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Polymer electrolytes with dual-phase structure composed of NBR/SBR blend polymer

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A dual-phase polymer electrolyte without ionic impurities has been prepared from pure poly(acrylonitrile-*co*-butadiene) rubber (NBR)/poly(styrene-*co*-butadiene) rubber (SBR) blend polymer. D.s.c. heating curves suggest that a dual-phase structure was constructed. The blend polymer electrolyte system attained high ionic conductivity of 7.2×10^{-4} S cm^{-1} when NBR/SBR 50/50 (w/w) film was saturated with 1 M $LiClO_4$ in 50/50 (v/v) γ-butyrolactone/1,2-dimethoxyethane solution.

(Keywords: polymer electrolyte; dual-phase structure; high ionic conductivity)

Introduction

Polymer electrolytes composed of poly(acrylonitrile-*co*-butadiene) rubber (NBR) and poly(styrene-*co*-butadiene) rubber (SBR) mixed latex have recently been investigated because of their high ionic conductivity and good mechanical strength$^{1-3}$. These superior characteristics result from dual-phase structure, in which highly polar NBR is selectively impregnated with lithium salt solution, forming ion-conductive channels, whereas a non-polar SBR is not impregnated, forming supporting polymer matrices. However, commercially available latices typically include ionic impurities and reactive groups (e.g. surfactants, initiator fragments and hydroxyl and amino groups, etc.), which may reduce the long-term stability of electrochemical devices. Thus, investigation of the dual-phase polymer electrolyte without ionic impurities is required.

This communication shows that a dual-phase polymer electrolyte can also be prepared from pure NBR/SBR blend polymer. Pure NBR and SBR polymers used in this work were synthesized by suspension polymerization and solution polymerization, respectively. D.s.c. heating curves suggest that a dual-phase structure was formed. The blend polymer electrolyte system attained high ionic conductivity of 7.2×10^{-4} S cm^{-1} when NBR/SBR 50/50 (w/w) film was saturated with 1 M $LiClO_4$ in 50/50 (v/v) γ-butyrolactone (γ-BL)/1,2-dimethoxyethane (DME) solution.

Experimental

Pure NBR and SBR were purchased from Nippon Zeon Co., Ltd. Their poly(butadiene) contents were 60% (w/w) and 75% (w/w), respectively. The NBR and SBR were dissolved in tetrahydrofuran and mechanically mixed using a standard technique, dried at room temperature for several hours, and vacuum dried at 378 K for 24 h to form polymer blend films. The resultant film was immersed in 1 M $LiClO_4$ in γ-BL solution or 1 M $LiClO_4$ in 50/50 (v/v) γ-BL/DME solution to obtain blend polymer electrolyte film. The lithium salt solutions were reagent grade ($H_2O < 30$ ppm), available from Mitsubishi Petrochemical Co., Ltd. The amount of absorbed solution in the films was controlled by varying the immersion time. After immersion, the films were still rubber-like and retained tensile strength.

Ionic conductivity was measured by the standard a.c. impedance method in the frequency range from 20 Hz to 1 MHz using a Hewlett Packard 4284A Precision LCR Meter. Two parallel stainless steel discs (10 mm in diameter) were used as electrodes. D.s.c. heating measurements were carried out at 20 K min^{-1} after cooling the film to 113 K with a Perkin Elmer DSC7 Differential Scanning Calorimeter.

Results and discussion

Figure 1 shows d.s.c. heating curves for NBR/SBR 50/50 (w/w) blend polymer films before becoming swollen with 1 M $LiClO_4/\gamma$-BL solution (curve 1), swollen with 27% (w/w) of 1 M $LiClO_4/\gamma$-BL solution (curve 2), and swollen with 40% (w/w) of 1 M $LiClO_4/\gamma$-BL solution (curve 3). In curve 1, there are two endothermic shoulders at 235 and 256 K and these are attributed to the glass transitions of SBR and NBR, respectively. This profile suggests that NBR and SBR are not mixed at the molecular scale and should exist as separate phases in the blend polymer film. Curve 2 shows only one shoulder at about 230 K, which is assigned to the SBR phase. Highly polar NBR phase should be impregnated and plasticized with the lithium salt solution, so the glass transition shoulder of NBR at 256 K in curve 1 disappears. On the other hand, the non-polar SBR phase is not swollen and plasticized, so the SBR shoulder remains. These results suggest that the NBR phase is selectively swollen with the solution, building ion-conductive pathways, while the SBR phase is not swollen, forming a mechanically supportive polymer matrix. Furthermore, there is no peak attributed to the absorbed lithium salt solution. In curve 3, however, an exothermic peak at 195 K and an endothermic peak at 220 K are clearly visible and can be attributed to crystallization and melting of the

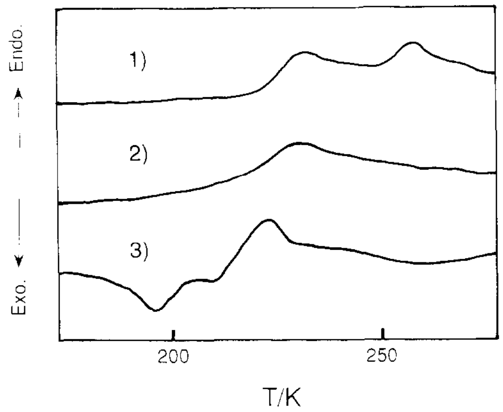

Figure 1 D.s.c. heating curves for NBR/SBR 50/50 (w/w) blend polymer electrolyte films: 1, blend polymer film before becoming swollen with 1 M $LiClO_4/\gamma$-BL solution; 2, blend polymer film swollen with 27% (w/w) of 1 M $LiClO_4/\gamma$-BL solution; 3, blend polymer film swollen with 40% (w/w) of 1 M $LiClO_4/\gamma$-BL solution

Table 1 Solution contents and ionic conductivities of NBR/SBR 50/50 (w/w) blend polymer electrolytes

Lithium salt solution	Solution contents (%, w/w)	Ionic conductivity ($S cm^{-1}$)
1 M $LiClO_4/\gamma$-BL	17	2.3×10^{-7}
	30	1.2×10^{-5}
	36	1.2×10^{-4}
	38	1.0×10^{-4}
	40	2.0×10^{-4}
	42	2.3×10^{-4}
1 M $LiClO_4/\gamma$-BL/DME	21	7.6×10^{-7}
	24	1.1×10^{-6}
	33	2.7×10^{-5}
	37	2.3×10^{-4}
	41	4.5×10^{-4}
	45	6.5×10^{-4}
	49	7.2×10^{-4}

$LiClO_4/\gamma$-BL solution, respectively[2]. This implies that the phase transition of absorbed solution in the NBR may critically change in the solution content range between 27 and 40% (w/w). Below the threshold, the majority of the absorbed solution interacts so strongly with the polar NBR matrix that freezing and melting of the solution cannot occur. In contrast, above the threshold a 'free' lithium salt solution[2,4] exists. This behaviour is consistent with that of NBR/SBR mixed latex systems[2], in which the threshold of the solution content was reported to be between 29 and 37% (w/w).

Table 1 gives ionic conductivities and solution contents of blend polymer electrolytes (NBR/SBR 50/50, w/w) for both the 1 M $LiClO_4/\gamma$-BL system and the 1 M $LiClO_4$ dissolved in 50/50 (v/v) γ-BL/DME cosolvent system. For both systems, ionic conductivity increases with increasing the solution content. The maximum solution content of 49% (w/w) for the $LiClO_4/\gamma$-BL/DME system is larger than that of 42% (w/w) for the $LiClO_4/\gamma$-BL system. A similar result was reported in the NBR/SBR latex polymer electrolyte system, i.e. the maximum solution content of the previous system was 61% (w/w) for $LiClO_4/\gamma$-BL/DME and 49% (w/w) for $LiClO_4/\gamma$-BL[2]. This phenomenon can be explained in terms of solubility effects. The solubility parameters of γ-BL and DME are 25.8 and 17.6 $MPa^{1/2}$, respectively[5]. Adding weakly polar DME to γ-BL lowers the polarity of the solution and it approaches the polarity of the SBR. The solubility parameter of styrene–butadiene copolymer is between 16.6 and 19.0 $MPa^{1/2}$ (ref. 5). Therefore, it is possible that a small amount of the solution permeates the SBR phase as well as the NBR phase[2]. The highest ionic conductivities of 2.3×10^{-4} and 7.2×10^{-4} $S cm^{-1}$ were achieved with the 1 M $LiClO_4/\gamma$-BL and 1 M $LiClO_4/\gamma$-BL/DME solution systems, respectively. The blend polymer electrolyte films retained rubber-like consistency with mechanical strength, despite the presence of a large amount of lithium salt solution. In future work, dependence of the microscopic morphology on ionic conductivity of this and other blend systems will be reported in more detail.

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