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Structural and Ionic Conductivity Studies of Solid Polymer Electrolyte Based on Poly(methyl methacrylate)-Grafted Natural Rubber Integrated with Ammonium Nitrate

Hamidah Shabri[1], Muhammad Asyraf Al-Wafiy Lauthfi[1], Muhammad Izzat Jaafar[1], Nabilah Akemal Muhd Zailani[1], Sharifah Nafisah Syed Ismail[1], Ab Malik Marwan Ali[2] and Khuzaimah Nazir[1]*
[1]Faculty of Applied Sciences, Universiti Teknologi MARA, Cawangan Perlis, Kampus Arau,
02600 Arau, Perlis
[2]Faculty of Applied Sciences, Universiti Teknologi MARA, Shah Alam, 40450 Shah Alam,
Selangor, Malaysia
*Corresponding author (e-mail: khuzaimahnazir@uitm.edu.my)

Given the mounting popularity of energy storage demands, there is an escalating focus on investigating polymer electrolytes (PEs) based on natural rubber (NR) due to their eco-friendly nature and low-cost production. The 30% poly(methyl methacrylate) (PMMA) grafted onto natural rubber (NR), also known as (MG30) is an excellent alternative of polymer host with prominent properties such as flexibility that allow fantastic electrode-electrolyte contact, but the modified natural polymer possess low ionic conductivity. Therefore, introducing dopant salt forming a polymer host-salt system is one of the ways to tackle this challenge. This study centered around solid polymer electrolytes (SPEs) of MG30, produced via solution casting method while doping different concentrations of NH_4NO_3 (5, 10, 15, 20, 25, 30, 35, and 40 wt.%). Attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) spectra changes in peak intensity, wavenumber shifting, emergence of new peak, justifying the polymer host-inorganic salt interaction. AC impedance spectroscopy is utilized to heighten the conductivity of the MG30-NH_4NO_3 samples, in which the incorporation of NH_4NO_3 into the polymer matrix enhanced the ionic conductivity up 6.36×10^{-6} S cm^{-1} at room temperature for the sample composition MG30(70):NH_4NO_3(30).

Keywords: 30% PMMA-g-NR; NH_4NO_3; EIS; ATR-FTIR

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The increasing demand for sophisticated portable electronic devices nowadays has driven extensive research in energy storage technology such as rechargeable batteries and supercapacitors [1]. One of the key components in developing these devices is the electrolytes, where it is crucial for ionic conduction [2]. Commercial devices commonly implement liquid-state electrolytes due to their notable low-temperature performance. Despite the advantages, liquid-state electrolytes possess major drawbacks concerning safety features, electrochemical instability, and leakage [3]. Thus, solid-state electrolytes with thermal stability properties and offer good safety features have been proposed to address the limitation encountered by the liquid-state electrolytes [3].

The implementation of polymer in developing solid-state electrolytes was discovered in the 1970s, where Fenton and coworkers incorporated alkali metal salts into synthetic polymer, namely poly(ethylene oxide) (PEO) and achieved conductivity up to 10^{-5} S cm^{-1} [4]. To produce good polymer electrolytes, the selection of polymer is crucial to obtain good film flexibility and its role as a host allowing for ion migration [5–7]. Other unique properties possessed by polymers include good elasticity, good insulator, corrosion resistance, and cheaper [8]. Though, the sustainable development goals have led to the substitution of synthetic polymers to natural polymers [9].

Among varieties of natural polymers, natural rubber, produced by rubber tree or scientifically known as Hevea Brasiliense, is an inexhaustible resource in nature. The production of natural rubber from Malaysia in 2020 is approximately 0.5 million tons or 2% from the total production of natural rubber globally [10]. **Figure 1(a)** represents the structure of poly(cis-1,4-isoprene) from natural rubber that exhibits superior mechanical properties including high tensile strength and high flexibility. Moreover, it is abundant in nature and the production cost of the natural rubber is low [11]. Despite its uniqueness, natural rubber is not suitable to be adopted as a polymer host for solid polymer electrolytes due to its non-polar characteristics that are vital for ionic conduction. Hence, modification by grafting polymers

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that possess polar groups onto natural rubber was done. It is essential to highlight that commercially available modified natural rubbers encompass 30% poly(methyl methacrylate)-grafted natural rubber (PMMA-g-NR), commonly referred to as MG30. The MMA monomers of the MG30 provides coordinating sites for ions from doping salt due to the existence of oxygen atoms from carbonyl (C=O) and ether (C-O-C) groups, as shown in **Figure 1 (b)**, resulting in the formation of polymer-salt complexes [12, 13]. To add on that, MG30 has another attractive characteristic to be used as polymer host, which is good elasticity. This characteristic can help in forming a free-standing and flexible thin film that has good contact with the electrode [12].

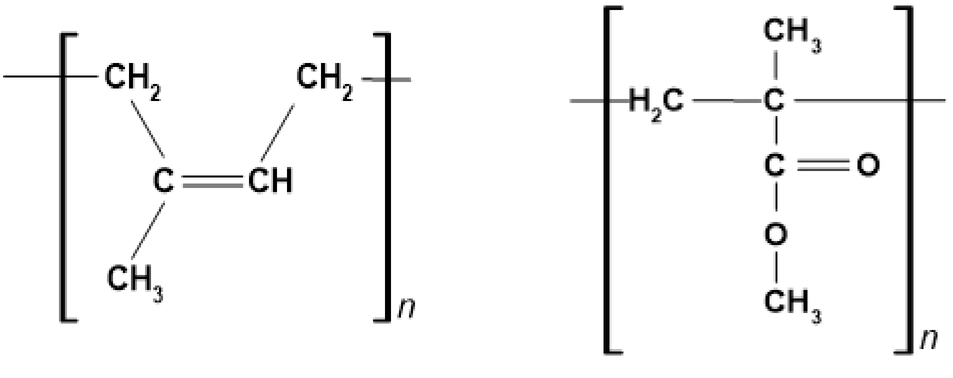
The selection of both polymer host and salt is vital as complexation from both elements will determine the result such as ionic conductivity that is a significant factor to develop the polymer electrolyte into energy storage applications. Numerous researches have utilized lithium doping onto grafted-NR polymer electrolyte [18]. However, the development of long-term sustainable energy storage technology needs alternatives other than lithium salt as the dopant salt. On the other hand, ammonium is a more abundant resource compared to lithium, thus it is generally less expensive than lithium [19]. Furthermore, it is more environmentally friendly than lithium [20]. Previous study by Moniha and co-workers [21] in 2018 has reported that 1.0 g of I-carrageenan doped with 0.4 wt.% of NH_4NO_3 possess a maximum conductivity up to 1.46×10^{-3} S cm^{-1}. Highest conductivity values of 2.66×10^{-3} S cm^{-1} for 1.0 g of natural tree gum with 0.5 wt.% of NH_4NO_3 [22], 10.5×10^{-6} S cm^{-1} for NaAlg/polyvinyl alcohol (PVA) with 15 wt.% of NH_4NO_3 [23], 2.48×10^{-6} S cm^{-1} for PEO/graphene oxide (GO) with 35 wt.% of ammonium triflate ($NH_4CF_3SO_3$) [1], and 2.05×10^{-5} S cm^{-1} for MG30/ GO with 15 wt.% of $NH_4CF_3SO_3$ reported confirms that the incorporation of doping salt into polymer system contributes to increasing conductivity of the polymer electrolytes.

Despite many studies done on natural polymers incorporated with ammonium salt-based polymer electrolytes, there is no information available for the MG30-NH_4NO_3 based solid polymer electrolytes system. Thus, this study will be focusing on the ionic conductivity and structural properties of MG30-NH_4NO_3 solid polymer electrolytes by using electrical impedance spectroscopy (EIS) and attenuated total reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) analysis.

EXPERIMENTAL

Chemicals and Materials

In this study, the materials used are MG30 as the polymer host, obtained from Green HPSP (M) Sdn. Bhd., ammonium nitrate (NH_4NO_3) as the dopant salt, and tetrahydrofuran (THF) as the solvent. Both NH_4NO_3 and THF were purchased from A.R. Alatan Sains (K) Sdn. Bhd.



(a) (b)

Figure 1. Chemical structure of (a) cis-1,4 polyisoprene and (b) PMMA structure [14–17].

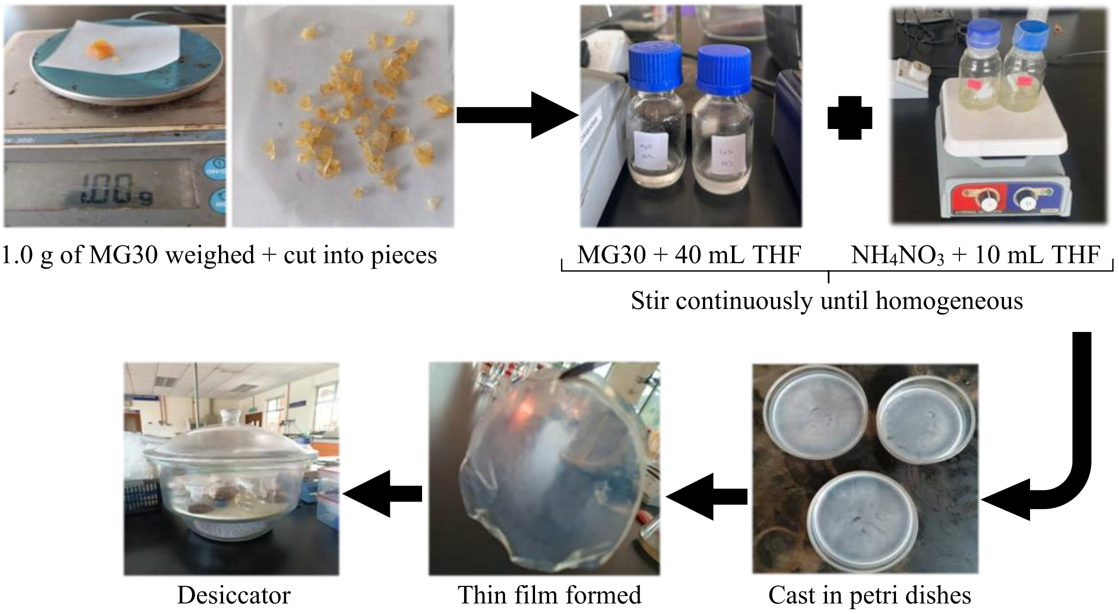


Figure 2. Preparation of polymer films incorporated with NH_4NO_3.

Solid Polymer Electrolytes Preparation

Polymer electrolytes films were prepared by solution casting method, as illustrated in **Figure 2.**

1.0 g of MG30 was weighed and cut into small cubes before being stirred continuously in 40 mL of THF at room temperature until homogeneous. Different compositions of NH_4NO_3 (5, 10, 15, 20, 25, 30, 35, and 40 wt.%) were stirred separately in 10 mL of THF for 24 hours to ensure complete dissolution of salt. Next, the salt solutions were added into homogeneous MG30 and stirred for another 24 hours. Then, they were poured into petri dishes and left to evaporate in the fume hoods at room temperature for 24 hours to form solvent-free films. The solvent-free films obtained were peeled and stored in a desiccator for further characterization. **Table 1** presents the composition of solid polymer electrolytes based on MG30 and NH_4NO_3.

Characterization Techniques

ATR-FTIR analysis was used to verify the polymer host-inorganic salt interaction. The Perkin Elmer ATR-FTIR spectrometer was used to discover the functional groups presence from samples by ranging wavenumber from 600 cm^{-1} to 4000 cm^{-1} with scanning resolution of 2 cm^{-1}. The ionic conductivity of the samples was measured by using HIOKI 3532-50 LCR HiTESTER. All samples were cut into 1.50 cm diameter and their thickness were measured by using a micrometre screw gauge. They were then placed into position between stainless steel electrodes and the data collected within frequency between 50 Hz to 1 MHz at room temperature.

Table 1. MG30:NH_4NO_3 composition of the solid polymer electrolytes.

Sample	Composition ratio (MG30:NH_4NO_3) (wt.%)
Pure MG30	100:0
A1	95:5
A2	90:10
A3	85:15
A4	80:20
A5	75:25
A6	70:30
A7	65:35
A8	60:40

Table 2. Vibration mode of NH_4NO_3.

Wavenumber (cm^{-1})	Assignment	References
3200 – 3500	Asymmetric stretching of N-H	[25,30]
1448	Asymmetric stretching of N-O and bending of N-H	[25]
1372	Asymmetric stretching of N-O	[25]
1042	Symmetric stretching of N-O	[25]
829	Bending of N-O	[25]

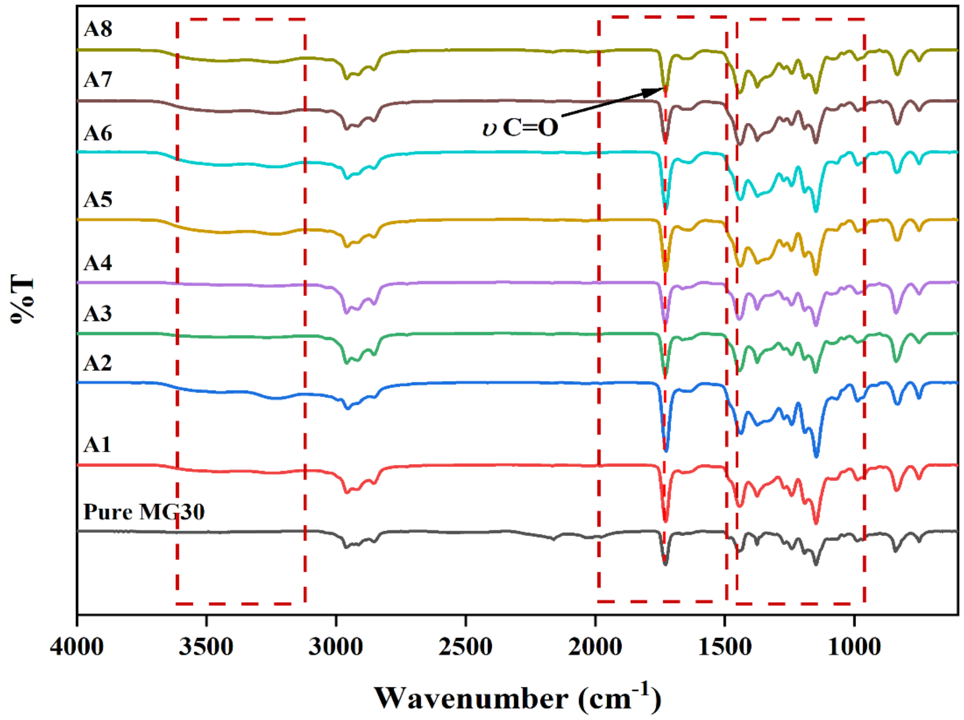


Figure 3. ATR-FTIR spectra for solid polymer electrolytes films.

RESULTS AND DISCUSSION

Structural Studies

ATR-FTIR analysis has been conducted to study the complexation between MG30 with different compositions of ammonium salt. The characteristic peaks of NH_4NO_3 (N-H andN-O) were tabulated in **Table 2** [17].

Figure 3 shows ATR-FTIR spectra of pure MG30 and MG30 doped with different compositions of NH_4NO_3 salts.

The main region of interest appeared at wavenumber 1730 to 1750 cm^{-1} and wavenumber 1000 to 1300 cm^{-1}. The existence of oxygen atoms that act as the electron donor to coordinate with ionic dopant salt in these regions originated from carbonyl (C=O) group and ether (C-O-C) group [17]. Analysis of these spectra through examination of peaks shifting, peak intensity, and absence or appearance of new peaks led to deeper understanding of polymer-salt interaction, delivering key insights of conductivity enhancement of the polymer electrolytes. New peaks appeared at 3200 to 3400 cm^{-1} which, assigned to asymmetric N-H stretching, become broaden with the addition of NH_4NO_3 confirmed the existence of ammonium salt in the polymer-salt system [22]. Sharp peak at 1729 cm^{-1} representing C=O stretching was observed to increase in intensity and shifted around 2 to 3 cm^{-1} affirms the formation of $NH_4^+ \leftarrow O=C$ complexes [24,25]. Peaks at 1447 cm^{-1} representing O-CH_3 asymmetric deformation shifted around 4 to 8 cm^{-1} confirms the interactions between ammonium ions of the dopant salt and oxygen atoms in the MMA structure from the polymer host. Peaks between 1270 to 1350 cm^{-1} downshifted around 4 cm^{-1} from its origin indicates the interaction has occurred at vibration mode of the ether (C-O-C) group [17, 26, 27].

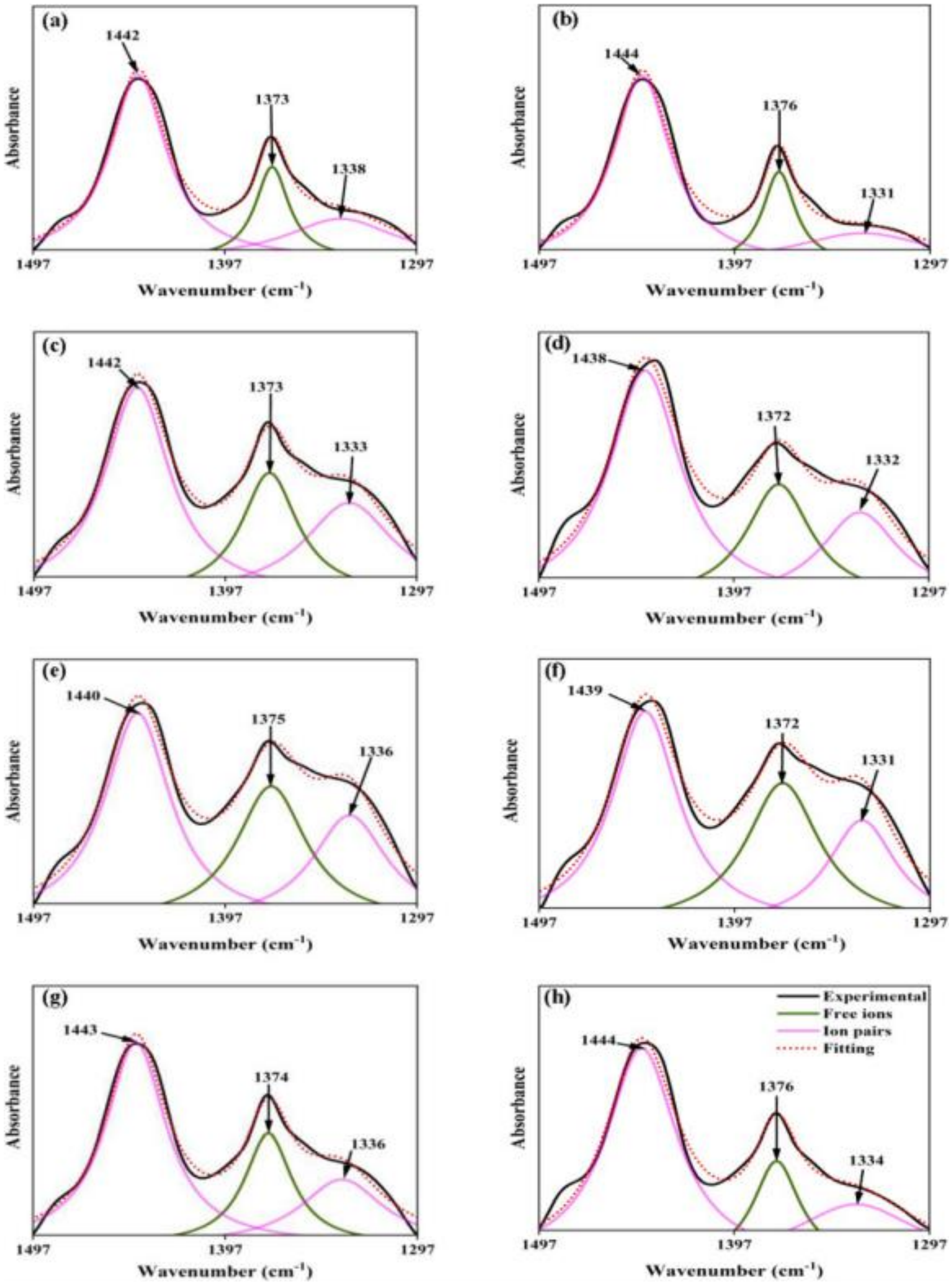


Figure 4. FTIR deconvolution of (a) A1, (b) A2, (c) A3, (d) A4, (e) A5, (f) A6, (g) A7, and (h) A8.

Deconvolution of ATR-FTIR spectra has been performed for specific regions of overlapped spectra by using OriginPro software (Gaussian-Lorentz function) [28]. The peaks in the chosen region between 1297 to 1450 cm^{-1} correspond to N-O and N-H stretching vibration from NH_4NO_3 salt and C-O-C vibration from the polymer host. The alteration in peak wavenumber suggests the complexes between MG30 and NH_4NO_3 [25]. Information on the ion dissociation and ion aggregation has been investigated by analyzing the deconvolution of ATR-FTIR spectra. **Figure 4** shows that free ions peak at 1372 cm^{-1} meanwhile the ion pairs peak at 1331 and 1439 cm^{-1}. The free ions represent the dissociated ions from the ammonium salt meanwhile ion pairs represent the aggregated ions from the polymer-salt system. The percentage of free ions can be calculated by using Equation (1) [28]:

$$Free\ ions\ \% = \frac{Area\ of\ free\ ions\ peak}{Total\ area\ of\ free\ ions\ peak\ and\ ion\ pairs} \quad (1)$$

Figure 5 depicts the percentage of free ions increased when doped with NH_4NO_3 up to 30 wt.%. The ionic conductivity of the solid polymer electrolytes is enhanced by the rise of ion dissociation from NH_4^+. However, the addition of NH_4NO_3 at higher salt concentration (35 and 40 wt.%) has lowered the ionic conductivity to 1 magnitude order due to the increase in the formation of ion aggregation [28, 29].

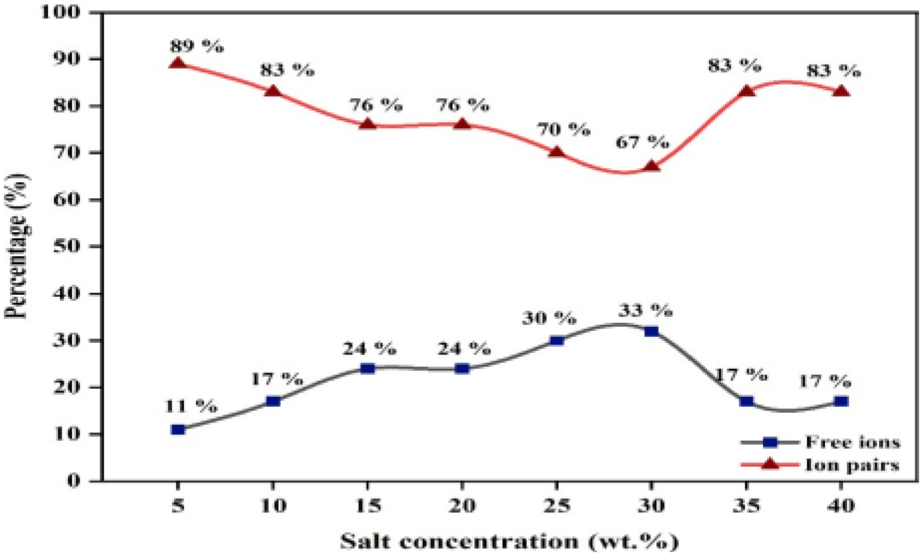


Figure 5. Percentage of free ions and ion pairs for different salt's composition.

Table 3. Conductivity of the films at room temperature.

Sample	σ (Scm^{-1})
Pure MG30	7.51×10^{-9}
A1	1.70×10^{-8}
A2	8.10×10^{-8}
A3	2.10×10^{-7}
A4	3.90×10^{-7}
A5	5.39×10^{-7}
A6	6.36×10^{-6}
A7	1.48×10^{-7}
A8	1.13×10^{-7}

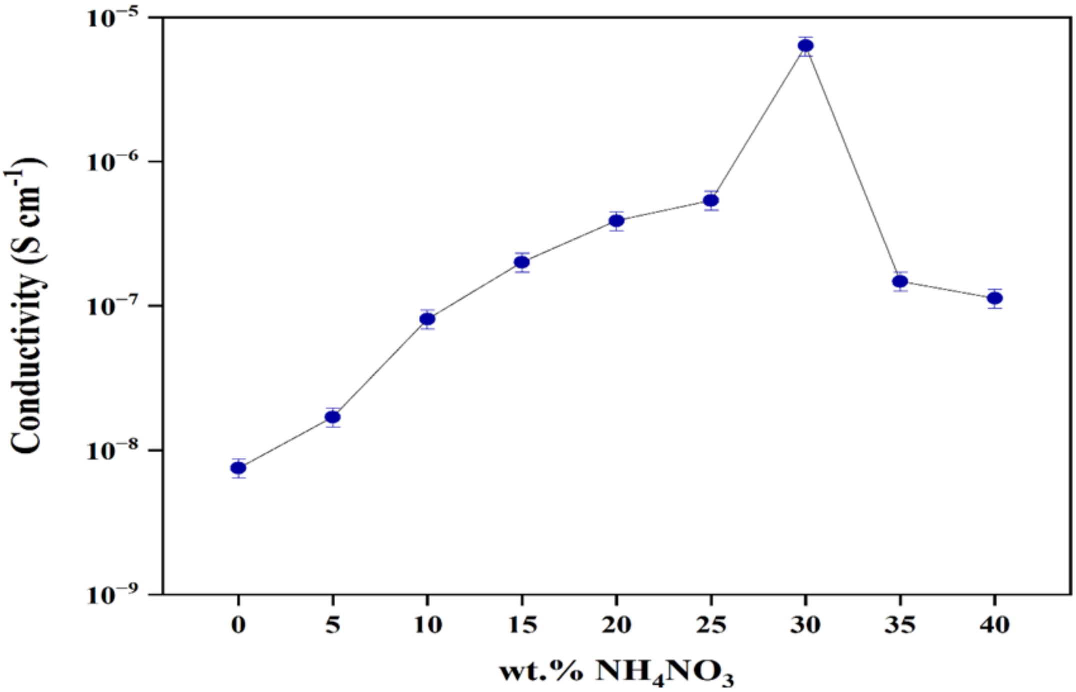


Figure 6. Conductivity of sample films at room temperature.

Ionic Conductivity Studies

The ionic conductivity can be calculated by using Equation (2) [31]:

$$\sigma = \frac{l}{AR_b} \tag{2}$$

Where l is the thickness of film, A is the contact area of film and electrode, and σ is the ionic conductivity. Bulk resistance, R_b, can be calculated from the interception of a semicircle or spike on the real axis of the impedance plot [28,32]. The conductivity of solid polymer electrolytes at room temperature as a function of increasing NH_4NO_3 compositions is shown in **Table 3** and **Figure 6**. The ionic conductivity rises from 7.51 × 10^{-9} S cm^{-1} to 1.70 × 10^{-8} S cm^{-1} upon the addition of 5 wt.% of NH_4NO_3. The ionic conductivity value further increased up to 6.36 × 10^{-6} S cm^{-1} with the addition of 30 wt.% of NH_4NO_3. The enhancement of the ionic conductivity is contributed by the increasing number of ion dissociation in the polymer-salt system as discussed in the structural studies section. The incorporation of dopant salt, NH_4NO_3, into the polymer matrix has introduced numbers of free ions that interact with polar groups from the MG30, leading to ion dissociation, thus enhancing the ionic conductivity [25, 32]. Still, beyond the addition of 30 wt.% of NH_4NO_3, the ionic conductivity decreases to 1 magnitude order. The decreasing value of conductivity is attributed to the ion aggregation, which limits the mobility of the ion within the polymer-salt system [29, 33].

CONCLUSION

New solid polymer electrolytes based on 30% poly (methyl methacrylate)-grafted natural rubber (MG30) integrated with ammonium nitrate (NH_4NO_3) at different compositions have been prepared by using solution casting techniques. The interaction of the polymer host, MG30 with dopant salt, NH_4NO_3 has been explained by using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analysis. The ion dissociation and ion aggregation have been studied from the ATR-FTIR analysis, which correlated with the increasing and decreasing value of ionic conductivity. The incorporation of 30 wt.% of NH_4NO_3 into the polymer matrix has enhanced the ionic conductivity up to 6.36 × 10^{-6} S cm^{-1}. The highest ionic conductivity correlated with the highest percentage of free ions, indicating that the increasing number of dissociated ions enhanced the ion mobility within the polymer backbone, thus increasing the ionic conductivity of the polymer electrolytes. Further investigation on the surface morphology, crystallinity, thermal properties, and other electrical properties, and modification by incorporation of plasticizer or nanofiller need to be done to study its potential in the energy storage application.

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