Dual-Phase Polymer Electrolyte with Enhanced Mechanical Strength

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ABSTRACT: The effect of the heat treatment on the tensile properties and the dynamic moduli of polymer matrix films and polymer electrolytes were studied to further increase the mechanical properties. The crosslinking of latex particles brought about their improvements by heating. We have fabricated the polymer electrolyte with a tensile strength of 3.0 MPa, together with a conductivity above 1 mS/cm for application to a lithium secondary battery. This polymer electrolyte had the highest tensile strength among the known gel polymer electrolytes having conductivity over 1 mS/cm, although mechanical properties of plasticized polymer electrolytes have rarely been reported. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1835–1839, 1999

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INTRODUCTION

Polymer electrolytes have been of great interest due to their possible applications in lithium batteries.[1–4] In particular, gel polymer electrolytes are attractive since high ionic conductivity over 1 mS/cm can be obtained when they are highly plasticized. Although both high ionic conductivity and high mechanical strength are required in battery applications, the mechanical strength of gel polymer electrolyte is reduced when the plasticizer content is high. In an attempt to meet these demands, we have proposed dual-phase polymer electrolyte (DPE).[5–8] One of the phases, the supporting phase, in DPE maintains the mechanical strength and the other phase produces ionic pathways of high conductivity. The ion-conductive phase consists of high-polarity polymer plasticized with a lithium salt solution (lithium salt–organic solvent), while the supporting phase is made of low-polarity polymer. In this way, we can increase the plasticizer content in the conductive phase, resulting in a high conductivity, with little damage to the supporting phase. DPE is prepared from a random mixture of high-polarity and low-polarity latex particles. The cast film, composed of fused latex particles, is fully impregnated with a lithium salt solution, which permeates into the high-polarity polymer phase, producing a DPE structure.

We have previously fabricated a DPE with a conductivity of 1 mS/cm and tensile strength of 0.5 MPa from latex mixtures of poly(styrene-*co*-butadiene) rubber (SBR) and poly(acrylonitrile-*co*-butadiene) rubber (NBR).[8] When we tried to apply them to coin-type lithium secondary batteries, we found that although we could make real batteries using thick films, thin films were too

Table I   Characteristics of SBR and NBR Latices

		Particle Size	
	Content of Butadiene (wt %)	Average Particle Diameter (μm)[c]	Standard Deviation (μm)
SBR	50[a]	0.082	0.028
NBR	61[b]	0.084	0.021

[a] Measured from the ratio of the peak areas of ^{1}H-NMR measurement.
[b] Measured from the ratio of the peak areas of ^{13}C-NMR measurement.
[c] Volume average.

weak mechanically to process for coin-type cells. In this article, we therefore try to further increase the mechanical strength while maintaining the high ionic conductivity over 1 mS/cm. We focused on the boundary domains of coalesced SBR latex particles and introduced a crosslinking structure to reinforce the boundary domains. We evaluate the change in mechanical properties (tensile strength and dynamic modulus) produced by this crosslinking and discuss its effect on them along with conductivities.

EXPERIMENTAL

The SBR is partially copolymerized with monomers containing a carboxyl group and a hydroxyl group, which are assumed to react with each other or between themselves on heating, forming crosslinking between adjacent SBR polymer chains. A carboxyl group is also introduced into the NBR by copolymerization. The characteristics of the SBR and NBR latices are summarized in Table I. Particle diameters of SBR and NBR latices were measured on a Particle Distribution Measure LA-910 (Horiba, Ltd). He-Ne laser, and tungsten lamps were used as light sources.

DPE films were prepared in the same manner as previously reported.[5–8] The SBR and NBR latices were first mixed with a 50/50 weight ratio. The mixture was then cast and dried at room temperature for 24 h. The cast films were then subjected to various heat treatments, as described later. Polymer matrix films obtained in this way were immersed in a lithium salt solution of 1M LiAsF$_6$–ethylene carbonate (EC)–pro-

pylene carbonate (PC)–2-methyl tetrahydrofuran (2-MTHF) (volume ratio of EC to PC to 2-MTHF = 1 : 1 : 2) until the films were fully impregnated; thus, DPE films were obtained. This impregnation process was conducted in an Ar atmosphere (H$_2$O < 10 ppm), and the lithium salt solution was of battery grade (H$_2$O < 30 ppm) purchased from Tomiyama Chemical Co., Ltd.

Tensile behaviors of polymer matrices and DPEs were evaluated on an Instron Model 4204 Tensile Testing Instrument. Specimens were cut into dumbbell-shaped test pieces. The crosshead speed of the test fixture was 20 mm/min.

The dynamic mechanical properties were measured on an automatic dynamic viscoelastomer rheovibron DDV-25FP. A measuring step of 2°C min was employed over a temperature range of 20 to 300°C, and frequency was 3.5 Hz.

The ionic conductivity was measured by the complex impedance method on a Hewlett Packard 4284A LCR Meter using stainless steel disc electrodes (10 mm in diameter).

RESULTS AND DISCUSSION

After thorough vacuum-drying at 105°C, the polymer matrix (SBR–NBR) was heat-treated in vacuum at 150°C. The stress–strain curves for the polymer matrix films with heating time from 0 to 45 h are shown in Figure 1. All of the curves show

Figure 1   Effect of crosslinking on stress–strain curve of SBR–NBR polymer matrix films.

Figure 2 Effect of crosslinking on E' temperature of SBR polymer matrix films.

typical behavior of rubbery material,[9–12] as follows: in the initial small strain region, the stress increases linearly with the strain, corresponding to the rubber elasticity; the samples then extends smoothly with a smaller stress increase in the following intermediate region; finally, a steep increase in stress is observed, which is caused by highly extended polymer chains. Since both SBR and NBR are typical rubbers, such a behavior of the polymer film is quite reasonable.

Even without the 150°C heating, the tensile strength at break is 9.8 MPa. This high tensile strength for an SBR–NBR blend reflects the crosslinking in the SBR and NBR, which is inherently formed in an emulsion polymerization.[11] The stress–strain curve rises with heating time, and the tensile strength simultaneously increases to as high as 12.3 MPa for 5 h of heating while the elongation at break point continues to decrease. Such a behavior is expected when the crosslink density is increased, indicating the formation of crosslinking in the latex particles by heating.

To verify this additional crosslinking of SBR, we investigated the change in the crosslink density of SBR. The relationships between the moduli (E') and the absolute temperatures (T) of SBR films with various heating times are shown in Figure 2. These films have T_gs at around 273 K. In principle, E' shows a linear relationship with the absolute temperature in the region, which shows the entropy elasticity. In Figure 2, the region, in which E' shows a linear relationship with

the absolute temperature, is observed from 460 to 470 K at 20 h of heating (□), while that region is observed around 475 K without heating (△). Generally, the slope of E' versus temperature through rubber plateau is in proportion to the crosslink density, as follows:

$$E' = 3RT\left(\frac{v_e}{V}\right) \qquad \left(\frac{v_e}{V}\right) : \text{crosslink density}$$

The slope of E' versus temperature for 20 h of heating (□) is larger than that for 0 h of heating (△) by 1.5 times. This indicates the crosslinking density of SBR increases by 50%. This additional crosslinking takes place mainly in the boundary domains of SBR particles since the polar crosslinking groups, introduced in a latex particle, are distributed along the particle boundary.[13–15]

Stress–strain curves for DPEs fully impregnated are shown in Figure 3. The 150°C heating-time dependency on the conductivity and the saturated plasticizer ($1M$ LiAsF$_6$–EC/PC–2-MTHF) content for the DPEs are also plotted in Figure 4. In the stress–strain curve for the DPE without the 150°C-heating, the modulus, which is calculated from the slope in the first region, greatly decreases compared with that for the latex film before impregnation (Fig. 1, 0 h). This is due to the plasticization. This DPE contains 71% of plas-

Figure 3 Effect of crosslinking on stress–strain curve of SBR–NBR DPE fully impregnated with $1M$ LiAsF$_6$–EC–PC–2-MTHF.

Figure 4 Conductivity and plasticizer ($1M$ LiAsF$_6$–EC–PC–2-MTHF) content versus 150°C heating time for the DPE fully impregnated.

ticizer, and most of it is selectively accommodated in the NBR phase, as previously determined by X-ray microanalysis.[6] Therefore, the NBR phase loses mechanical strength (This is confirmed by a control experiment, in which the fully impregnated NBR gel is so fragile that it breaks easily upon handling, and the plasticizer content of NBR cannot be found); thus, the only SBR comes to bear all the mechanical support. With the further strain applied to the second region, the plasticization considerably reduces the stress, and the test piece breaks at 270% elongation before the third region, in which the stress rises. Obviously, the SBR phase breaks at this point. We suspect that this occurs in boundary domains of the fused SBR particles because the boundary domains contain polar components like emulsifiers. Some of the plasticizer then permeates into this domain, which was also found previously by the microanalysis.[6] Thus, the structural integrity degrades. With 20 h of heating, the tensile strength increases to 3.0 MPa while the DPE maintains high conductivity over 1 mS/cm, as shown in Figure 4. This is six times the value that we previously reported[8] and an order of magnitude higher than ever reported by others for plasticized polymer electrolytes having conductivity above 1 mS/cm.[17] The marked increase in tensile strength may be caused by the crosslinking introduced into the SBR phase, in particular, its particle boundary domain by heating. Further heating (45 h of heating) results in a significant reduction in tensile strength as well as elongation. It may be caused

by the decomposition of the SBR phase with a sufficient thermal energy. The excess crosslinking also occurs by the fact that the plasticizer content decreases at 45 h of heating, as shown in Figure 4. (This is also confirmed by the experimental fact that the plasticizer content of the fully impregnated NBR gel is 89% at 20 h of heating and decreases to 85% at 45 h of heating.) The ionic conductivity also decreases for that.

CONCLUSION

We have fabricated a DPE with a tensile strength of 3.0 MPa, together with a conductivity above 1 mS/cm, by heat treatment. This considerable improvement in mechanical strength may be achieved by the crosslinking in the boundary domains of the latex particles. This DPE has the highest tensile strength among the known gel polymer electrolytes having conductivity over 1 mS/cm, although mechanical properties of plasticized polymer electrolytes have rarely been reported.

Recently, it became possible to make a coin-type lithium secondary battery using our improved DPE with a thickness of 36 μm due to its high mechanical strength. Results of the performances of cells will be reported later. We will also try to improve the DPE in terms of the mechanical and conducting properties for application to batteries.

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