Nano-Ordered Sea-Island Phase Separation of Ion-Conductive Elastomer Blends Based on NBR and Polyether Electrolytes

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Received November 27, 2012; Accepted June 11, 2013
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Abstract To create novel antistatic polymer materials, we prepared ion-conductive elastomer blends consisting of commercial NBR (with acrylonitrile (AN) content of 18 and 33% (NBR18, NBR33)) with nano-ordered domains of polyether electrolyte. In this study, we prepared blend samples using two different methods, solvent-casting and mechanical mixing methods. The oligo-[(ethylene oxide)-co-(propylene oxide)] methacrylate (M(EO/PO)) was mixed and polymerized in the NBR matrix including KSCN. Obtained elastomer blends showed relatively good conductivity more than $10^{-7}$ S cm$^{-1}$ and the difference in the conductivity of the cast samples under dry and wet conditions was especially very small, and the ratio of conductivity under dry and wet condition of NBR18 blends was lower than 0.06. The TEM images indicated that the order of sea-island phase separation in blend samples may effect on the ion-conductive behavior under different humidity conditions. Moreover, the NBR33 with 30 wt% of PM(EO/PO) sample showed the conductivity of the order of $10^{-6}$ S cm$^{-1}$, and we considered that the large interface between NBR33 and polyether electrolyte domains may effect the increase in the conductivity.

Keywords Ionic conductivity, Solid polymer electrolyte, Elastomer blend, Antistatic, Phase separation, NBR

Introduction

Polymer electrolytes are noteworthy soft materials as novel ionic conductors, since they have good safety characteristics (not flammable, no leakage), and their flexibility and light weight are particularly useful in solid-state lithium-ion secondary batteries. Ionic conduction in poly(ethylene oxide) (PEO)-metal salt complexes was first discovered in 1973, and there have since been many studies of PEO-based electrolytes with a reduced degree of crystallinity and improved salt solubility. Unfortunately, these electrolytes suffer from relatively low conductivity, not exceeding $10^{-5}$ S cm$^{-1}$ at room temperature. On the other hand, from the view point of semi-conductors, we think that these polyether-based electrolytes can be one of novel attractive antistatic materials.

It is well known that there are mainly three types of antistatic materials; polymer composites filled with conductive fillers such as carbon black (CB), surface coating of liquids or oligomers and polymer blends such as Pelestat. The polymer/CB composites have widely been studied, but the control of CB dispersion in polymer and discrepancies of the conductivity are crucial problems. The coating technique is usually temporary effective on the surface and it is difficult to keep the effect for a long time. Therefore, we focused on the polymer blend technique using ion-conductive polymer electrolytes, and expected precise control of the homogeneous conductivity. However, the conductivity of polyether-based electrolytes is very sensitive to the environmental humidity, because the electrolytes consist of hydrophilic polyether and metal salt. To overcome the problem for the humidity, we have previously studied novel polymer blends with NBR and polyether-based electrolytes. Whereas the conductivity of polyether-LiClO$_4$ without NBR under wet condition ($\sigma_{\text{wet}}$) was more than 10-times higher than that under dry condition ($\sigma_{\text{dry}}$), the difference ($\sigma_{\text{wet}}/\sigma_{\text{dry}}$) in the conductivity of NBR/polyether electrolytes blend samples was very small. We considered that it is due to the formation of nano-ordered phase separated structure in the blend samples. However, the Li salt (LiClO$_4$) used in the previous study is impractical because of its explosive property. Therefore, in this study, we used KSCN as a salt for the preparation of ion-conductive elastomer blends which are based on the NBR and amorphous polyether, studied effects of humidity conditions on the conductive behavior and characterized the phase separated...
structure of the blend samples. The aim of this study is to achieve good antistatic performance for the blend samples, more than $10^{-8}$ S cm$^{-1}$ conductivity and less than 1.0 $|\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})|$ which means an indicator of the humidity dependence of the conductivity.

**Experimental**

**Materials**

Acrylonitrile-butadiene rubbers (Nipol NBR, Zeon Co.) with acrylonitrile (AN) content of 18 and 33% (NBR18, NBR33) were obtained from company and used as a base elastomer. Oligo-[(ethylene oxide)-co-(propylene oxide)] methacrylate (Blemmer 50PEP-30, M(EO/PO)) was donated from NOF Co. and used as a monomer for the radical polymerization. The catalyst for the polymerization of M(EO/PO), $\alpha \alpha \alpha \alpha$-azobisisobutyronitrile(AIBN, 97%), was purchased from Kanto Chemical Co. Potassium thiocyanate (KSCN, 98%) as a salt was purchased from Kanto Chemical Co. and dried in vacuo at 70°C before use.

**Sample Preparation**

Ion-conductive elastomer blend samples were prepared by two methods; one is solvent-casting method and the other is mechanical mixing method. Outline of the solvent-casting method is shown in Figure 1. In this method, NBR, M(EO/PO) (including 1 mol% of AIBN) and KSCN were dissolved in THF, and vigorously stirred at room temperature for 24 h to obtain homogeneous solutions. The homogenous solutions were cast onto Teflon® petri dishes at room temperature and dried under low pressure for 6 h, and in vacuo for 48 h. After the solvent removal, the dried samples were kept on a programmable hotplate under dry N$_2$ at 100°C for 24 h to obtain polymerized samples. In case of the mechanical mixing method, NBR was mixed on a two-roll mill with M(EO/PO) (including 1 mol% of AIBN)-KSCN solution at room temperature for 30 min. The mixture was compressed at 120°C for 1.5 h to obtain a 2 mm-thick sheet. Salt concentration of NBR/PM(EO/PO) blend samples was all fixed at 5 wt% to the NBR/PM(EO/PO).

**Measurements**

Ionic conductivity of all samples was determined by a DC volume resistivity measurement system using a Keithley 487 picoammeter/voltage source. For the dry condition measurements (<2% RH), the cell was placed in an oven where the temperature was controlled between 30 and to 60°C under dry N$_2$ gas. The samples were all cut in size of 15×15 mm and were sandwiched between two stainless steel electrodes. For the wet condition measurements (>95% RH), the samples were first kept under high humidity environment (>99% RH) for 2 days. The wet sample was then used for the cell preparation and measured in the oven under the wet condition. Transmission electron microscopy (TEM) observation was made on some NBR18/PM(EO/PO) samples which were stained with OsO$_4$. The thin sections (app. 70 nm thick) were prepared using a cryomicrotome equipped with a glass knife at ~100°C. The sections were then mounted on a 100-mesh copper grid coated with a supporting elastic carbon membrane. The TEM observations were carried out using a JEM-2100 microscope (JEOL Ltd.) at an accelerating voltage of 200kV.

**Results and Discussion**

All blend samples were obtained as homogeneous and flexible films, (e.g. a 70/30 blend photograph of NBR18/PM(EO/PO) in Figure 1). Water uptakes of the dependence on PM(EO/PO) content for the NBR18 blends are shown in Figure 2. The blend samples on the SS electrode were kept under high humidity environment at approximately 99% RH for 2 days, and then they were taken out into air.

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**Figure 1.** Outline of the preparation procedure for a NBR18/PM(EO/PO) blend by the solvent-casting method.
and was weighted immediately. The value of water uptake increased drastically with increasing the PM(EO/PO) content in blend samples. The 30/70 blend sample showed the maximum value, approximately 70 wt%, and this is due to the hydrophilic property of the PM(EO/PO) side chains. In our previous study\(^\text{(14)}\), the water uptakes of NBR18 blend samples were only 4–7 wt%, because the samples were sandwiched between Cu electrodes and the measurement cell was prepared before the exposure to humidity. In this study, the exposure condition is very severe, and it is clear that the water uptakes is are basically proportional to the hydrophilic polyether content. However, the sample prepared by the mechanical mixing method had a slightly lower value, and these differences may be due to the morphology of the blend samples.

Temperature dependences of ionic conductivity for the cast and mechanically mixed NBR18 samples with 30 wt% of PM(EO/PO) are shown in Figure 3. The conductivity of polyether electrolytes usually increases with increasing temperature, because the ionic migration occurs via the segmental motion of polyether chains. As seen in Figure 3, the conductivity clearly increases with increasing temperature, and this indicates that the ionic migration in blend samples depends on the segmental motion. The $\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})$ of the cast sample was very small, 0.05 at 30°C, and the values slightly increased with increasing temperature from 30 to 60°C. On the other hand, the $\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})$ value of the mechanically mixed sample was quite large, more than 2.0 at 30°C, although the mixed sample in the dry condition showed similar order of conductivity with the cast sample.

In order to visualize the effects of the preparation methods on the morphology of the blend samples, we tried to examine the TEM images of the two samples as shown in Figure 4. The dark regions are the NBR phase which was stained with OsO\(_4\), and the light regions are the PM(EO/PO) phase. As seen in Figure 4(a), the blend sample prepared by the solvent casting method has a nano-ordered sea-island phase separated structure, and the domain size of PM(EO/PO) is estimated to be less than 50 nm. Moreover, the size and shape of the island domains seem to be very uniform. On the other hand, the blend sample prepared by the mechanical mixing method shows the distorted phase separation with relatively large size distribution approximately 100–200 nm, of the PM(EO/PO) domains. These indicate that the order and uniformity of the sea-island phase separation may effect the ion-conductive behavior of the blend samples under the different humidity conditions. The difference in morphology of blend samples using different preparation methods can also be seen in the NBR/monomer mixtures before the polymerization\(^\text{(15)}\).

The PM(EO/PO) content dependences of the conductivity for NBR18/PM(EO/PO) and NBR33/PM(EO/PO) blends in dry and wet conditions are shown in Figure 5. The difference in the $\sigma_{\text{dry}}$ of the NBR18/PM(EO/PO) samples was relatively small, whereas the $\sigma_{\text{wet}}$ increased with increasing the polyether content. The blend samples with more than 50 wt% of PM(EO/PO) were able to show good conductivity, and the sample with 70 wt% of PM(EO/PO) showed conductivity higher than the order of $10^{-6}$ S cm\(^{-1}\).
in the wet condition, but the $|\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})|$ value increased and was higher than 0.5. The remarkable point is the very low $|\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})|$ value (app. 0.05) in blend samples with lower than 30 wt% of PM(EO/PO). These samples are suitable for the antistatic material because of the low $|\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})|$ values, and the relatively good conductivity to be close to $10^{-7}$ S cm$^{-1}$. Moreover, the NBR18 sample with 20 wt% PM(EO/PO) showed the good antistatic performance, $0.7 \times 10^{-7}$ S cm$^{-1}$ conductivity, and the $|\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})|$ value of 0.05 at 30°C. On the other hand, the NBR33 blend samples showed a greater conductivity than the NBR18 system. Especially, the NBR33 with 30 wt% of PM(EO/PO) sample showed the conductivity of the order of $10^{-6}$ S cm$^{-1}$, and the significantly low $|\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})|$ value (app. 0.001). Here, we focused on the nitrile (CN) groups in the NBR. It is known that the polymers possessing CN groups such as NBR$^{16-18}$ and PAN$^{19,20}$ can dissolve many types of alkali metal (Li) salts and show good conductivities. Considering the fundamental properties of the CN group in the electrolyte materials, it has the strong electron withdrawing nature and can easily interact with Lewis acids such as alkali metal cations. Furthermore, it is necessary to note that the low nitrile NBR containing a small amount of CN groups becomes softer and has the lower glass transition temperature ($T_g$) than the high-nitrile NBR. The $T_g$ of the neat NBR18 and NBR33 used in this study is $-65^\circ$C and $-40^\circ$C, respectively, and there is a large difference affecting the ionic migration in the blend samples. However, comparing the two blend systems using NBR18 and NBR33, the NBR33 samples showed higher conductivity and the 20/80 blend had the maximum conductivity of approximately $7.7 \times 10^{-7}$ S cm$^{-1}$ at 30°C. The $|\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})|$ value of the NBR33 blend samples was also very small, and the values were less than 0.1. These indicate that the ionic migration in the blend samples mainly occurs in the polyether phase. According to the large difference in the conductivity between the NBR18 and NBR33 systems, we consider that the existence of the interface between the NBR and polyether electrolyte domains should effect the entire condition in the blend samples. The CN groups may contribute to dissociate salts and to diffuse K ions by the strong electron withdrawing property.

**Conclusion**

We prepared NBR/PM(EO/PO) blends using solvent-casting and mechanical mixing methods, and measured their ion-conductive properties under different temperature and humidity conditions. The $|\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})|$ value of the NBR18 cast sample was very small, 0.05 at 30°C. On the other hand, the $|\log (\sigma_{\text{wet}}/\sigma_{\text{dry}})|$ value of the mechanically mixed sample was very large, more than 2.0 at 30°C. From the TEM images, the cast sample had the nano-ordered sea-island and fine phase separated structure with...
less than 50 nm-sized PM(EO/PO) domains. However, the mechanically mixed sample showed distorted phase separation with relatively large size distribution. These indicate that the order and uniformity of sea-island phase separation should effect the ion-conductive behavior of the blend samples under different humidity conditions. Moreover, the NBR33 with 30 wt% of PM(EO/PO) sample showed the conductivity of the order of $10^{-6}$ S cm$^{-1}$, and the significant low $|\log(\sigma_{\text{wet}}/\sigma_{\text{dry}})|$ value of approximately 0.001. According to the large difference in the conductivity between NBR18 and NBR33 systems, we considered that increasing the content of the CN groups which may contribute to dissociate salts and to diffuse K ions by the strong electron withdrawing property may effect the increase in the conductivity.

**Acknowledgement**

One of authors (Y.T.) acknowledges financial support from the Eno Science Foundation.

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