Available online at www.sciencedirect.com
ScienceDirect
Solid State Ionics 177 (2006) 3251 – 3257
SOLID STATE IONICS
www.elsevier.com/locate/ssi

Ionic conductivity of highly deproteinized natural rubber having various amount of epoxy group mixed with lithium salt

Warunee Klinklai [a], Seiichi Kawahara [b,*], Edy Marwanta [c], Tomonobu Mizumo [c], Yoshinobu Isono [b], Hiroyuki Ohno [c]

[a] *Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi, Klong 6, Thanyaburi, Pathumthani 12110 Thailand*
[b] *Department of Chemistry, Faculty of Engineering, Nagaoka University of Technology, 1603-1, Kamitomioka, Nagaoka, Niigata 940-2188 Japan*
[c] *Department of biotechnology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588, Japan*

Received 5 February 2006; received in revised form 5 July 2006; accepted 8 August 2006

Abstract

Ionic conductivity of highly deproteinized natural rubber having various amount of epoxy group (LEDPNR) mixed with lithium bis (trifluoromethane sulfonyl) imide (LiTFSI) salt was investigated through impedance analysis with respect to salt concentration, glass transition temperature and epoxy group content. The LEDPNR was prepared from depolymerization of epoxidized natural rubber (ENR) latex, which was prepared by deproteinization of natural rubber latex with proteolytic enzyme and surfactant followed by epoxidation with fresh peracetic acid. The resulting LEDPNR was found to have 10–57 mol% epoxy group, low M_n and low T_g. The conductivity of LEDPNR/LiTFSI mixture was dependent on LiTFSI salt concentration and glass transition temperature (T_g). The highest ionic conductivity *versus* salt concentration for the mixtures was found to be due to amount of effective carrier ion and the highest mobility of segment of LEDPNR at a suitable LiTFSI concentration. The ionic conductivity of LEDPNR/LiTFSI mixtures was further dependent on epoxy group content.

Keywords: Liquid epoxidized DPNR; LiTFSI; Ionic conductivity; Polar epoxy group; Polymer electrolyte

1. Introduction

Deproteinized natural rubber (DPNR) having epoxy group is an important polymer electrolyte useful for fabrication of ionics devices such as polymer battery. This may be because it provides an effective conduction path of carrier ions, i.e. Li^+, with little effect of water that is attracted with proteins present in natural rubber. Since water causes serious problems such as dendrite formation in the electrolyte and corrosions of electrode, it is important to remove the proteins from natural rubber. In previous works, we proposed highly deproteinized natural rubber [1] and hyper-deproteinized natural rubber [2], which contained about 0.1 and 0.02 wt.% proteins, respectively, being less than about 2 wt.% proteins present in untreated natural rubber. Therefore, the epoxidized natural rubber prepared from deproteinized natural rubber was adopted as a polar rubber-electrolyte because it showed low glass transition temperature (T_g), large amount of polar epoxy group and fewer amount of the proteins, being necessary to prepare polymer electrolyte used for solid polymer electrolyte (SPE). However, to prepare the polymer electrolyte from DPNR, it may be important to increase epoxy group content without raising T_g, since the ionic conductivity of SPE is dependent on amount of charge carrier and mobility of ions.

In previous works [3,4], extensive effort has been devoted to improve the ionic conductivity of SPE with respect to amount of charge carrier and mobility of ions, which were related to the salt concentrations, polar group, the T_g or melting temperature (T_m) of SPE, respectively. Thus, low T_g and T_m have been required for the SPE, even though it contains polar substituents that resulted in higher T_g and T_m. To solve the problems, oligomer

---

* Corresponding author. Tel.: +81 258 47 9301; fax: +81 258 47 9300.
E-mail address: kawahara@chem.nagaoka.ac.jp (S. Kawahara).

0167-2738/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.ssi.2006.08.006

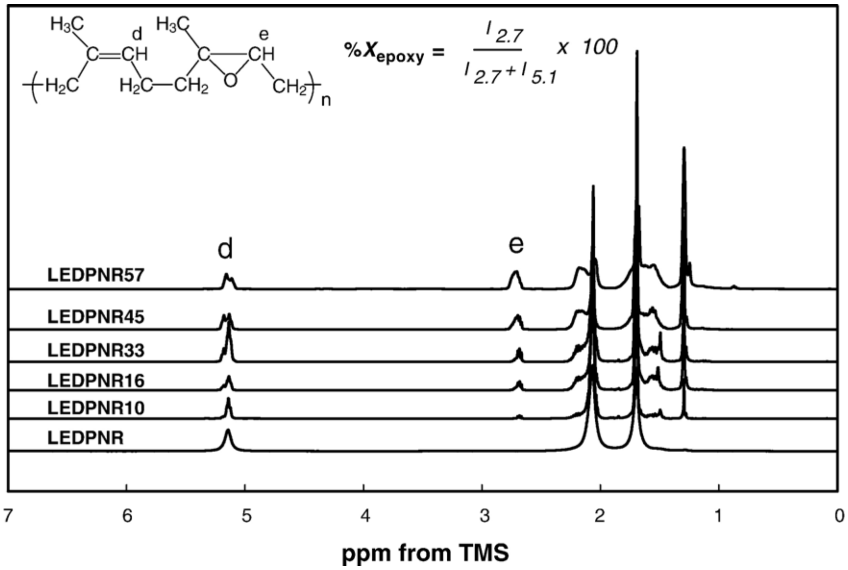

Fig. 1. ^{1}H-NMR spectra for LEDPNR, LEDPNR10, LEDPNR16, LEDPNR33, LEDPNR45 and LEDPNR57, respectively.

electrolyte has been prepared by living anionic polymerization of ethylene oxide [5–8]. However, the ionic conductivity of the resulting polyethylene oxide (PEO) based electrolyte was low at room temperature since PEO crystallize at ambient temperature [9]. The ionic conductivity may increase as a polar rubbery material is used as a conducting medium, since it has not only polar substituents to transport ion but also low T_g to enhance the mobility.

In our previous works [10,11], Liquid DPNR having epoxy group (LEDPNR) mixed with alkaline lithium salt was applied to transport lithium ion. The ionic conductivity of LEDPNR having 33 mol% epoxy group mixed with 20 wt.% LiTFSI salt was about 10^{-6} S cm^{-1} at 323 K. Since, the ionic conductivity is expected to be a function of amount of epoxy group, it is necessary to optimize the amount of the epoxy group and mobility of the rubbery electrolyte after mixing it with alkaline salt.

In the present work, the ionic conductivity of LEDPNR with various epoxy group contents mixed with LiTFSI salt was investigated by impedance analysis to optimize the amount of ion for the rubbery electrolyte. A change in ionic conductivity was associated with salt concentration, T_g, and epoxy group content of the rubbery electrolyte.

2. Experimental

2.1. Sample preparation

The rubber latex used in this study was high ammonia natural rubber (NR) latex. Deproteinization of the rubber was made by incubation of the latex with 0.04 wt.% proteolytic enzyme (KP-3939, KaO), and 1 wt.% sodium dodecyl sulfate (SDS) for 24 h at 311 K followed by centrifugation. The cream fraction was redispersed into 1 wt.% SDS solution and washed twice by centrifugation.

DPNR, pre-cooled at 278 K, was epoxidized in the latex stage with freshly prepared peracetic acid for 4 h at pH 5–6. After completion of the reaction, pH of the solution was adjusted to 7.1.

Depolymerization of the epoxidized rubber was carried out by incubation of the latex with ammonium persulfate ($(NH4)_2S_2O_8$) and propanol at 338 K for 10 h. The resulting latex was coagulated with methanol followed by purification with toluene and methanol, and dried up at 303 K for a week under reduced pressure.

The LEDPNR was mixed with salts to prepare polymer-salt electrolyte film. The salts used in the present study were lithium bis(trifluoromethane sulfonyl)imide (LiTFSI). The rubbers after drying for at least a week were dissolved in dried tetrahydrofuran, THF. The solution was mixed with the salts followed by casting onto Teflon sheets to prepare film specimens for the measurement of ionic conductivity. The resulting film was dried under reduced pressure at 323 K for 24 h.

2.2. Measurement

Measurements of molecular weight and molecular weight distribution of the rubber were made by a TOSOH size exclusion chromatography, consisting of a TOSOH CCPD pump, a RI-8012 Differential Refractometer and a UV-8011 UV detector. The measurement was made at room temperature and the flow rate of the mobile phase, THF, was 0.5 ml/min. The molecular weights were estimated on the basis of the molecular weight of standard polystyrene.

^{1}H-NMR measurement was carried out with a JEOL EX-400 NMR spectrometer at the pulse repetition time of 7 sec for 45° pulse. The rubber was dissolved in deuterated chloroform. The epoxy group content was estimated from intensity ratio of the characteristic signals at 2.7 ppm and 5.1 ppm, respectively [10].

DSC measurement was made with a Seiko Instrument DSC 220 differential scanning calorimeter over the temperature range of 153 K to 373 K at the heating rate of 10 K/min. Rubber samples of about 10 mg were encapsulated in an aluminium pan. The midpoint temperature was used as the T_g of the sample.