

Polymer electrolytes with a dual-phase structure composed of poly(acrylonitrile-co-butadiene)/poly(styrene-co-butadiene) blend films impregnated with lithium salt solution

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Dual-phase polymer electrolytes that possess good mechanical strength and high ionic conductivity were prepared by mechanically mixing a poly(acrylonitrile-co-butadiene) rubber (NBR) and poly(styrene-co-butadiene) rubber (SBR) binary solution and casting polymer blend films. The films were swollen with lithium salt solutions (e.g. 1 M LiClO₄ in γ -butyrolactone) to obtain dual-phase polymer electrolyte films. As the mixing rate increases, the average domain size of the NBR and SBR in the film decreased, levelling off at a mixing rate of $>10\,000\text{ rev min}^{-1}$ as it approached the value of $5\ \mu\text{m}$. A mechanically strong film was obtained by reducing the domain size to less than one-fifth of the film thickness. On the other hand, the ionic conductivity depended on the fraction of NBR in the NBR/SBR matrix rather than on the domain size of the film. Thus high ionic conductivity ($>10^{-4}\text{ S cm}^{-1}$) could be achieved with an NBR weight fraction of over 50% (w/w). Additionally, transmission electron microscope observation and differential scanning calorimetric analysis showed evidence that a dual-phase structure was created, in which the NBR phase provided an ion-conductive pathway and the SBR acted as a mechanically supportive matrix. Quantitative analysis of ionic conductivity suggested that a 'free' lithium salt solution absorbed in the matrix caused the high ionic conductivity of the polymer electrolyte.

(Keywords: polymer electrolyte; dual-phase structure; domain size control)

INTRODUCTION

Much research has been done with the goal of creating polymer electrolyte materials with high ionic conductivity, good mechanical strength and good electrochemical stability. Mixed systems comprising a polymer with low glass transition temperature such as poly(ethylene oxide) and a lithium salt have been investigated extensively, because a lithium ion dissociated in the polymer matrix can move easily due to the segmental motion of the polymer chains and the film still possesses good tensile strength^{1,2}. However, the typical ion conductivity values are of the order of 10^{-5} S cm^{-1} at room temperature, which is too low for many applications. Polymer electrolytes composed of a polar polymer providing a host matrix for a lithium salt solution have also been studied because of their liquid-like conductivity ($>10^{-3}\text{ S cm}^{-1}$ at room temperature)¹⁻⁴. This system can be easily prepared by swelling a 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 remains unreliable. Thus, it has been difficult to prepare polymer electrolytes that possess both high ionic conductivity and good mechanical strength.

One approach to solving this problem is to use dual-phase polymer electrolytes in which one phase provides high ionic conductivity but is mechanically weak, whereas the other phase provides mechanical strength. Previous reports proposed a polymer electrolyte designed to contain two phases: a highly polar region (impregnated with a lithium salt solution) that forms continuous ion-conductive channels, and a non-polar region that forms the supporting polymer matrix⁵⁻⁸. Highly polar regions are formed by using poly(acrylonitrile-co-butadiene) rubber (NBR) latex particles and non-polar regions are formed with poly(styrene-co-butadiene) rubber (SBR) latex particles. Various microscopic analyses have provided evidence that a dual-phase structure was created in the electrolyte film under these conditions. A rubbery film with good tensile strength and high ionic conductivity of the order of 10^{-3} S cm^{-1} was obtained, which was practicable for many applications.

Although materials with high ionic conductivity and good mechanical strength can be obtained from latex materials, commercially available latices typically include ionic impurities and reactive groups (e.g. surfactants, initiator fragments and hydroxyl and amino groups), which may reduce the long-term stability

of electrochemical devices. Thus, a dual-phase polymer electrolyte without ionic impurities needs to be investigated from the application point of view. Another communication will show that a dual-phase polymer electrolyte can also be prepared from a pure NBR/SBR blend polymer⁹. The pure NBR and SBR polymers used in that work are synthesized, respectively, by suspension polymerization and solution polymerization.

This paper extends the other research⁹ and systematically investigates a dual-phase polymer electrolyte comprising an NBR/SBR blend polymer from the standpoints of its mechanical properties and ionic conductivity. Domain size and polarity in the NBR/SBR blend polymer film were controlled so as to obtain both good mechanical strength and high ionic conductivity. The domain size can be controlled as a function of: (1) the mixing rate of the NBR/SBR polymer solution and (2) the evaporation rate of the solution. The polarity of the film can be controlled by varying the composition of the binary NBR/SBR matrix. This work also explores the dual-phase nature of the blend polymer electrolyte by transmission electron microscopic (TEM) observation and differential scanning calorimetric (d.s.c.) analysis. The origin of high ionic conductivity is quantitatively analysed as a function of the lithium salt solution content in the electrolyte.

EXPERIMENTAL

Pure NBR and SBR were supplied by Nippon Zeon Co. Ltd. Their polybutadiene contents were 60% (w/w) and 75% (w/w), respectively. The NBR and SBR were dissolved in tetrahydrofuran (THF) and mixed mechanically for 1 h using an SMT Co. homogenizer with various rotating rates, and dried at 325 K in an oven with an N₂ gas flow to form a polymer blend film. The resultant film was immersed in a solution of either 1 M LiClO₄ in propylene carbonate (PC), 1 M LiClO₄ in γ -butyrolactone (γ -BL) or 1 M LiClO₄ in 50/50 (v/v) γ -BL/1,2-dimethoxyethane (DME) to obtain a blend polymer

electrolyte film. These lithium salt solutions were reagent-grade (H₂O < 30 ppm) and were purchased from Mitsubishi Petrochemical Co. Ltd. The amount of absorbed solution in the films was controlled by varying the immersion time.

Optical microscope (OM) measurements were carried out using a Nikon Biophot optical microscope. Cross-sections were prepared by cutting the sample film with a microtome using the standard technique.

TEM measurements were carried out using a Hitachi H-600 microscope. The accelerating voltage was 100 kV. The sample that included 1 M LiClO₄/ γ -BL was prepared after evaporating the γ -BL completely. A thin section was prepared by the standard wet process and was stained with OsO₄ vapour⁷.

D.s.c. measurements were carried out at 20 K min⁻¹ with a Perkin-Elmer DSC7 differential scanning calorimeter after cooling the film to 113 K. During the measurement, the sample was mounted in a sealed aluminium pan to prevent the solution from evaporating.

Ionic conductivity was measured using the standard a.c. impedance method in the frequency range from 20 Hz to 1 MHz with a Hewlett-Packard 4284A Precision LCR Meter. Two parallel stainless-steel discs (10 mm in diameter) were used as electrodes.

Stress *versus* strain was measured using an Instron model 4204 testing instrument. Dumbbell-shaped test pieces were used for the measurement.

RESULTS AND DISCUSSION

Domain size control

We first controlled the size of the NBR and SBR domains in the film (NBR/SBR 50/50 w/w) as a function of the mixing rate of the homogenizer. Optical microscope images of the NBR/SBR film are shown in *Figure 1* as a function of the mixing rate. Elliptical domains are visible in all of the images, although it is difficult to identify whether they are NBR or SBR. As the mixing

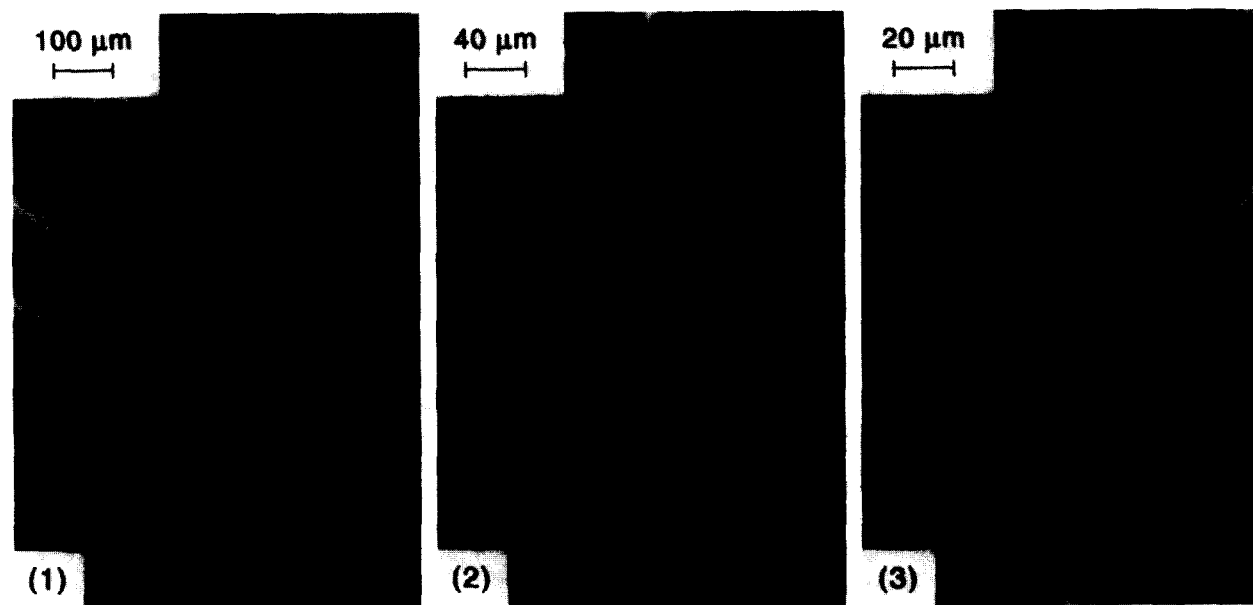


Figure 1 Optical microscope images of the NBR/SBR blend polymer matrix prepared by mixing NBR/SBR blend polymer solution at the following rates: (1) 200 rev min⁻¹, (2) 3000 rev min⁻¹, (3) 10 000 rev min⁻¹

rate increases, the domains become well dispersed and the average size decreases. In Figure 2, the average domain size in the film is plotted against the mixing rate. The average domain size is estimated from the images by directly measuring the major axis of the ellipse. As the mixing rate increases, the size sharply decreases, levelling off ($> 10\,000$ rpm) as it approaches the value of $5\ \mu\text{m}$. This result suggests that the domain size of this system can be controlled in the range between 5 and $100\ \mu\text{m}$ by using this mechanical mixing method. The NBR and SBR seem to be dissolved macroscopically in the polymer blend solution at low mixing rates, but microscopically each polymer chain may cling and form a cluster with itself in the blend solution. These clusters can possibly be made smaller by mixing the blend solution more speedily, resulting in a blend film that has small domains.

We then varied the evaporation time of the THF solvent to see what effect this would have on the domain size. The time was controlled by varying the temperature and N_2 gas flow in an oven. The evaporation time in this study is defined as how long it takes the solvent content in the film to become less than $0.1\%(\text{w/w})$. Figure 3 shows the relationship between the average domain size in the film and the evaporation time. The film was prepared by mixing the blend polymer solution at a rate of $10\,000\ \text{rev min}^{-1}$. It is safe to say that the domain size is independent of the evaporation time in this case. Once the NBR and the SBR are well mixed in the solvent, aggregation of the polymer does not appear to proceed further during solvent evaporation.

Dependence of the domain size on the NBR/SBR film strength

Figure 4 shows the stress-strain curves for the NBR/SBR 50/50 w/w blend polymer electrolyte films as a function of the average domain size. All the electrolyte films were saturated with $42\%(\text{w/w})$ $1\ \text{M LiClO}_4/\gamma\text{-BL}$ solution and are $100\ \mu\text{m}$ thick. We choose the composition of NBR/SBR 50/50 w/w for the polymer matrix because this electrolyte system with high

ionic conductivity ($>10^{-4}\ \text{S cm}^{-1}$) makes it practicable for applications. When this electrolyte is applied to electronic devices, a trade-off between two effects—low resistivity and good mechanical strength—is required. This electrolyte system needs a film thickness of over $50\ \mu\text{m}$ to obtain a self-standing film, but it needs a film of less than $200\ \mu\text{m}$ to obtain a low resistivity film; thus we selected a standard film thickness of $100\ \mu\text{m}$. Films with small domains ($< 20\ \mu\text{m}$) show almost the same mechanical behaviour and have good tensile strength, whereas films with large domains (near $100\ \mu\text{m}$) have very poor tensile strength. This implies that the domain size should be less than one-fifth of the film thickness to obtain good mechanical strength. When the film has a domain size close to the film thickness (i.e. a mechanically weak NBR domain swollen with the lithium salt solution exists throughout the film thickness), the film is mechanically weak and is easily broken at the NBR domains.

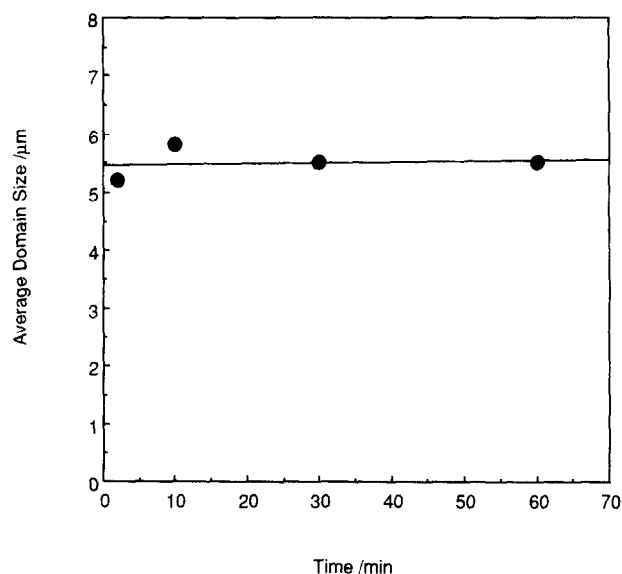


Figure 3 Relationship between the average domain size in the film and the evaporation time of the solution

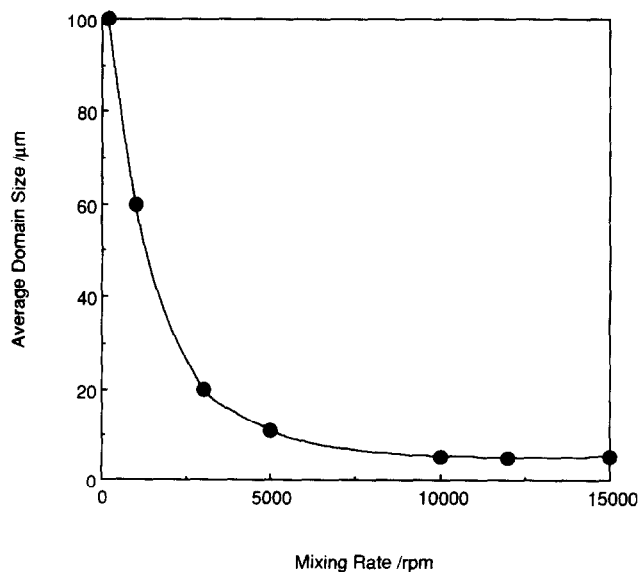


Figure 2 Relationship between the average domain size in the film and the mixing rate

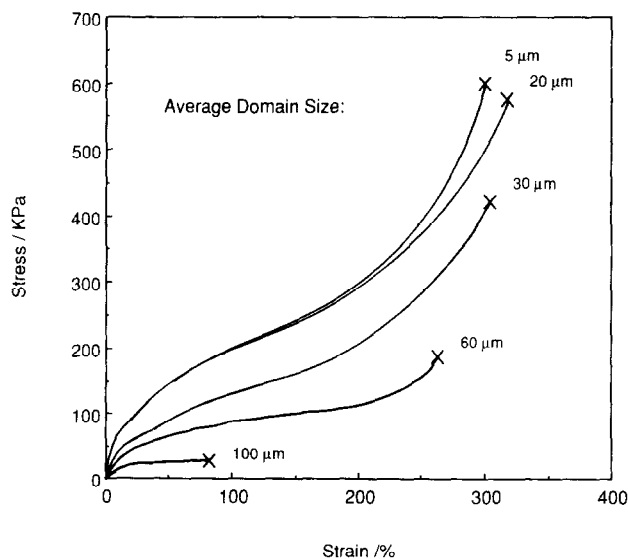


Figure 4 Stress-strain curves for the NBR/SBR 50/50 w/w blend polymer electrolytes saturated with $\text{LiClO}_4/\gamma\text{-BL}$ as a function of the average domain size in the film

Effect of domain size and polarity in the NBR/SBR film on ionic conductivity

Ionic conductivity of various NBR/SBR composition films saturated with 1 M LiClO₄/γ-BL is plotted logarithmically in Figure 5 as a function of both the average domain size and the lithium salt solution content (the percolation curve). The lithium salt solution contents of 10, 14, 20, 23, 31, 41 and 47% (v/v) in the figure, respectively, correspond to NBR contents of NBR/SBR polymer matrices of 5, 10, 15, 20, 30, 50 and 70% (w/w) that are saturated with 1 M LiClO₄/γ-BL solution. Lithium salt solution content at the saturation point increased with increase in the NBR in the matrix due to increase in polarity. The volume percentage was calculated by use of the density of 1 M LiClO₄ in γ-BL solution at 298 K, i.e. 1.19⁷. The percolation curve profile reflects the dimensionality of conduction and the manner in which the conducting phase (the NBR swollen with lithium salt solution) and the insulating phase (the SBR) are mixed¹⁰⁻¹³. Polymer electrolyte films with small domains (<20 μm) show typical three-dimensional (3D) conduction; a jump is visible at a lithium salt solution content of 20% (v/v)⁷. For the film with large domains (100 μm), in contrast, the curve shows high ionic conductivity even at small amounts of solution content and does not show the jump. This probably results from ID ion conduction; this film has large NBR domains and has ready-made continuous ion pathways throughout the film even when the NBR fraction (the lithium salt solution fraction) is very small.

In the lithium salt solution content range above 35% (v/v), however, all systems have a similar curve profile and the ionic conductivity gradually increases as the polar NBR fraction increases. This indicates that ionic conductivity depends upon the polarity of the NBR/SBR matrix rather than the domain size in the film; thus high ionic conductivity (>10⁻⁴ S cm⁻¹) can be achieved in all systems when the NBR content is above 50% (w/w) (the lithium salt solution content is above 41% (v/v)).

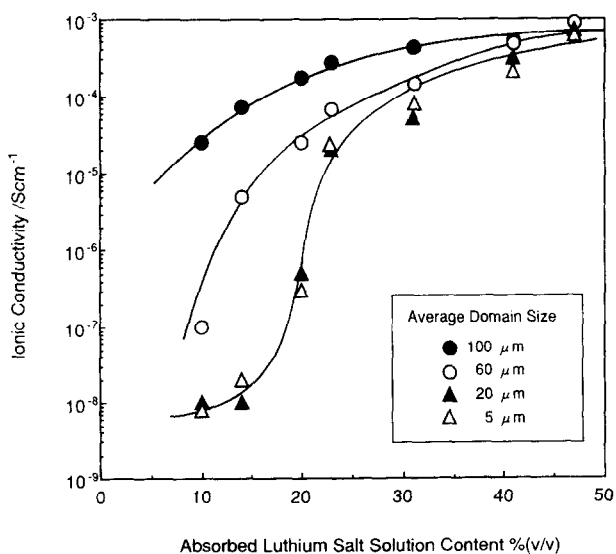


Figure 5 Relationship between lithium salt solution volume percentage and ionic conductivity of polymer electrolyte for various NBR contents in the matrix at the saturation point

TEM observation of the dual-phase structure before and after swelling with lithium salt solution

A TEM image of the polymer matrix (NBR/SBR 50/50 w/w) before impregnation with the lithium salt solution is shown in Figure 6a. The matrix was prepared by mixing the polymer blend solution at 200 rev min⁻¹. The dual-phase structure is clearly seen: one phase is deeply stained; the other phase is lightly stained. Previous research on NBR/SBR mixed latex systems has confirmed microscopically that the deeply stained regions are SBR and lightly stained regions are NBR⁷.

Figure 6b shows the TEM image of the polymer electrolyte film after swelling with a lithium salt solution (1 M LiClO₄/γ-BL) and evaporation of the γ-BL. Two phases (deeply and lightly stained) are still seen after swelling. Careful analysis of the TEM image in Figure 6b also indicated that small voids (white, spotty regions) occurred almost exclusively in the lightly stained phase (the NBR phase). These voids are probably caused by evaporation of the high-boiling-point solvent, γ-BL, and provide evidence that swelling and ionic conduction occur only in the polar NBR phase. The solubility parameters of the γ-BL, polyacrylonitrile, polystyrene and polybutadiene are approximately 25.8, 30, 18 and 17 MPa^{1/2}, respectively¹⁴. On the assumption that the solubility parameters of NBR and SBR decrease in proportion to the increase in the polybutadiene content, the solubility parameter values of NBR (polybutadiene 60% (w/w) and SBR polybutadiene 75% (w/w)) in this case are approximately 23 and 17 MPa^{1/2}, respectively. Therefore, it is reasonable to expect the γ-BL to permeate selectively in the NBR phase but not to permeate in the SBR phase.

Calorimetric analysis⁹

Figure 7 shows d.s.c. heating curves for NBR/SBR 50/50 (w/w) blend polymer films prepared by mixing at 200 rev min⁻¹: curve (1) represents a blend polymer film before becoming swollen with a 1 M LiClO₄/γ-BL solution; curve (2) is for a blend polymer film swollen with 27% (w/w) of a 1 M LiClO₄/γ-BL solution; and curve (3) is for a blend polymer film swollen with 40% (w/w) of a 1 M LiClO₄/γ-BL solution. 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 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. The highly polar NBR phase appears to have been impregnated and plasticized by the lithium salt solution, so the glass transition shoulder of the NBR at 256 K 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 and forms a mechanically supportive polymer matrix. This also agrees well with the microscopic evidence of the TEM image shown in Figure 6b.

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 these can be attributed,

respectively, to crystallization and melting of the $\text{LiClO}_4/\gamma\text{-BL}$ solution⁶. This implies that a critical change in the phase transition of the absorbed solution in the NBR may occur somewhere in the solution content

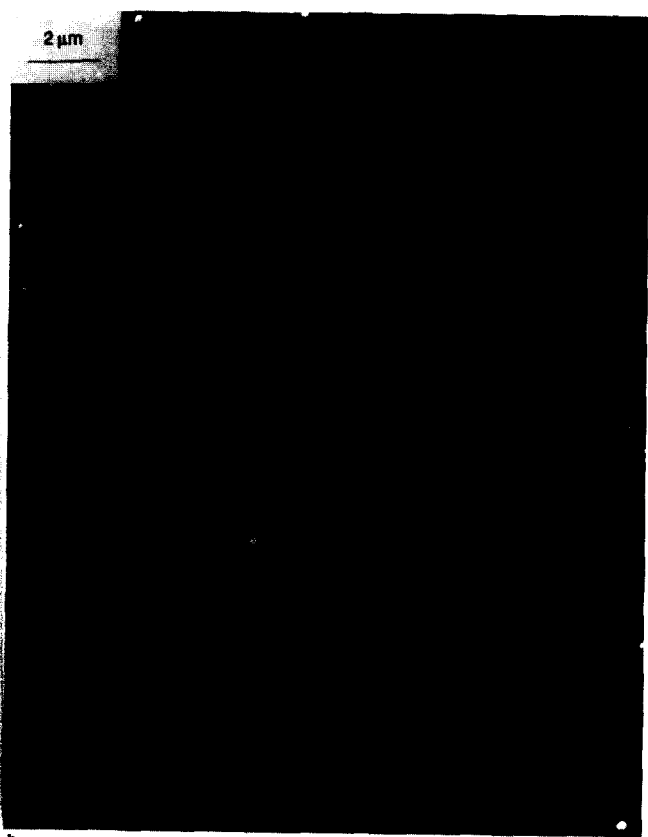
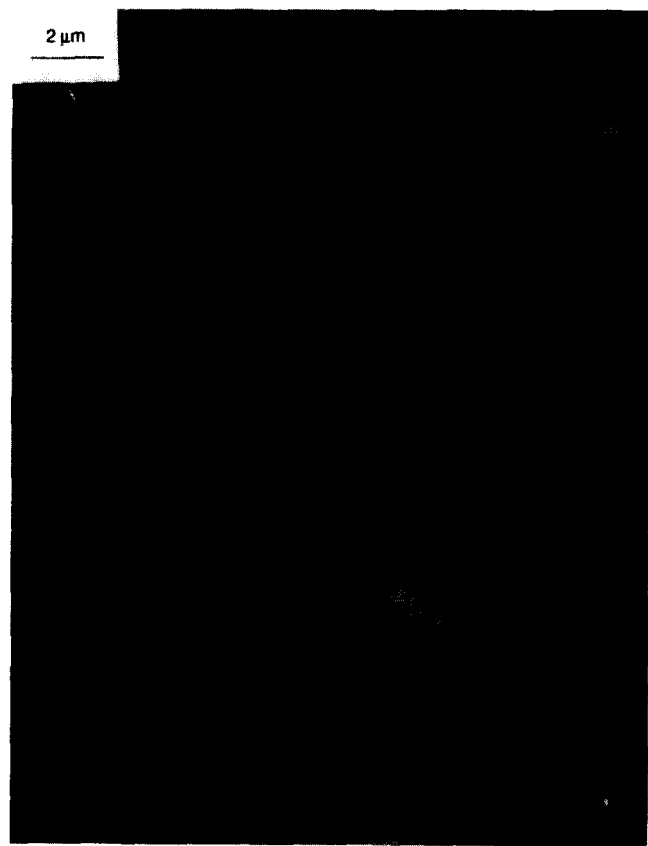


Figure 6 TEM images of the NBR/SBR 50/50 w/w polymer matrix (a) before and (b) after impregnation with 1 M $\text{LiClO}_4/\gamma\text{-BL}$

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. Above the threshold, in contrast, a 'free' lithium salt solution exists^{6,15}. This behaviour is consistent with that of NBR/SBR mixed latex systems, in which the threshold of the solution content was reported to be between 29% and 37% (w/w)⁶.

Ion-conductive behaviour

Figure 8 shows the ionic conductivity of the polymer electrolyte (NBR/SBR 50/50 w/w) logarithmically versus the solution content for the 1 M LiClO_4/PC , 1 M $\text{LiClO}_4/\gamma\text{-BL}$ and 1 M $\text{LiClO}_4/\gamma\text{-BL}/\text{DME}$. The

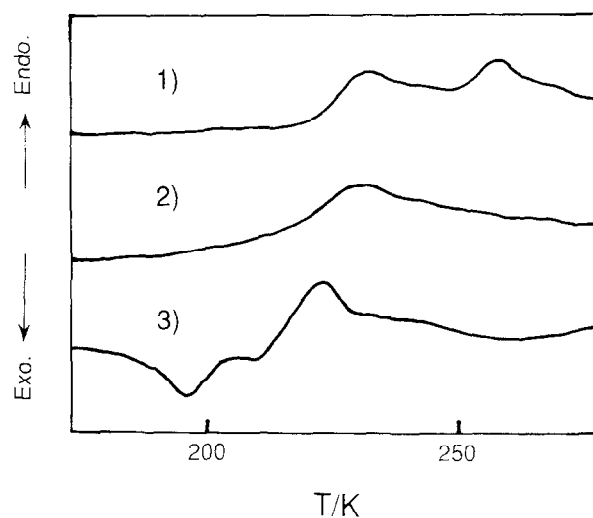


Figure 7 D.s.c. heating curves for NBR/SBR 50/50 w/w blend polymer electrolyte films: (1) blend polymer film before becoming swollen with 1 M $\text{LiClO}_4/\gamma\text{-BL}$ solution; (2) blend polymer film swollen with 27% (w/w) of 1 M $\text{LiClO}_4/\gamma\text{-BL}$ solution; and (3) blend polymer film swollen with 40% (w/w) of 1 M $\text{LiClO}_4/\gamma\text{-BL}$ solution

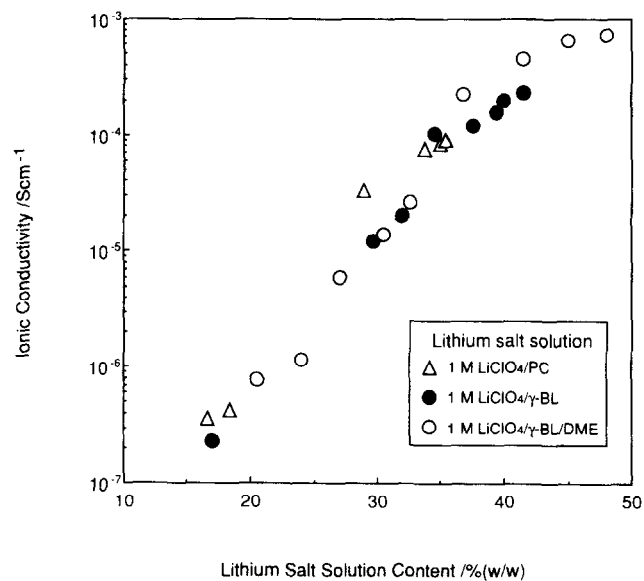


Figure 8 Ionic conductivity of NBR/SBR 50/50 w/w polymer electrolytes versus lithium salt solution content for 1 M LiClO_4/PC , 1 M $\text{LiClO}_4/\gamma\text{-BL}$ and 1 M LiClO_4 dissolved in 50/50 (v/v) $\gamma\text{-BL}/\text{DME}$ solutions

maximum solution content is 35.5% (w/w) for the 1 M LiClO₄/PC, 41.5% (w/w) for the 1 M LiClO₄/γ-BL and 48% (w/w) for the 1 M LiClO₄/γ-BL/DME systems. A similar phenomenon was found in a previous polymer electrolyte system prepared by mixing NBR and SBR latices. The maximum solution content of that electrolyte system was 49% (w/w) for a LiClO₄/γ-BL system and 60.5% (w/w) for a LiClO₄/γ-BL/DME system⁶.

This phenomenon can be explained in terms of the solubility effect, i.e. the affinity between the matrix polymer and the absorbed solution. Both PC and γ-BL are relatively polar solvents, with PC the more polar of the two; the solubility parameter of PC is 27.2 MPa^{1/2} and that of γ-BL is 25.8 MPa^{1/2}. For a polymer matrix, the solubility parameters of the NBR and SBR in this work are 23 and 17 MPa^{1/2}, respectively, which is mentioned in the previous section. A control experiment showed that a small amount of PC and γ-BL—2% (w/w) for PC and 5% (w/w) for γ-BL at the saturation point—can permeate into SBR. Thus, the majority of the absorbed solution is present in the polar NBR phase. The difference of polarity between PC and NBR is larger than that between γ-BL and NBR, and the PC is too polar to permeate the NBR phase. This appears to be one reason why γ-BL is absorbed in the NBR/SBR polymer matrix rather than PC. On the other hand, DME is less polar than γ-BL—its solubility parameter is 17.6 MPa^{1/2} (ref. 14). Adding DME to γ-BL lowers the polarity of the solution so that it can also permeate the SBR phase as well as the NBR phase. Hence, the largest amount of solution is absorbed by the γ-BL/DME system in this series. The maximum ionic conductivity achieved was 8.9 × 10⁻⁵ S cm⁻¹ with the PC, 2.3 × 10⁻⁴ S cm⁻¹ with the γ-BL and 7.2 × 10⁻⁴ S cm⁻¹ with the γ-BL/DME.

At low solution contents (<35% (w/w)), all systems show almost the same ionic conductivity. In contrast, at higher solution contents (>35% (w/w)), the γ-BL/DME system shows higher conductivity than the γ-BL system. These results are similar to those obtained in a previous NBR/SBR mixed latex system and are due to the presence of the 'free' lithium salt solution above 35% (w/w)⁶. D.s.c. heating curves in Figure 7 also suggest the presence of the 'free' lithium salt solution above a solution content of 40% (w/w). Furthermore, in Figure 8, the slope of the curve in the low solution content region (<35% (w/w)) apparently differs from that in the high content region (>35% (w/w)). Ionic conductivity is plotted linearly in Figures 9a and 9b against the solution content density in the ranges below and above 0.54. The solution content density is the ratio of the absorbed lithium salt solution weight to the NBR/SBR polymer matrix weight. This value is proportional to the number of carrier ions in the electrolyte, because the absorbed lithium salt solution includes a constant ion concentration, i.e. a 1 M LiClO₄/γ-BL or a 1 M LiClO₄/γ-BL/DME solution. Solution content density of 0.54 corresponds to the absorbed solution content of 35% (w/w). Straight lines are visible in Figure 9b for both solution systems, while Figure 9a shows a curved profile. This indicates that the ionic conductivity of the present electrolyte swelling with >35% (w/w) is proportional to the number of ions in the film. In general, ionic conductivity of a liquid electrolyte such as a lithium salt solution

obeys the following equation:

$$\delta = nqu \quad (1)$$

where δ , n , q and u , respectively, denote ionic conductivity, the number of carrier ions, their charge number and their mobility. The carrier ions in this system are Li⁺ and ClO₄⁻ and both are monovalent, so the charge number of the ions is 1. If the absorbed 'free' lithium salt solution predominates the ionic conductivity, it is reasonable that Figure 9b should obey equation (1) and show a straight line. The slopes of the straight lines are proportional to the mobility of the ions, and the slope is 1.03 for the γ-BL system and 1.35 for the γ-BL/DME system. According to equation (1), the ionic conductivity of a lithium salt solution such as 1 M LiClO₄/γ-BL or 1 M LiClO₄/γ-BL/DME is proportional to the mobility of ions because the number of ions and their charge number are constant. The ionic conductivities of 1 M LiClO₄/γ-BL and 1 M LiClO₄/γ-BL/DME solutions are 1.1 × 10⁻² and 1.4 × 10⁻² S cm⁻¹, respectively. The ratio of the slopes, i.e. 1.03 to 1.35 (0.76), agrees well with the ratio of the

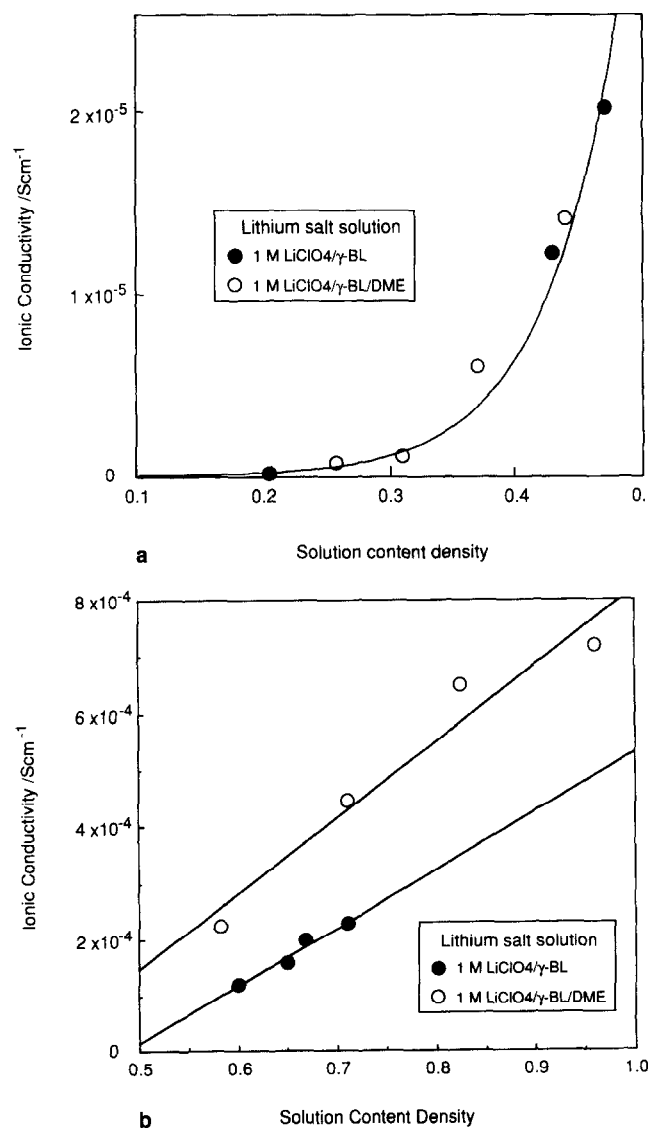


Figure 9 Ionic conductivity of a polymer electrolyte (NBR/SBR 50/50 w/w) versus 1 M LiClO₄/γ-BL and 1 M LiClO₄/γ-BL/DME solution content densities in the range (a) below 0.54 and (b) above 0.54

ionic conductivities, i.e. 1.1×10^{-2} to 1.4×10^{-2} (0.79). This suggests that a polymer electrolyte swollen >35% (w/w) lithium salt solution exhibits ion-conductive behaviour similar to that of the lithium salt solution itself (the absorbed 'free' lithium salt solution).

CONCLUSIONS

Dual-phase polymer electrolytes that possess good mechanical strength and high ionic conductivity were obtained by controlling the domain size and the polarity in NBR/SBR blend polymer films. The domain size could be controlled by varying the mixing rate and a film with good mechanical strength was obtained by reducing the domain size to less than one-fifth of the film thickness. The ionic conductivity depended on the saturated lithium salt solution content in the NBR/SBR matrix, and high ionic conductivity ($>10^{-4} \text{ S cm}^{-1}$) was achieved when the NBR content in the matrix was above 50% (w/w). TEM observation and d.s.c. analysis provided evidence that a dual-phase structure is created, in which the NBR phase provides an ion-conductive pathway and the SBR acts as a mechanically supportive matrix. Quantitative analysis of ionic conductivity suggested that a 'free' lithium salt solution absorbed in the polymer matrix causes the high ionic conductivity.

REFERENCES

- 1 MacCallum, J. R. and Vincent, C. A. 'Polymer Electrolyte Reviews I', Elsevier Applied Science, London, 1987
- 2 MacCallum, J. R. and Vincent, C. A. 'Polymer Electrolyte Reviews II', Elsevier Applied Science, London, 1989
- 3 Abraham, K. M. and Alamgir, M. *J. Electrochem. Soc.* 1990, **137**, 1657
- 4 Lundsgaards, J. S., Yde-Andersen, S., Koksang, R., Shackle, D. R., Austin, R. A. and Fauteux, D. 'Secondary International Symposium on Polymer Electrolytes' (ed. B. Scrosati), Elsevier Applied Science, London 1990
- 5 Matsumoto, M., Ichino, T., Rutt, J. S. and Nishi, S. *J. Electrochem. Soc.* 1993, **130**, L151
- 6 Matsumoto, M., Ichino, T., Rutt, J. S. and Nishi, S. *J. Electrochem. Soc.* 1994, **141**, 1989
- 7 Matsumoto, M., Ichino, T., Rutt, J. S. and Nishi, S. *J. Polym. Sci. (A) Polym. Chem. Edn.* 1994, **32**, 2551
- 8 Matsumoto, M., Rutt, J. S. and Nishi, S. *J. Electrochem. Soc.* 1995, **142**, 3052
- 9 Matsumoto, M. *Polym. Commun.* 1995, **36**, 3243
- 10 Webman, I., Jortner, J. and Cohen, M. H. *Phys. Rev. (B)* 1976, **14**, 4737
- 11 Scher, H. and Zallen, R. *J. Chem. Phys.* 1970, **532**, 3759
- 12 Webman, I., Jortner, J. and Cohen, M. H. *Phys. Rev. (B)* 1975, **16**, 2885
- 13 Kirkpatrick, S. *Rev. Mod. Phys.* 1973, **45**, 574
- 14 Barton, A. F. M. 'Handbook of Solubility Parameters and Other Cohesion Parameters', CRC Press, Boca Raton, FL, 1991
- 15 Yoshida, H., Hatakeyama, T. and Hatakeyama, H. *Polymer* 1990, **31**, 693