

INFLUENCE OF PMMA ON PROPERTIES OF POLYMER ELECTROLYTE BASED ON EPOXIDIZED DEPROTEINIZED NATURAL RUBBER

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Abstract

The effect of co-polymer, i.e. poly(methyl methacrylate) (PMMA), and doping salt, i.e. lithium trifluoromethanesulfonate (LiCF_3SO_3) in the epoxidized rubber-polymer blends preparation was evaluated. The electrolyte membrane was developed through solution casting method in the presence of 0-50wt.% of LiCF_3SO_3 . The influence of LiCF_3SO_3 on chemical interaction and structure, ionic conductivity, mechanical properties, and glass transition temperature (T_g) of 45%-epoxidized deproteinized natural rubber (EDPNR45)-PMMA (80/20) membrane was determined using several techniques, i.e. F-IR, universal testing machine, multipotentiostat, and DSC. Infrared analysis showed that lithium salts might formed coordination bonds with the oxygen atoms of PMMA and EDPNR45. Ionic conductivity of EDPNR45/ LiCF_3SO_3 blends have been evaluated and the highest conductivity (σ) was obtained in the presence of 35 wt.% of lithium trifluoromethanesulfonate ($1.71 \times 10^{-5} \text{S.cm}^{-1}$). The PMMA content's effect was also evaluated on the properties of EDPNR45/ LiCF_3SO_3 . The highest conductivity and mechanical strength values at EDPNR45/PMMA ratio of 80/20. Enhancing trend of T_g was obtained with the increase of PMMA and salt concentration. FTIR characterization also confirms the interaction of salt with EDPNR45 and PMMA.

Keywords: EDPNR, PMMA, LiCF_3SO_3 , Polymer Electrolyte Substrate

1. Introduction

In this era, polymer electrolyte substrates are widely investigated due to the applicability of these materials in energy devices, such as in lithium batteries [1, 2]. The reason behind this phenomenon is due to the effective path of Li^+ or dopant salt presents in those materials [3, 4].

Previous study mentioned that the utilization of polar rubbery material is quite important to improve the electrolyte membrane ionic conductivity, this is due to some advantages, i.e. as a polar material it will be able to be used for transporting Li^+ , and rubbery material commonly has low T_g value that able to enhance the mobility of Li^+ [2, 5, 6]. The combination of the low T_g and T_m values of polymer electrolyte substrates and the optimum amount of salt ion is believed to be able to improve its ionic conductivity [7-11]. After the incorporation of dopant ion, the T_g value of polymeric material normally will increase, in this regards the low T_g of polymeric material is required.

Natural polymer that has elastomer property, i.e. natural rubber latex (NRL) and its derivatives, can be utilized for this purpose, this is caused by its wide applications, i.e. tire, glove, seal, gasket, mounting, etc [12, 13]. NRL cannot be directly applied for this purpose due to the presence of $\text{C}=\text{C}$ bonds that can cause this material to be quite reactive into oxygen, sunlight, and heat; also, it will easily interact with the hydrophobic solvents, i.e. toluene, xylene, etc. Structure modification, i.e. polar group modification (epoxy group) on the natural rubber structure is

needed, this kind of modification is able to improve its hydrophilicity without reducing the other properties of NRL, i.e. elasticity, T_g , tensile modulus and tensile strength [12, 14].

Several issues related to the utilization of epoxidized natural rubber (ENR) as polymer electrolyte substrate have been reported, i.e. the presence of protein during the preparation of epoxidized natural rubber lead to the inaccurate result obtained during the measurement as the effect of the interaction of protein with water [5, 15, 16]. In general, ENR prepared from NRL normally will have a soft and tacky characteristic, these properties cause some difficulties to handle this material. To overcome these issues, in this study the ENR was prepared using urea deproteinization method to obtain a hyper-deproteinized natural rubber (DPNR) which has 0.002wt.% of protein [14, 17] (ENR in this study was called as EDPNR45, due to the degree of epoxidation in this study which was about 45%), which normally in the natural rubber latex before deproteinization contains 2wt.% of protein. With this significant decrease of protein content, we believed the result obtained during the measurement would be more accurate.

In order to resolve the softness and tackiness issues of ENR, PMMA was selected for blends with the ENR. Several researches have been conducted under this topic to observe the mechanical properties, compatibility and its ability to be utilized as polymer electrolyte substrates [18-22]. The blends obtained between ENR and PMMA have good interfacial interaction, and in the last

decade several studies have dealt with the good properties of ENR/PMMA blends for the fuel cell application [18, 23].

In this study, a dopant salt of lithium (lithium trifluoromethanesulfonate, LiCF_3SO_3) was blended with EDPNR45, the presence on lithium ion in the blends can help to enhance the ionic conductivity property. In this study, to produce the electrolyte membrane, the dopant salt, PMMA, and EDPNR45 were mixed in various ratios. Spectroscopy analysis, i.e. FT-IR, was performed to determine the shifting of specific functional group of membranes. Multipotentiostat was utilized to evaluate the ionic conductivity (σ) of the membranes. Universal testing machine was used to assess the mechanical properties of membranes. The glass transition temperature of membranes also determined in this study through thermal analysis using DSC.

2. Experimental

2.1. Materials

Natural rubber latex (NRL) in this study was obtained from Dau Tieng Rubber Corporation, Viet Nam. Sodium dodecyl sulphate ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$, SDS) was purchased from Fisher Scientific UK Ltd (United Kingdom). Urea ($\text{CO}(\text{NH}_2)_2$) was obtained from Nacalai Tesque, Inc (Japan). Acetic anhydride ($\text{C}_4\text{H}_6\text{O}_3$), hydrogen peroxide (H_2O_2), PMMA (Mw \sim 120 kDa), lithium trifluoromethanesulfonate (LiCF_3SO_3), and tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$, THF) were obtained from Sigma Aldrich (Singapore).

2.2. Hyper-deproteinization of natural rubber latex

The hyper-deproteinization of high ammonia natural rubber latex (HANR) was performed by following protocol [14, 17]. The HANR with dry rubber content (DRC) \sim 60 wt.% was added with urea and SDS with final concentration of each chemical was 0.1 and 1.0wt.%, respectively. This mixture was then incubated for an hour at room temperature. The separation of cream fraction was performed through centrifugation and re-dispersed in 1.0wt.% of SDS solution for twice and in each step, the cream fraction was separated by centrifugation. The obtained cream fraction of DPNR was then diluted to obtain DPNR latex which had 10 wt.% of DRC and it was stabilized with 1.0wt.% of SDS.

2.4. The epoxidation of deproteinized natural rubber latex (EPDNR)

The pH of the obtained DPNR (100g, DRC \sim 10wt.%) was adjusted to 5.5 using acetic acid solution (1 v/v.%), and pre-cooled at 10°C . The epoxidation was performed by adding 50mL peracetic acid. After 90 min, the pH reaction was adjusted to 7.1 by adding 0.01M NaOH solution. The resulting EDPNR45 latex was coagulated and purified by pouring the latex into methanol. The purified latex was then dried using vacuum oven at 30°C [2, 6, 14].

2.5. The effect of dopant salt (LiCF_3SO_3) on the EDPNR45 film

The effect of dopant salt on the characteristic of EDPNR45 was evaluated by preparing EDPNR45 film by mixing EDPNR45 solution with a specific amount of LiCF_3SO_3 (0-50wt.%) to prepare polymer-salt electrolyte solution. The mixture of EDPNR45/ LiCF_3SO_3 was poured onto Teflon surface and allowed to evaporate slowly.

2.6. The effect of poly(methyl methacrylate) on the EDPNR45/ LiCF_3SO_3 film

The solution of EDPNR45/PMMA (100/0; 90/10; 80/20; and 70/30) blends was also prepared in the presence of LiCF_3SO_3 of 35wt.%. The membrane was obtained by pouring the solutions onto Teflon surface and allowed to evaporate slowly.

2.7. Characterizations

The spectra of EDPNR45 blends was recorded on the ALPHA Platinum ATR (Bruker). The sample was scanned between a wavenumber 4000 to 400cm^{-1} . The tensile strength and elongation at break properties of the elastomeric membrane were carried out through ISO 37:2017 and evaluated using Stograph VG5E (Toyoseiki, Japan) equipped with 5-kN load cell at speed 10 mm/min. The ionic conductivity was measured by the complex impedance method using an Ultimate versatile multipotentiostat VSP 300 (Biologic Sciences Instrument). The DSC measurement was carried out on a Seiko Instrument DSC 220 apparatus. The thermograms were recorded on raising the temperature from -100 to 100°C at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

3. Result and discussion

3.1 The properties of epoxidized (hyper)-deproteinization natural rubber (EDPNR45)

The total nitrogen content of the non-DPNR and DPNR was achieved by Kjeldahl method (ISO 1656:1996).

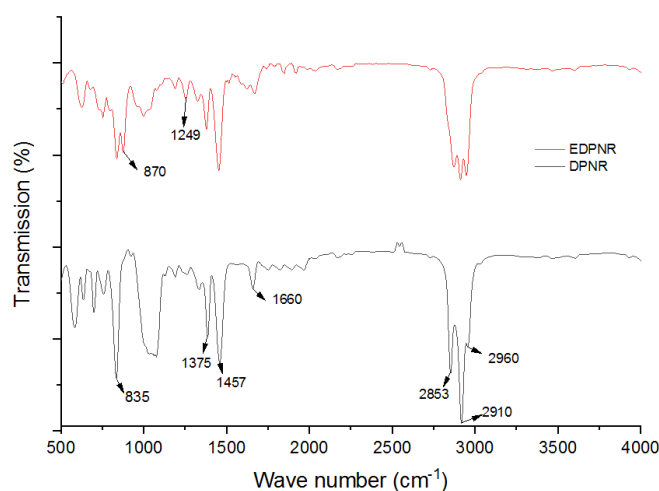


Figure 1. FT- IR spectra of DPNR and EDPNR.

The nitrogen content of HANR was decreased from 0.3800 to 0.0028wt.% after being treated and incubated with the mixture of urea and SDS at room temperature for 1 hour. After treated with the peracetic acid, the band oxirane group that indicated the present of epoxy ring was appeared at 1249 and 870cm^{-1} [24], and the band that indicated the present of isoprene was found at 1600 and 835cm^{-1} [25]. In DPNR spectrum, there were several absorption bands, i.e. at 1660, 1459, 1375, and 835cm^{-1} that referred to $\text{C}=\text{C}$ stretching, $-\text{CH}_2-$ deformation, methyl $\text{C}-\text{H}$ deformation and $=\text{C}-\text{H}$ deformation, respectively. Other absorption bands also appeared at 2960, 2910, and 2853cm^{-1} were assigned to $=\text{CH}$ stretching, $-\text{CH}_3$ asymmetry stretching, and $-\text{CH}_2$ symmetry stretching. The estimated epoxy group percentage

in EDPNR was about 45 mol% (EDPNR45) that determined by the following equation [26].

$$X_{epoxy} = \frac{A_{870}}{(A_{835} + A_{870})} \quad (\text{Eq. 1})$$

Figure 2 shows the DSC thermograms of DPNR and EDPNR45. That revealed the T_g value of DPNR and EDPNR45, which was about -62.29 and -21.48°C, respectively.

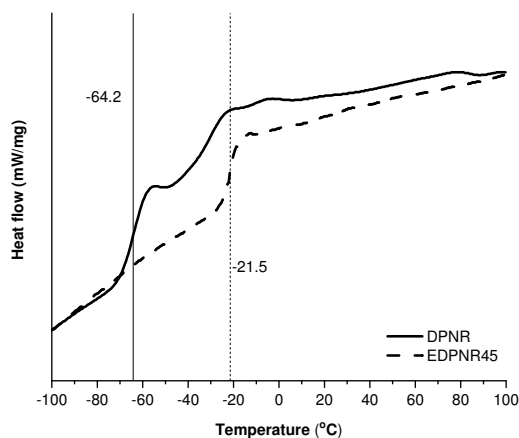


Figure 2. DSC thermograms of DPNR and EDPNR45.

EDPNR45 still had low T_g value (<RT, room temperature) that indicated EDPNR45 still had elastomer property just like DPNR. Supported by the presence of high percentage of epoxy group (45mol%) and low proteins content (~0.002wt.%), it made EDPNR45 is suitable to be used as polymer electrolyte substrate.

3.2 The ionic conductivity of EDPNR45 mixed with various concentrations of LiCF₃SO₃

The effect of the lithium salt content on the ionic conductivity (σ) property of the electrolyte membrane is shown in Figure 3. The enhancement of σ value of EDPNR45/LiCF₃SO₃ in the incorporation of small amount of LiCF₃SO₃ could be associated to the enhance of the effective carrier ion amount [2, 27]. On the other hand, at the higher amount of LiCF₃SO₃ induced to the decrease of σ value that could be due to the segmental motion constraint of EDPNR45 [23]. The highest ionic conductivity was obtained at the addition of 35wt.% of LiCF₃SO₃ with value about $1.71 \times 10^{-5} \text{S.cm}^{-1}$. However, the obtained film of EDPNR45/ LiCF₃SO₃ were very soft, tacky and difficult to peel off.

The present of segmental motion constraint was examined by measuring the T_g of EDPNR45/LiCF₃SO₃. Transition glass temperature of EDPNR45/LiCF₃SO₃ versus the amount of LiCF₃SO₃ that was added into EDPNR45, ranging from 0–50wt.%, is shown in Figure. 4. The glass transition temperature of EDPNR45/LiCF₃SO₃ enhance as the amount of LiCF₃SO₃ rose, this phenomenon can be associated to the pseudo-crosslinking of EDPNR45. The similar result was reported in the previous study that prepared PEO/LiTFSI and PEO/sulfonamide salt hybrid [28, 29].

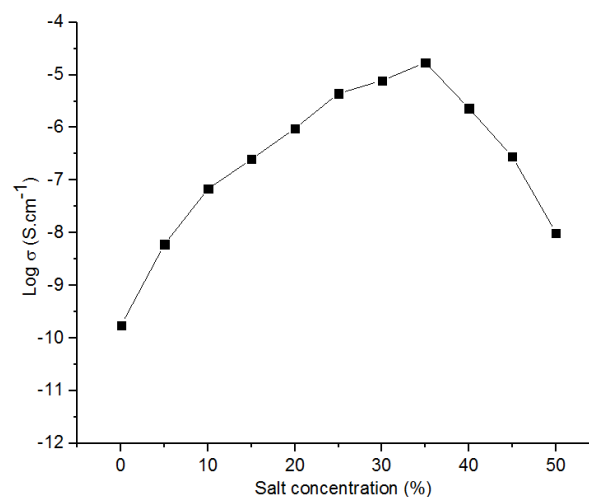


Figure 3. Ionic conductivity for EDPNR45 as a function of salt concentration.

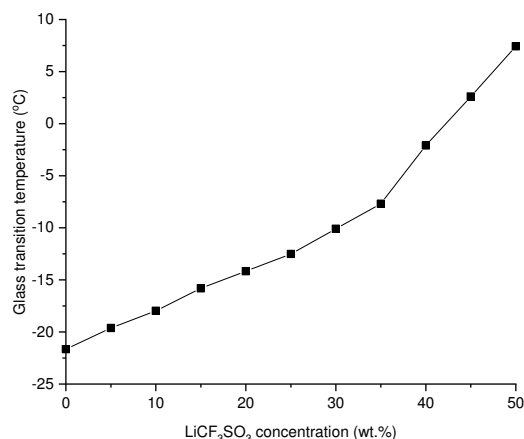


Figure 4. T_g value of EDPNR45/ LiCF₃SO₃ at various amount of salt.

3.3 Effect of PMMA content on the properties of EDPNR45/LiCF₃SO₃

The salt concentration of LiCF₃SO₃ was fixed at 35wt.%, while PMMA content was varied to study the effect of addition of PMMA into EDPNR45/LiCF₃SO₃ polymer electrolyte substrate by monitoring their ionic conductivity, thermal and mechanics properties.

Films that obtained from EDPNR45/PMMA/ LiCF₃SO₃ solutions appeared homogeneous at room temperature. Figure 5 shows a single T_g value was obtained when the content of PMMA used blend with EDPNR45 of about 10-20wt.%. This indicated that there was no microphase separation occurred in the blend system, and the value of T_g increased when the PMMA content increased. However, when the PMMA content that added into blend was about 30wt.% of PMMA, two T_g values were obtained indicating the phase separation might be occurred in this amount of PMMA. Compare to the previous studies, the presence of two

T_g values indicated that at this ratio of the polymer electrolyte blend was not forming a homogeneous mixture [30, 31].

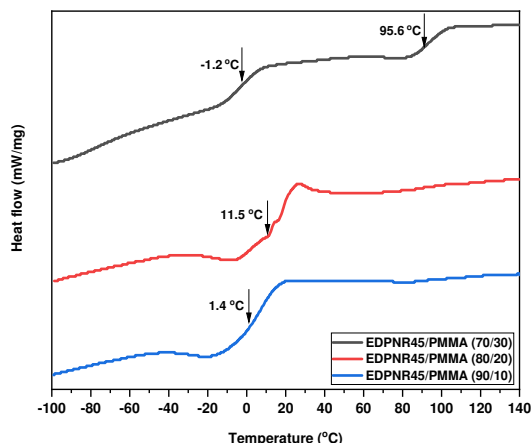


Figure 5. Effect of PMMA content on DSC thermograms of EDPNR45/LiCF₃SO₃.

Table 1. Effect of PMMA content on ion conductivity of EDPNR45/LiCF₃SO₃.

DPNR/PMMA	Film thickness (mm)	δ (S.cm ⁻¹)	Appearance
100/0	0.29	1.45 x 10 ⁻⁵	slightly stick to surface, difficult to peel off, transparent film
90/10	0.30	1.71 x 10 ⁻⁵	not stick to surface, easy to peel off, transparent film
80/20	0.31	2.94 x 10 ⁻⁵	not stick to surface, easy to peel off, transparent film
70/30	0.30	6.58 x 10 ⁻⁶	not stick to surface, easy to peel off, hazy films

Table 1 lists ionic conductivity data and appearance film of the polymer electrolyte substrates of EDPNR45/PMMA/LiCF₃SO₃. It was found that when the ratio of PMMA was higher than EDPNR45, the ionic conductivity of the films rose up to 2.94 x 10⁻⁵ S.cm⁻¹ and the value started to decrease when the PMMA content was 30wt.%. Increased concentration of PMMA in the blend could enhance the oxygen number that obtained from carbonyl group [23]. The presence of this oxygen atom could hinder the migration of lithium ion in the blends due to the high chances of the coordinate bond formation between the oxygen atom and lithium ion [32, 33]. The ionic conductivity value decreased at PMMA 30wt.% content because the obtained polymer electrolyte film was inhomogeneous and might cause the phase separation

occurred. This statement was supported by the T_g value in Figure. 5, that showed at the 30wt.% of PMMA, the blend system had two T_g values, e.g. T_{g1} = -1.2°C (EDPNR45 phase) and T_{g2} = 96,5°C (PMMA phase). The phase separation led to the formation of opaque or hazy films for this blend ratio. The mechanical properties results of the electrolyte membrane were shown in the Table 2.

Table 2. Effect of PMMA content on the mechanical properties of EDPNR45/LiCF₃SO₃.

Sample	Tensile strength (MPa)	Elongation at break (%)
EDPNR45	3.5	869
PMMA	43.8	8.2
65wt.% EDPNR45: 35wt.% LiCF ₃ SO ₃	4.0	789
65wt.% (90wt.% EDPNR45: 10wt.% PMMA): 35wt.% LiCF ₃ SO ₃	5.8	745
65wt.% (80wt.% EDPNR45: 20wt.% PMMA): 35wt.% LiCF ₃ SO ₃	6.9	690
65wt.% (70wt.% EDPNR45: 30wt.% PMMA): 35wt.% LiCF ₃ SO ₃	5.5	615

Table 2 data confirms that PMMA basically could improve the flexibility of EDPNR45/LiCF₃SO₃ films. A further addition of PMMA in the sample, resulting to the mechanical strength being further increased. However, the mechanical properties of blends started to decrease when the PMMA content was 30%, this could be due to the phase separation phenomenon.

3.4 Fourier transform infrared analysis

Figure 6 shows the FT-IR spectra of PMMA, EDPNR45/LiCF₃SO₃, and EDPNR45/PMMA/LiCF₃SO₃ films. Two new bands, at 1367 and 1032cm⁻¹, were found in the EDPNR45/PMMA blend and EDPNR spectra after the addition of LiCF₃SO₃. These bands was confirmed as the vibrational of CF₃ and SO₃ from the LiCF₃SO₃, respectively [23]. The absorption bands at 2853, 2918 and 2965cm⁻¹ that identified as -CH₂ symmetry stretching, -CH₃ asymmetry stretching and =CH stretching were found in EDPNR45/LiCF₃SO₃. In the presence of PMMA, these bands have shifted and changed into two bands at 2895 and 2954cm⁻¹. This phenomenon can be caused by the effect of the absorbing of CH₃ symmetrical stretching of PMMA at 2953cm⁻¹. The presence of specific bands at 689 and 691cm⁻¹ was confirmed as the vibration of LiO₂ symmetric [34]. These bands indicated that the lithium salt dissolved in the EDPNR45 and EDPNR45/PMMA matrices and created a coordination bond between Li⁺ and oxygen ions in the epoxy group. The other coordinating effect of the lithium salt in the EDPNR45 blends was also found affecting chemical shift. As the example, the epoxy band in the EDPNR film that appeared at 1249cm⁻¹ was found shifting to 1255cm⁻¹ in the EDPNR45/PMMA/LiCF₃SO₃. Bands at 1660 and 1729cm⁻¹ that were assigned as -C-O-C epoxy group of EDPNR45 and C=C in PMMA, respectively were found as a broaden band in the blend of EDPNR45/PMMA/LiCF₃SO₃, also a new band at 3604cm⁻¹ was appeared that assigned for hydrogen bonding.

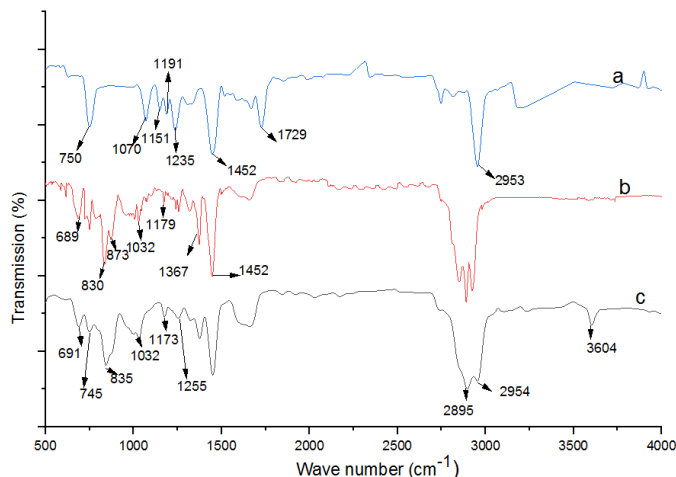


Figure 6. FT- IR spectrum of (a) FT- IR spectrum of PMMA, (b) FT- IR spectrum of EDPNR45/LiCF₃SO₃, and (c) FT- IR spectrum of EDPNR45/PMMA/LiCF₃SO₃.

4. Conclusions

EDPNR45 were prepared and obtained by epoxidation DNR with 50mL freshly prepared peracetic acid. The ionic conductivity of EDPNR45/LiCF₃SO₃ was dependent on salt concentration, Tg. At lower salt concentration, the ionic conductivity increased as the effective carrier ion increased. In contrast, at higher salt concentration, the ionic conductivity was governed by the segmental motion of EDPNR45. The highest ionic conductivity for EDPNR45/LiCF₃SO₃ was about $1,71 \times 10^{-5} \text{Scm}^{-1}$ at 323K. However, the film has low tensile strength and high elongation at break and it is not easy to form free standing film from pure EDPNR45. PMMA has been used to add into the electrolytic film to improve mechanical and conductive properties. The highest conductivity and tensile strength achieved in this work is $2.94 \times 10^{-5} \text{S.cm}^{-1}$, 6.9MPa, respectively at EDPNR45/PMMA ratio of 80/20 and 35wt% of LiCF₃SO₃. Because EDPNR45 can be prepared from natural resource but not from petroleum, it will be useful as an ionic conducting medium for solid polymer electrolyte.

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References

- [1] S.F. Mohammad, N. Zainal, S. Ibrahim, N.S. Mohamed, Conductivity Enhancement of (Epoxidized Natural Rubber 50)/Poly(Ethyl Methacrylate)-Ionic Liquid-Ammonium Triflate, *Int. J. Electrochem. Sci.*, 8 (2013) 6145-6153.
- [2] W. Klinklai, Ionic conductivity of highly deproteinized natural rubber having epoxy group mixed with alkali metal salts, *Solid State Ion.*, 168 (2004) 131-136.
- [3] P.G. Bruce, F. Krok, C.A. Vincent, Preparation and characterisation of PEO-Hg(ClO₄) complexes and some thoughts on ion transport in polymer electrolytes, *Solid State Ion.*, 27 (1988) 81-88.
- [4] P.V. Wright, Electrical conductivity in ionic complexes of poly(ethylene oxide), *Br. Polym. J.*, 7 (1975) 319-327.

- [5] R. Idris, M.D. Glasse, R.J. Latham, R.G. Linford, W.S. Schlindwein, Polymer electrolytes based on modified natural rubber for use in rechargeable lithium batteries, *J. Power Sources*, 94 (2001) 206-211.
- [6] W. Klinklai, S. Kawahara, T. Mizumo, M. Yoshizawa, J. Tangpakdee Sakdapipanich, Y. Isono, H. Ohno, Depolymerization and ionic conductivity of enzymatically deproteinized natural rubber having epoxy group, *Eur. Polym. J.*, 39 (2003) 1707-1712.
- [7] G.G. Cameron, J.L. Harvie, M.D. Ingram, G.A. Sorrie, Ion migration in liquid polymer electrolytes, *Br. Polym. J.*, 20 (1988) 199-202.
- [8] G.G. Cameron, M.D. Ingram, K. Sarmouk, Conductivity and viscosity of liquid polymer electrolytes plasticized by propylene carbonate and tetrahydrofuran, *Eur. Polym. J.*, 26 (1990) 1097-1101.
- [9] P. Manaresi, M.C. Bignozzi, F. Pilati, A. Munari, M. Mastragostino, L. Meneghello, A. Chiolle, Polymer electrolytes based on polyesters of thiodipropionic acid: 1. Synthesis, characterization and ionic conductivity measurements, *Polymer*, 34 (1993) 2422-2426.
- [10] D.J. Bannister, G.R. Davies, I.M. Ward, J.E. McIntyre, Ionic conductivities of poly(methoxy polyethylene glycol monomethacrylate) complexes with LiSO₃CH₃, *Polymer*, 25 (1984) 1600-1602.
- [11] A. Vallée, S. Besner, J. Prud'Homme, Comparative study of poly(ethylene oxide) electrolytes made with LiN(CF₃SO₂)₂, LiCF₃SO₃ and LiClO₄: Thermal properties and conductivity behaviour, *Electrochim. Acta*, 37 (1992) 1579-1583.
- [12] Q. Ali, W. Taweepreda, K. Techato, Preparation and characterization of polymer electrolyte membrane from chloroacetate chitosan/chitosan blended with epoxidized natural rubber, *Polym. Test.*, 82 (2020).
- [13] H. Ismail, S.M. Shaari, N. Othman, The effect of chitosan loading on the curing characteristics, mechanical and morphological properties of chitosan-filled natural rubber (NR), epoxidised natural rubber (ENR) and styrene-butadiene rubber (SBR) compounds, *Polym. Test.*, 30 (2011) 784-790.
- [14] P.T. Nghia, N. Siripitakchai, W. Klinklai, T. Saito, Y. Yamamoto, S. Kawahara, Compatibility of liquid deproteinized natural rubber having epoxy group (LEDPNR)/poly (L-lactide) blend, *J. Appl. Polym. Sci.*, 108 (2008) 393-399.
- [15] J. Garbarczyk, W. Jakubowski, M. Wasiucionek, Effect of selected mobile ions on moisture uptake by beta' alumina, *Solid State Ion.*, 9-10 (1983) 249-253.
- [16] A. Lauenstein, A. Johansson, J. Tegenfeldt, Water Absorption of the Polymer Electrolyte Systems Pb(CF₃SO₃)₂PEO_n and Zn(CF₃SO₃)₂PEO_n, *J. Electrochem. Soc.*, 141 (1994).
- [17] W. Klinklai, T. Saito, S. Kawahara, K. Tashiro, Y. Suzuki, J.T. Sakdapipanich, Y. Isono, Hyperdeproteinized natural rubber prepared with urea, *J. Appl. Polym. Sci.*, 93 (2004) 555-559.
- [18] W.D.N. Ayutthaya, S. Poompradub, Thermal and mechanical properties of poly(lactic acid)/natural rubber blend using epoxidized natural rubber and poly(methyl methacrylate) as co-compatibilizers, *Macromol. Res.*, 22 (2014) 686-692.
- [19] J. James, G.V. Thomas, K.P. Pramoda, S. Thomas, Transport behaviour of aromatic solvents through styrene butadiene rubber/poly [methyl methacrylate] (SBR/PMMA) interpenetrating polymer network (IPN) membranes, *Polymer*, 116 (2017) 76-88.
- [20] R. Jaratrotkamjorn, C. Khaokong, V. Tanrattanakul, Toughness enhancement of poly(lactic acid) by melt blending with natural rubber, *J. Appl. Polym. Sci.*, 124 (2012) 5027-5036.
- [21] C. Nakason, W. Pechurai, K. Sahakaro, A. Kaesaman, Rheological, mechanical and morphological properties of thermoplastic vulcanizates based on NR-g-PMMA/PMMA blends, *Polym. Adv. Technol.*, 16 (2005) 592-592.
- [22] M.Z. Sharil Fadli, A.L. Famiza, SiO₂ Filler as Interface Modifier in PMMA/ENR 50 Electrolytes, *Adv. Mat. Res.*, 812 (2013) 120-124.
- [23] F. Latif, M. Aziz, N. Katun, A.M.M. Ali, M.Z. Yahya, The role and impact of rubber in poly(methyl methacrylate)/lithium triflate electrolyte, *J. Power Sources*, 159 (2006) 1401-1404.
- [24] O.S. Dahham, N.N. Zulkepli, Robust interface on ENR-50/TiO₂ nanohybrid material based sol-gel technique: Insights into synthesis, characterization and applications in optical, *Arab. J. Chem.*, 13 (2020) 6568-6579.

- [25] S. Kawahara, W. Klinklai, H. Kuroda, Y. Isono, Removal of proteins from natural rubber with urea, *Polym. Adv. Technol.*, 15 (2004) 181-184.
- [26] J.E. Davey, M.J.R. Loadman, A Chemical Demonstration of the Randomness of Epoxidation of Natural Rubber, *Br. Polym. J.*, (1984) 134-138.
- [27] M. Yoshizawa, E. Marwanta, H. Ohno, Preparation and characteristics of natural rubber/poly(ethylene oxide) salt hybrid mixtures as novel polymer electrolytes, *Polymer*, 41 (2000) 9049-9053.
- [28] J.-F.L. Nest, A. Gandini, H. Cheradame, Crosslinked Polyethers as Media for Ionic Conduction, *Br. Polym. J.*, (1998) 253-268.
- [29] Y. Tominaga, N. Takizawa, H. Ohno, Effect of added salt species on the ionic conductivity of PEO/sulfonamide salt hybrids, *Electrochim. Acta*, 45 (2000) 1285-1289.
- [30] A.M. El-Hadi, The effect of additives interaction on the miscibility and crystal structure of two immiscible biodegradable polymers, *Polímeros*, 24 (2014).
- [31] J. Zhao, M.D. Ediger, Y. Sun, L. Yu, Two DSC Glass Transitions in Miscible Blends of Polyisoprene/Poly(4-tert-butylstyrene), *Macromolecules*, 42 (2009) 6777-6783.
- [32] S.A.M.N. M. S. Su'ait, A. Ahmad, H. Hamzah, M. Y. A. Rahman, Preparation and characterization of blended solid polymer electrolyte 49% poly(methyl methacrylate)-grafted natural rubber:poly(methyl methacrylate)-lithium tetrafluoroborate, *J. Solid State Electrochem.*, (2012) 2275-2282.
- [33] M.D. Glasse, R. Idris, R.J. Latham, R.G. Linford, W.S. Schlindwein, Polymer electrolytes based on modified natural rubber, *Solid State Ion.*, 147 (2002) 289-294.
- [34] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part A: Theory and Applications in Inorganic Chemistry*, John Wiley & Sons, Inc., Hoboken, New Jersey, Canada.