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Preparation and characteristics of natural rubber/poly(ethylene oxide) salt hybrid mixtures as novel polymer electrolytes

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Abstract

Poly(ethylene oxide) (PEO) of molecular weight 1000 (PEO_{1000}) containing lithium benzenesulfonate (LiBs) (PEO_{1000}/LiBs), PEO derivatives having benzenesulfonate groups on both chain ends (PEO_{1000}–$(BSLi)_2$), or 1-ethyl-2,3-dimethylimidazolium bromide (ImB), were each blended with natural rubber (NR). The ionic conductivity was measured from AC impedance values. The ionic conductivity of the mixture of NR and PEO_{1000}/LiBs (40 wt%) was about 10^{-6} S cm^{-1} at 50°C; this mixture retained rubbery physical characteristics. At NR content of 10 wt%, the ionic conductivity of the mixture (NR/PEO_{1000}/LiBs) was 2.7×10^{-5} S cm^{-1} at 50°C, approximately 10 times higher than that of the bulk PEO/LiBs mixture. For mixtures of NR and PEO_{1000}–$(BSLi)_2$, no improvement in ionic conductivity by mixing was found. The ionic conductivity of the mixture of NR and ImB was about 10 times higher than for the bulk of PEO_{1000}–$(BSLi)_2$ at a NR content of 10 wt%. We propose that the ionic conductivity of the mixture increases when an ion conducting matrix containing simple salt is added. On the other hand, the DSC curve for NR/PEO derivatives showed two T_gs based on the separate components, suggesting phase separation of the PEO derivative in the NR phase. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Natural rubber; Poly(ethylene oxide); Ionic conductivity

1. Introduction

Since ion conducting polymers have become applicable in energy devices such as lithium batteries, many types of solid polymer electrolytes have been investigated. Most ion conducting polymers have been developed as a mixture of inorganic salts and polyethylene(oxide) (PEO) derivatives [1–3]. PEO can dissolve many different inorganic salts in considerable amounts because of the large polarization charge on the ether oxygen, and can transport dissociated ions by the segmental motion of the main chain. However, these PEO/salt mixtures become stiff with considerably reduced segmental motion when a small excess of inorganic salt is added, and the resulting carrier ion mobility decreases because of the elevated T_g [4,5]. To overcome these drawbacks we have been synthesizing PEO derivatives having negatively charged groups on the chain end, such as carboxylate [6,7], benzenesulfonate [8], sulfonate [9], or sulfonamide groups [10]. Since these PEO/salt hybrid systems enter an amorphous phase when the molecular weight of the PEO part is around 1000, a relatively high cation conductivity of about 10^{-5} S cm^{-1} is observed at room temperature. However, it is difficult to combine high ionic conductivity with good mechanical properties.

Much effort has been devoted to PEO-based composite polymer electrolytes with inorganic fillers such as TiO_2, SiO_2, $BaTiO_3$ [11–16]. Composite polymer electrolytes containing a small amount of inorganic filler have an ionic conductivity of about 10^{-4} S cm^{-1} at 50°C, which is higher than for the corresponding bulk PEO-based polymer electrolytes. They had improved mechanical properties and good stability of the electrode surface. The PEO/$LiClO_4$ mixture with 10 wt% TiO_2 had an excellent transference number (Li^+) of 0.6 [11]. However, the effect of inorganic fillers on improving the conductivity of PEO-based composite polymer electrolytes has never been studied. To improve mechanical properties, synthetic rubber has been mixed with some ion conducting materials. The system composed of poly(acrylonitrile-*co*-butadiene) (NBR)/poly (styrene-*co*-butadiene) (SBR)/$LiClO_4$ latex films with γ-butyrolactone (γ-BL) has been studied, for example [17,18]. The polar NBR provided the path for ion conduction and the non-polar SBR gave the desired mechanical property. This blended system had an ionic conductivity of about 10^{-3} S cm^{-1} at room temperature. Unfortunately, this strategy does not work for ordinary carrier ions, or employ organic solvent, and is therefore problematic.

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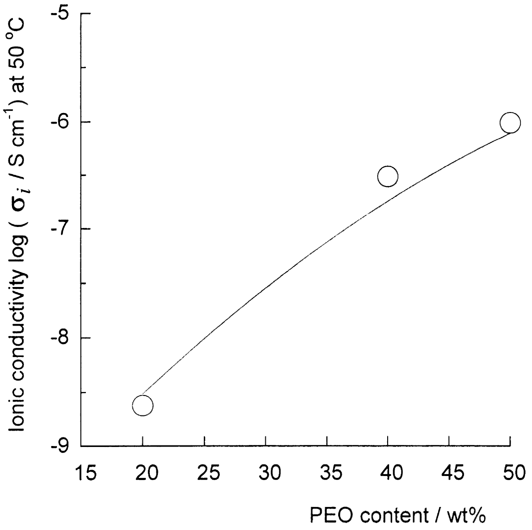

Fig. 1. Effect of PEO/LiBs content on the ionic conductivity of the mixture of NR and PEO/LiBs at 50°C.

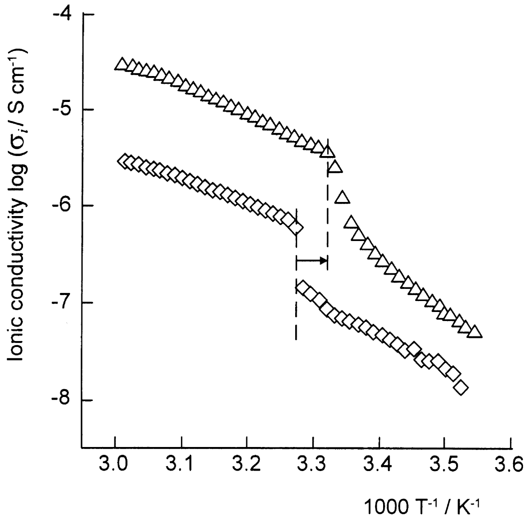

Fig. 2. Temperature dependence of the ionic conductivity for PEO/LiBs (S) and NR/PEO/LiBs (K) (PEO/LiBs content: 90 wt%).

We have also tried adding ion conducting characteristics to natural rubber (NR). NR can be superior to synthetic rubbers in its lightweight and degree of elongation. A new type of polymer electrolyte having excellent elasticity is expected when the ion conducting path is designed in the NR. To that end, some ion conducting materials are examined in this paper. Salts that are molten at room temperature have recently been recognized as unique ionic liquids. It was reported recently that room temperature molten salts were obtained with imidazolium cation [19–21]. A high ionic conductivity was expected and was often found [21]. A composite of NR and these ion conducting materials should be a new and useful polymer electrolyte.

2. Experimental

2.1. Materials

NR was donated by Prof. Y. Tanaka of Tokyo University of Agriculture and Technology. Latex, as a lyophilized NR suspension, was used in our study. PEO oligomer with an average molecular weight of 1000 (PEO_{1000}) was purchased from NOF Co. Ltd. Lithium triflate ($LiCF_3SO_3$) and lithium benzenesulfonate (LiBs) were purchased from Aldrich and from Kanto Chem. Co. PEO containing salt of 5 mol% to oxyethylene (OE) unit, which showed the greatest ionic conductivity, was used as an ion conducting additive.

A PEO derivative having charges on both chain ends, specifically PEO-benzenesulfonate lithium salt (PEO_{1000}–$(BSLi)_2$) [8], was also used. 1-Ethyl-2,3-dimethylimidazolium bromide (ImB) was prepared by the reaction of 1,2-dimethylimidazole and bromoethane in acetonitrile. The product was purified by the precipitation method with dehydrated diethylether. The structure of this compound was confirmed by ^1H NMR spectroscopy.

NR was dissolved in chloroform, and a series of ion conducting materials was added. The mixture was stirred to enforce homogeneity. The resulting solution was cast on a Teflon sheet, and the film was prepared by drying under reduced pressure.

2.2. Methods

The ionic conductivity was measured by the complex-impedance method using an impedance analyzer (Solartron model 1260; Schlumberger). The dynamic ionic conductivity measurement system was developed in our laboratory; details are given in Ref. [22]. All measurements were performed in a glove box filled with dry nitrogen gas in the temperature range 10–60°C.

The DSC measurement was carried out with the DSC-120 (SEIKO Instruments) at a heating rate of 10°C min^{-1} and a temperature range from -100 to $+200$°C.

3. Results and discussion

The PEO_{1000}/LiBs mixture was added to NR, and the ionic conductivity was evaluated as shown in Fig. 1. The ionic conductivity of NR and the PEO/salt mixture system containing 20 wt% of PEO_{1000}/LiBs was low, about 10^{-9} S cm^{-1} at 50°C. However, when 40 wt% of PEO_{1000}/LiBs was added to NR, the ionic conductivity of the mixture at 50°C improved to about 10^{-6} S cm^{-1}. This is almost the same ionic conductivity as the bulk PEO_{1000}/LiBs. The mechanical property of this mixture was similar to the NR itself, actually showing rubber elasticity. When 40–50 wt% PEO containing salts was added to NR, the NR obtained both ion conducting properties and rubber elasticity.

Since the ionic conductivity of NR was improved by adding PEO/LiBs mixture, the system having excess PEO/salt mixture was also analyzed, in the expectation of high

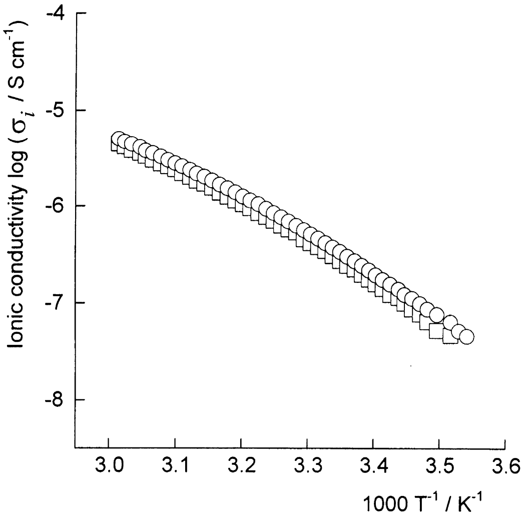

Fig. 3. Temperature dependence of the ionic conductivity for PEO–$(BSLi)_2$ (A) and NR/PEO–$(BSLi)_2$ (W)(PEO–$(BSLi)_2$ content: 90 wt%).

ionic conductivity. Fig. 2 shows the temperature dependence of the ionic conductivity for NR/PEO_{1000}/LiBs (PEO_{1000}/LiBs: 90 wt%). The ionic conductivity for PEO_{1000}/LiBs is also shown in Fig. 2 (S) as a reference. Since this mixture contains a small amount of NR, it did not exhibit rubber-like properties. The ionic conductivity of NR/PEO_{1000}/LiBs was 2.70×10^{-5} S cm^{-1} at 50°C, about 10 times higher than that of bulk PEO_{1000}/LiBs. Similar conductivity enhancement has been reported in PEO-based composite polymer electrolytes with inorganic fillers [11–16]. Inorganic fillers suppress crystallization of the PEO matrix. Furthermore, it is possible that fast ion conducting paths exist in the surface of inorganic fillers. A dramatic decrease in ionic conductivity was observed at around 30°C in both PEO_{1000}/LiBs and NR/PEO_{1000}/LiBs. This jump is due to the crystallization of PEO. The crystallization temperature of PEO shifted to the lower temperature side in the NR/PEO_{1000}/LiBs mixture. Crystallization of PEO was also suppressed by contact with NR. Since a part of PEO are surrounded by NR, the crystallization of PEO shifted to lower temperature side. Owing to the considerable effect, it is suggested that NR and PEO_{1000}/LiBs should be in the micro phase separation.

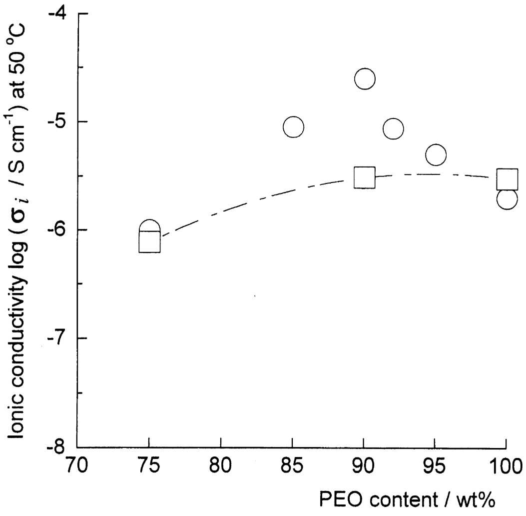

Fig. 4. Effect of PEO derivatives content on the ionic conductivity of the mixture of NR and PEO derivatives at 50°C.(W: PEO/LiBs. A: PEO–$(BSLi)_2$).

This improvement of ionic conductivity in the PEO derivative by the addition of NR was analyzed by changing the PEO derivative. Fig. 3 shows the temperature dependence of the ionic conductivity for PEO_{1000}–$(BSLi)_2$ and NR/PEO_{1000}–$(BSLi)_2$ (PEO_{1000}–$(BSLi)_2$; 90 wt%). We aimed to study the effect of fixed and free anions by using PEO derivatives with a benzenesulfonate anion on the chain end. PEO_{1000}–$(BSLi)_2$ showed an upper convex curve in the Arrhenius plots of the ionic conductivity, a typical consequence of ion migration in the viscous matrix. There was no dramatic decrease in ionic conductivity due to crystallization of PEO. PEO_{1000}–$(BSLi)_2$ is an amorphous material and its property is maintained when it is dispersed in the NR matrix. In the case of the PEO/salt hybrid, the ionic conductivity of the mixture is almost the same as for the hybrid, but a higher ionic conductivity than in the bulk was not observed at any mixing ratio.

Since a higher ionic conductivity of the NR mixture was observed than in the bulk when a simple PEO/salt mixture was used, the effect on the ionic conductivity of the amount of PEO derivative was investigated in detail for the NR/PEO derivative mixture system. The ionic conductivity of the NR/PEO derivative mixture system is shown in Fig. 4 for differing compositions. In the case of PEO/salt mixture, the ionic conductivity increased up to 90 wt%. An ionic conductivity higher than for the PEO_{1000}/LiBs system was observed when the PEO_{1000}/LiBs content is between 85 and 95 wt%, and the maximum value was found at 90 wt%. At this composition the NR content was 10 wt%, and the ionic conductivity of the mixture was about 10 times higher than for the bulk. This is a large difference, which cannot be explained by experimental error. A detailed explanation awaits further experiment.

On the other hand, for the PEO_{1000}–$(BSLi)_2$ hybrid, the ionic conductivity never exceeds the bulk ionic conductivity at any ratio of NR to hybrid. A low molecular weight salt was considered to be effective in producing this anomalous improvement in ionic conductivity. Accordingly, low molecular weight organic molten salt was added to NR. Since molten salt is liquid, it shows very high ionic conductivity. The ionic conductivity of 1-ethyl-2,3-dimethylimidazolium bromide (ImB) was about 10^{-4} S cm^{-1} at 50°C. Fig. 5 shows the ionic conductivity of the mixture at differing NR content. At a NR fraction of 5 and 10 wt%, the ionic conductivity of the mixture was 10 times higher than for the bulk molten salt, and the mixture showed the same tendency as NR/PEO_{1000}/LiBs. Although detailed studies have not yet been carried out, the ionic conductivity of some electrolyte

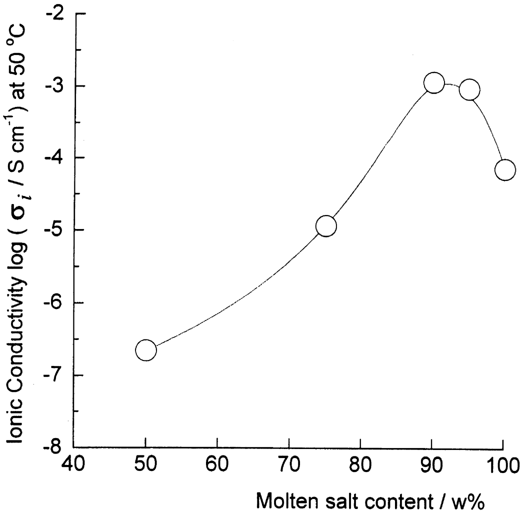

Fig. 5. Effect of molten salt (ImB) content on the ionic conductivity of the mixture of NR and molten salt at 50°C.

materials increases when these ion conducting matrices are mixed with a small amount of NR.

Fig. 6 shows DSC curves for NR, PEO_{1000}/LiBs, and NR/PEO_{1000}/LiBs mixture (PEO_{1000}/LiBs; 90 wt%). The T_g of NR and PEO_{1000}/LiBs are, −65 and −57°C, respectively. According to the DSC measurement of NR/PEO_{1000}/LiBs, two T_gs were observed, suggesting micro phase separation. When PEO and NR were mixed, the mixture separated into two phases, but PEO can be mixed homogeneously with NR in the presence of LiBs. We then tried to blend NR and PEO by using $LiCF_3SO_3$ instead of LiBs. NR and PEO_{1000}/$LiCF_3SO_3$ were stirred until homogeneous solution was obtained in chloroform. NR and PEO_{1000}/$LiCF_3SO_3$ were then gradually separated by removing the solvent. The aromatic benzene ring may play an important role in mixing NR and PEO; PEO interacts with the benzenesulfonate anion and lithium cation, and NR interacts with benzene ring. NR is soluble in benzene, supporting the hypothesis. In addition, we have reported that not only cation, but also anion, interacts with the polyether chain [23]. DSC measurements of the mixture of PEO/salt hybrids, PEO_{1000}–$(BSLi)_2$ and NR was carried out. As a result two T_gs of NR and PEO_{1000}–$(BSLi)_2$ were observed at −64 and −35°C, respectively, a similar result to the PEO/salt mixture. Thus, NR/PEO_{1000}–$(BSLi)_2$ mixture also forms a micro phase separation structure.

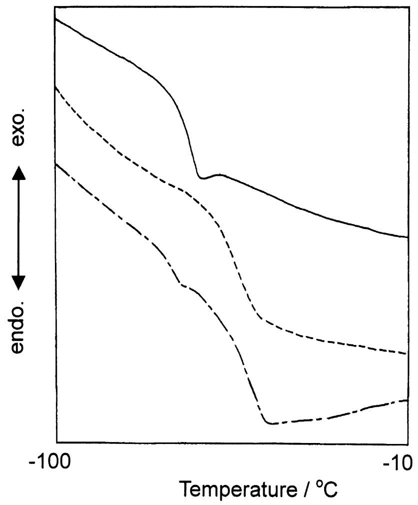

Fig. 6. DSC curves for NR/PEO/LiBs. Scan rate: 10°C min^{-1}. NR: —. PEO/LiBs: – – –. NR/PEO/LiBs: — – —.

Table 1
Effect of elongation on the ionic conductivity (σ_i) for NR/PEO/LiBs

Elongation	$\sigma_i \times 10^{-7}$ at 50°C (S cm^{-1})
None	6.82
⊥ 200%[a]	7.99
‖ 200%[b]	11.7

[a] ⊥ the ionic conductivity perpendicular to the elongation direction.
[b] ‖ the ionic conductivity parallel to the elongation direction.

To study the elasticity of the NR/PEO derivative mixture system, the mixture was cast from chloroform solution on a Teflon sheet, and a film was prepared by gentle drying. The mixture of NR and PEO derivatives showed the highest ionic conductivity, as stated, at a NR content of 10 wt%. However, since it is difficult to obtain an elastic mixture at this ratio, mixture containing 25 wt% NR was used to evaluate the elasticity. The elastic limit of both NR/PEO_{1000}/LiBs and NR/PEO_{1000}–$(BSLi)_2$ was 300 and 400%, respectively, a little lower than that of NR (600%).

Since our experiments imply phase separation of NR in the mixture, orientation of the conduction domain should occur with elongation. The ionic conductivity of NR/PEO_{1000}/LiBs (PEO_{1000}/LiBs: 75 wt%) film was measured using a comb-shaped gold electrode. The ionic conductivity was 6.82×10^{-7} S cm^{-1} at 50°C. The ionic conductivity of films elongated (200%) vertically or parallel to the gold electrode is shown in Table 1. The ionic conductivity of the vertical and parallel elongated samples was, respectively, 1.17×10^{-6} and 7.99×10^{-7} S cm^{-1} at 50°C. The ionic conductivity was almost the same as before elongation, indicating that the conduction path in the film is independent of the deformation.

When PEO containing salts was added to NR, NR was found to conduct ions and have the elasticity of rubber. To our knowledge, NR/PEO mixtures having this combination have not been reported for solvent-free polymer electrolytes. It is also worth increasing the ionic conductivity of some materials by adding a little NR. Mixtures of NR and ion conducting materials are expected to provide flexible polymer electrolytes.

4. Conclusion

PEO_{1000}/LiBs, PEO_{1000}–$(BSLi)_2$, or ImB were blended with natural rubber (NR) to produce novel ion conductive materials. When PEO_{1000}/LiBs was added at 40 wt% to NR, the ionic conductivity of the mixture was approximately 10^{-6} S cm^{-1} at 50°C. This value was almost the same as that of bulk PEO_{1000}/LiBs. The mechanical property of the NR/PEO mixture system is similar to pure NR. At a NR content of 10 wt%, the ionic conductivity of the mixture is 2.7×10^{-5} S cm^{-1} at 50°C, some 10 times higher than for the bulk. Enhancement of the ionic conductivity of ImB was found when NR was mixed in. According to the DSC measurements, these mixtures appear to show micro phase separation. The ionic conductivity of a film of the NR/PEO_{1000}/LiBs system was virtually unchanged on stretching.

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