Preparation and Characterization of Polymerizable Deep Eutectic Solvents Ionic Conductive Elastomers

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Abstract. To investigate the influence of different molar ratios of raw materials on the performance of Ionic Conductive Elastomers (ICE) based on Polymerizable Deep Eutectic Solvents (PDES), this study employed a UV-initiated in-situ polymerization method. Polymerizable Deep Eutectic Solvents, synthesized by Choline chloride -acrylic acid with molar ratios of 1:1.7, 1:1.6, and 1:1.5, served as raw materials for the preparation of ionic conductive elastomers. Various modern instruments were employed to analyze and test their properties. The results indicate that as the molar ratio of acrylic acid in the raw materials decreases, the conductivity of the ionic conductive elastomers doubles (reaching 0.838 mS·m⁻¹), but their mechanical properties are somewhat affected. Furthermore, UV testing demonstrates high light transmittance and UV shielding advantages. This suggests that adjusting the performance of ICE by controlling the molar ratio of raw materials can meet the requirements of different applications.

Keywords: Polymerizable Deep Eutectic Solvents, Ionic Conductive Elastomer, Choline Chloride, Acrylic Acid, Conductivity.

1. Introduction

Ionic Conductive Elastomers (ICE) have attracted significant attention from researchers due to their excellent flexibility, elasticity, and high conductivity. They hold promising applications in flexible smart wearables, energy harvesting and storage, touch screen devices, among others [1-5]. Traditional ionic conductive materials primarily rely on ionic liquids, induced polymerization through liquid metals to form ICE [6]. However, the prospects of traditional ionic liquids are limited due to their high cost and significant toxicity, despite their low volatility and crystallization resistance [7-9]. Therefore, the urgent need to develop high-performance ICE with minimal environmental and human health hazards cannot be overstated.

Compared to ionic liquids, Deep Eutectic Solvents (DES) composed of Hydrogen Bond Donors (HBD) and Hydrogen Bond Acceptors (HBA) are recognized as a new type of green solvent due to their low cost, low toxicity, biodegradability, and ideal thermal stability and recyclability [10-13]. Polymerizable Deep Eutectic Solvents (PDES) is an emerging DES characterized by the polymerizability of its HBD or HBA components. ICE produced from PDES exhibits high transparency, good conductivity, and long-term stability. Li et al. have demonstrated the application of PDES-based ICE with polymerizable acrylic acid as the HBD in flexible sensor biomimetic skin [14]. Compared to widely used hydrogel materials, ICE based on PDES offers higher stability and greater suitability for extreme operating environments [15-17]. Therefore, research on PDES-based Ionic Conductive Elastomers holds significant importance.

This study employs polymerizable acrylic acid as the HBD and choline chloride as the HBA to produce PDES. In this material, the conductive ions are hydrogen ions and chloride ions, and the ratio of choline chloride to acrylic acid affects the degree of polymerization and the number and activity of conductive ions. Therefore, by preparing ICE with different ratios, this paper investigates the extent to which raw material proportions affect its electrical and mechanical properties. It summarizes the performance changes of ICE with variations in raw material ratios, providing reference significance for material selection in fields such as flexible smart wearables in the future.
2. Experiment

2.1. Reagents and Instruments

Reagents: Choline chloride, Shanghai Aladdin Biochemical Technology Co., Ltd. Acrylic acid, Shanghai Titan Scientific Co., Ltd. Polyethylene glycol diacrylate (PEGDA), Shanghai EEn Chemical Technology Co., Ltd. 2-Hydroxy-4’-(2-hydroxyethoxy)-2-methylpropiophenone (photoinitiator 2959), Shanghai Titan Scientific Co., Ltd.


2.2. Preparation of Ionic Conductive Elastomers (ICE)

According to the molar ratios of choline chloride to acrylic acid (1: 2, 1: 1.7, 1: 1.6, and 1: 1.5), a certain amount of choline chloride and acrylic acid is weighed and placed in a sealed round-bottom flask. The mixture is heated in a 100°C oil bath and stirred with a magnetic stirrer for one hour until it becomes a transparent and stable solvent. A specific amount of photoinitiator 2959 and crosslinking agent PEGDA is added to the solution. The solution is then transferred to a reagent bottle and subjected to ultrasonic dispersion at 720W power for 30 minutes until a transparent and stable PDES is formed. The PDES is poured into a mold and exposed to ultraviolet light for one minute to form PDES-based ionic conductive elastomers.

2.3. ICE Testing and Characterization

Chemical Structure Analysis: Utilizing a Nicolet 6700 Fourier Transform Infrared Spectrometer (FEI, USA), ICE is characterized in attenuated total reflection mode with a scanning range of 4000 to 400 cm\(^{-1}\) and 32 scans.

Optical Properties Testing: Employing a UV2600 UV-Visible Spectrophotometer (Shimadzu, Japan) using an integrating sphere method to characterize ICE, with wavelength detection ranging from 200 to 1400 nm.

Electrical Properties Testing: Utilizing a CEI660E Electrochemical Workstation (Shanghai Chenhua Instrument Co., Ltd.) to sample ICE at different positions for testing. The frequency range is 0 to 10\(^6\) Hz, temperature is 20°C, and relative humidity is 30% to 35%. Electrochemical impedance spectroscopy is conducted to calculate conductivity.

Mechanical Properties Testing: Using a WDW-20B Microcomputer-Controlled Electronic Universal Testing Machine (Shanghai Lishi Company) to measure the mechanical properties of ICE. The gauge length is set to 5mm, and the tensile speed is 10mm·min\(^{-1}\).
3. Result and Discussion

3.1. Dissolution Performance Analysis

Figure 2. Comparison of the Dissolution Performance of PDES with Three Different Molar Ratios (Choline Chloride: Acrylic Acid)

When using different ratios of acrylic acid and choline chloride, the flowability of the resulting PDES also varies. As seen in Figure 2, when the ratio of choline chloride to acrylic acid is higher than 1:2, PDES exhibits good flowability. When the ratio is 1:1.6, PDES shows a noticeable viscosity. However, when the ratio reaches 1:1.5, upon removing the heated PDES from the heat source, it quickly crystallizes within a very short period, making it impossible to proceed with subsequent polymerization for ICE preparation. This may be due to the insufficient number of hydrogen ion donors when the ratio of acrylic acid is too low, resulting in an inadequate formation of hydrogen bonds to maintain a low eutectic state, leading to rapid crystallization upon removal from the heat source. Therefore, when producing ICE, the molar ratio of choline chloride to acrylic acid should exceed 1:1.6.

3.2. Infrared Spectroscopy Analysis

Figure 3. FT-IR spectra of the samples

As observed in Figure 3, at a frequency of 3250 cm$^{-1}$, PDES prepared with a ratio of 1:1.6 exhibits a stronger peak, possibly due to an increase in -OH groups in choline chloride. At a frequency of 1750 cm$^{-1}$, PDES prepared with a ratio of 1:2 shows a more prominent C=O peak, attributed to an excess of acrylic acid. From the infrared spectra, we can observe that the molar ratio significantly affects the chemical bonds of the material, thereby influencing its properties to a certain extent.
3.3. Optical Property Analysis

Figure 4. UV-vis spectra of the samples

Figure 4 depicts the optical performance test results of ICE, showing the transmittance curve of ICE in the range of 250 to 800 nm. It can be observed that PDES exhibits high transmittance in the visible light range, approaching 90%. This feature makes PDES promising for applications such as touch screen devices that require high transparency. Additionally, it is evident from the graph that PDES has excellent shielding properties against ultraviolet light (250 to 400 nm). Therefore, ICE holds potential applications in the field of ultraviolet shielding.

3.4. Electrical Property Analysis

Figure 5. Conductivity of the samples

Choline chloride not only serves as a hydrogen ion acceptor, combining with the donor acrylic acid to form PDES, but also its ions (H+ and Cl-) contribute to the ion conductivity of ICE. As depicted in Figure 5, as the ratio of choline chloride to acrylic acid decreases from 1:2 to 1:1.6, the conductivity of ICE increases from 0.343 mS·m⁻¹ to 0.838 mS·m⁻¹, doubling the conductivity. It is evident that among different ratios of PDES capable of forming ICE, lower proportions of acrylic acid result in higher conductivity of ICE. This may be attributed to the polymer network formed by acrylic acid after polymerization, which hinders the movement of conductive ions. Therefore, with a decrease in the ratio of acrylic acid, the hindrance to the movement of conductive ions decreases, leading to a significant increase in conductivity.
3.5. Mechanical Property Analysis

![Figure 6](image)

*Figure 6. Tensile image of the samples*

![Figure 7](image)

*Figure 7. Stress-Strain image of the samples*

PDES primarily relies on the polymerization of acrylic acid to form a reinforced network structure, hence the mechanical properties of ICE are often determined by acrylic acid. As indicated in Section 2.3, with a decrease in the proportion of acrylic acid, the reduction in polymerization degree leads to increased freedom of movement for positive and negative ions within ICE. However, this decrease in polymerization degree significantly impacts its mechanical properties. From Figure 7, it is evident that when the ratio of choline chloride to acrylic acid is 1:2, ICE exhibits the highest stress value of 0.422 MPa and the maximum strain value of 345%. However, as the proportion of acrylic acid decreases, both stress and strain of ICE decrease significantly. When the ratio of choline chloride to acrylic acid is 1:1.6, stress and strain of ICE decrease to 0.296 MPa and 199%, respectively. It is clear that the electrical and mechanical properties of ICE prepared from choline chloride and acrylic acid cannot be simultaneously optimized. Therefore, in practical production, the proportion of these components should be adjusted according to the specific performance requirements to produce products that meet the intended use.

4. Conclusion

In the present study, Polymerizable Deep Eutectic Solvents (PDES) were synthesized using choline chloride and acrylic acid in varying molar ratios. Subsequently, these PDES with different
ratios were transformed into ionic conductive elastomers (ICE) using UV-initiated in-situ polymerization. Various analytical instruments were then employed to analyze and characterize their chemical structure and key physical properties, exploring the influence of different molar ratios of raw materials on their performance.

In PDES produced from choline chloride and acrylic acid, a lower molar ratio of acrylic acid results in higher conductivity of the resulting ICE. Among the samples capable of forming ICE, when the molar ratio of choline chloride to acrylic acid is 1:1.6, the highest conductivity of 0.838 mS·m⁻¹ is achieved. However, there is a decrease in mechanical properties (maximum stress reduced to 0.296 MPa and maximum strain reduced to 199%). Infrared analysis also confirms the influence of molar ratio on the structure and properties of PDES. Additionally, in the UV transmittance test, ICE produced from PDES exhibits high transmittance in the visible light range, approaching 90%, indicating significant potential for UV shielding applications.

References