INFLUENCE OF 6PPD ON THERMAL AGING AND IONIC CONDUCTIVITY OF MG30 POLYMER ELECTROLYTES

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Abstract

This study investigates the influence of N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine (6PPD) in retarding the thermal ageing of methyl-grafted natural rubber (MG30) polymer electrolytes (PEs). Like other rubber derivative products, MG30 is susceptible to thermal degradation due to elevated temperatures, which in turn causes physical ageing. This deterioration has an adverse effect on both the mechanical properties and the ionic conductivity of the electrolyte. In this work, MG30 PEs were subjected to thermal degradation at 100 °C for several days, and the ionic conductivity was observed. Impedance spectroscopy was used to analyse the temperature-dependent ionic conductivity of MG30-LiTf and MG30-6PPD-LiTf PEs. The results showed that the ionic conductivity increased as the temperature increased, following the Vogel-Tamman-Fulcher (VTF) model. Further exposing the electrolytes to heat treatment at a precise temperature of 100 °C for several days led to a progressive decline in the conductivity of ions over time, likely due to the phenomenon of physical ageing. The MG30-6PPD electrolytes exhibited longer conductivity relaxation, indicating greater resilience to physical aging compared to MG30 PEs. The findings provide crucial insights into the thermal durability and potential applications of these polymer electrolytes in electrochemical devices.

Keyword:methyl-grafted natural rubber, polymer electrolyte, thermal aging, 6PPD

Introduction

Energy storage is a major concern in today's global quest for sustainable and resilient energy systems. As renewable energy sources like solar and wind are intermittent, they require energy storage to balance supply and demand. In the modern world, the requirement for environmental sustainability has driven a continuous search for "green materials". As a result, bio-based polymers have gained greater acceptance due to their potential application as efficient substitutes of conventional synthetic polymers (Whba et al., 2024). Among the biopolymer, Methyl-grafted natural rubber (MG) surge as a bright candidate to be applied as polymer electrolytes especially for lithium-ion polymer batteries (Azaki et al., 2023; Jaafar et al., 2023; Kamarulazam et al., 2023; Mamat et al., 2020; Rajapaksha et al., 2023) and supercapacitor

(Perera et al., 2024; Rajapaksha et al., 2021; Rajapaksha et al., 2022) due to its strong mechanical stability, flexibility, high ionic conduction, and low cost production.

However, like other rubber product derivatives, MG is prone to degrade due to elevated temperature. As physical ageing is accelerated by heat (Li et al., 2003; Wang et al., 2022; Wang et al., 2021), the ageing process will cause the deterioration of polymer host on mechanical and structural properties. The consequences of degraded MG30, however, mainly devour the mechanical properties such as hardening, losing its elasticity and favourably cracking. This will damage the ionic motion pathway and decrease the ionic conductivity value as ionic motion in rubbery polymer electrolytes also depends on the polymer segmental motion (Nazir et al., 2021; Whba et al., 2020). Accordingly, it leads to bad electrode-electrolytes contact that may drop the performance of lithium-ion bio-polymer batteries (Shi et al., 2022).

Hence, it is important to retard MG polymer electrolytes degradation due to thermal aging. A recent work shows that 0.5 wt. % of N-(1,3- dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) antioxidant works well on retarding 30% MG (MG30) thermal aging (Aziz et al., 2023). Meanwhile, the relation between ionic conductivity and thermal aging can be explored by extending the knowledge from Kumar and Scanlon (1999) who formulated Equation (1) that shows the conductivity relaxation of electrolytes at a given temperature. The equation contains the most difficult aspect of physical aging due to the complexity and nonlinearity resulting from the collective effect of a large number of relaxation sites.

$$\sigma'(t) = \sigma(\infty) \pm \sum_{i=0}^{n} \sigma_i e^{-v_i t} \quad (1)$$

where:

$\sigma'(t)$ = theoretical conductivity at time t
$\sigma(\infty)$ = equilibrium conductivity
σ_i = relaxation amplitude
v_i = relaxation frequency ($1/t_i$)
t_i = relaxation time

Equation (1) is then reduced to Equation (2), with the assumption that only a single relaxation mechanism occurs at the early stage of physical aging.

$$\sigma(t) = \sigma'(t) - \sigma(\infty) = \sigma_o e^{-v_o t} \quad (2)$$

where:

$\sigma(t)$ = experimentally measured conductivity at time, t

A plot of ln $\sigma(t)$ vs. t should therefore yield a straight line from which the relaxation time, t_o, can be calculated from the information of the slope that represents the relaxation frequency. The validity of the assumption can be assessed from the experimental data of the MG30 electrolytes system with and without the presence of 6PPD. This work highlights the effect of 6PPD's presence onto the ionic conductivity of MG30 polymer electrolyte under thermal ageing.

Material and Method

MG30 as the polymer host was obtained from the Rubber Research Institute of Malaysia (RRIM), lithium trifluoromethanesulfonate (LiTF) as the doping salt was obtained from Sigma Aldrich and N-(1,3- dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) as an antioxidant

pallet was supplied by Centre West Industrial Supplies. Stocks solutions composing 1g of MG30 in a 40 ml of tetrahydrofuran (THF) was prepared. LiTF salt was taken in different stoichiometry weight percent (wt. %) in the ratio of 20, 25, 30, 35, 40, and 45 were dissolved in stocks solutions to form polymer electrolyte solution. The mixtures were continuously stirred with a magnetic stirrer for several hours at room temperature to ensure a complete dissolution of the salt. Then, the solutions were cast into different petri dishes and the films were allowed to form at room temperature. This process was repeated by adding 0.5 wt.% of 6PPD into the MG30 stock solutions.

These samples were put in a constant humidity chamber (ESPEC SH-221) at 40% RH and the temperature was varied from 303 K up to 373 K. The data for electrochemical impedance spectroscopy (EIS) was taken via in situ process by using HIOKI 3532-50 LCR Hi-tester interfaced into a computer with a frequency ranging from 50 Hz to 1 MHz at each selected temperature. During the test, the polymer electrolytes were sandwiched between two stainless steel blocking electrodes and the thermal aging condition was established by exposing the electrolyte samples in an enclosed coin cell at 100 ^{o}C for 24 hours. The ionic conductivity was calculated by utilising the same parameter obtained from the complex impedance plot and applying the same formula as Equation (2).

Results and Discussion

Effect of Salt Content on MG30-LiTf and MG30-6PPD-LiTf Polymer Electrolytes Systems Ionic Conductivity

Figure 1 shows the ionic conductivity of MG30-LiTf and MG30-6PPD-LiTf polymer electrolytes in function of LiTF concentration at 303 K. The ionic conductivity of MG30-LiTf increases with salt concentration, reaching an optimum conductivity 5.89 x 10^{-4} Scm^{-1} at 35 wt. % of LiTf. Beyond 35 wt. % of LiTf, the ionic conductivity of MG30-LiTf is decreasing. In contrast, even with the increasing salt content, the sample of MG30-6PPD-LiTf did not show any sign of decline in the ionic conductivity value. The increasing conductivity value, altogether with the rise of salt content percentage is due to the increasing number of free ions (Aziz et al., 2017; Roy et al., 2017).

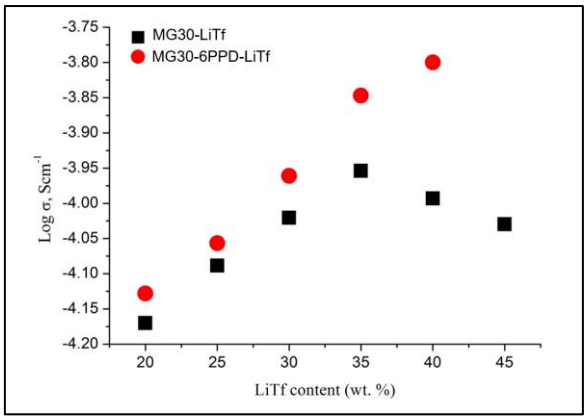

Figure 1 Ionic conductivity of MG30 and TMG30 electrolytes in function of LiTF concentration at 303 K

The MG30-6PPD-LiTf electrolytes have higher ionic conductivity value compared MG30LiTf electrolytes at same amount of LiTf content. The lone pair of electron which existed in the secondary amines of 6PPD may play a role in dissociating LiTf into ions (Polovková et al., 2006). However, the reaction cannot be proven in experimental works due to the small

amount of 6PPD content in the electrolytes systems (Aziz et al., 2017; 2018). The steady increase of the ionic conductivity value with a higher percentage salt content of MG30-6PPD-LiTf electrolytes systems presumed that 6PPD played a role in avoiding salt aggregation.

The decline in ionic conductivity value after 35 wt. % of MG30-LiTf may be due to the increasing number of ion aggregates and ion recombination which occurred at a higher percentage salt content in the polymeric system (Ravikumar et al., 2018).

Temperature Dependence Conductivity Studies of MG30-LiTf and MG30-6PPD-LiTf Polymer Electrolytes Systems

The study of temperature dependence conductivity on polymer electrolytes provides the ions transport mechanism information. The three highest point of MG30-LiTf and MG30-6PPD-LiTf polymer electrolytes ionic conductivity samples (30 wt.%, 35 wt.% and 40 wt.%) were selected in this test. The sample of MG30-6PPD beyond 40 wt.% LiTf, however, is not taken into calculation due to an undesired low mechanical stability. These samples were put in a constant humidity chamber at 40% RH and the temperature was varied from 303 K up to 373 K. 40% RH was chosen to replicate the humidity level condition in most electrochemical devices and the temperature was set to increase up to the most possible extreme electrolyte working temperature. The EIS data was taken via in situ process at each selected temperature. The ionic conductivity was calculated by utilising the same parameter obtained from the complex impedance plot and applying the same formula as Equation (2).

Figure 2 shows the calculated ionic conductivity of MG30 electrolytes in log conductivity vs 1000/T order. From **Figure 2**, all samples experienced increment in ionic conductivity alongside with the rise in temperature. The supplied heat energy may induce the mobile ion to move faster. The conservation of energy may take place to transform heat energy into kinetic energy in the mobile ion. Hence the ion moved faster and increased the rate of ion hopping from one site to another site, simultaneously increasing the ionic conductivity (Chandra, 2017). The same trend in the increasing ionic conductivity altogether with the rise in temperature also can be observed in MG30-6PPD electrolytes log ionic conductivity vs 1000/T graph as shown in **Figure 3**, which implied that the same coordination may occur.

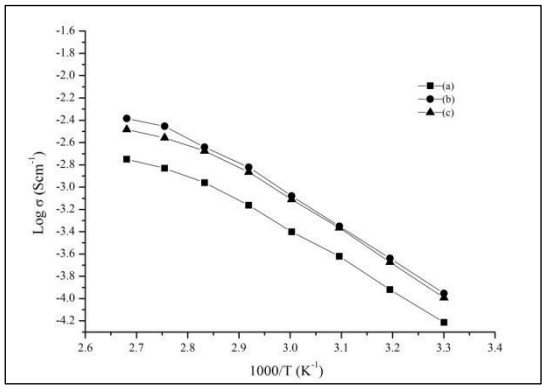

Figure 2 Arrhenius plot of MG30 polymer electrolytes at different LiTf concentration (a) 30 wt.%, (b) 35 wt.% and (c) 40 wt.%

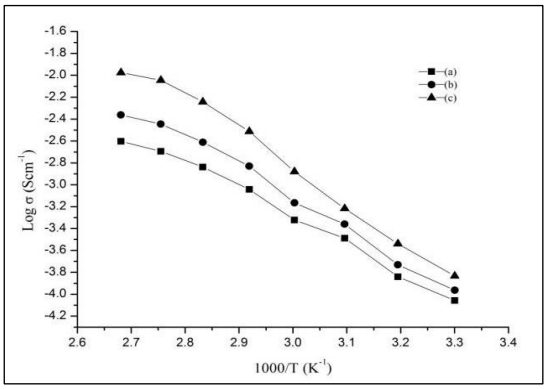

Figure 3 Arrhenius plot of MG30-6PPD polymer electrolytes at different LiTf concentration (a) 30 wt.%, (b) 35 wt.% and (c) 40 wt.

In polymer electrolytes, these thermally activated ion movement were typically described either in Arrhenius or Vogel-Tamman-Fulcher (VTF) behaviour. The plot in **Figures 2** and **3** had been formulated to follow Arrhenius temperature dependence expression.

The linear regression values, R^2 of each plotted graph in both figures were found at around 0.97 to 0.98 respectively, which were not too close to unity. Thus, the ion transport mechanism in both MG30-LiTf and MG30-6PPD-LiTf polymer electrolytes cannot be treated as a hopping mechanism. Meanwhile, **Figures 4** and **5** show the ionic conductivity plot in VTF expressions of MG30-LiTf and MG30-6PPD-LiTf respectively.

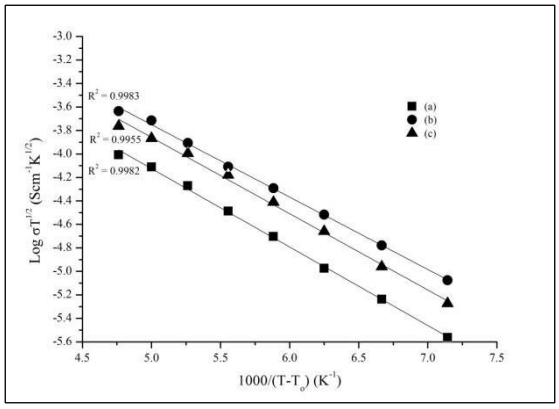

Figure 4 VTF plot of MG30 polymer electrolytes at different LiTf concentration (a) 30 wt.%, (b) 35 wt.% and (c) 40 wt.%

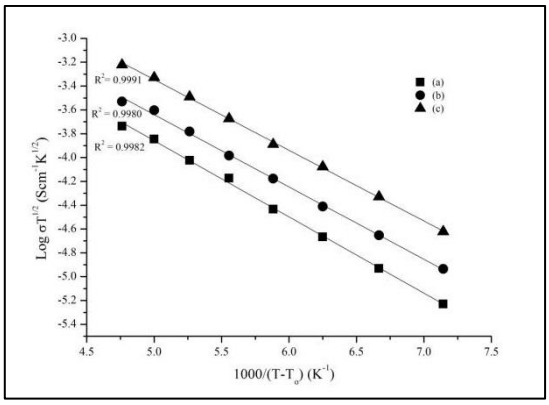

Figure 5 VTF plot of MG30-6PPD polymer electrolytes at different LiTf concentration (a) 30 wt.%, (b) 35 wt.% and (c) 40 wt.%

All plotted graph in both figures show the fitted R^2 at around 0.99 which indicates that the ion transport of both electrolytes systems obeyed the VTF expressions in all tested temperature ranges. Generally, the ion transport mechanism in VTF behaviour is mainly contributed by the movement of the dynamic segmental motion, or also known as the free volume law. According to the law, as the temperature is increased, the hike found in ionic conductivity is preferably caused by the intensification of the free volume space creation rate, which induced the ion to migrate faster (Mohammad et al., 2010). This behaviour may also be contributed in MG30 low T_g at around -64ºC.

At an elevated temperature, the rigid glassy state of MG30 structure transformed into a rubbery-like phase which offered more freedom in the polymer segmental motion. The fast wriggly polymer segmental motion at an elevated temperature may create continuous free space to allow ions to migrate faster. The pseudo-activation energy, E_a of these samples were calculated by fitting the conductivity with the empirical expression based on the free volume concept, which is related to VTF expression (Bohnke et al., 1993). **Table 1** shows the E_a of selected MG30 and MG30-6PPD based electrolytes. In an ascending order, the E_a could be listed as C40 < C35 < B35 < C30 < B40 < B30.

Table 1 The Ea value of highest MG30 and MG30-6PPD electrolytes systems

Polymer host	Notation	LiTf wt.%	Regression value, R^2	DC activation energy, E_a (eV)
MG30	B30	30	0.9983	0.1326
	B35	35	0.9955	0.1226
	B40	40	0.9982	0.1289
MG30-6PPD	C30	30	0.9991	0.1270
	C35	35	0.9980	0.1205
	C40	40	0.9982	0.1177

This order also matched with the respective ionic conductivity, establishing that the charge particle movement of highest ionic conductivity sample required the lowest amount of energy to move to an adjacent electrode.

Heat Treatment Conductivity Studies of MG30 and MG30-6PPD Polymer Electrolytes Systems

Polymers, especially amorphous polymer electrolytes undergo physical aging where the structure of the polymer changes with time, leading to significant effects on mechanical, molecular structure and electrical properties. This physical aging can be accelerated via heat treatment process under controlled conditions. Altogether with conductivities studies, the effect of physical aging onto highest ionic conductivity of each electrolyte group were taken to be tested.

Figures 6 and **7** show the heat treatment ionic conductivity of MG30 and MG30-6PPD electrolytes at 35 and 40 wt. % LiTf respectively. In both figures, it was clearly observed that all tested electrolytes ionic conductivity decreased over time. Therefore, physical aging may be suggested to have affected the electrolytes performance and occurred at a different rate.

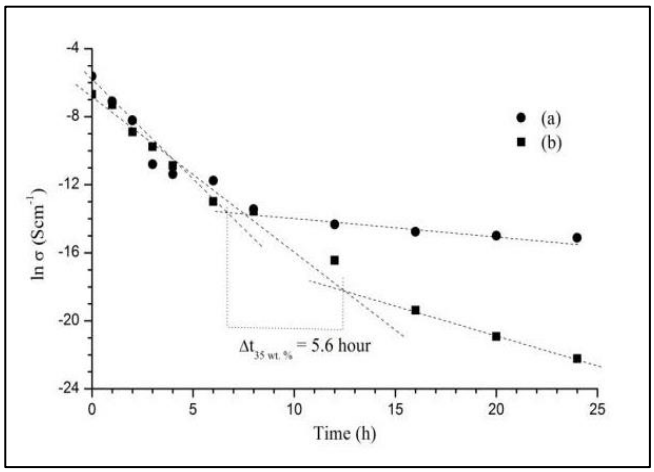

Figure 6 Time dependence ionic conductivity of electrolyes with 35 wt. % LiTf of (a) MG30 and (b) MG30-6PPD at 100 100°C heat treatment

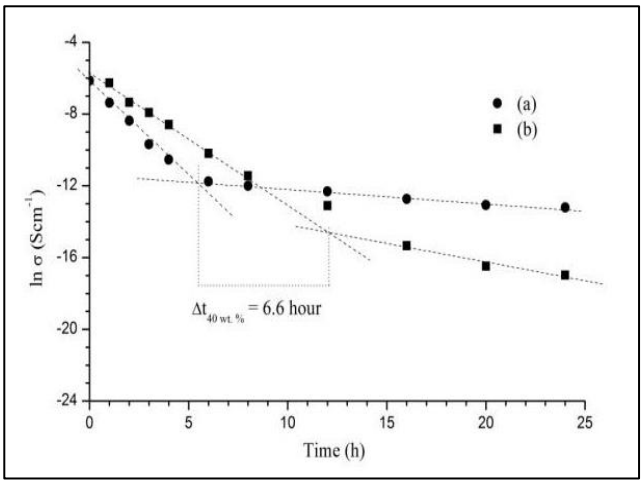

Figure 7 Time dependence ionic conductivity electrolyes with 40 wt. % LiTf of (a) MG30 and (b) MG30-6PPD at 100°C heat treatment

Two distinct trends of decreasing conductivity were observed on all samples, which are a steeper gradient at the early heat treatment and a gradual decline towards the longer heating time. The steeper gradient on the left implied that the electrolytes were experiencing a continuous degradation process. During this stage, as these amorphous electrolytes had transformed into the equilibrium state from nonequilibrium state, the relative displacement of structural elements and rearrangement of the molecular structure had rapidly occurred. Consequently, parts of the electrolytes lost their amorphous properties while increasing the degree of structural packing instead. Hence, the continuous free volume flow of ion became limited, and the ionic conductivity of the electrolytes decreased (Kumar et al., 2003).

The gradual declining slopes towards the longer heating time indicated that the electrolytes were reaching the equilibrium state. The conductivity at an equilibrium state may had run out of free volume model where the amorphous state of the electrolytes is almost wiped out due to the physical aging. The inclined point between the steep and the gradual line is known as relaxation time, T_o. T_o which signalled the internal stress of nonequilibrium state was being released and represented the beginning of initial phase of equilibrium state. The T_o can be a parameter to determine how strong or how long the electrolytes could stand against physical aging. The T_o obtained from the experimental data (T_{oE}) and theoretical approach (T_{oT}) using Equation (2) was tabulated in **Table 2**. The T_o obtained from MG30-6PPD electrolytes samples were higher than MG30 electrolytes which implied that the MG30-6PPD electrolytes were more resistant to physical aging due to the introduction of 6PPD. The difference between MG30 and MG30-6PPD electrolytes T_{oE}, Δt_{oE} revealed that the electrolytes with 6PPD (MG30-6PPD) were more resistant to physical aging by 5.6 to 6.6 hour for 35 and 40 wt. % respectively.

Table 2 Δt and relaxation time of MG30 and MG30-6PPD electrolytes

LiTf (wt. %)	Polymer host	V_o	T_{oT}	Δt_T	T_{oE}	Δt_E
35	MG30	0.9470	1.0560	0.2367	6.8	5.6
	MG30-6PPD	0.7706	1.2927		12.4	
40	MG30	0.9333	1.0715	0.5352	5.5	6.6
	MG30-6PPD	0.6224	1.6067		12.1	

The Δt_{oT} on the other hand, was read at 0.2367-hour for 35 wt. % LiTf and 0.5352-hour margin for 40 wt. % LiTf, proving that with MG30-6PPD electrolytes, it is more retard to experience physical aging. Even though both approaches showed that the electrolytes with 6PPD were superior in term of physical aging retardant, the experimental results exceeded the theoretical expectations with a significant value. The reason in T_{oE} delay may be due to the memory effect that took place during the physical aging build up process where the samples were left to cool down at room temperature several times and confronted mechanical deformation during the data taking process (Choi et al., 2012). However, the experimental data met the postulated theory where there was only one relaxation site at the early stage of physical aging to yield a straight-line form in ln $\sigma(t)$ vs. t where the T_{oT} can be calculated.

Conclusion

The investigation of the MG30-LiTf and MG30-6PPD-LiTf polymer electrolyte systems via heat treatment and conductivity experiments provided valuable insights into their thermal stability and behaviour in terms of ionic conductivity. The electrolytes underwent physical ageing, which was expedited by heat, leading to a discernible decrease in ionic conductivity as

time progressed. MG30-6PPD-LiTf electrolytes are found to be more resistant to physical ageing compared to MG30-LiTf electrolytes due to the 6PPD antioxidant protection mechanism. Temperature-dependent investigations revealed that the ionic conductivity exhibited an increase as the temperature rose, in accordance with the VTF behaviour. The findings highlighted the capability of MG30-6PPD-LiTf electrolytes to be functional in applications which needed increased thermal stability and extended operating lifespan. These results have enhanced our comprehension of the thermal and mechanical characteristics of polymer electrolytes, while also providing guidance for the development of electrochemical devices that are more efficient and long-lasting.

Ethics Statement

The research does not require research ethics approval

Authors Contribution

Ahmad Fairoz bin Aziz: Investigation, Methodology, Visualization, Data curation, Writing – original draft. Fadhlul Wafi bin Badruddin: Conceptualization, Writing – review & editing. Nur Hafiz Hussin: Conceptualization, Writing – review & editing Ab Malik Marwan Ali: Conceptualization, Methodology, Validation, Funding acquisition, Project administration.

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Conflict of interests

The authors agree that this research was conducted in the absence of any self-benefits, commercial or financial conflicts and declare the absence of conflicting interests with the funders.

References

Azaki, N. J., Ahmad, A., Hassan, N. H., Amirul, M., Mohd, A., Sukor, M., Ataollahi, N., & Lee, T. K. (2023). *Poly(methyl methacrylate) Grafted Natural Rubber Binder for Anodes in Lithium-Ion Battery Applications*. https://doi.org/10.1021/acsapm.3c00532

Aziz, A. F., Badruddin, F. W., Yahya, M. Z. A., & Ali, A. M. M. (2023). Study On 30% Methyl Grafted Natural Rubber Polymer Electrolytes Thermal Aging Via Ftir Study. *4th International Conference on Engineering and Computing Technologies (ICECT IV)*, *Icect Iv*, 36–40.

Aziz, A. F., Nazir, K., Ayub, S. F., Adam, N. I., Yahya, M. Z. A., & Ali, A. M. M. (2017). Effect of Phenylene Diamine Antioxidant on Physico-Chemical Properties of Methyl Grafted Natural Rubber Polymer Electrolytes. *Applied Mechanics and Materials*, *864*, 48–53. https://doi.org/10.4028/www.scientific.net/amm.864.48

Aziz, A. F., Nazir, K., Ayub, S. F., Adam, N. I., Yahya, M. Z. A., & Ali, A. M. M. (2018).

Electrochemical properties of polymer electrolytes treated with 6PPD on 30% poly(Methyl methacrylate) grafted natural rubber. *Malaysian Journal of Analytical Sciences*, *22*(3), 491–498. https://doi.org/10.17576/mjas-2018-2203-17

Bohnke, O., Frand, G., Rezrazi, M., Rousselot, C., & Truche, C. (1993). Fast ion transport in new lithium electrolytes gelled with PMMA. 1. Influence of polymer concentration. *Solid State Ionics*, *66*(1–2), 97–104. https://doi.org/10.1016/0167-2738(93)90032-X

Chandra, A. (2017). Temperature dependent ionic conductivity and cell performance studies of hot-pressed nanocomposite polymer electrolytes. *Composites Communications*, *4*(November 2016), 33–36. https://doi.org/10.1016/j.coco.2017.04.001

Choi, J., Ortega, A. M., Xiao, R., Yakacki, C. M., & Nguyen, T. D. (2012). Effect of physical aging on the shape-memory behavior of amorphous networks. *Polymer*, *53*(12), 2453–2464. https://doi.org/10.1016/j.polymer.2012.03.066

Jaafar, M. I., Firza, N., & Raghali, S. (2023). *Effect of Graphene Oxide on Poly (Methyl Methacrylate) -Grafted Natural Rubber Polymer Electrolytes*. *20*, 45–54.

Kamarulazam, F., Manogran, P., Goh, Z. L., Gerard, O., Said, Z., Zabidi, A. S., Bashir, S., Zulkarnain, M., Subramaniam, R., & Kasi, R. (2023). Exploring the Potential of Natural Rubber as Electrolytes and Electrodes for Advanced Energy Storage Applications. *Energy Technology*, *11*(11), 2300655. https://doi.org/https://doi.org/10.1002/ente.202300655

Kumar, B., Koka, S., Rodrigues, S. J., & Nookala, M. (2003). Physical aging effects on conductivity in polymer electrolytes. *Solid State Ionics*, *156*(1–2), 163–170. https://doi.org/10.1016/S0167-2738(02)00610-0

Li, S. D., Wang, C., Xu, K., & Peng, Z. (2003). Thermooxidative degradation methyl methacrylate-graft-natural rubber. *Journal of Applied Polymer Science*, *90*(5), 1227–1232. https://doi.org/10.1002/app.12669

Mamat, S., Haji, H., Sopian, K., Tian, L., Ahmad, A., & Matsumi, N. (2020). *Conductivity and Dielectric Behavior Studies on Solid Polymer Electrolyte Based Poly (methyl methacrylate) (PMMA) Grafted Natural Rubber (MG49) Polymer Blends*. *32*(4), 599–606.

Mohammad, S. F., Idris, R., & Mohamed, N. S. (2010). Conductivity studies of ENR based proton conducting polymer electrolytes. *Advanced Materials Research*, *129–131*, 561–565. https://doi.org/10.4028/www.scientific.net/AMR.129-131.561

Nazir, K., Ismail, S. N. S., Zailani, N. A. M., Yahya, M. Z. A., & Ali, A. M. M. (2021). Effect of ethylene carbonate (EC) plasticizer on epoxidized 30% poly(methyl methacrylate)-grafted natural based polymer electrolytes for lithium batteries. *AIP Conference Proceedings*, *2332*. https://doi.org/10.1063/5.0043681

Perera, K. S., Vidanapathirana, K. P., Adams, L. J., Hawes, C. S., & Balakrishnan, N. (2024). Symmetric double-layer capacitor with natural rubber and sodium salt-based solid polymer electrolyte and reduced graphene oxide electrodes. *Journal of Energy Storage*, *97*(PA), 112683. https://doi.org/10.1016/j.est.2024.112683

Polovková, J., Kortišová, I., Gatial, A., & Breza, M. (2006). On the dehydrogenation of N,N′-substituted p-phenylenediamine antioxidants. I. N-Phenyl-N′-isopropyl-p-phenylenediamine (IPPD). *Polymer Degradation and Stability*, *91*(8), 1775–1780. https://doi.org/10.1016/j.polymdegradstab.2005.11.016

Rajapaksha, H. G. N., Perera, K. S., & Vidanapathirana, K. P. (2021). A novel redox capacitor with a natural rubber-based solid polymer electrolyte for energy applications. *Ionics*, *27*(5), 2231–2239. https://doi.org/10.1007/s11581-021-03970-w

Rajapaksha, H. G. N., Perera, K. S., Vidanapathirana, K. P., Sandaruwani, P. M., & Siriwardana, S. (2023). Preparation of methyl grafted natural rubber and its application in super capacitor electrolytes. *Journal of Rubber Research*, *26*(5), 415–424.

Rajapaksha, N., Perera, K. S., & Vidanapathirana, K. P. (2022). *Analysis of electrochemical double-layer capacitors using a Natural Rubber-Zn based polymer electrolyte*. *8*(1), 41–57.

Ravikumar, B., Mynam, M., & Rai, B. (2018). Effect of Salt Concentration on Properties of Lithium Ion Battery Electrolytes: A Molecular Dynamics Study. *Journal of Physical Chemistry C*, *122*(15), 8173–8181. https://doi.org/10.1021/acs.jpcc.8b02072

Roy, A., Dutta, B., & Bhattacharya, S. (2017). Ion dynamics in NaBF4 salt-complexed PVC–PEO blend polymer electrolytes: correlation between average ion hopping length and network structure. *Ionics*, *23*(12), 3389–3399. https://doi.org/10.1007/s11581-017-2154-2

Shi, Y., Yang, N., Niu, J., Yang, S., & Wang, F. (2022). A Highly Durable Rubber-Derived Lithium-Conducting Elastomer for Lithium Metal Batteries. *Advanced Science*, *9*(16), 1–8. https://doi.org/10.1002/advs.202200553

Wang, M., Wang, R., Chen, X., Kong, Y., Huang, Y., Lv, Y., & Li, G. (2022). Effect of non-rubber components on the crosslinking structure and thermo-oxidative degradation of natural rubber. *Polymer Degradation and Stability*, *196*, 109845. https://doi.org/10.1016/j.polymdegradstab.2022.109845

Wang, X., Yang, K., Zong, C., & Zhang, P. (2021). The evolution of microstructure of Styrene-Isoprene-Butadiene Rubber during the thermal-oxidative aging process using In-situ FTIR way. *Polymer Degradation and Stability*, *188*, 109573. https://doi.org/10.1016/j.polymdegradstab.2021.109573

Whba, R. A. G., Tiankhoon, L., Su, M. S., Rahman, M. Y. A., & Ahmad, A. (2020). Influence of binary lithium salts on 49 % poly (methyl methacrylate) grafted natural rubber based solid polymer electrolytes. *Arabian Journal of Chemistry*, *13*(1), 3351–3361. https://doi.org/10.1016/j.arabjc.2018.11.009

Whba, R., Su'ait, M. S., Sahinbay, S., Whba, F., & Ahmad, A. (2024). Natural rubber-based polymer electrolytes for electrochemical devices: Modification, challenges, advances, and perspectives. *Journal of Energy Storage*, *83*(February), 110593. https://doi.org/10.1016/j.est.2024.110593