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Thymol–Menthol Deep Eutectic Solvent as a Functional Additive for PEO-Based Solid Polymer Electrolytes

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Deep eutectic solvents (DESs) have emerged as an alternative strategy to enhance electrolyte performance when employed as additives. In the present study, a new solid-state polymer electrolyte based on polyethylene oxide (PEO) doped with thymol–menthol deep eutectic solvents (T:M DESs) was successfully prepared via solution casting technique. Prior to incorporation into the PEO matrix, the physical and spectroscopic properties of the T:M DES additives were investigated using density, surface tension analysis, and Fourier transform infrared spectroscopy (FTIR). The results revealed that the T:M 1:4 composition exhibited the density (0.91 g cm^{-3}) and surface tension (30 mN m^{-1}), due to higher menthol content which enhances intermolecular interactions, leading to a more organized molecular arrangement within the DES structure. The PEO-T:M electrolyte was analysed through FTIR, Thermogravimetric analysis (TGA), and Electrochemical Impedance Spectroscopy (EIS). FTIR analysis confirmed the successful incorporation of T:M DES into the PEO matrix through broadening and shifting of the hydroxyl (–OH) stretching band, indicating strong hydrogen bonding interactions between T:M and PEO. EIS revealed that the ionic conductivity of the PEO electrolyte increased gradually upon the incorporation of T:M DES additives. Among the various additive compositions, ratio 1:4 of T:M DES additive exhibited the highest ionic conductivity of $1.28 \times 10^{-6} \text{ Scm}^{-1}$. Overall, these findings highlight the promising role of thymol–menthol DES additives in improving the physicochemical properties and electrochemical performance of PEO-based electrolytes for potential

electrochemical application.

Keywords: Thymol-Menthol; PEO; Additive; Conductivity; SPEs

1.0 Introduction

Polymer electrolytes (PEs) have gained considerable attention for use in electronic and electrochemical devices due to their simple fabrication, low cost, flexibility, safety, and good electrochemical stability. Compared with conventional liquid electrolytes, PEs offer better mechanical stability and reduced risks of leakage, evaporation, and flammability, making them promising alternatives for safer electrochemical systems [1]. Among these, solid polymer electrolytes (SPEs) have attracted increasing attention due to their excellent safety and compatibility with solid-state electrochemical devices. However, they suffer from low ionic conductivity, brittleness and poor interfacial compatibility with electrodes which may limit their practical applications and performance [2].

Therefore, to enhance the ionic conductivity and flexibility of SPEs, numerous strategies have been explored, including physical treatment [3] and chemical addition [4]. Physical treatment incorporates different polymers and adding crosslinker into the electrolyte matrix to enhance ion transport and alter the physical structure of the polymer matrix [3]. Chemical addition methods have attracted great attentions recently which focus on adjusting the concentration and type of salts, adding plasticizers to facilitate ion movement, and including various additives to create an environment more conducive to ion transport [5,6].

In this context, deep eutectic solvents (DES) gaining attention to become a promising additive to improve the performance of polymer electrolytes in the recent years. It is widely used as alternatives to conventional organic solvents and ionic liquids (IL) in various fields such as electrochemical application. This is due to the increasing demands for eco-friendly processes within the framework of green and sustainable chemistry, and the recognition of the remarkable and advantageous properties of DES. DES show similar physicochemical properties to IL such as high density, high solubility, high conductivity, and thermal stability [7]. DESs also offers much cheaper and safer for their use as solvents because low toxicity and have been synthesize as “green”

solvents in numerous applications, including synthesis of polymers and nanomaterials. DES have shown potential as additives for polymer-based electrolytes, creating new possibilities for their use in diverse electrochemical applications.

Literally, these solvents have shown high solubility with polymers, such as polyethylene oxide (PEO), protein, and chitin, through the formation of strong hydrogen bond interactions. Several eutectic solvents such as N-methylacetamide (NMAC) and the lithium bis [(trifluoromethyl)sulfonyl]imid (LiTFSI), choline chloride (ChCl) and citric acid monohydrate (CAM), poly (1,3-dioxolane) and lithium salt, choline chloride/lactic acid were successfully used as additives in polymer-based electrolyte. In a previous study, deep eutectic solvents were integrated into PEO-based solid polymer electrolytes, where the in-situ formation of DES effectively suppressed PEO crystallinity and enhanced Li^+ mobility. The weakened coordination between ether oxygens and lithium ions facilitated greater salt dissociation, leading to a marked improvement in ionic conductivity ($2.1 \times 10^{-4} \text{ S cm}^{-1}$) and a higher lithium-ion transference number compared to conventional and ionic liquid-doped PEO electrolytes at 60°C [8]. In another study by Liang et al. [9], an in situ polymerized DES-based solid polymer electrolyte demonstrated high ionic conductivity ($\sim 1.89 \times 10^{-3} \text{ S cm}^{-1}$) and improved lithium-ion transport, alongside effective dendrite suppression, and excellent electrochemical stability.

Among the different types of DESs, hydrophobic deep eutectic solvents (hDESs) have attracted attention due to their low affinity toward water and low water miscibility, which allow them to maintain a separate phase in aqueous media. Their hydrophobic nature also provides favourable interactions with non-polar compounds, making them attractive for various applications [10]. In this context, thymol–menthol-based DES (T DES), a hydrophobic DES system, was selected as the additive in the present work. Despite numerous studies exploring the preparation of DES for electrochemical applications, however, until now, there has not been any attempt to exploit DES based on Thymol and Menthol yet as a liquid additive in PEO-polymer based system. Herein, in this work, eco-friendly solvents, thymol and menthol based deep eutectic solvents (T:M DESs) were produced for the first time in several ratios and was utilized as additive to be doped with polyethylene oxide (PEO), (PEO-T:M DESs), which served as the polymer host to improve the conductivity of resulting polymer matrix in electrolyte-based systems. The potential of the prepared DESs as green additive combined polyethylene oxide (PEO) polymers is an interesting

area of exploration as additive provides a π system and making it very attractive for a variety of electrolyte applications. Electron delocalization, intermolecular interaction and π - π stacking interactions are made possible by these synthesized additives which improve the characteristics of charge transport.

2.0 Materials and methods

2.1 Materials

Thymol with purity (> 98%), menthol (> 98%) and acetonitrile were obtained from Fluka Analytical (Germany). The polyethylene oxide (PEO) average Mv ~900, 000 (nominal) was purchased from Sigma-Aldrich (USA). All chemicals were employed without undergoing additional purification.

2.2 Instrumentation

Fourier transform infrared spectroscopy (FTIR) (Spectrum 400 Perkin Elmer, Waltham, MA, USA) was conducted at a resolution of $\pm 4\text{ cm}^{-1}$ and in the spectral range of 4000–400 cm^{-1} . This was done to investigate the functional groups of the prepared materials. Surface tension analysis was performed using a torsion balance. Measurements were taken at 298.15 K and 1 atm using a platinum ring (Du Noüy ring) with a circumference of 4 cm. A densitometer (Oscillating U-tube digital densitometer DDM 2910) was used to measure the density of the prepared DESs at 298.15 K and 1 atm. Thermogravimetric Analysis (TGA) was meticulously performed using the Perkin Elmer analyzer, spanning a temperature range of 30–600°C with a controlled flow rate of 10°C/min.

2.3 Preparation of T:M DESs

The thymol and menthol based deep eutectic solvent (T:M DESs) (Fig. 1) was synthesized using a heating approach adopted from Santana et al. [11] Briefly, thymol and menthol were heated at 60 °C with constant stirring in molar ratios of 1:1, 1:2, 1:3, 1:4, 2:1, 3:1, and 4:1 until a colorless liquid formed. This liquid was then allowed to cool to room temperature.

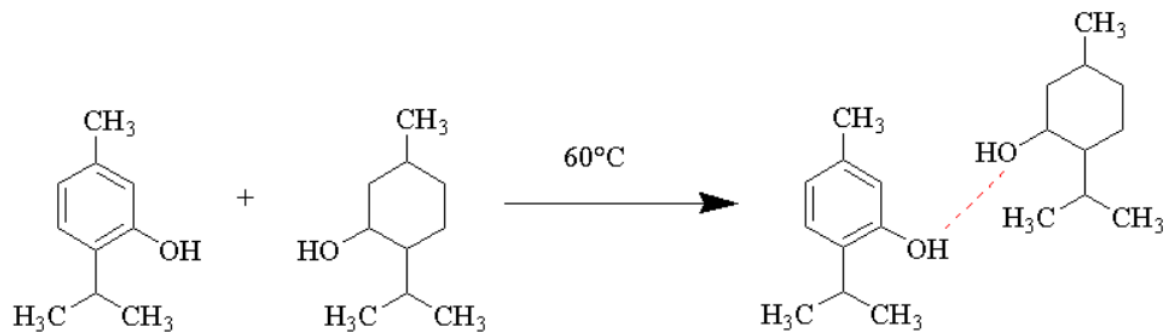


Fig. 1. The schematic preparation of T:M DESs in molar ratio 1:1 and schematically interaction of the T:M 1:1 component.

2.4 Preparation of PEO electrolyte

The preparation of PEO-T:M DESs electrolyte was adapted from [8]. Briefly, 4.0 g of polyethylene oxide (PEO) was dissolved with 85 mL of acetonitrile. The mixture was continuously stirred for 5 hours to ensure that all the PEO was completely dissolved in acetonitrile and form a homogeneous mixture. After that, the solution was cast to a petri dish and placed at room temperature overnight for drying purpose.

2.4 Preparation of PEO-T:M DESs electrolyte

The preparation of PEO-T:M DESs electrolyte as shown in Fig. 2 was adapted from [8]. Briefly, 4.0 g of polyethylene oxide (PEO) was dissolved with 85 mL of acetonitrile. The mixture was continuously stirred for 5 hours to ensure that all the PEO was completely dissolved in acetonitrile and form a homogeneous mixture. Then, the prepared PEO electrolyte with T:M DES was prepared by dropwise each of 5 mL of T:M DES at various molar ratios with PEO solution. The mixture was maintained stirring continuously for 5 hours to achieve a homogeneous solution. After that, the solution was cast to a petri dish and placed at room temperature overnight for drying purpose to form PEO-T:M DES electrolyte films. Table 1 shows the thymol–menthol ratios in PEO–T:M DES electrolytes.

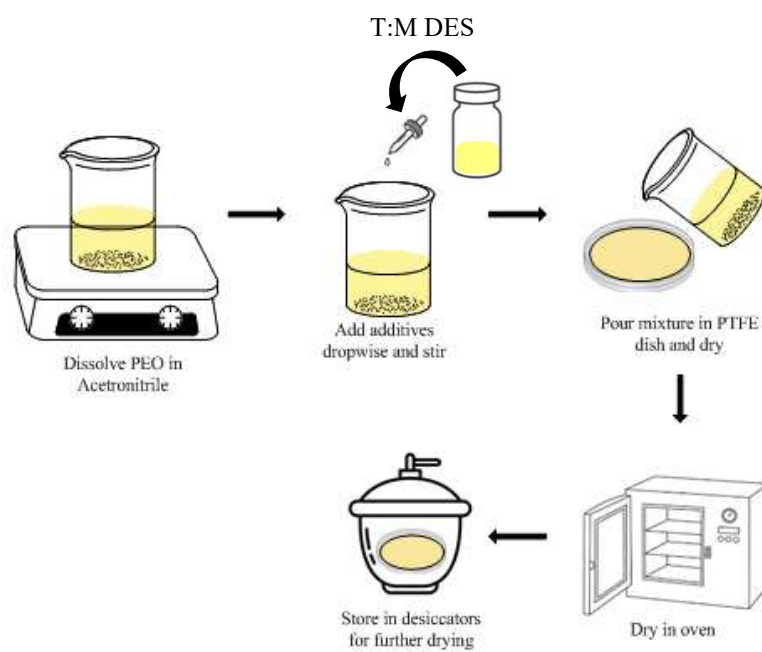


Fig. 2. The preparation process of PEO-T:M DES electrolytes.

Table 1: Thymol–menthol ratios in PEO–T:M DES electrolytes

PEO-T:M DESs electrolytes	Ratio of thymol:menthol
PEO-T:M 1:1 DES	1:1
PEO-T:M 1:2 DES	1:2
PEO-T:M 1:3 DES	1:3
PEO-T:M 1:4 DES	1:4

2.4.1 Electrochemical impedance spectroscopy (EIS)

Electrical Impedance Spectroscopy (EIS) was employed to investigate the electrical properties of the prepared solid polymer electrolytes (SPEs). The ionic conductivity of polymer electrolyte films, with and without additives, was evaluated using a HIOKI Hi-Tester (model 3570) over a frequency range of 50 Hz to 1 MHz, following a procedure similar to that reported by Rahamathullah et al. [12]. Prior to impedance measurements, the thickness of each SPE film was measured using a thickness gauge (OEM brand). The films were then sandwiched between two stainless steel blocking electrodes with a radius of 1 cm. Impedance measurements were subsequently measured at room temperature across the specified frequency range to evaluate the ionic conductivity performance of the newly prepared PEO-T:M DESs electrolyte. The ionic conductivity, σ was calculated using the relation in Eq. 1.

$$\sigma = \frac{t}{R_b A} \quad (1)$$

where, σ is the ionic conductivity, t (cm) is the thickness of the sample, R_b is bulk resistance obtained from the plotting of negative imaginary impedance ($-Z_i$) versus real part (Z_r) of impedance and A (cm²) is the surface area of electrode-electrolyte contact area of SPE.

3.0 Results and discussion

3.1 Visual observation and physical properties of T:M DESs

Thymol and menthol-based deep eutectic solvent (T:M) was prepared using T:M molar ratios of 1:1, 1:2, 1:3, and 1:4 in order to find the optimized liquid state which is stable at room temperature. Table 2 shows the average molecular weight and visual observations of the different mixtures of T:M DESs. As described in Table 2, a colorless liquid was formed for T:M with molar ratio 1:1 to 1:4 at room temperature. Density, surface tension, and FTIR analyses of these liquids were then carried out to confirm the characteristics and structure of synthesized T:M DESs. The average molecular weight of T:M was calculated according to Eq. 2.

$$M_{T:M} = X_{HBA} M_{HBA} + X_{HBD} M_{HBD} \quad (2)$$

where $M_{T:M}$ is the molecular weight of T:M in g mol⁻¹, M_{HBA} is the molecular weight of hydrogen bond acceptor (HBA) in g mol⁻¹, M_{HBD} is the molecular weight of hydrophobic bond donor (HBD) in g mol⁻¹, X_{HBA} is the ratio of HBA and X_{HBD} is the ratio of HBD.

Table 2: Average molecular weight and visual observations of the different mixtures of T:M DESs.

DES		Abbreviation of DES	Molar ratio		Molecular weight of components (g/mol)		Mole weig DE (g/r
HBD	HBA		HBD	HBA	HBD	HBA	
Thymol	Menthol	1:1	1	1	150.22	156.27	306
		1:2	1	2	150.22	312.54	462
		1:3	1	3	150.22	468.81	619
		1:4	1	4	150.22	625.08	775

The density of synthesized DESs is dependent largely on the density of their constituents. Thus, the density of the prepared DESs was determined and the results are shown in Figure 2 (A). The density of DESs decreases from 0.934 to 0.91 g cm⁻³ at 298.15 K with increasing content of menthol in the DES. This is probably due to the density of menthol (0.890 g cm⁻³) being lower than thymol (0.960 g cm⁻³) at 298.15 K. Therefore, a higher content of menthol in the DESs would contribute to a lower density of DES [13]. Moreover, the structure of the constituents also could considerably influence the density of DESs [14,15]. Thus, upon analyzing the density sequence for prepared T:M DESs, it becomes apparent that the hydrogen bond strength between T:M 1:1 is the highest, followed by T:M 1:2, T:M 1:3, and finally T:M 1:4.

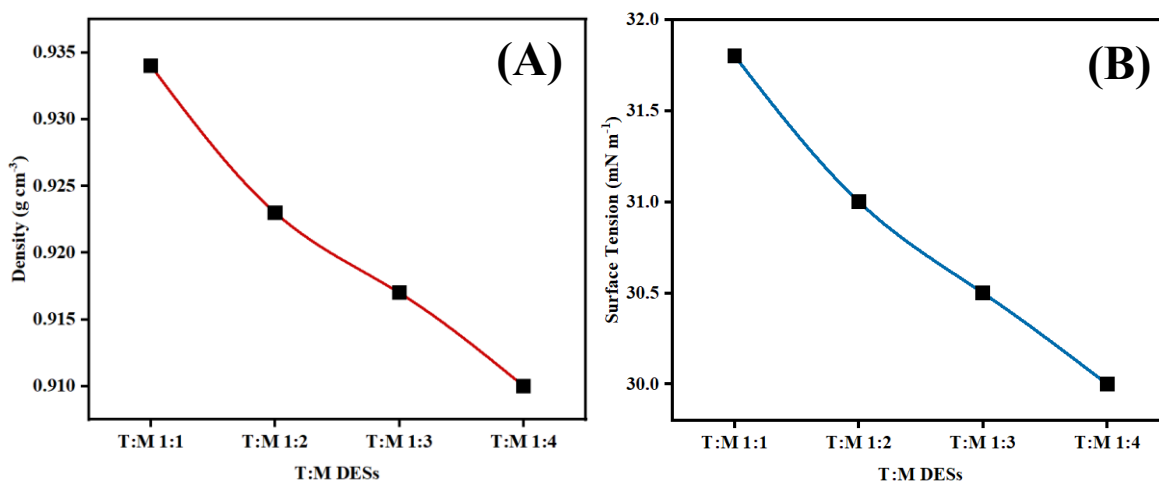


Fig. 2: (A) Density and (B) surface tension of the prepared T:M DESs.

Surface tension is another important physical characteristic of DES to characterize as it affects the interaction strength in the mixture [16]. In this study, the DESs surface tension with varying thymol to menthol molar ratio (1:1 to 1:4) is measured. Generally, the surface tension of the DES is weak because their constituents are uncharged and any other cohesive forces present is weak [17]. The molar ratio of constituents can however still influence the surface tension of the DESs [18]. As seen in Figure 2 (B), the surface tension of the prepared DES is ordered as T:M 1:1 (31.8 mN m⁻¹) > T:M 1:2 (31 mN m⁻¹) > T:M 1:3 (30.5 mN m⁻¹) > T:M 1:4 (30 mN m⁻¹). T:M 1:1 has higher surface tension, than the other DESs as it has strongest hydrogen-bonding interaction

as was corroborated with interaction energy result.

Solubility of polyethylene oxide (PEO) in T:M DESs was carried out at molar ratios of 1:1, 1:2, 1:3, and 1:4. During blending of T:M DESs with PEO, polymer swelling was observed after approximately 30 minutes, after which the samples transformed into a translucent gel across all ratios (Fig. 3). As shown in the figure, PEO was successfully dissolved in all tested T:M DESs. The use of low-viscosity DESs in this application enhances mass transfer between the solute and solvent by promoting more frequent intermolecular collisions during the dissolution process. This indicates that the formation of new molecular hydrogen bonds between T:M DESs and the polymer constituents increases, thereby improving the solubility of the polymer under investigation [19,20]. These results suggest that the studied DESs have potential as organic additives in PEO-based electrolytes due to their good solubility with this polymer.

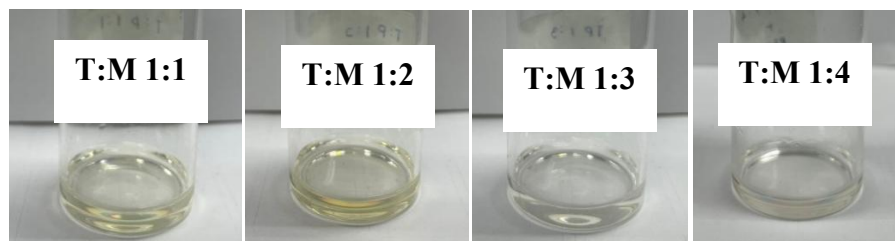


Fig. 3: Solubility behavior of PEO in T:M DESs at different molar ratios (1:1, 1:2, 1:3, and 1:4).

3.2 FTIR of PEO-T:M DESs

FTIR spectroscopy was used to analyze the functional groups present in T:M DESs, PEO film, and series of PEO-T:M DESs films as presented in Fig. 4. The FTIR spectrum of the T:M 1:1 DES exhibits characteristic absorption bands corresponding to both thymol and menthol components. The hydroxyl $\nu(\text{-OH})$ stretching vibrations of thymol and menthol are observed at 3172 and 3158 cm^{-1} , respectively. The intense absorption bands at 2956-2865 cm^{-1} are attributed to the stretching vibrations of methyl $\nu(\text{-CH}_3)$ groups. Peaks appearing at 1417 cm^{-1} for thymol and 1418 cm^{-1} for menthol are associated with methyl group bending vibrations [13]. In addition, the absorption band at 1428 cm^{-1} indicates the presence of aromatic ring structures from thymol, while the band at 1026 cm^{-1} corresponds to the cyclohexane ring of menthol [21]. Notably, the observed broadening and slight shifts in the hydroxyl stretching bands across all T-M spectra are indicative of hydrogen bonding interactions between thymol and menthol, confirming intermolecular interactions rather than the formation of new chemical compounds [22].

The FTIR spectrum of PEO film exhibits characteristic absorption bands associated with its polymeric backbone. The broad band observed around 3326 cm^{-1} is attributed to the stretching vibration of hydroxyl $\nu(\text{-OH})$ end groups and absorbed moisture. The prominent bands at 2892 cm^{-1} arise from alkyl $\nu(\text{C-H})$ groups stretching vibrations, while the strong absorption band near 1083 cm^{-1} corresponds to the ether $\nu(\text{C-O})$ stretching vibration, which is a characteristic feature of PEO. Additional bands appearing at approximately 1479 and 1402 cm^{-1} are assigned to CH_2 bending [23]. Moreover, PEO-T:M systems were prepared by combining PEO with T:M DES at different molar ratios, and their FTIR spectra were subsequently analyzed. The FTIR spectrum of PEO-T:M exhibits changes in peak intensity compared to the individual FTIR spectrum of T:M and PEO as shown in Fig. 4, confirming the incorporation of T:M DES into the PEO matrix to form the electrolyte systems.

The hydroxyl $\nu(\text{-OH})$ stretching bands of the individual components appear at 3158–3172 cm^{-1} for T:M 1:1 and at approximately 3326 cm^{-1} for pure PEO. Upon formation of the PEO-T:M electrolytes, the $\nu(\text{-OH})$ stretching region becomes significantly broader and shifts to higher wavenumbers, appearing in the range of 3431–3472 cm^{-1} for all PEO-T:M compositions. This pronounced band broadening, compared to those of pure T:M and PEO, indicates strong

intermolecular interactions between the hydroxyl groups of T:M DES and the ether oxygen groups of PEO, confirming successful incorporation and interaction within the electrolyte matrix. Moreover, the $\nu(\text{C-H})$ stretching vibrations of the methyl groups in T:M DES appear as medium-intensity bands in the range of $2956\text{--}2865\text{ cm}^{-1}$, whereas pure PEO exhibits a very weak $\nu(\text{C-H})$ stretching band at approximately 2892 cm^{-1} [23]. Upon incorporation of T:M DES into the PEO matrix, weak $\nu(\text{C-H})$ stretching bands are observed in the PEO-T:M electrolytes at 2880, 2891, 2885, 2868, and 2867 cm^{-1} for the different ratios of T-M. The reduced intensity of these bands compared to pure T:M DES is attributed to the dilution of DES components within the PEO matrix and the overlapping of C-H stretching vibrations from both PEO and T:M constituents.

Furthermore, in the ether stretching region, the T:M 1:1 DES exhibits a medium-intensity absorption band at 1089 cm^{-1} , while pure PEO shows a relatively weak band at 1083 cm^{-1} corresponding to the $\nu(\text{C-O})$ stretching vibration of the polymer backbone [23]. Upon incorporation of T:M DES into the PEO matrix, the PEO-T:M electrolytes display pronounced, sharp, and highly intense absorption bands in the range of $1098\text{--}1106\text{ cm}^{-1}$ for all compositions. The enhancement in peak intensity, together with the slight shift to higher wavenumbers compared to pure PEO, indicates strong intermolecular interactions between the ether oxygen atoms of PEO and the hydroxyl groups of the T:M DES.

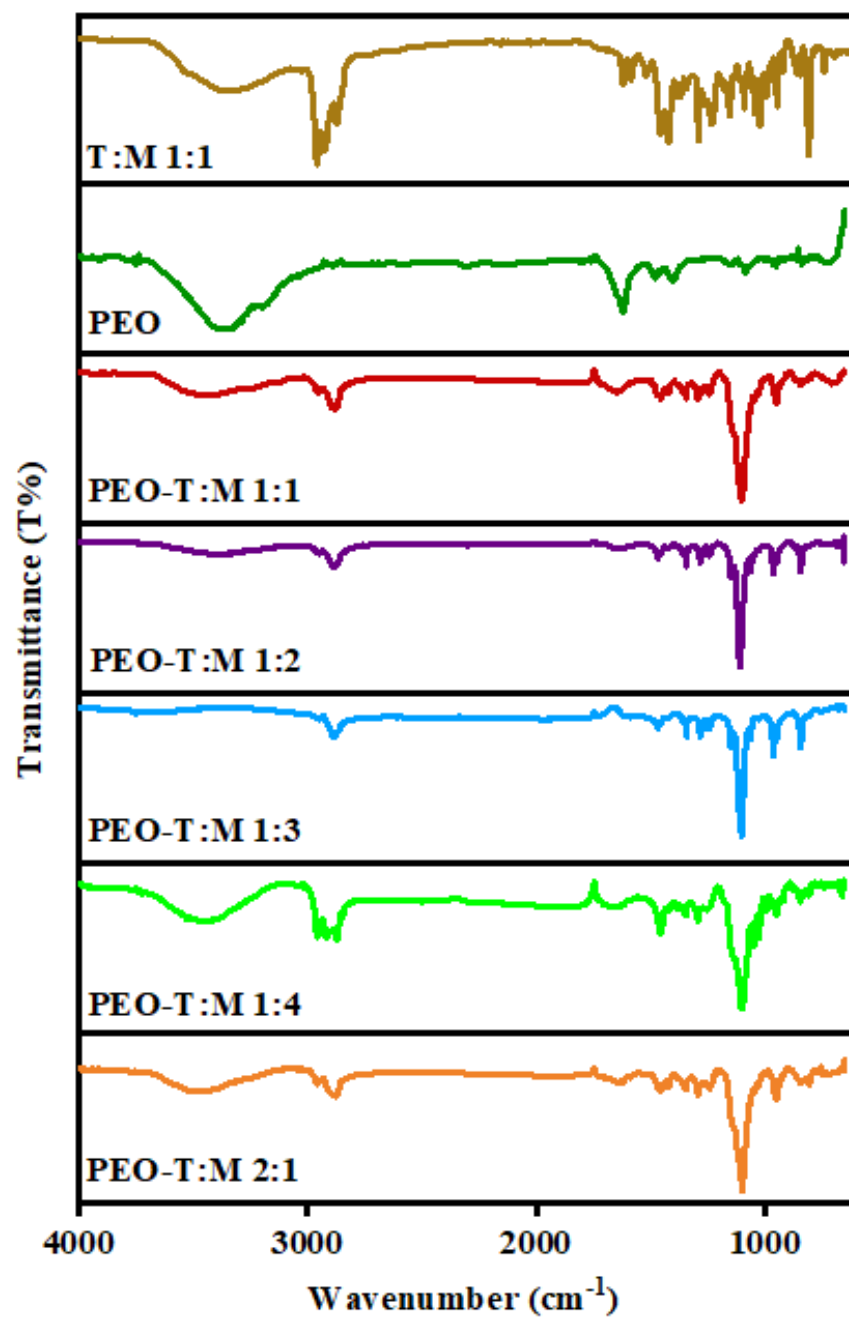


Fig. 4: Overlay FTIR spectra of T:M 1:1, PEO, and PEO-T:M in various ratios.

3.3 TGA of PEO-T:M DESs

The thermal stability of the prepared PEO electrolytes containing T:M DESs were evaluated using thermogravimetric analysis (TGA). This technique was employed to determine the decomposition temperature and the amount of residual mass remaining after complete thermal degradation over a range of temperatures. The TGA and derivative thermogravimetric (DTG) curves revealed distinct thermal degradation patterns for T:M 1:1, PEO, and the PEO-T:M 1:1 as presented in Fig. 5 (A & B). PEO-T:M 1:1 was selected as the representative sample among all the other PEO-T:M electrolyte films.

T:M 1:1 shows a single degradation step starting at 92.81°C (T_{onset}) and finishing at 175.51°C (T_{offset}) with a sharp endothermic DTG peak around 168.39°C. The onset decomposition temperature represents the temperature at which thermal degradation begins and was utilized to determine the highest temperature at which the T:M system remains in a stable liquid state without undergoing decomposition [24]. TM 1:1 undergoes almost complete mass loss (99.38 %) with negligible residual char (0.62 %), indicating total decomposition of T:M 1:1. These results demonstrate that TM 1:1 alone possesses poor thermal stability and requires incorporation into a polymer matrix to enhance its thermal resistance for electrolyte applications.

For PEO film, no major mass loss until was observed up to approximately 240°C. However, a major weight loss of about 89.71% was then observed sharply within the temperature range of 243.54 – 474 °C, indicating that the film remains thermally stable only up to around 240 °C. This substantial mass loss is likely associated with the degradation of the PEO polymer backbone, combustion of the organic phase, and thermal dehydration of inorganic components. Beyond 500°C, no further weight loss was detected, suggesting the completion of thermal decomposition of the PEO [25].

For the PEO-T:M 1:1 electrolyte, the TGA and DTG curves exhibit a clear two-step thermal degradation behavior, indicating the successful incorporation of T:M into the PEO matrix. The first degradation stage occurs between 95.85 and 224.69 °C, with a DTG peak at 156.84 °C and a corresponding weight loss of 52.98%. This initial mass loss is attributed primarily to the thermal decomposition of the T:M DES component in the electrolyte, which occurs at a slightly higher onset temperature compared to pure T:M 1:1. The shift in T_{onset} suggests an improvement in the thermal stability of T:M upon interaction with the PEO, likely due to hydrogen bonding and

molecular confinement within the polymer matrix [26].

The second degradation stage is observed in the temperature range of 309.85–414.39 °C, with a maximum degradation temperature ($T_{\max}$) at 378.39 °C and an associated weight loss of 40.33%. This stage corresponds to the thermal decomposition of the PEO polymer, consistent with the degradation behavior of PEO, although occurring at a slightly lower temperature. The overall degradation profile indicates that the presence of T:M modifies the thermal behavior of PEO by reducing its decomposition temperature. After complete degradation, a residual char of 6.69% remains, which is lower than that of pure PEO, further confirming the contribution of the T:M 1:1 component. Overall, the two-step degradation pattern demonstrates that incorporation of T:M into the PEO matrix alters the thermal stability while maintaining sufficient resistance for solid polymer electrolyte applications [27].

Overall, although the incorporation of T:M 1:1 slightly reduces the thermal stability of PEO, the PEO–T:M 1:1 electrolyte exhibits significantly improved stability compared to pure T:M 1:1 and remains thermally stable well above typical operating temperatures of polymer electrolytes, confirming its suitability for solid-state electrolyte applications. Table 3 shows the thermal analysis data of T:M 1:1, PEO, and PEO-T:M 1:1.

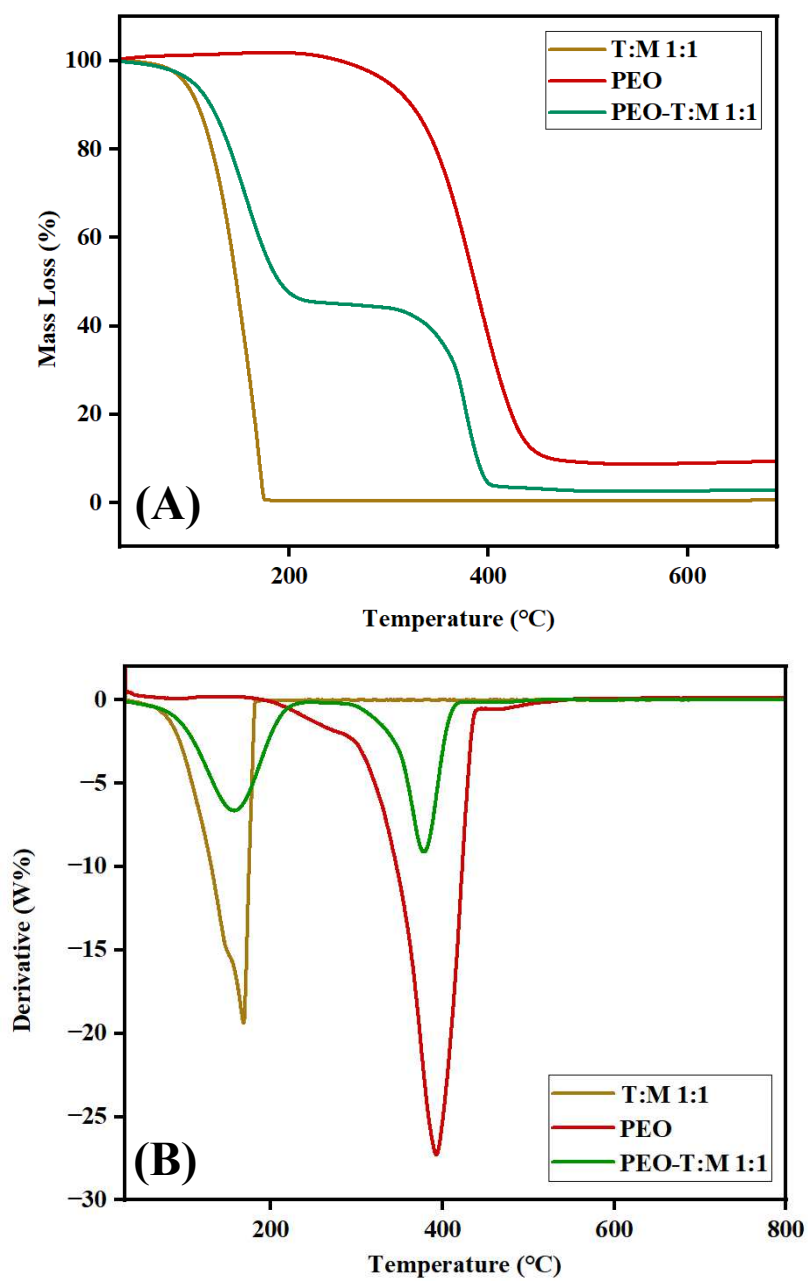


Fig. 5: (A) TGA and (B) DTG thermograms of T:M 1:1, PEO, and PEO-T:M 1:1.

Table 3: Thermal analysis data of T:M 1:1, PEO, and PEO-T:M 1:1.

Compounds		T _{onset} (°C)	T _{offset} (°C)	T _{max} (°C)	Weight loss (%)	Residue (%)
T:M 1:1		92.81	175.51	168.39	99.38	0.62
PEO		243.54	477.74	392.34	89.71	10.29
PEO-T:M 1:1	First degradation	95.85	224.69	156.84	52.98	6.69
	Second degradation	309.85	414.39	378.39	40.33	

3.4 Electrochemical performances of polymer electrolytes

Electrochemical Impedance Spectroscopy (EIS) stands as a pivotal technique in the characterization of polymer electrolytes, which serve as critical components in various electrochemical devices, including batteries, fuel cells, and sensors [28]. EIS offers unparalleled insights into the electrochemical behavior and transport mechanisms within polymer electrolytes by measuring their impedance response to alternating current (AC) perturbations over a range of frequencies.

Fig. 6 shows the Cole-Cole plot for the prepared PEO-T:M DESs electrolyte. The plot shows a combination of semicircle at higher frequency region and inclined spike at lower frequency region for the PEO electrolyte (without T:M DES additive), indicating the highest bulk resistance. The inclined spike later then disappeared and the semicircle diameter decreased with increasing ratio of T:M DES additive, consistent across all the prepared electrolyte films. According to Samsudin et al. [29], the diameter of the depressed semicircle determines the charge

transfer resistance. The decreased of semicircle diameter reflects a reduction in bulk resistance, indicating that the electrolyte film become more conductive. This conductive property is the result of enhancement in the number density of charge carriers and the efficiency of synthesized additive in dissociating PEO matrix, which has been proved through the interaction in FTIR spectrum [30].

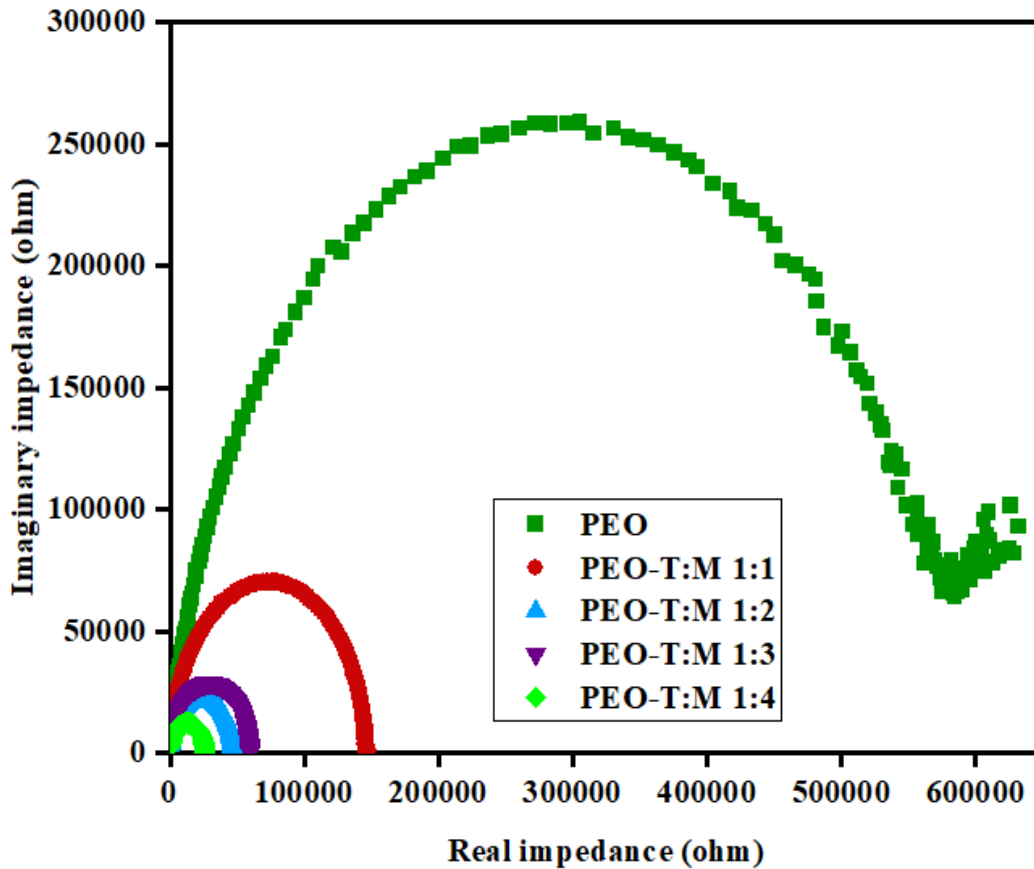


Fig. 6: Cole-Cole plot of PEO and PEO-T:M in various ratios.

The conductive property of the prepared PEO-T:M DESs electrolyte can be further observed through the plot of ionic conductivity with different ratio of T:M DES additive (Fig. 7). The ionic conductivity of pure PEO electrolyte was $8.25 \times 10^{-8} \text{ Scm}^{-1}$, which found similar orders of magnitude ($10^{-8} - 10^{-9} \text{ Scm}^{-1}$) reported by Ahmed & Abdullah, [31] and Liu et al. [32]. As observed in Fig. 7, the ionic conductivity increases about two orders of magnitude upon addition of T:M DES additives into PEO electrolyte film. The highest ionic conductivity was obtained for

ratio 1:4 (T:M DES additive) with the value of $1.28 \times 10^{-6} \text{ Scm}^{-1}$. This result indicates that adding a suitable molar ratio of menthol is important in enhancing ion conduction process. At 1:4 ratio, the T:M DES additive exhibits the lowest viscosity which help in increase polymer chain flexibility and free volume for ion movement to increase the ionic conductivity of polymer electrolyte [33]. In addition to that, the presence of aromatic moiety in thymol and higher number of electrons donating from hydroxyl group further promotes the mobility of ion through electron delocalization, which therefore contributes in enhanced ionic conductivity of PEO based electrolyte [34,12]. The findings imply that the designated T:M DESs-based moiety has a potential to be employed as additive materials towards the performance enhancement for electrochemical interests.

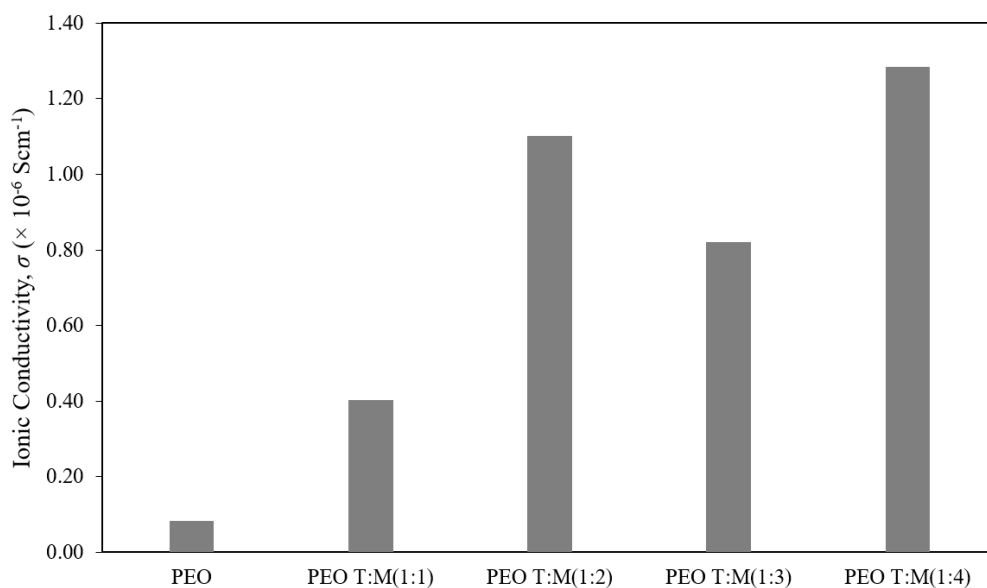


Fig. 7: Ionic conductivity of the prepared PEO-T:M DES electrolyte.

4.0 Conclusion

The thymol and menthol-based deep eutectic solvent (T:M DESs) has been successfully prepared, and characterized with liquid behavior formation of prepared DESs was obtained with T:M DESs at molar ratios of 1:1, 1:2, 1:3 and 1:4 and their physicochemical characteristics were compared. The interaction energy and physical properties of T:M DESs in terms of density and surface tension measurements are highly affected by the changing composition of HBA (menthol). These solvents were successfully applied as the additive in solid polymer electrolytes based on Polyethylene oxide (PEO) as Electrochemical Impedance Spectroscopy (EIS) revealed that the highest ionic conductivity was obtained by the system consisting of T:M DESs with molar ratio of 1:4 (T:M 1:4), with a magnitude of $(1.02 \times 10^{-6} \text{ S/cm})$, hence validating the prospects of the materials to be further experimented as an alternative electrolyte in various electrochemical devices. This incorporation of T:M DESs as additives effectively enhanced ionic transport in PEO-based electrolytes while offering a greener and more sustainable alternative to conventional additives. However, further work is needed to improve ionic conductivity, thermal stability, and interfacial compatibility for practical applications. Overall, this study validates the potential of PEO-T:M DESs electrolytes as a viable and environmentally friendly alternative for electrochemical devices, while also providing a foundation for future optimization in terms of conductivity, stability, and practical applicability.

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