

Preparation and Characterization of Solid Polymer Electrolyte Based on Epoxidized Jackfruit Gum

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Abstract

An attempt to prepare a solid polymer electrolyte from jackfruit gum was made. Jackfruit gum (JG) was purified and subjected to epoxidation process. Lithium perchlorate (LiClO_4) was dispersed in JG and epoxidized jackfruit gum (EJG). The structural characterizations were made through NMR spectroscopy and gel permeation chromatography. Ion conductivity and melting point of JG/ LiClO_4 and EJG/ LiClO_4 were measured. Obtained results indicated that epoxy group was introduced in JG and chain scission did not occur during the epoxidation. Ion conductivity of EJG/ LiClO_4 in epoxidized natural rubber matrix was about 100 times higher than that of JG/ LiClO_4 in epoxidized natural rubber matrix. EJG and LiClO_4 formed a liquid crystal. These may suggest the strong interaction between epoxy groups in EJG and LiClO_4 .

Keywords: jackfruit gum, epoxidation, solid polymer electrolyte, structural characterization, thermal properties.

1. Introduction

Research on polymers as a solid electrolyte in lithium batteries has attracted the attention of many scientists around the world for more than three decades [1,2]. Solid polymer electrolytes used in lithium ion batteries need a structure that ensures the transportation of lithium ion. These polymers are required to have flexible chains which contain some functional groups such as oxide, amide, carbonate, epoxy group and so on [3]. Recently, scientists around the world have paid attention on oligomer electrolytes which have short and flexible chains [4]. In the present research, we propose a solution to replace synthesized oligomer electrolyte with the respect to safety and friendliness of materials for the environment. We reported a new approach to prepare solid polymer electrolytes for lithium-ion battery based on natural oligomer.

In the present research work, jackfruit gum was taken into account. It is revealed that chemical constituents of a jackfruit gum are composed of residues soluble in acetone, other rubber-like soluble in petroleum ether and poly(*cis*-isoprene) as in the case of natural rubber. Jackfruit gum extracted from ripen fruits is very sticky and flexible [5]. This suggests that jackfruit gum contains the short and flexible polymer chain. This is an ideal material supporting for the mobility of conducting species, for example lithium ion. In order to increase the mobility of lithium ion, it is necessary to add functional groups to poly (*cis*-

isoprene) in jackfruit gum. Among the known chemical modification methods of poly(*cis*-isoprene), epoxidation which converts C = C double bonds into epoxy groups is widely reported. This functional group is capable of forming the complex with lithium ions and allowing lithium ions to transport in the polymer matrix.

In this work, we carried out the purification of jackfruit gum, followed by the epoxidation. Lithium perchlorate (LiClO_4) was dispersed into purified and epoxidized jackfruit gums. The structural characterizations of resulting samples were carried out through NMR spectroscopy and gel permeation chromatography. The properties of LiClO_4 /epoxidized jackfruit gum mixture which are important to solid polymer electrolyte in lithium batteries, i.e. thermal properties and ion conductivity were investigated.

2. Experiments

2.1. Preparation of materials

Jackfruit gum was extracted from ripen jackfruit which was harvested in summer in the North of Vietnam. The gum was mixed in an excess amount of methanol (Duc Giang Ltd.co., 99 w/w%) followed by the centrifugation at 9000 rpm in 30 minutes at 15°C. The obtained precipitation was washed by dissolving in toluene (Duc Giang Ltd.co., 99 w/w%), then coagulating in an excess amount of methanol. The washing process was repeated twice to obtain purified jackfruit gum (JG). The procedure was illustrated in Figure 1.

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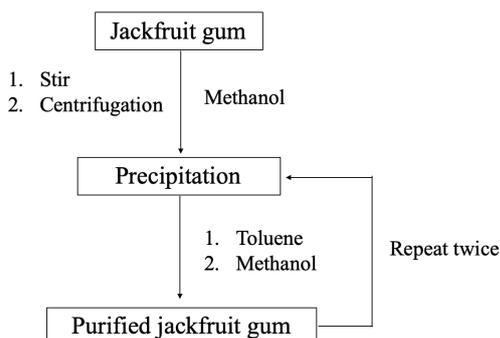


Fig. 1. The schema of jackfruit gum purification.

Epoxidation of JG was carried out in tetrahydrofuran (THF, Sigma Aldrich, 99.9 w/w%) using fresh peracetic acid. Fresh peracetic acid was prepared by adding hydrogen peroxide (Sigma Aldrich, 30 w/w%) into acetic anhydride (Sigma Aldrich, 99 w/w%) at 0°C, followed by stirring gently at 40°C for 90 minutes. JG which was dissolved in THF to get the concentration of 2 w/v% was epoxidized with fresh peracetic acid at 5°C for 1 hour. After the reaction, the resulting mixture was coagulated in an excess amount of methanol then centrifuged at 9,000g for 30 minutes. The obtained coagulant was dried in reduced pressure for a week at room temperature to obtain epoxidized jackfruit gum (EJG). The procedure of epoxidation was shown in Figure 2.

Epoxidized natural rubber (ENR) was prepared according to our procedure [6]. The epoxy group content of the resulting ENR is 21 mol%. ENR and EJG (or JG) were dissolved in toluene (Nacalai Tesque, 99.9 w/w%) to obtain solutions. The weight ratio of ENR/EJG (or ENR/JG) was 2:1. Various lithium perchlorate (LiClO_4 , Merck, 99.9 w/w%) salt solutions of THF were prepared separately. Then, the ENR and EJG solution and a LiClO_4 solution were mixed together to obtain a homogenous solution. The solution was casted onto a glass ring mold with Teflon substrate. The solvent was allowed to evaporate in a fume cupboard at room temperature. The resulting films were used for ion conductivity measurement.

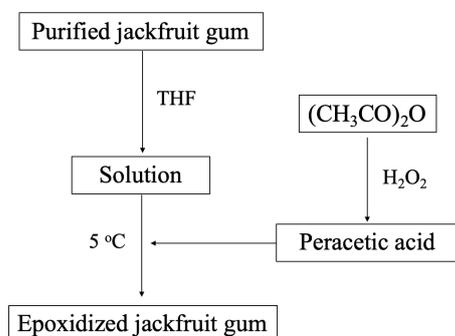


Fig. 2. The schema of epoxidation of jackfruit gum.

EJG or JG was dissolved in THF to prepare a homogeneous solution. Thereafter, various amount of lithium perchlorate was added in EJG/THF solution, then ultrasonicated. The solvent was allowed to evaporate in a fume cupboard at room temperature. The obtained mixtures were used for DSC measurement.

2.2. Characterization of materials

The structural characterization of materials was made through NMR spectroscopy. The samples were dissolved in benzene- D (C_6D_6 , Nacalai Tesque Inc., 99.9 w/w%). NMR measurement for the solutions was carried out on a JEOL FT-NMR ECA-400 at 25°C.

Molecular weight and molecular weight distribution of JG and EJG were measured with a TOSOH GPC consisting of a TOSOH CCPD pump; RI-8012 differential refractometer and UV-8011 UV detector. The measurement was made at room temperature with the flow rate of the mobile phase, i.e. THF, of 0.5 ml/min. Standard polyisoprenes purchased from PSS Polymer Standards Service GmbH (Mainz, Germany), were used for preparing a calibration curve.

Ion conductivity of the sample was measured using a Solartron 1260 Frequency Response Analyzer at 25°C.

DSC measurements for the samples were performed using a DSC 7020 (SII NanoTechnology Inc.). The sample packed into an aluminum pan was heated from -80 to 90°C at a heating rate of 10°C/min.

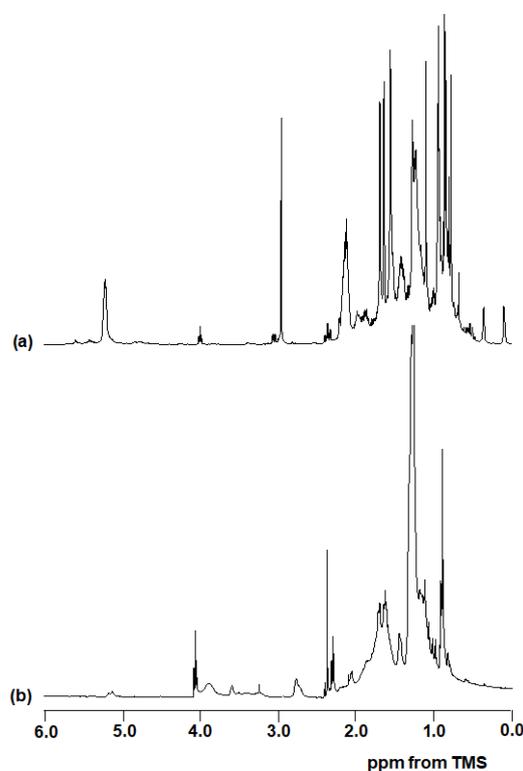


Fig. 3. ^1H -NMR spectrum of (a) JG, (b) EJG.

3. Results and discussion

3.1. NMR spectrum

$^1\text{H-NMR}$ spectrum of JG before and after epoxidation is illustrated in Figure 3. The JG spectrum showed the characteristic signals of cis-polyisoprene at 5.13, 2.15 and 1.75 ppm, which correspond to olefinic proton (H-C), methylene proton ($-\text{CH}_2-$) and methyl proton (cis- CH_3), respectively. The other signals in the spectrum was assigned to protons of fatty acids and proteins as reported in our previous work [7].

After epoxidation, the signals at 5.13, 2.15 and 1.75 ppm were found to reduce. In addition, a new signal appeared at 2.70 which was assigned to methine proton of resulting epoxy group [8]. These evidences may confirm that epoxy group was successfully introduced to JG.

3.2. GPC

Figure 4 shows the molecular weight distribution of JG and EJG. Both samples showed a unimodal distribution and symmetrical with a narrow polydispersity index. It implied that JG contains oligomers with the similar length of chain. Furthermore, the molecular weight did not change after epoxidation. This may suggest that epoxidation did not cause chain scission in oligomer chain of JG.

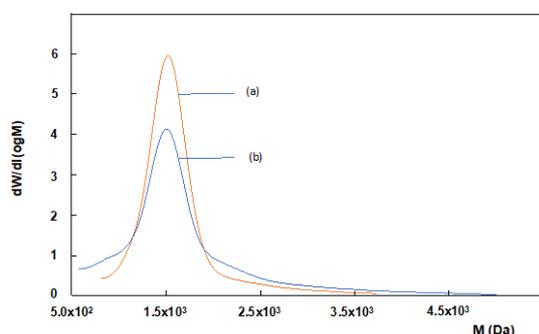


Fig. 4. Molecular weight distribution of the samples (a) JG, (b) EJG.

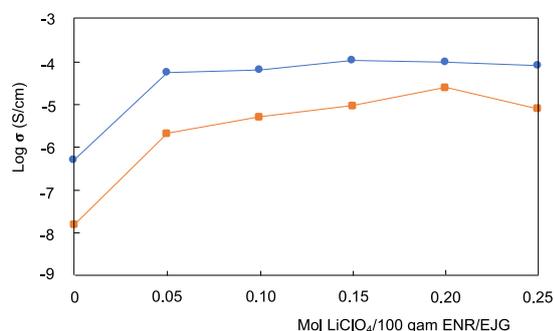


Fig. 5. Logarithm of ion conductivity vs amount of lithium perchlorate in the samples ■ JG/ENR, ● EJG/ENR.

3.3. Ion conductivity

Ion conductivity was studied as a function of concentration of conducting species, i.e. LiClO_4 . Figure 5 shows the ion conductivity of samples containing various amount of LiClO_4 . When the amount of LiClO_4 increased, the conductivities of JG/ENR and EJG/ENR went up. This behavior is quite general in salt-containing polymers. The conductivity of JG/ENR achieved the highest value with 0.20 mol LiClO_4 , whereas that of EJG/ENR achieved the highest value with 0.15 mol LiClO_4 . This is explained that as the salt concentration increased, ions available for conduction also increased and hence ion conductivity also increased. However, when the amount of LiClO_4 in JG/ENR and EJG/ENR was higher than the optimum value, the ion conductivities of the samples reduced. This may be considered that ion pairs carrying neutral charge were formed when the amount of LiClO_4 was too high. Thereby the available number of free charges for conduction reduced and hence the conductivity decreased.

The ion conductivities of EJG/ENRs were found to higher than those of JG/ENRs. When LiClO_4 was present in the samples, the conductivities of JG/ENRs are in the order of 10^{-6} S/cm, whereas those of EJG/ENRs in the order of 10^{-4} S/cm. In previous work [9], Klinklai and co-workers reported that ion conductivity of LiClO_4 in liquid epoxidized natural rubber was in the order of 10^{-6} . In this work, we found that EJG could remarkably improve the ion conductivity of LiClO_4 in ENR. This behavior may confirm that epoxy groups in EJG supports the mobility of lithium ion.

3.4. DSC thermograms

The DSC thermogram of samples is illustrated in Figure 6. For EJG, the thermogram shows melting point at 76.0°C . The worthy note is that the melting point peak is quite broad, implying that EJG may be partially crystalline material [10]. When LiClO_4 was added into EJG, a new melting point appeared at -12.5°C . The low temperature side of the melting peak is almost a straight line, which may correspond to a liquid crystal. This may be due to the strong interaction between LiClO_4 and epoxy group in EJG. In addition, the melting peak of EJG at 76.0°C became smaller. These may be evident that LiClO_4 was well dispersed in EJG and formed a crystal liquid substance. When the amount of LiClO_4 is excess, it cannot disperse more in EJG. As a result, a new peak can be observed at 52.2°C in the DSC thermogram of EJG/0.20- LiClO_4 . LiClO_4 , which may refer to the existence of a new phase. This is in good agreement with the result from ion conductivity measurement in which suggested that ion pairs were formed when the amount of LiClO_4 was too high.

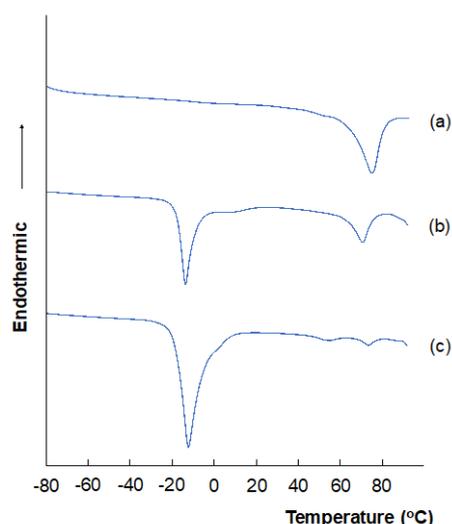


Fig.6. DSC thermogram of (a) EJG, (b) EJG/0.05-LiClO₄, (c) EJG/0.20-LiClO₄.

4. Conclusion

Epoxy group was successfully introduced to JG. The molecular weight of JG did not change after the epoxidation. LiClO₄ can well disperse in JG and EJG. Epoxy group in EJG facilitated the mobility of lithium ion and therefore ion conductivity of EJG/LiClO₄ was significantly improved. EJG interacted LiClO₄ to form a liquid crystal.

Acknowledgements

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