Studies on Conductivity of Acrylonitrile-Butadiene Rubber/LiClO$_4$ Composite and Its Modification by Adding Epoxy Resin

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ABSTRACT: Solid polymer electrolytes based on acrylonitrile-butadiene rubber (NBR) and LiClO$_4$ were prepared and their conductivity was evaluated. The effect of nitrile group —CN/LiClO$_4$ mole ratio on the conductivity was investigated. The maximum conductivity of 1.21×10^{-4} S cm^{-1} (20°C) was achieved in the NBR/LiClO$_4$ composite at the —CN/LiClO$_4$ mole ratio of 1/2.5, which was in accordance with the strongest coordination between —CN and Li$^+$ indicated by Fourier transform infrared spectrometry measurement. The conductivity was further increased by two to three times when 30 phr epoxy resin was introduced into NBR, and the conductivity could retain around the maximum value with the —CN/LiClO$_4$ mole ratio ranged from 1/2.5 to 1/3.5, while the conductivity of NBR/LiClO$_4$ composite existed a decrease in the same range. Field emission scanning electron microscopy and atomic force microscopy characterization showed that epoxy resin significantly improved the dispersion of LiClO$_4$, leading to better surface smoothness of NBR/epoxy resin/LiClO$_4$ composite film and contributing to the increase of ionic conductivity. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2340–2345, 2010

Key words: acrylonitrile-butadiene rubber; epoxy resin; ionic conductivity

INTRODUCTION

Since Wright[1] discovered ionic conductivity in poly(ethylene oxide) (PEO)/Na$^+$ composites in 1975 and Armand et al.[2] proposed the application of solid polymer electrolyte (SPE) in lithium batteries, numerous research concerning SPE, especially on the improvement of ionic conductivity, has been widely reported.[3–7] SPE is typically based on various polymer matrix, such as PEO, polymethyl methacrylate (PMMA), and polyacrylonitrile (PAN), into which several ionic salts are readily dissolved.[8] The solubility of salt, by virtue of the coordinative interaction between metal ions and the polar groups of polymer matrix, is of vital importance in determining the ionic conduction of SPE.[9] Recently, research are mainly focused on the development of gel-type polymer electrolyte (GPE), which is made by immobilizing salt and nonaqueous solvents in polymer matrix.[10,11] GPE has high-ionic conductivity but also has some deficiencies, such as poor mechanical properties, the restriction of ions diffusion caused by entanglement of polymer chains,[10] reactivity of polar solvents with lithium electrode,[12] and the leakage of excess liquid electrolytes.

Polymer blending is an effective method to avoid the deficiencies associated with poor mechanical properties and the leakage of liquid electrolytes.[12–14] Furthermore, if the polymers can be compatible with each other, and the composites film can have better surface smoothness after blending, it will provide higher conductivity.

In SPE, accompanying with thermal movement of polymer chains, the ions transport is achieved via the continuous dissolving and reforming complex between ions and polar groups in polymer.[15] Considering that rubber material is an excellent potential matrix because of its low-glass transition temperature (T_g) and good flexibility. Acrylonitrile-butadiene rubber (NBR) is a kind of noncrystalline rubber with high polarity and excellent elasticity. Butadiene units provide soft segments with high flexibility and capability of segmental motion, while nitrile units provide high polarity, which is useful for salt dissociation.[16,17] Furthermore, the interaction between nitrile group (—CN) and Li$^+$ ion is considered to be very suitable for the stabilization of high conducting amorphous ionic clusters.[18,19] Therefore, NBR is considered as a potential polymer matrix for SPE.

In this work, solid NBR-based electrolytes were fabricated by solvent casting, where solvent was

slowly removed from a homogeneous solution of NBR and LiClO$_4$ salt. Considering the special properties of epoxy resin and its good compatibility with NBR,[20] the electrolytes matrix used was further expanded to NBR/epoxy resin blend. The addition of epoxy resin may affect the dispersion of LiClO$_4$ in polymer matrix and improve the surface smoothness of composites film, so it is worthy to investigate the effect of epoxy resin on the conductivity of NBR/LiClO$_4$ composite.

EXPERIMENTAL

Materials

NBR with acrylonitrile content of 35 wt % (N230S) was kindly supplied by Japan Synthetic Rubber Company. LiClO$_4$ (AR) was supplied by Sinopharm Chemical Reagent. Bisphenol-A type epoxy resin (E-06), with epoxy equivalent weight of 2000 g/eq, was supplied by Tianyuan Group Shanghai Resin Factory.

Sample preparation

NBR was first dissolved in methyl ethyl ketone and precipitated in methanol for purification. The precipitated material was washed with methanol for several times before vacuum drying at 45°C for 24 h. Then, both NBR and LiClO$_4$ with various ratios, were dissolved in tetrahydrofuran, placed at room temperature for 6 h and then vigorously stirred for 10 min to obtain homogenous solutions. Films with thickness of 0.3–0.5 mm were obtained by casting the homogenous solutions in Teflon slot die.

Purified NBR, LiClO$_4$, and epoxy resin were dissolved in tetrahydrofuran, and the epoxy resin content was 30 phr (based on the 100 phr NBR). Then, the same procedures were conducted as mentioned earlier.

Measurements

Fourier transform infrared spectrometry

Fourier transform infrared (FTIR) spectrometry was conducted with Paragon 1000 FTIR (Perkin Elmer) from 400 to 4000 cm^{-1} at room temperature. Samples in tetrahydrofuran were dropped on a KBr crystal and dried to obtain transparent thin films before FTIR measurement.

Conductivity

Conductivity was measured by the complex-impedance method using a Solartron 1260 Frequency Response Analyser and 1287 Electrochemical Interface, in the frequency range from 0.1 Hz to 1.0 MHz

at 20°C. The samples were sandwiched between two stainless steel electrodes. The conductivity was calculated from the bulk electrolyte resistance value (R_b).

Field emission scanning electron microscopy

Morphology of the composites was studied by field emission scanning electron micros (FESEM; JSM-7401F JEOL, Japan). Images were taken from cryogenically fractured surfaces of specimens. The fracture surfaces were sputter coated with gold for observation.

Atomic force microscopy

Surface morphology was imaged by Nanoscope IIIa Multimode atomic force microscopy (AFM; Digital Instruments, USA) in tapping mode. The spring constant of the cantilever was 40 N/m and the measured resonant frequency was 300 kHz. The roughness parameters R_q (root-mean-square roughness, RMS) and R_a (arithmetic mean roughness) were calculated according to the following equations[21]:

$$R_q = \sqrt{\frac{\sum_{i=1}^{N} (Z_i - Z_{\text{ave}})^2}{N}} \quad (1)$$

$$R_a = \frac{\sum_{i=1}^{N} |Z_i - Z_{\text{ep}}|}{N} \quad (2)$$

where R_q is the standard deviation of the Z-values (the height of surface points) within a given area, R_a, the arithmetic average of the deviations from the center plane, Z_{ave}, the average Z-value within the given area, Z_{ep}, the Z-value of the center plane, Z_i, the current Z-value, and N, the number of points within a given area.

RESULTS AND DISCUSSION

NBR/LiClO$_4$ composite

Conductivity

The conductivity of NBR/LiClO$_4$ composite is plotted as a function of —CN/LiClO$_4$ mole ratio (Fig. 1). The conductivity of NBR/LiClO$_4$ composite increases with increasing LiClO$_4$ content, and goes through the maximum value of 1.21×10^{-4} S cm^{-1} at the —CN/LiClO$_4$ mole ratio of 1/2.5, which is five orders of magnitude higher than that of pure NBR (2.64×10^{-9} S cm^{-1}). Further increasing LiClO$_4$ content leads to a slight decrease of conductivity. Superfluous LiClO$_4$ may lead to serious aggregation, and those aggregates are prone to migrating to the
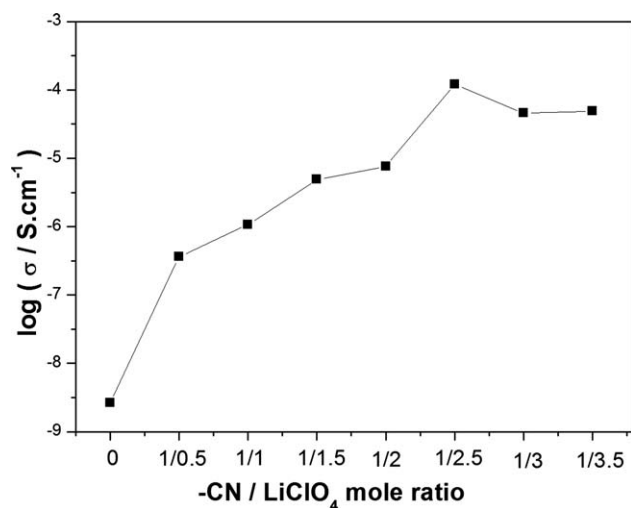
Figure 1 Effect of $-CN/LiClO_4$ mole ratio on the conductivity of NBR/LiClO_4 composite.

film surface, resulting in poor smoothness of the film. Therefore, the conductivity of NBR/LiClO_4 composite slightly decreases at high LiClO_4 content.

FTIR study

FTIR spectra of NBR/LiClO_4 composite with different $-CN/LiClO_4$ mole ratios is recorded to confirm the interaction between NBR and lithium salt (Fig. 2). The peak at 2237 cm^{-1} corresponds to the stretching vibration of free $-CN$ in NBR. After the addition of LiClO_4, a new shoulder peak appears at 2263 cm^{-1} and it becomes stronger with increasing amount of LiClO_4. The spectroscopic studies on polymer electrolytes have demonstrated that polymer containing nitrile group could form complex with metal cations.[18,22,23] According to these studies, the new peak at 2263 cm^{-1} indicates the interaction between nitrile
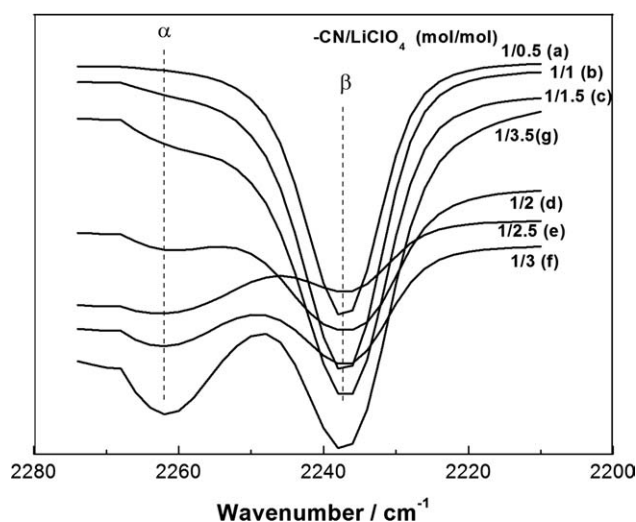
TABLE I
Peak Area Ratio of α (Coordination Absorption) to α + β (Gross $-CN$ absorption) in Figure 1

$-CN/LiClO_4$ (mol/mol)	Peak area ratio of α to α + β
1/0.5	0
1/1	1/805
1/1.5	1/67
1/2	1/20
1/2.5	1/2.7
1/3	1/5.5
1/3.5	1/4.9

group and Li$^+$ ion, which is probably attributed to the electron donating nature of the nitrile group. It is known that the cation-coordinating macromolecule is generally the major component in polymer electrolytes, and ionic transfer occurs in amorphous regions of the material, assisted by segmental motions of the polymer matrix.[22,24] Therefore, in NBR/LiClO_4 composite, it is the interaction between nitrile group and Li$^+$ ion that promotes the dissolving and dissociation process of lithium salts. Table I exhibits the area ratio of the coordination absorption to the gross $-CN$ absorption, indicating the relative intensity of the peak at 2263 cm^{-1}. The relative intensity, which suggests the amount of dissociated Li$^+$ ion, is related to the increasing amount of LiClO_4. When the $-CN/LiClO_4$ mole ratio is 1/2.5, the area ratio achieves the maximum value, corresponding to the maximum conductivity of NBR/LiClO_4 composite (Fig. 1).

NBR/Epoxy Resin/LiClO_4 composite

Conductivity

The conductivity of NBR/epoxy resin/LiClO_4 composite is plotted as a function of $-CN/LiClO_4$ mole ratio (Fig. 3). The addition of epoxy resin obviously

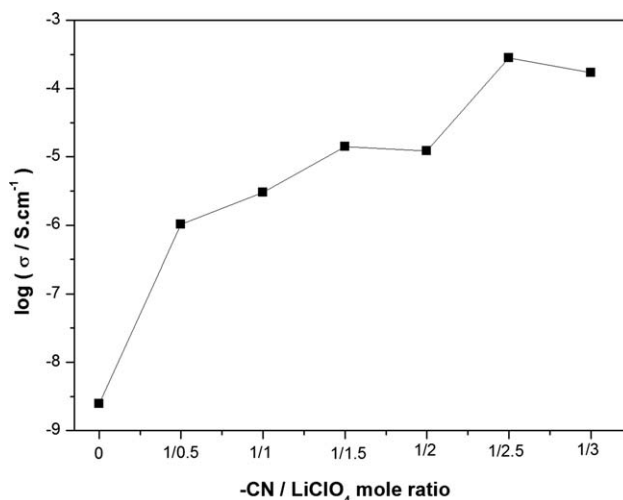**Figure 2** FTIR spectra of the $-CN$ stretching mode in NBR bulk with $-CN/LiClO_4$ mole ratio of (a) 1/0.5, (b) 1/1, (c) 1/1.5, (d) 1/2, (e) 1/2.5, (f) 1/3, and (g) 1/3.5.

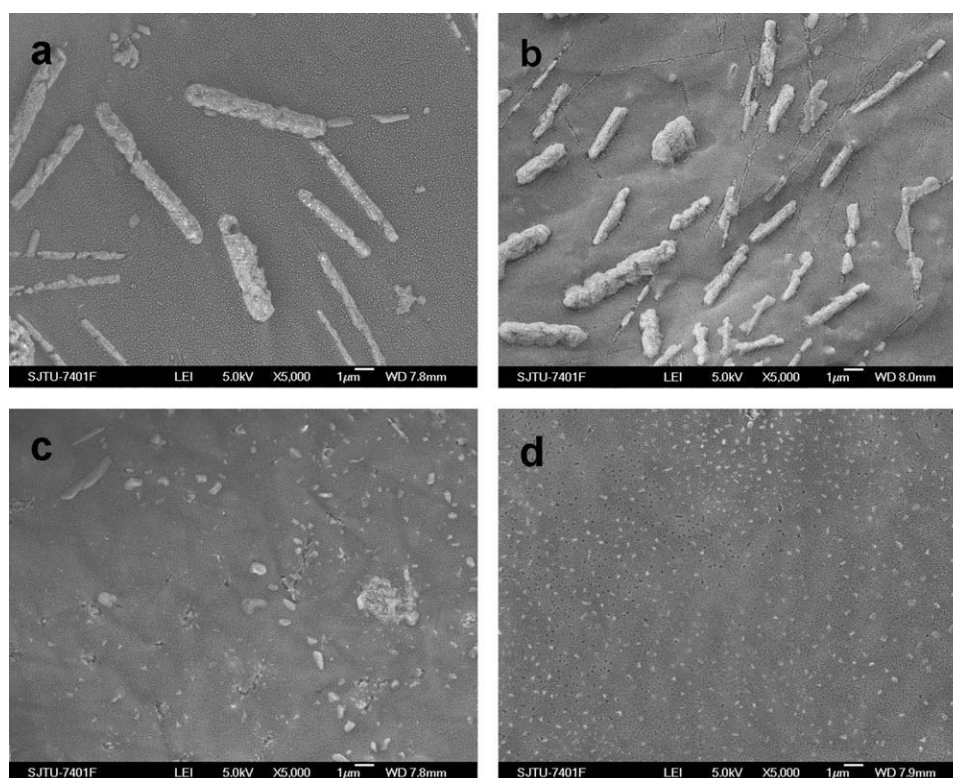**Figure 3** Effect of $-CN/LiClO_4$ mole ratio on the ionic conductivity of NBR/epoxy resin/LiClO_4 composite.

Figure 4 FESEM images of NBR/LiClO$_4$ and NBR/epoxy resin/LiClO$_4$ composites: (a) NBR/LiClO$_4$ ($-$CN/LiClO$_4$ = 1/1.5 (mol/mol)), (b) NBR/LiClO$_4$ ($-$CN/LiClO$_4$ = 1/2.5 (mol/mol)), (c) NBR/epoxy resin/LiClO$_4$ ($-$CN/LiClO$_4$ = 1/1.5 (mol/mol)), and (d) NBR/epoxy resin/LiClO$_4$ ($-$CN/LiClO$_4$ = 1/2.5 (mol/mol)).

improves the conductivity of NBR/LiClO$_4$ composite by two to three times at the same $-$CN/LiClO$_4$ mole ratio. The maximum conductivity of 2.81 × 10^{-4} S cm^{-1} is obtained at the $-$CN/LiClO$_4$ mole ratio of 1/2.5, the same ratio as that of NBR/LiClO$_4$ composite. With further increasing LiClO$_4$ content, the conductivity of NBR/epoxy resin/LiClO$_4$ composite retain around the maximum value, which can not be achieved in the NBR/LiClO$_4$ composite. FTIR spectra of NBR/epoxy resin/LiClO$_4$ composite has been investigated, but the characteristic peaks of nitrile group have little change compared with those of NBR/LiClO$_4$ composite in Figure 1, suggesting epoxy resin does not affect the interaction between nitrile group and Li$^+$ ion. By contrast, the aforementioned increase of conductivity after the addition of epoxy resin should be attributed to the improved dispersion of LiClO$_4$ and better surface smoothness of electrolyte film, which will be discussed in following section.

Field emission scanning electron microscopy

The morphology of NBR/LiClO$_4$ composite with and without epoxy resin at the $-$CN/LiClO$_4$ mole ratio of 1/1.5 and 1/2.5 is investigated for at these two mole ratios the most significant difference and

the maximum value of conductivity existing, respectively (Fig. 4). Epoxy resin significantly affects the dispersion of LiClO$_4$ in polymer matrix. In the NBR/LiClO$_4$ composite, most of LiClO$_4$ are dispersed as acicular particles with clear interfacial boundaries in the NBR matrix [Fig. 4(a,b)]. By contrast, in the NBR/epoxy resin/LiClO$_4$ composite, the acicular LiClO$_4$ particles have been cut into granular ones embedded in the polymer matrix [Fig. 4(c,d)], whose size is generally comparable with the transverse size of acicular ones in Figure 4(a,b). Such phenomenon indicated that epoxy resin can improve the dispersion of LiClO$_4$ and thus increase the interfacial area between LiClO$_4$ and polymer matrix, leading to better dissolution of LiClO$_4$ and stronger coordination between $-$CN and Li$^+$, which is in accordance with the measurements of conductivity.

Atomic force microscopy

The surface morphology of NBR/LiClO$_4$ and NBR/epoxy resin/LiClO$_4$ films, with the $-$CN/LiClO$_4$ mole ratio of 1/1.5 and 1/2.5, are represented by the tapping mode AFM images (Fig. 5). The light and dark areas in the AFM images correspond to peaks and troughs, respectively. The surfaces of NBR/epoxy resin/LiClO$_4$ films [Fig. 5(c,d)] are smoother
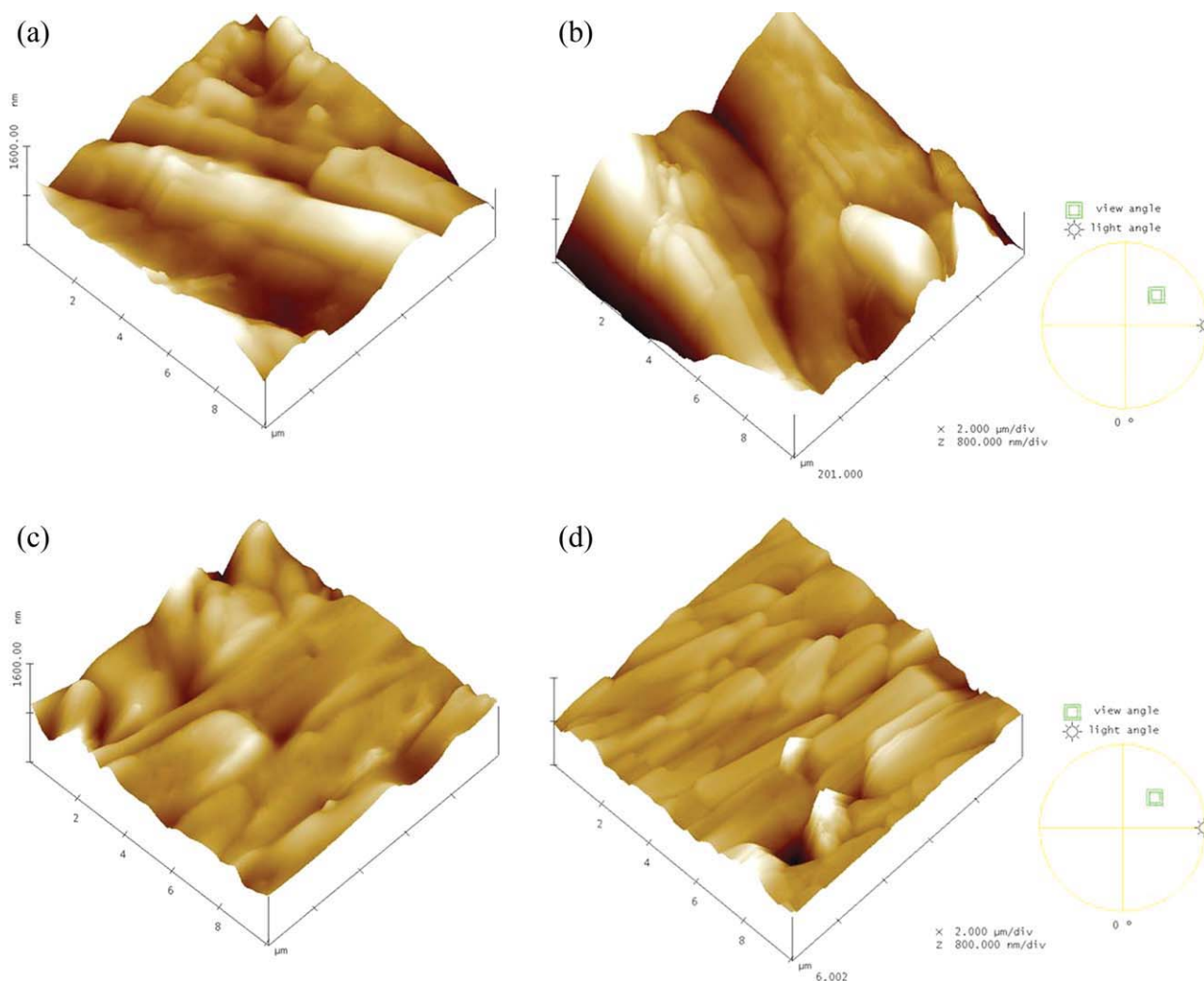
Figure 5 AFM images of NBR/LiClO$_4$ and NBR/epoxy resin/LiClO$_4$ composites: (a) NBR/LiClO$_4$ (—CN/LiClO$_4$ = 1/1.5 (mol/mol)), (b) NBR/LiClO$_4$ (—CN/LiClO$_4$ = 1/2.5 (mol/mol)), (c) NBR/epoxyresin/LiClO$_4$ (—CN/LiClO$_4$ = 1/1.5 (mol/mol)), and (d) NBR/epoxyresin/LiClO$_4$ (—CN/LiClO$_4$ = 1/2.5 (mol/mol)). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

than that of NBR/LiClO$_4$ composites [Fig. 5(a,b)]. Statistical analyses of the AFM images were performed to obtain further information about the surface roughness of NBR/LiClO$_4$ and NBR/epoxy resin/LiClO$_4$ films (Table II). The roughness parameters of NBR/epoxy resin/LiClO$_4$ films are about one third of that of NBR/LiClO$_4$ films. It has been proved that better surface smoothness of electrolyte film could provide better contact with the electrodes in battery, contributing to higher conductivity.[25] The observed results are well in agreement with the measurements of conductivity.

TABLE II
Roughness Parameters Obtained from AFM Images of Composites

Samples	—CN/LiClO$_4$ mole ratio	RMS roughness (R_q) (nm)	Mean roughness (R_a) (nm)
NBR/LiClO$_4$	1/1.5	207.83	167.80
	1/2.5	222.56	176.40
NBR/epoxy resin/LiClO$_4$	1/1.5	58.64	42.22
	1/2.5	71.64	47.54

The scanning surface area: 100 µm^2.

CONCLUSIONS

SPEs based on NBR/LiClO$_4$ composite was prepared. The NBR/LiClO$_4$ composite with the nitrile group (—CN)/LiClO$_4$ mole ratio of 1/2.5 showed the maximum conductivity of 1.21×10^{-4} S cm^{-1} (20°C) in the experimental range in this article. Fourier transform infrared spectrometry demonstrated an obvious coordination occurred between —CN and Li$^+$, and thus favored the dissolution and dissociation of Li$^+$ in NBR matrix, contributing to the high conductivity of NBR/LiClO$_4$ composite. The addition of 30 phr epoxy resin further increased the conductivity of NBR/LiClO$_4$ composite by two to three times. Furthermore, their conductivity could retain around the maximum value with the —CN/LiClO$_4$ mole ratio ranged from 1/2.5 to 1/3.5. Morphology investigation showed that LiClO$_4$ was dispersed as granular particles instead of acicular ones in the presence of epoxy resin. Epoxy resin significantly improved the dispersion of LiClO$_4$ in the polymer matrix, leading to lower roughness parameters (R_q and R_a). All of these factors favored the increase of conductivity.

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