.15 mol/L LiClO₄/PC solution.

is too polar to permeate the NBR phase. Thus, the majority of the absorbed solution is present mainly in the more polar ECO phase. The NBR phase supports the polymer matrix while the ECO phase forms continuous ion-conductivity channels.

Equivalent Circuit

The typical complex impedance spectrum for the new DPE film is shown in Figure 2. The open squares in the figure are the experimental data. The bulk impedance loci appeared to be a superposition of two semicircles having different time constants. There is also a low-frequency spur in the spectrum, caused by the boundary impedance. Taking the morphology of the new DPE film into account, we assume an equivalent circuit in order to interpret the profile of the bulk impedance loci, as shown in Figure 3.

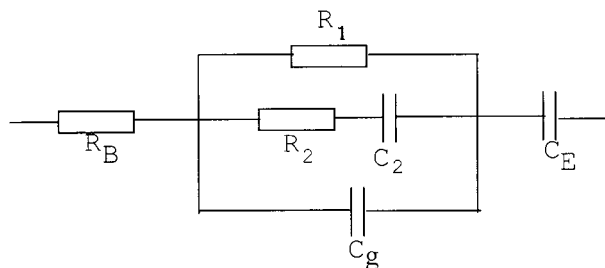


Figure 3 Equivalent circuit to interpret complex impedance spectra of the DPE in the present study.

R_B is the resistance of the LiClO₄/PC solution and R_1 is the resistance of the continuous conductive pathway formed by the ECO phase. A series combination of resistor R_2 and capacitor C_2 represents the blocked conductive pathways, while C_g corresponds to the geometrical capacitance determined by the dielectric constant and geometry of the sample. The R_1 and the R_2-C_2 are connected to the geometrical capacitance C_g in parallel. They should result in a complex impedance diagram of two merged semicircles. C_E is the double-layer capacity of the electrode and sample. To confirm the validity of the assumed equivalent circuit, we simulated the complex impedance diagram. The results are shown by the solid line in Figure 2. The simulated diagram is seen to agree well with the experimental data. The low-frequency intercept of the simulated diagram with

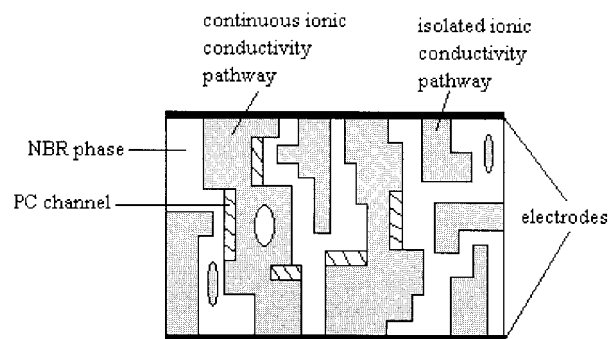


Figure 4 Schematic microstructure of ionic conductivity pathways in the DPE.

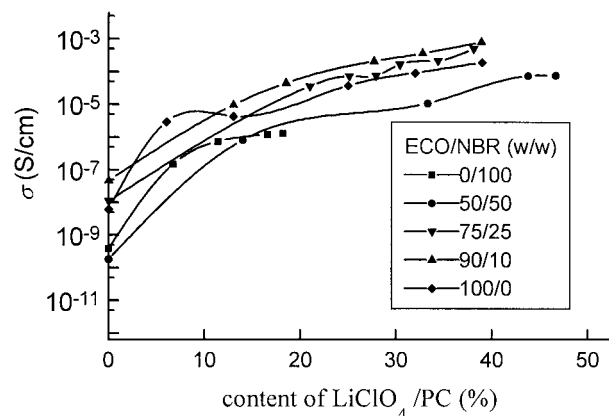


Figure 5 Ionic conductivity σ as a function of LiClO_4/PC content for DPEs at 298 K.

the real axis corresponds to the bulk resistance R of the sample. This value was then used in conjunction with room-temperature geometrical measurements. The ionic conductivity σ of the sample may be calculated from eq. (1):

$$\sigma = d/(RS) \quad (1)$$

where d is the thickness of the sample and S is the area of the electrode. As is evident from the above discussion, it should be possible to describe the microstructure of the new DPE by a schematic diagram, as shown in Figure 4.

Ionic Conductivity at Room Temperature

The ionic conductivity of the DPE/ LiClO_4/PC hybrid films depends on the content of LiClO_4 , ECO, and PC. Figure 5 shows the relation between the ionic conductivity σ and the content of LiClO_4/PC . In general, it is well known that the ionic conductivity of an electrolyte is directly proportional to the number of carrier ions and their mobility. Hence, the ionic conductivity σ of the present

electrolyte is proportional to the content of the LiClO_4/PC solution. On the other hand, Figure 5 also shows that σ is dependent on the ECO/NBR blend ratio. The more ECO the DPEs contains, the higher ionic conductivity the system has, because more continuous ionic conductivity pathways form in the system. But it is interesting to observe that the σ of the ECO gel electrolyte is lower than those of the DPEs (ECO/NBR = 90/10 and 75/25); perhaps there was a small PC channel between the ECO phase and the NBR phase, which is in agreement with the impedance analysis. Moreover, Li^+ moves faster in PC than in the ECO phase, so the σ of the DPE was higher than was the σ of the ECO gel electrolyte. Besides, it can be seen from Table I that the ionic conductivity increases with increasing concentration of LiClO_4 , because the carrier number increases in the dual-phase system.

CONCLUSIONS

Based on the commercially available polymers ECO and NBR, a new type of dual-phase polymer electrolyte film with high ionic conductivity and good mechanical strength was developed. The ionic conductivity depends on the content of the LiClO_4/PC solution and the ECO/NBR blend ratio. A high conductivity ($> 10^{-3}$ S/cm) at 298 K was achieved when the ECO content in the matrix was 90% (w/w), the concentration of LiClO_4/PC solution was 3 mol/L, and the weight percent of LiClO_4/PC was 40% (w/w). The impedance spectrum provided evidence that a dual-phase structure was created, in which the ECO phase provides an ion-conductive pathway and the NBR phase acts as a supportive matrix. It is worth noticing that our findings suggested that the high ionic conductivity of DPE films is governed not only by the free lithium salt solution

Table I. Ionic Conductivity of the DPE (ECO/NBR = 90/10) with Different Concentrations of the LiClO_4/PC Solution

Concentration of LiClO_4/PC Solution (mol/L)	LiClO_4/PC Content (%)	Conductivity (298 K) (S/cm)
2	32.8	3.7×10^{-4}
2	38.9	8.3×10^{-4}
3	35.7	7.6×10^{-4}
3	40.1	1.3×10^{-3}

absorbed in the matrix but also by the nature of the polymer matrix.

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