

SYNTHESIS AND MICROSTRUCTURAL STUDIES OF ORGANOGELE FOR FLEXIBLE ELECTRONIC APPLICATIONS

Thesis Submitted to the University of Calicut for the Award of
DOCTOR OF PHILOSOPHY IN CHEMISTRY

by

GOKUL G. K.

under the supervision of

DR. SUDHEESH PARATHAKKATT



Department of Chemistry

The Zamorin's Guruvayurappan College, Calicut

December 2025

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Place: Kozhikode

Date: 11.05.2026

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DECLARATION

I hereby declare that the work presented in the thesis entitled “**SYNTHESIS AND MICROSTRUCTURAL STUDIES OF ORGANOGEL FOR FLEXIBLE ELECTRONIC APPLICATIONS**” is based on the original work done by me under the guidance of **Dr. Sudheesh Parathakkatt**, Associate Professor, Department of Chemistry, The Zamorin’s Guruvayurappan College, Calicut and has not been included in any other thesis submitted previously for the award of any degree. The contents of the thesis are undergone plagiarism check using iThenticate software at C.H.M.K. Library, University of Calicut, and the similarity index found within the permissible limit. I also declare that the thesis is free from AI-generated contents.




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This is to certify that the Ph.D. thesis entitled "*Synthesis and Microstructural Studies of Organogel for Flexible Electronic Applications*" submitted by Mr. **Gokul G. K.**, Research Scholar, Department of Chemistry, The Zamorin's Guruvayurappan College, Kozhikode, has been modified in accordance with the recommendations of the adjudicators. All the suggestions and corrections pointed out by the adjudicators have been duly incorporated into the revised copy of the thesis. It is further certified that the contents of the thesis in both the hard copy and the soft copy are one and the same.


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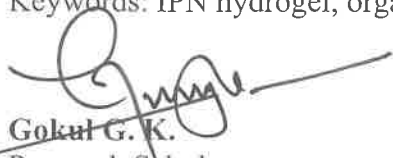
Gokul G. K.

ABSTRACT

SYNTHESIS AND MICROSTRUCTURAL STUDIES OF ORGANOGEL FOR FLEXIBLE ELECTRONIC APPLICATIONS

The increasing demand for flexible, wearable, and bio-integrated electronic devices has accelerated the development of soft and mechanically compliant materials capable of sustaining large deformations while maintaining electrical functionality. Conventional rigid electronic materials often exhibit mechanical incompatibility with soft substrates and biological tissues, limiting their applicability in flexible electronic systems. Conductive hydrogels and organogels have emerged as promising alternatives due to their tissue-like softness, flexibility, and ability to support ionic charge transport; however, their practical use is often restricted by poor mechanical strength and limited environmental stability. In this study, interpenetrating polymer network (IPN) hydrogels and organogels based on polyacrylamide (PAAm) reinforced with natural polysaccharides, namely pectin and gellan gum (GG), were successfully developed using a dual crosslinking and post-synthesis solvent displacement strategy. The combination of covalent crosslinking within the PAAm network and ionic coordination between calcium ions and the polysaccharide chains imparted enhanced mechanical strength, flexibility, and structural stability to the hydrogel systems. Subsequent solvent displacement with polyols, including glycerol and ethylene glycol, effectively transformed the hydrogels into organogels with significantly improved anti-freezing, anti-dehydration, and thermal stability. Comprehensive characterisation using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), swelling studies, and mechanical testing confirmed the formation of robust dual-network architectures and strong hydrogen-bonding interactions between the polymer networks and polyol solvents. The rheological analysis provided detailed insight into the viscoelastic behaviour and network stability of the gels. Mechanical evaluations demonstrated substantial improvements in tensile strength and elasticity, while anti-freezing and solvent-retention studies highlighted the superior environmental tolerance of the organogels. Ionic conductivity measurements over a wide temperature range revealed stable and efficient ion transport, including at sub-zero temperatures. Overall, the results demonstrate that PAAm-based polysaccharide-reinforced IPN organogels offer a mechanically robust, environmentally resilient, and ionically conductive material platform, making them promising candidates for flexible electronics, wearable sensors, and low-temperature soft electronic applications.

Keywords: IPN hydrogel, organogel, flexible electronics, polysaccharide, conductive hydrogels



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SYNTHESIS AND MICROSTRUCTURAL STUDIES OF ORGANOGEL FOR FLEXIBLE ELECTRONIC APPLICATIONS

ശരീരത്തിൽ ധരിക്കാവുന്നതും വഴക്കമുള്ളതും ജൈവസംയോജനം സാധ്യമായതുമായ ഇലക്ട്രോണിക് ഉപകരണങ്ങളുടെ ആവശ്യം അടുത്തകാലത്ത് ഗണ്യമായി വർദ്ധിച്ചുവരികയാണ്. ഈ പ്രവണത, വൈദ്യുത പ്രവർത്തനക്ഷമത നിലനിർത്തിക്കൊണ്ട് തന്നെ വലിയ തോതിലുള്ള രൂപമാറ്റങ്ങളും യാന്ത്രിക സമ്മർദ്ദങ്ങളും സഹിക്കാൻ കഴിയുന്ന മൃദവായ പദാർത്ഥങ്ങളുടെ വികസനത്തിന് ശക്തമായ പ്രചോദനം നൽകിയിട്ടുണ്ട്.

പരമ്പരാഗതമായ ദൃഢതയേറിയ ഇലക്ട്രോണിക് മെറ്റീരിയലുകൾ പലപ്പോഴും മൃദവായ പ്രതലങ്ങളുമായും ജൈവ കലകളുമായും ആവശ്യമായ ചേർച്ച കാണിക്കാറില്ല; ഇതുവഴി ഫ്ലെക്സിബിൾ ഇലക്ട്രോണിക് സംവിധാനങ്ങളിൽ അവയുടെ ഉപയോഗം പരിമിതപ്പെടുന്നു. ഇതിന് വിപരീതമായി, ടിഷ്യൂകൾക്ക് സമാനമായ മൃദത്വം, വഴക്കം, കൂടാതെ അയോണിക് ചാർജ് ട്രാൻസ്പോർട്ടിനെ പിന്തുണയ്ക്കുന്ന കഴിവ് എന്നിവ കാരണം വൈദ്യുത ചാലകതയുള്ള ഹൈഡ്രോജെലുകളും ഓർഗാനോജെലുകളും പ്രതീക്ഷാജനകമായ ബദലുകളായി ഉയർന്നുവന്നിട്ടുണ്ട്. എന്നിരുന്നാലും, കറഞ്ഞ യാന്ത്രിക ശക്തിയും പരിമിതമായ പാരിസ്ഥിതിക സ്ഥിരതയും കാരണം ഇവയുടെ ദീർഘകാല പ്രായോഗിക ഉപയോഗം ഇപ്പോഴും വെല്ലുവിളിയായി തുടരുന്നു.

ഈ പഠനത്തിൽ, പോളിഅക്രിലമൈഡ് അടിസ്ഥാനമാക്കിയതും പെക്റ്റിൻ , ജെല്ലിൻ ഗം തുടങ്ങിയ പ്രകൃതിദത്ത പോളിസാക്കറൈഡുകൾ ഉപയോഗിച്ച് ബലപ്പെടുത്തിയതുമായ ഇന്റർപെനേട്രേറ്റിംഗ് പോളിമർ നെറ്റ്‌വർക്ക് ഹൈഡ്രോജെലുകളും ഓർഗാനോജെലുകളും വിജയകരമായി വികസിപ്പിച്ചു. ഡ്യൂവൽ ക്രോസ്‌ലിങ്കിംഗ്, പോസ്റ്റ്-സിന്തസിസ് സോൾവെന്റ് ഡിസ്‌പ്ലേസ്‌മെന്റ് എന്നീ രീതികളാണ് ഇതിനായി അവലംബിച്ചിട്ടുള്ളത്.

പോളിഅക്രിലമൈഡ് നെറ്റ്‌വർക്കിനുള്ളിലെ കോവാലന്റ് ക്രോസ്‌ലിങ്കിംഗും പോളിസാക്കറൈഡ് ചെയിനുകളും കാൽസ്യം അയോണുകളും തമ്മിലുള്ള അയോണിക് കോർഡിനേഷനും സംയോജിപ്പിച്ചതിലൂടെ ഹൈഡ്രോജെൽ സിസ്റ്റങ്ങൾക്ക് മെച്ചപ്പെട്ട യാന്ത്രിക ബലം, വഴക്കം, ഘടനാപരമായ സ്ഥിരത എന്നിവ കൈവരിക്കാൻ സാധിച്ചു. ഗ്ലിസറോൾ, എഥിലീൻ ഗ്ലൈക്കോൾ തുടങ്ങിയ പോളിയോളുകൾ ഉപയോഗിച്ചുള്ള ലായക വിസ്ഥാപന പ്രക്രിയയിലൂടെ ഹൈഡ്രോജെലുകളെ വളരെ താഴ്ന്ന താപനിലയിൽ സ്ഥിരത പുലർത്തുന്നതും , നിർജ്ജലീകരണത്തോട് പ്രതിരോധശേഷിയുള്ളതും , കൂടാതെ മികച്ച താപ സ്ഥിരതയുമുള്ള ഓർഗാനോജെലുകളായി പരിവർത്തനം ചെയ്യാനായി.

ഫോറിയർ ട്രാൻസ്ഫോം ഇൻഫ്രാറെഡ് സ്പെക്ട്രോസ്കോപ്പി, സ്കാനിംഗ് ഇലക്ട്രോൺ മൈക്രോസ്കോപ്പി, സ്വെല്ലിംഗ് പഠനങ്ങൾ, മെക്കാനിക്കൽ പരിശോധനകൾ എന്നിവ ഉപയോഗിച്ചുള്ള സമഗ്രമായ വിശകലനം, ശക്തമായ ഡ്യൂവൽ-നെറ്റ്‌വർക്ക് ഘടനകളുടെ രൂപീകരണവും പോളിമർ നെറ്റ്‌വർക്കുകളും പോളിയോൾ ലായകങ്ങളും തമ്മിലുള്ള ശക്തമായ ഹൈഡ്രജൻ-ബോണ്ടിംഗ് ബന്ധങ്ങളും സ്ഥിരീകരിച്ചു. റിയോളജിക്കൽ വിശകലനം ജെലുകളുടെ വിസ്കോഇലാസ്റ്റിക് സ്വഭാവത്തെയും നെറ്റ്‌വർക്ക് സ്ഥിരതയെയും കുറിച്ച് വിശദമായ അവബോധം നൽകി. മെക്കാനിക്കൽ പഠനങ്ങൾ ടെൻസൈൽ ശക്തിയിലും ഇലാസ്റ്റിക്തയിലും ഗണ്യമായ പുരോഗതി പ്രകടമായപ്പോൾ, ആന്റി-ഫ്രീസിംഗ് കൂടാതെ ലായക സംരക്ഷണ പഠനങ്ങൾ ഓർഗാനോജെലുകളുടെ മികച്ച പാരിസ്ഥിതിക അതിജീവന ശേഷിയെ വ്യക്തമായി അടയാളപ്പെടുത്തി. വ്യത്യസ്ത താപനിലകളിൽ നടത്തിയ അയോണിക് വൈദ്യുത ചാലകത പരിശോധനകൾ , പൂജ്യത്തിന് താഴെയുള്ള താപനിലകളിലും പോലും സുസ്ഥിരവും കാര്യക്ഷമവുമായ അയോൺ വിനിമയം ഉണ്ടെന്ന് വ്യക്തമാക്കുന്നു.

ചുരുക്കത്തിൽ, പോളിസാക്കറൈഡ് ഉപയോഗിച്ച് ബലപ്പെടുത്തിയ പോളിഅക്രിലമൈഡ് അധിഷ്ഠിത ഓർഗാനോജെലുകൾ നല്ല യാന്ത്രിക ബലം, മികച്ച പാരിസ്ഥിതിക സ്ഥിരത, കൂടാതെ ഫലപ്രദമായ അയോണിക് ചാലകത എന്നിവ കൈവരിച്ച വസ്തുക്കളാണ്. അതിനാൽ, ഫ്ലെക്സിബിൾ ഇലക്ട്രോണിക്സ്, വെയറബിൾ സെൻസറുകൾ, കറഞ്ഞ താപനിലയിൽ പ്രവർത്തിക്കുന്ന സോഫ്റ്റ് ഇലക്ട്രോണിക് ഉപകരണങ്ങൾ എന്നിവയ്ക്ക് ഇവ അനുയോജ്യമാണ്.

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Gokul G. K.
Research Scholar


Dr. Sudheesh Parathakkatt
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List of Abbreviations

AAm Acrylamide

CMC Carboxymethyl Cellulose

CNTs Carbon Nanotubes

CS Chitosan

DN Double Network

DSC Differential Scanning Calorimetry

EG Ethylene Glycol

ECH Electron Conductive Hydrogel

FTIR Fourier Transform Infrared Spectroscopy

GG Gellan Gum

GL Glycerol

GO Graphene Oxide

HM High Methoxyl

IPN Interpenetrating Polymer Network

IUPAC International Union of Pure and Applied Chemistry

LM Low Methoxyl

PAAm Polyacrylamide

PAMPS Poly(2-acrylamido-2-methylpropanesulfonic acid)

PANI Polyaniline

PDMS Polydimethylsiloxane

PEG Polyethylene Glycol

PET Polyethylene Terephthalate

PI Polyimide

PNIPAAm Poly(N-isopropylacrylamide)

PPy Polypyrrole

PVA Polyvinyl Alcohol

rGO Reduced Graphene Oxide

SEM Scanning Electron Microscopy

TGA Thermogravimetric Analysis

XG Xanthan Gum

Preface

The rapid evolution of flexible and wearable electronic technologies has intensified the need for soft, mechanically compliant, and electrically functional materials capable of sustaining large deformations and operating under diverse environmental conditions. Conventional rigid electronic materials, while offering excellent electrical performance, often exhibit a pronounced mechanical mismatch with soft substrates and biological tissues, thereby restricting their applicability in next-generation wearable, implantable, and biointegrated electronic systems. In this context, polymeric hydrogels and organogels have emerged as promising candidates because of their inherent softness, high flexibility, and ability to support ionic transport. A central objective of this work is to investigate the role of network architecture, ionic coordination, and solvent composition in governing the structure–property relationships of these materials. Particular emphasis is placed on the development of organogels through solvent displacement using polyols such as glycerol and ethylene glycol, which impart anti-freezing and anti-drying characteristics while preserving mechanical integrity and electrochemical performance. Systematic studies involving swelling behaviour, microstructural analysis, thermal stability, mechanical and rheological properties, as well as temperature-dependent ionic conductivity, are carried out to establish a comprehensive understanding of the material behaviour under varying environmental conditions. The thesis is organized into six chapters. Chapter 1 provides a detailed introduction and critical review of the literature related to flexible electronics, conductive hydrogels, and organogels. It discusses the classification of hydrogels based on origin, compo-

sition, and crosslinking mechanism, with particular emphasis on polysaccharide-based systems. The chapter highlights the significance of interpenetrating and double-network hydrogels in improving mechanical robustness and reviews recent advances in ionic conductive hydrogels and organogels. The scope and objectives of the present research are clearly outlined at the end of the chapter. Chapter 2 describes the materials, chemicals, and experimental methodologies employed in this study. It details the preparation protocols for PAAm hydrogels, PAAm-pectin and PAAm-gellan gum hydrogels, and their corresponding organogels fabricated via solvent displacement using glycerol and ethylene glycol. This chapter also outlines the characterization techniques used to evaluate swelling behaviour, microstructure, chemical interactions, thermal stability, mechanical and rheological properties, anti-freezing and anti-dehydration performance, and ionic conductivity. Chapter 3 focuses on the development and comprehensive characterization of PAAm-pectin interpenetrating polymer network hydrogels and organogels. The chapter discusses the mechanism of network formation through covalent crosslinking of PAAm and ionic coordination between pectin and calcium ions. Detailed analyses of FTIR spectra, scanning electron microscopy, swelling behaviour, mechanical performance, and rheological properties are presented. The anti-freezing behaviour, solvent retention capability, thermal stability, and temperature-dependent ionic conductivity of pectin-based organogels are systematically investigated and discussed. Chapter 4 presents the fabrication and physicochemical characterization of PAAm-gellan gum hydrogels and organogels. The chapter examines the role of gellan gum concentration, calcium ion coordination, and polyol content on the structural, mechanical, and electrochemical properties of the gels. Comparative discussions on microstructure, swelling characteristics, tensile properties, rheological behaviour, thermal stability, solvent retention, anti-freezing performance, and ionic conductivity are provided to elucidate the structure-property relationships of gellan gum-based systems. Chapter

5 offers a comparative analysis of PAAm–pectin and PAAm–gellan gum hydrogels and organogels. This chapter systematically contrasts the influence of biopolymer type and solvent system on morphology, swelling behaviour, mechanical strength, viscoelastic properties, solvent retention, anti-freezing characteristics, and ionic conductivity. The comparative evaluation highlights the advantages and limitations of each biopolymer system in the context of flexible electronic applications. Chapter 6 summarises the key findings of the research and presents the overall conclusions drawn from the study. The chapter also outlines prospective directions for future research, emphasising the potential extension of these organogel systems toward multifunctional, sustainable, and high-performance soft materials for advanced flexible and bioelectronic devices. It is anticipated that the outcomes of this thesis will contribute to a deeper understanding of polysaccharide-reinforced IPN hydrogels and organogels, and will aid in the rational design of mechanically robust, environmentally tolerant, and ionically conductive soft materials for next-generation flexible electronic applications.

Chapter 1

Introduction and Review of Literature

1.1 Introduction

Flexible electronics are a class of electronic devices and circuits designed to maintain functionality under mechanical deformation (Lu et al., 2025; Corzo et al., 2020). Flexible electronics possess advantages such as lightweight design, superior mechanical flexibility, and conformability, compared to conventional rigid electronic systems. These features make them highly suitable for a broad spectrum of applications, including wearable devices, flexible displays, implantable medical systems, and conformal sensors (Omiyale et al., 2025; Katiyar et al., 2023). Recent years have witnessed growing interest in innovative materials and advanced fabrication methods for integrating high-performance electronic components onto flexible substrates. This progress has significantly broadened the application landscape of flexible electronics, extending to flexible sensors (Gao et al., 2021; Trung and Lee, 2016), energy harvesting systems (Fan et al., 2012; Ma et al., 2021), energy storage devices (Han, Wang, Mao, Yin, Zhong, Yiming, Hu, Jia, Nian, Qu et al., 2020), and flexible display technologies (Lee and Mooney, 2001). Furthermore, recent technological advances in artificial intelligence, cloud computing, augmented reality, and virtual reality have accelerated progress in flexible electronic technologies. In parallel, the growing emphasis on personal health monitoring has stimulated the development of flexible electronics capable of inter-

facing biological tissues with synthetic electronic systems (Heikenfeld et al., 2018; Yang and Gao, 2019).

The mechanical mismatch between conventional electronic materials and biological tissues remains one of the principal challenges in the development of flexible bioelectronics. The commonly used materials in flexible electronics are polyimide (PI), polyethylene terephthalate (PET), polydimethylsiloxane (PDMS), and silicone (MacDonald, 2015; Li, Han, Hu and Zhang, 2023). These materials exhibit a mechanical mismatch with soft and hydrated tissues and organs in the human body. While these materials provide excellent mechanical flexibility and long-term durability, they often lack biocompatibility, which limits their direct integration with living tissues for long-term biomedical applications (Qian et al., 2021; Balakrishnan et al., 2022; Chitrakar et al., 2022).

Due to their soft nature and high water content, the hydrogels exhibit mechanical characteristics similar to biological tissues. Hence, they have emerged as promising materials for the development of flexible electronics designed for biological applications. Hydrogels are three-dimensional, crosslinked polymeric networks capable of absorbing and retaining large amounts of water while maintaining their structural integrity (Chirani et al., 2015; Yang, 2022). The high water content, soft tissue-like behaviour, and biocompatibility make hydrogels suitable for diverse applications in biomedicine, tissue engineering, agriculture, environmental science, and smart materials. Incorporating conductive components into hydrogel networks imparts electrical functionality, making them suitable for bioelectronic applications (Hu et al., 2023; Zhang, Tan, Lao, Gao and Yu, 2023). Conductivity, together with self-healing ability, tunable mechanics, and biofunctionalisation potential, makes hydrogels highly suitable for advanced bioelectronic applications (Li, Liu, Wei, Yang, Ren and Li, 2023).

1.1.1 Classification of hydrogel

Based on their origin, hydrogels are classified into natural, synthetic, and hybrid systems (Vasile et al., 2020; Garnica-Palafox and Sánchez-Arévalo, 2016). Natural hydrogels are fabricated using biopolymers, which are usually derived from plants or animals. The presence of a large number of reactive sites on the molecular chain of biopolymers facilitates the fabrication of hydrogels. Because of their excellent biocompatibility and similarity with biological systems, natural hydrogels are highly suitable for biomedical applications. These hydrogels have been widely used in wound healing, tissue engineering, and drug-delivery applications. Moreover, the biodegradable nature, natural abundance, and sustainability of natural hydrogels expand their potential applications in various fields (Khansari et al., 2017). Despite their potential, the poor mechanical strength and low structural stability of natural hydrogels limit their practical applications (Kasai et al., 2023). Hydrogels fabricated from synthetic or man-made polymers are classified as synthetic hydrogels. PEG (polyethylene glycol), PVA (polyvinyl alcohol), PAAm (polyacrylamide), and PNIPAAm (poly(N-isopropylacrylamide)) are common examples of polymers used to prepare synthetic hydrogels. These hydrogels exhibit remarkable mechanical strength, reproducibility, and controlled purity but lack biocompatibility and biodegradability (Madduma-Bandarage and Madihally, 2021; Hameed et al., 2024).

Hybrid hydrogels, created by blending natural and synthetic polymers, are designed to combine the excellent biocompatibility and biodegradability of natural materials with the superior mechanical strength provided by synthetic polymers (Vasile et al., 2020; Khattak et al., 2025). Hybrid hydrogels fabricated using synthetic polymers such as PVA, PAAm, and PEG, blended with biopolymers like alginate, chitosan, and starch, are widely employed for biomedical applications.

Based on the composition, hydrogels are classified into homopolymers, copolymers, semi-interpenetrating networks (semi-IPNs), and interpenetrating networks

(IPNs). Homopolymer hydrogels consist of a polymer network composed of identical monomer units. whereas copolymer hydrogels contain polymer networks formed from two or more distinct monomer units (Singhal and Gupta, 2016; Dhara, 2024). Semi-IPN hydrogels are formed when a linear polymer is incorporated into a cross-linked network, creating interactions between the two components (Zoratto and Matricardi, 2018; Zambili et al., 2025). The IUPAC definition referred to semi IPN is “A polymer comprising one or more networks and one or more linear or branched polymer(s) characterised by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules.” IPN hydrogels comprise two independently cross-linked networks interwoven together, which enhances mechanical strength and stability. IUPAC defines an IPN as “A polymer comprising two or more networks that are at least partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken. A mixture of two or more pre-formed polymer networks is not an IPN.” The semi-IPN and IPN can be differentiated as “Semi-interpenetrating polymer networks are distinguished from interpenetrating polymer networks because the constituent linear or branched polymers can, in principle, be separated from the constituent polymer network(s) without breaking chemical bonds.”

Based on the crosslinking mechanism, hydrogels are classified into physical, chemical, and hybrid gels (Thakur et al., 2018; Bustamante-Torres et al., 2021). The polymer networks in physical gels are cross-linked by non-covalent interactions, such as hydrogen bonding, ionic interactions, hydrophobic forces, or van der Waals forces (Garg et al., 2016). Such reversible physical interactions enable efficient energy dissipation when the material undergoes mechanical deformation. These hydrogels can undergo reversible gel-to-sol transitions when exposed to external stimuli such as temperature, pH, or ionic strength. They often display self-healing ability and can swell substantially without losing their structural in-

tegrity. Examples include agarose, gelatin, chitosan, and PEG derivatives. The preparation of physical hydrogels is comparatively easy and does not require toxic crosslinking agents, but they exhibit poor mechanical performance and reduced long-term stability (Chamkouri et al., 2021).

In chemical hydrogels, the polymer networks are covalently crosslinked, providing enhanced mechanical strength and structural stability. These hydrogels are widely used for load-bearing applications, tissue engineering, and wound dressing applications (Picchioni and Muljana, 2018; Maitra et al., 2014). The preparation of chemical hydrogels is relatively complex and may involve toxic crosslinking agents or initiators. As they are usually less responsive to external stimuli not used for the fabrication of stimuli-responsive hydrogels. Hybrid hydrogels combine physical and chemical crosslinking to balance mechanical stability with stimulus-responsiveness. They can respond to environmental triggers while maintaining structural integrity, offering tunability in mechanical, swelling, and functional properties. Examples include PVA–alginate, gelatin–PEG, and chitosan-based chemically reinforced hydrogels. While hybrid hydrogels provide enhanced performance for smart drug delivery, tissue scaffolds, and wound healing, their synthesis is more complex, and careful selection of crosslinkers is essential to achieve the desired properties (Kasai et al., 2023).

Due to their natural abundance, low cost, excellent biocompatibility, inherent nontoxicity, and renewable origin, hydrogels derived from polysaccharide materials have attracted considerable research interest in recent times. The presence of reactive functional groups such as hydroxyl ($-\text{OH}$), carboxyl ($-\text{COOH}$), and amine ($-\text{NH}_2$) in their molecular backbone enables chemical modification and functionalisation. These intrinsic features make polysaccharides highly suitable for the design and development of advanced functional materials, particularly in biomedical and environmental applications. Polysaccharide-based biopolymers such as alginate, chitosan, cellulose, hyaluronic acid, and agarose are widely used natural

polymers for the fabrication of hydrogels (Dave and Gor, 2018; Mittal et al., 2013; Li and Lin, 2021).

Hydrogels formed via single chemical or physical crosslinking often suffer from poor mechanical strength and limited energy dissipation, rendering them soft, brittle, and weak (Duan and Zhang, 2017). Such limitations significantly constrain the practical applications of polysaccharide-based hydrogels. Over the past few decades, extensive research efforts have been devoted to improving the mechanical strength of hydrogels by designing innovative network architectures and introducing diverse energy dissipation mechanisms, including double-network (DN) hydrogels (Huang, Li, Luo, Gao, Mao and Li, 2021), nanocomposite hydrogels (Wu, Zhang, Zhang, Li, He, Qin and Yang, 2022), sliding-ring hydrogels (Noda et al., 2014), hydrophobic association hydrogels (Jiang et al., 2019), and tetra-arm polymer hydrogels (Asai et al., 2012). Among these, double-network hydrogels composed of interpenetrating or semi-interpenetrating polymer networks have been shown to exhibit significantly higher strength and toughness compared to either individual network (Liang et al., 2017; Xu, Jerca and Hoogenboom, 2021).

Gong *et al.* first developed a chemically cross-linked poly(2-acrylamido-2-methyl-propanesulfonic acid) (PAMPS)/polyacrylamide (PAAm) double-network hydrogel through a two-step continuous free-radical polymerization process. In this design, PAMPS formed the first network while PAAm constituted the second, significantly enhancing the mechanical properties, with a toughness of 10^2 – 10^3 J m⁻², tensile stress of 1–10 MPa, and strain of 1000–2000% (Gong et al., 2003). In this context, the double-network strategy that combines chemical and physical crosslinking offers a promising approach to the design of polysaccharide-based hydrogels with enhanced mechanical strength, toughness, and long-term stability (Li and Lin, 2021; Zhang, Shi and Zhou, 2023). This approach harnesses the synergistic effect of two interpenetrating polymer networks to significantly enhance mechanical strength and durability, making the hydrogels suitable for a

broad spectrum of demanding applications (Wang, Chen, Chen and Wei, 2023).

Yang and Yuan (2019) developed a Li^+ /agar/PAM ionic double-network hydrogel using a rapid one-pot method. The double-network architecture imparts exceptional mechanical strength and stretchability ($> 1600\%$), along with robust ionic conductivity, making it a promising candidate for soft, wearable electronics (Yang and Yuan, 2019). J. Zhu et al. reported a double-network PAAm-Guar gum hydrogel whose unique architecture markedly enhanced its mechanical performance. The DN hydrogel exhibited a fracture stress of 843 kPa and an extensibility of 1400%, demonstrating that the synergistic interaction between the Guar gum and PAAm networks significantly strengthens the material. Additionally, the hydrogel showed self-recovery under small deformations and self-reinforcement under large deformations, highlighting the mechanical advantages conferred by the double-network design (Zhu et al., 2016).

Chang et al. developed double-network hydrogels combining natural cellulose and synthetic poly(N-isopropylacrylamide) (PNIPAAm) to achieve enhanced mechanical and thermal performance. In their design, the cellulose hydrogel, formed by chemical crosslinking in a NaOH/urea aqueous solution, served as the primary network, while the secondary PNIPAAm network was introduced via in situ polymerization and crosslinking. This DN architecture significantly improved the hydrogel's toughness, elasticity, and resilience, while preserving its inherent thermoresponsive behaviour (Chang et al., 2011). Ang et al. fabricated an ionically-covalently cross-linked chitosan/polyacrylamide (CS/PAAm) double-network hydrogel, demonstrating the effectiveness of hybrid crosslinking in enhancing mechanical performance. The resulting hybrid ionic-covalent DN hydrogel exhibited superior mechanical strength, high elasticity, and remarkable fracture energy due to efficient energy dissipation (Yang et al., 2018).

Anionic polysaccharides, including alginate (Li, Chen, Yang and Zhang, 2023), pectin (Abdullah et al., 2018), carrageenan (Álvarez-Viñas et al., 2022), hyaluronic

acid (Burdick and Prestwich, 2011; Luo et al., 2023), and xanthan gum (Njuguna and Schoenherr, 2022), are commonly employed in hydrogel fabrication due to the presence of negatively charged functional groups such as carboxylate and sulfate moieties. These functional groups enable the formation of hydrogel networks through ionic crosslinking with multivalent cations or through covalent modification. The availability and reactivity of these groups make anionic polysaccharides versatile building blocks for constructing hydrogels via various crosslinking strategies.

Wang et al. (2019) synthesized alginate–polyacrylamide hydrogels via a one-pot method using multivalent ionic and covalent crosslinking. Hydrogels crosslinked with trivalent cations (Fe^{3+} , Al^{3+}) exhibited superior mechanical strength compared to those with divalent cations (Ca^{2+} , Ba^{2+}). Increased ionic or chemical crosslinker concentrations enhanced compressive properties up to an optimal point. These tough hydrogels show potential for biomedical applications such as load-bearing tissues (Wang et al., 2019). Sun et al. (2019) developed a multifunctional hydrogel-based strain sensor using ionically and covalently crosslinked networks of polyacrylamide, sodium alginate, and Ca^{2+} ions. The hydrogel exhibits excellent mechanical properties, broad sensing range (20–800% strain), high transparency, biocompatibility, and self-recovery. It enables accurate, real-time monitoring of complex human motions, offering strong potential for wearable and eco-friendly strain-sensing devices (Sun et al., 2019).

Fan et al. (2020) developed a dual physically crosslinked carrageenan-polyacrylamide (PAAm/CAR) hydrogel with excellent toughness, conductivity, and self-healing ability. The hydrogel demonstrated strong mechanical properties, fast recovery, and strain sensitivity, making it suitable for detecting both large-scale human motions and subtle physiological signals in wearable sensing applications (Fan et al., 2020). Zhang et al. (2020) developed a dual physically crosslinked CMC– Fe^{3+} /PAAm hydrogel with excellent mechanical strength, toughness, and

self-recovery, enabled by Fe^{3+} coordination and hydrophobic interactions. The hydrogel exhibits high conductivity (1.82 S/m), strong strain sensitivity (gauge factor = 4.02), and fast response, making it a promising material for flexible and stretchable strain sensors to monitor human motion (Zhang, Wu, Qin, Sun, Zhang, Yu, Yao, He, Dong, Yao et al., 2020).

Zhu et al. (2020) developed a transparent, ionic, semi-interpenetrating network hydrogel composed of sodium carboxymethylcellulose (CMC) and polyacrylamide (PAAm). The hydrogel exhibits excellent transparency (98.2%), strong adhesion, high sensitivity (gauge factor = 3.15), and repeatability over 500 cycles. Its real-time response and ability to detect both subtle and large deformations make it ideal for wearable strain sensors in human motion monitoring and soft robotics (Zhu et al., 2020). Huang et al. (2020) developed a multifunctional electronic skin (e-skin) hydrogel composed of a covalently cross-linked polyacrylamide (PAAm) network and a coordinatively cross-linked xanthan gum (XG)/ Fe^{3+} network. The hydrogel exhibits tunable mechanical strength, high stretchability, and sensitive strain responsiveness, along with excellent adhesion, antibacterial properties, and biocompatibility. It functions effectively as a wearable sensor for detecting human motion and physiological signals, with potential applications in wound healing, soft robotics, and next-generation wearable electronics (Huang, Liu, Chi, Jiang, Xu, Qu, Zhao, Li, Chen, Chen et al., 2021).

Among these anionic polysaccharides, pectin is particularly noteworthy due to its natural abundance and structurally intricate composition. It is primarily extracted from agricultural by-products such as apple pomace and citrus peels. Its molecular backbone consists mainly of D-galacturonic acid (GalA) units connected via α -(1 $\rightarrow$ 4)-glycosidic linkages. A fraction of the carboxyl groups along the polygalacturonic acid chain are esterified with methyl groups, forming the basis for classifying pectin into two main types: high methoxyl (HM) pectin and low methoxyl (LM) pectin. HM pectins primarily stabilize their structure through

hydrogen bonding and hydrophobic interactions, while LM pectins form networks via ionic crosslinking with divalent cations such as calcium ions (Ca^{2+}), resulting in a more robust and stable gel network (Liu et al., 2007; Tummalapalli et al., 2016; Jantrawut et al., 2013).

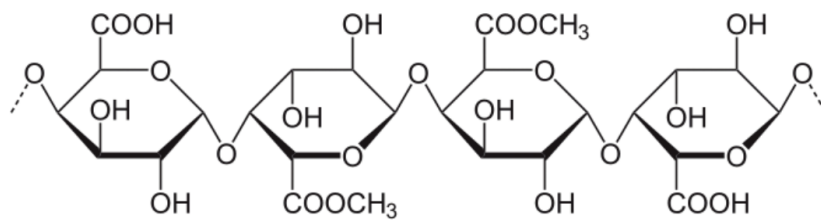


Figure 1.1: Chemical structure of pectin

The “egg-box” model describes the ionic crosslinking mechanism in low methoxyl (LM) pectin when exposed to divalent cations like calcium ions (Ca^{2+}). In this model, the negatively charged carboxyl groups on adjacent pectin chains interact with Ca^{2+} ions, forming junction zones. These zones are formed by the alignment of two antiparallel polygalacturonic acid chains, where Ca^{2+} ions fit into spaces between them, similar to eggs in an egg carton. This organized binding stabilizes the network, leading to the formation of a three-dimensional gel. Rui Niu et al. developed a hybrid pectin- Fe^{3+} /polyacrylamide DN hydrogel using a simple two-step strategy, in which Fe^{3+} ions were incorporated into the pectin network to form strong yet reversible ionic crosslinks. This design resulted in a hydrogel exhibiting high tensile strength (0.9 MPa), large elongation at break (1300%), and excellent stiffness (elastic modulus ≈ 1.46 MPa), along with superior toughness (fracture energy ≈ 3785 J/m²). Additionally, the hydrogel demonstrated remarkable fatigue resistance, notch insensitivity, recoverability, and a water absorption capacity of 85%. The combination of reversible Fe^{3+} -pectin complexation and covalently crosslinked polyacrylamide network endowed the material with both strength and resilience, making it a promising candidate for load-bearing tissue repair and other biomedical applications (Niu et al., 2017). Shengping Dai et al.

developed a poly(acrylic acid) (PAA)–pectin double-network hydrogel reinforced through dynamic hydrogen bonding and metal–carboxylate coordination. The hydrogel exhibited high stretchability (1214%), rapid self-healing (94% within 2 h), and excellent recovery, making it suitable for flexible pressure and strain sensors in electronic skin applications (Dai et al., 2019). A tough physical hydrogel was developed by Zhi Wei Kenny Low et al., composed of poly(vinyl alcohol) (PVA) and ionic pectin (CaP), forming an interpenetrating network. The hydrogel showed a threefold increase in tensile modulus and fracture energy compared with pristine PVA. Its reversible physical crosslinks enabled heating-induced network dissociation, and the inclusion of pectin improved cell adhesion and proliferation, with implantation studies confirming biocompatibility and tissue conformity (Low et al., 2020).

In recent times, there has been growing interest in microbial polysaccharides due to their diverse functional capabilities, extensive industrial uses, and their ability to be produced sustainably on a commercial scale. Gellan gum (GG) is a natural, biocompatible exopolysaccharide produced through microbial fermentation by the bacterium *Sphingomonas elodea* (formerly *Pseudomonas elodea*, ATCC 31461), which is commonly associated with the aquatic plant *Elodea canadensis*.

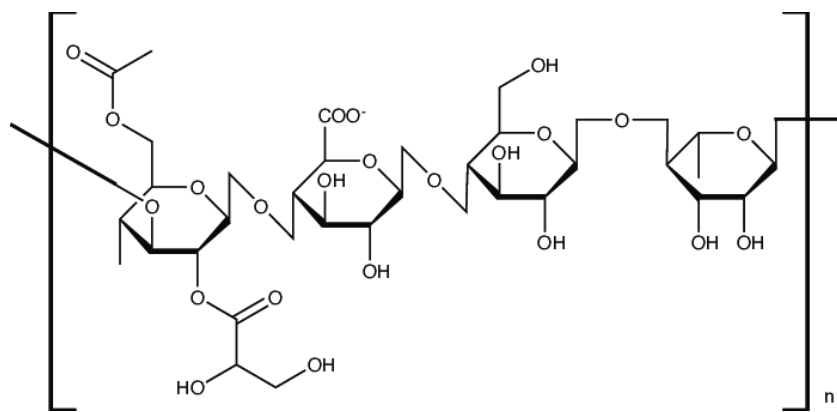


Figure 1.2: Chemical structure of Gellan gum

Gellan gum (GG) is a linear, anionic, high molecular weight polysaccharide (500 kDa), composed of repeating tetrasaccharide units. Each unit consists of

two glucose residues, one glucuronic acid, and one rhamnose residue, arranged in the following sequence: 1,3- β -D-glucose (Glc) – 1,4- β -D-glucuronic acid (GlcA) – 1,4- β -D-glucose (Glc) – 1,4- α -L-rhamnose (Rha). Gellan gum (GG) is available in two primary forms. The natural form, which retains its high acyl content, is commonly referred to as high acyl gellan gum. The second form, known as low acyl gellan gum, is derived by removing the acyl groups. Both the acetylated and deacetylated forms of gellan gum are capable of gelation through a thermally induced transition from a random coil conformation at high temperatures to an ordered double-helix structure upon cooling. In gellan gum, ionic crosslinking takes place when divalent cations (e.g., Ca^{2+}) form bridges between carboxylate groups of glucuronic acid residues on adjacent polymer chains, facilitating double helix aggregation and stabilizing the three-dimensional gel network (Verma et al., 2012; Abdl Aali and Al-Sahlany, 2024; Bacelar et al., 2016).

Liu et al. (2020) developed a gellan gum–polyacrylamide hybrid hydrogel with high stretchability, notch-insensitivity, and self-healing capability. The physically cross-linked gellan gum network, reinforced by hydrogen bonding and ionic associations, acted as sacrificial bonds, while thermoreversible gelation enabled recoverability. The hydrogel showed excellent strain sensitivity and was effectively used as a flexible strain sensor for monitoring both large and subtle human motions (Liu et al., 2020). An interpenetrating network hydrogel consisting of gellan gum and polyacrylamide was developed by W. Li et al. using chemical crosslinking combined with Mg^{2+} ion immersion. The incorporation of Mg^{2+} ions and the dual-network structure significantly enhanced the hydrogel’s mechanical performance, increasing tensile strength from 86 to 392 kPa, elongation at break from 84 to 231%, and crosslinking density from 4.3 to 7.2 mol/m³ compared with pure GG hydrogel. The hydrogel also shows potential for skin wound healing applications (Li et al., 2021).

1.2 Conductive hydrogels

Conductive hydrogels have emerged as promising materials for flexible electronics due to their excellent conductivity and mechanical flexibility (Xu et al., 2020). They are hybrid materials that combine the mechanical softness and flexibility of hydrogels with the electrical functionality of conductive materials. Conductive hydrogels are fabricated by incorporating conductive materials such as metals, conductive carbonaceous nanomaterials, conductive polymers, or ions into the hydrogel matrix (Liu, Omar, Li, Zhou, Zhang, Yan, Haick, Guo, Someya and Wang, 2025).

1.2.1 Fabrication of conductive hydrogels

Metals have gained considerable attention in the fabrication of conductive hydrogels due to their high electrical conductivity. Because of their high conductivities, unique optical and catalytic properties, silver and gold nanoparticles have been widely employed for the fabrication of metal-based conductive hydrogels (Rong et al., 2018; Wang et al., 2020). However, inorganic metal particles often undergo sedimentation and aggregation within polymer matrices, which affects the mechanical and electrical properties of the hydrogel. Moreover, the presence of metals interferes with the polymerisation process, thereby deteriorating the mechanical properties of hydrogels. The intrinsic incompatibility between the metallic component and the hydrogel also restricts the practical applications of metal-based hydrogels (Li et al., 2022).

Due to their excellent conductivity, mechanical properties, and environmental stability, carbon-based materials like carbon nanotubes (CNTs), graphene, graphene oxide (GO), and reduced graphene oxide (rGO) have been widely employed for the fabrication of conductive hydrogels (Li et al., 2017; Zhang and Zhao, 2009). Carbon-based materials commonly used in the fabrication of conductive hydrogels, such as carbon nanotubes (CNTs) and graphene, possess large specific

surface areas and high aspect ratios. Hence, a low concentration of these materials is sufficient to impart electrical conductivity to hydrogels (Liu et al., 2018). As a result of their hydrophobic nature and low solubility, the incorporation of these materials into hydrogel matrices is challenging. Moreover, weak interfacial interactions between these materials and hydrogels further limit their potential applications (Wang et al., 2020; Sun et al., 2020).

Conductive polymers have been widely recognized as promising materials for the fabrication of conductive hydrogels. Due to their ease of fabrication and tunable electrical properties, conductive polymers such as polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene), and poly(styrene sulfonate) (PEDOT:PSS) are commonly used for the fabrication of conductive polymer-based hydrogels. Compared with conventional electronically conductive materials, conductive polymers provide superior mechanical flexibility, better biocompatibility, and improved solubility, which favors their integration into hydrogel systems (Wang et al., 2016; Stejskal and Bober, 2018).

1.2.2 Ionic conductive hydrogels

Direct incorporation of soluble inorganic salts into the hydrogel matrix is a common approach for fabricating ionic conductive hydrogels. The high water content and microporous structure of hydrogels enable ions to move freely across the network, resulting in efficient ionic conductivity (Mo et al., 2025; Liu, Wang, Fu, Wang, Zhan, Sheng, Yang and Liu, 2025). In contrast to electron conductive hydrogels (ECHs), which rely on electron migration, ionic conductive hydrogels rely on mobile ions within the hydrated polymer network (Liang et al., 2023; He et al., 2024). This ion-based conduction mechanism offers distinct advantages in terms of flexibility, transparency, and compatibility with biological systems (Chen et al., 2021; Dechiraju et al., 2022).

With rapid advancements in flexible electronic devices, ionic-based conductive

hydrogels have emerged as versatile materials for various flexible electrochemical solid-state ionic devices. These include applications in solid-state batteries, supercapacitors, solid oxide fuel cells, and a range of wearable sensors (Liu, Fu, Jin, Cheng, Li, Zhao, Liu and Tian, 2025; Fang et al., 2025). From a macroscopic perspective, hydrogels resemble solids but exhibit liquid-like characteristics at the microscopic level. Moreover, hydrogels provide abundant pathways for ion migration as a result of their 3D network structure and continuous water phase. This unique structure enables the development of highly effective ionic-conducting hydrogel materials.

On the basis of the role of ions, ion-conductive hydrogels are classified into free ion-based and crosslinked ion-based hydrogels. In free-ion-based hydrogels, the ions act as mobile charge carriers without contributing to the structural framework of the hydrogel network. In contrast, crosslinked ion-based hydrogels employ multivalent ions that serve a dual function. These ions not only enable ionic conductivity but also act as ionic crosslinkers, strengthening and stabilizing the hydrogel structure. This dual function improves both the mechanical integrity and the conductive performance of the hydrogel, making crosslinked ion-based systems particularly promising for high-performance applications such as strain sensing and flexible electronics.

Crosslinked ion-based ionic conductive hydrogels offer several advantages compared to free ion-based hydrogels. Incorporation of multivalent ions as crosslinkers enhances the mechanical strength of the hydrogel network. As a result, the material exhibits better structural stability along with superior stretchability, toughness, and resistance to mechanical deformation. In contrast, free ion-based hydrogels often suffer from poor mechanical integrity due to the absence of additional crosslinking reinforcement. Crosslinked ion-based systems exhibit improved long-term stability, as immobilized crosslinking ions reduce the risk of ion leaching and maintain consistent ionic conductivity over time. The dual role of crosslinked ions,

as both charge carriers and structural crosslinkers, allows for better integration of mechanical and electrical performance, making these hydrogels more suitable for demanding applications such as wearable sensors, soft robotics, and bioelectronics. Additionally, crosslinked ion-based hydrogels can often be tailored to achieve tunable properties by adjusting the type and concentration of multivalent ions, offering greater design flexibility compared to systems relying solely on free ion doping. Certain natural polymers, such as agar (Yang and Yuan, 2019) and gelatin (Fu et al., 2024), which form hydrogels through physical means, are examples of free ion-based hydrogels, whereas alginate, κ -carrageenan, and hyaluronic acid (HA), which require ionic crosslinking to form stable hydrogels, are examples of crosslinked ion-based hydrogels (Tang et al., 2020).

Electron-conductive hydrogels (ECHs) fabricated using conductive polymers, metals, or carbon-based materials are generally opaque. In contrast, ion-based conductive hydrogels are typically transparent, as they conduct electricity through mobile ions without incorporating opaque conductive fillers. Their transparency allows for visual inspection of both the internal structure of the device and the underlying skin, which is essential for real-time monitoring and diagnostic functions (Periyasamy et al., 2025). Consequently, ionic conductive hydrogels have attracted significant research interest. This combination of conductivity and transparency makes ionic conductive hydrogels a promising material. They are particularly well-suited for next-generation optoelectronic, bio-integrated, and wearable systems where both electrical performance and optical clarity are required.

Ionic conductive hydrogels are highly valued for their biocompatibility and environmental sustainability, making them ideal for biomedical applications, wearable devices, and green technologies. Their water-based composition closely mimics biological tissues, and the ionic components—typically benign salts such as Na^+ , K^+ , or Ca^{2+} —are non-toxic, minimizing the risk of adverse reactions and enabling safe interfacing in bioelectronics, tissue engineering, and biosensing. Environmen-

tally, these hydrogels are more sustainable than many synthetic conductive materials: they reduce reliance on hazardous solvents, are often made from abundant, biodegradable natural polymers (e.g., alginate, agar, hyaluronic acid), and can be recycled or degraded in natural environments. This combination of performance, biocompatibility, and environmental sustainability positions ionic conductive hydrogels as a promising alternative to conventional electronics that rely on heavy metals, non-renewable resources, or toxic chemicals, supporting the development of next-generation sustainable and high-performance devices (Wu, Luo, Cuthbert, Shokurov, Chu, Feng and Menon, 2022).

Ionic conductive hydrogels (ICHs) exhibit exceptional flexibility and stretchability, as their conductivity relies on mobile ions rather than rigid conductive networks. Unlike electronically conductive hydrogels (ECHs), which can become brittle when filler networks break under strain, ICHs maintain continuous ionic transport even under large deformations, making them highly suitable for flexible electronics applications. The stretchability and mechanical performance of ICHs can be tuned by adjusting ion concentration, polymer network structure, or crosslinking density, allowing customisation for specific applications. Their ionic conductivity is highly controllable, depending on ion type and concentration, polymer network characteristics, crosslinking degree, and environmental factors such as pH and temperature, enabling precise optimization for sensors, actuators, and energy storage devices. Moreover, ICHs perform reliably in hydrated or moist conditions, and their capacitive, non-Faradaic charge transport reduces the risk of unwanted electrochemical reactions, further enhancing their suitability for bio-integrated and wearable applications.

Despite their promising functional properties, ionic conductive hydrogels (ICHs) exhibit notable limitations in thermal stability and long-term performance, which restrict their practical application in dynamic or harsh environments. The ionic conductivity of these materials is inherently dependent on the presence of water,

which serves as the medium for ion transport. Consequently, ICHs are highly sensitive to temperature fluctuations. At sub-zero temperatures, the aqueous phase within the hydrogel network is prone to freezing, leading to crystallization of water molecules. This phase transition significantly hinders ion mobility and reduces the hydrogel’s conductivity, flexibility, and mechanical integrity (Lei et al., 2023; Li et al., 2022). Conversely, at elevated temperatures, water loss via evaporation becomes predominant. As the water content diminishes, the ionic conductivity decreases due to reduced ion mobility, and the hydrogel matrix may undergo shrinkage, loss of elasticity, and structural degradation. These temperature-dependent changes limit the effective operational window of ICHs, typically confining them to environments near ambient conditions.

Long-term stability of ICHs is also significantly influenced by water loss over time. Since ionic conduction depends on the continuous presence of free water molecules for ion transport, gradual evaporation under ambient or operational conditions leads to a steady decline in conductivity. Additionally, water evaporation can cause structural contraction, increased stiffness, and reduced elasticity of the hydrogel matrix, ultimately degrading both the mechanical and electrical performance. Therefore, the susceptibility to dehydration poses a major limitation for the prolonged use of ICHs in real-world applications, particularly in open-air or dry conditions (Lee et al., 2025; Yang et al., 2021). Improving the environmental stability of hydrogels, particularly their freeze-tolerance and resistance to dehydration, is critical for expanding their applicability in wearable electronics, biomedical devices, and soft robotics.

The long-term stability of hydrogels can be improved by sealed packaging or encapsulation (Herrmann et al., 2021; Cai and Yu, 2025). This method typically employs moisture-impermeable materials such as silicone elastomers and polyurethane films. This encapsulation not only prevents water evaporation but also protects the hydrogels from contaminants and mechanical damage. However,

these additional barriers increase the thickness and reduce the flexibility and biocompatibility of the hydrogels. Moreover, the complexity and cost of achieving reliable, high-quality encapsulation can hinder large-scale or low-cost production of hydrogel-based devices. These limitations restrict the practical application of encapsulated hydrogels, particularly in flexible electronics.

The temperature tolerance of the hydrogel electrolytes can be enhanced by increasing the concentration of dissolved salts (Jiang et al., 2025; Zhang et al., 2019). However, these high concentrations of salts lead to undesirable reactions and material erosion (Su et al., 2014; Deng et al., 2018). This results in the deterioration of the electrochemical performance of the material. This limits the long-term practical application of hydrogels in extreme environmental conditions.

The long-term stability and temperature tolerance of hydrogels can be enhanced by the incorporation of ionic liquids (ILs) (Zang et al., 2017). ILs are low-melting salts with negligible vapor pressure, which reduces water evaporation and improves drying resistance (Ghorbanizamani et al., 2022). Their inherent ionic conductivity ensures efficient ion transport, while their thermal and electrochemical stability prevents ice formation, enabling reliable performance even under sub-zero conditions (Jian et al., 2021). However, the high cost, potential cytotoxicity, and complex synthesis of some ILs can limit their practical use, especially in large-scale or biomedical applications (Lu et al., 2020). Moreover, their high viscosity and reduced ionic conductivity at sub-zero temperatures restrict their effectiveness in fabricating hydrogels with temperature tolerance (Na et al., 2017; Feng et al., 2018).

1.3 Organogel

Due to their excellent anti-freezing and anti-dehydration properties, organogels have gained significant attention in recent years (Lee et al., 2025; Yadav et al., 2024). These hybrid materials combine the advantages of traditional hydrogels

with enhanced environmental stability provided by organic solvents (Zhao et al., 2023; Zhao, Wang, Feng, Yang, Wang, Zhang, Zhang and You, 2025). Solvents such as glycerol (Aggarwal et al., 2025; Wang, Li, Li, Sun, Li, Murto, Wang and Xu, 2025), ethylene glycol (Xu et al., 2025; Ge et al., 2025), dimethyl sulfoxide (DMSO) (Ye et al., 2025; Ramirez et al., 2025), and sorbitol (Wei et al., 2025; Zheng et al., 2025) are commonly used for the fabrication of organogels. These solvents can form extensive hydrogen bonding interactions with the functional groups within the polymer networks of the hydrogels. This enables them to function as anti-freezing agents while simultaneously suppressing water evaporation from the polymer network. This helps the hydrogels maintain their mechanical flexibility and functional performance under extreme environmental conditions.

There are two widely accepted methods for the fabrication of organogel. The first one is a one-step in-situ gelation process carried out in an organic–water binary solvent system, allowing uniform dispersion of the organic component during network formation (Hu et al., 2018; Rong et al., 2017; Shi et al., 2017). The second method is a post-synthesis solvent-exchange process. In this approach, a preformed hydrogel is immersed in an organic solvent, allowing gradual replacement of water by the organic solvent (Lou et al., 2019; Zhou et al., 2018). The solvent exchange method for fabricating organogels offers several advantages over in-situ gelling, particularly in terms of versatility and process simplicity. This method allows conventional hydrogels to be transformed into organogels without altering the original polymerization conditions, making it broadly compatible with a wide range of hydrogel systems. This approach avoids interference of organic solvents with gelation chemistry, which can be problematic in in situ methods. Additionally, solvent exchange enables controlled incorporation of organic solvents by tuning parameters such as soaking time and solvent concentration, allowing for the precise adjustment of anti-freezing and anti-dehydration properties. Since the hydrogel network is already established, this method typically preserves the

original morphology and mechanical integrity of the material (Li, Deng and Zhou, 2020; Tang et al., 2024).

Q. Rong et al. reported an anti-freezing conductive organogel consisting of poly(vinyl alcohol) (PVA) networks, PEDOT:PSS, and a H₂O/ethylene glycol (EG) solvent system. The EG facilitated the formation of hydrogen bonds and dense crystalline domains, conferring enhanced mechanical strength. Due to the anti-freezing property of the H₂O/EG binary solvent, the hydrogel maintained flexibility and strain-sensitive performance at temperatures as low as -40°C (Rong et al., 2017). Wu et al. (2019) developed anti-freezing and anti-drying organogels using a solvent-replacement method with ethylene glycol/glycerol, enabling stable, ultra-stretchable, and self-healing strain sensors. These sensors show a high gauge factor (6), operate over a wide strain range (0.5–950%), and remain functional from -18°C to 25°C and even after nine months in ambient air, offering a promising approach for wearable electronics (Wu et al., 2019).

Cheng et al. (2019) developed a flexible, anti-freezing organogel strain sensor using Fe³⁺-crosslinked carboxymethyl cellulose (CMC) and polyacrylamide in a water/ethylene glycol system. The sensor exhibited excellent mechanical strength (fracture energy of 5238 kJ m^{-3}), high sensitivity (gauge factor = 1.4 for 0–30% strain), and a rapid response time (0.98 s), enabling detection of subtle human motions. This CMC-based organogel holds strong potential for next-generation wearable and bioelectronic applications (Cheng et al., 2019). J. Li et al. prepared a xanthan gum-Fe³⁺/polyacrylamide-glycerol (XG-Fe³⁺/PAAm-Gl) organogel via in situ polymerization and solvent-exchange methods. The xanthan gum network introduced covalent crosslinking, ionic coordination, and hydrogen bonding, resulting in ultra stretchability (1769%) and high tensile strength (1.5 MPa). In addition, the water–glycerol binary solvent provided excellent anti-drying and anti-freezing properties, enabling the hydrogel to maintain stretchability ($> 500\%$), good conductivity, and transparency even at -40°C (Yu et al., 2021).

A poly(vinyl alcohol)/sodium alginate/poly(ethylene glycol) (PVA/SA/PEG) organogel electrolyte was fabricated by Hu. et. al. via a freeze–thaw process followed by soaking in saturated NaCl solution. The PEG component enhanced the hydrogel’s mechanical properties, recyclability, and self-healing ability, while the combination of PEG and NaCl conferred low-temperature resistance. A flexible supercapacitor fabricated using this organogel as the gel electrolyte demonstrated stable performance even at -15°C (Hu et al., 2021). X. Li et al. developed a flexible supercapacitor based on a PAMPS/PAAm double-network organogel electrolyte (OHE) soaked in LiCl/ethylene glycol. The OHE exhibited ionic conductivities of 1.9 mS cm^{-1} at -20°C and 22.9 mS cm^{-1} at 25°C , demonstrating broad temperature adaptability (-20 to 80°C) and excellent mechanical robustness. Moreover, its anti-drying stability and enhanced interfacial compatibility ensured remarkable durability under high-temperature conditions (Li, Lou, Wang, Sun, Li and Liu, 2020).

N. Lu et al. fabricated an organogel electrolyte by partially replacing water in a hydroxypropyl cellulose/poly(vinyl alcohol) (HPC/PVA) hydrogel with a LiClO_4 water–glycerol mixture. The incorporation of glycerol and inorganic salts effectively inhibited ice formation at subfreezing temperatures. A flexible supercapacitor assembled with this anti-freezing organogel electrolyte exhibited excellent mechanical strength and electrochemical stability even under low-temperature conditions (Lu et al., 2020). Zhu et al. developed a hybrid crosslinking strategy to prepare a stretchable and transparent sodium alginate–poly(acrylamide) (SA–PAAm) hydrogel, which was further converted into an organogel through solvent replacement. The hybrid physical–covalent double-network structure, combined with hydrogen bonding interactions introduced by the glycerol–water binary solvent, endowed the SA–PAAm organogel (SPOH) with remarkable properties, including anti-freezing capability (-20°C), stability (> 2 days), high transparency, ultrastretchability (1600%), and high ionic conductivity (17.1 mS cm^{-1})

(Zhu et al., 2022).

Despite considerable advances in conductive hydrogels for flexible electronics, their practical application is still limited by poor mechanical stability, dehydration, and freezing at sub-zero temperatures. Although double-network and IPN hydrogels have demonstrated improved performance, studies on pectin- and gellan gum-based IPN organogels remain limited. In addition, systematic investigations on the influence of glycerol and ethylene glycol on the structural, mechanical, thermal, and ionic conductive properties of such organogels are limited. Therefore, the development of mechanically robust, anti-freezing, and ionically conductive PAAm–pectin and PAAm–gellan gum organogels is of significant research interest for flexible electronic applications.

Both pectin and gellan gum are anionic polysaccharides known for their biocompatibility, renewability, and ability to form ionic crosslinks with multivalent metal ions, which can significantly enhance the toughness and self-recovery behaviour of polymer networks. Integrating these polysaccharides with PAAm can create hybrid organogels that combine the elasticity and strength of synthetic polymers with the functional versatility of natural polymers. Furthermore, the introduction of organic solvents such as glycerol or ethylene glycol is expected to impart anti-freezing and anti-drying properties, expanding their potential use in flexible electronics, soft actuators, and biomedical applications under extreme environmental conditions. Thus, exploring pectin and gellan gum as functional natural components provides a sustainable and effective route toward next-generation high-performance organogels. Based on the available literature, no studies have been reported on the fabrication of PAAm–pectin and PAAm–gellan gum interpenetrating network (IPN) organogels, highlighting the novelty and significance of the proposed research.

1.4 Scope and objective

Ionic conductive hydrogels are widely recognized as promising materials for flexible and bioelectronic devices because their soft, water-rich networks provide good ionic conductivity and mechanical compliance. However, their practical applications are restricted by poor environmental tolerance. At sub-zero temperatures, freezing of the aqueous phase severely suppresses ion mobility and compromises flexibility, while at elevated temperatures or during long-term storage, water evaporation leads to dehydration, shrinkage, and a progressive loss of conductivity and mechanical performance. These limitations can be addressed by partially replacing water in the hydrogel network with suitable organic solvents, which can inhibit ice formation and reduce evaporation, thereby improving anti-freezing and anti-drying stability.

Conventional single-network hydrogels typically exhibit low mechanical strength and limited resistance to deformation. Incorporation of double-network architectures, particularly those integrating a synthetic polymer network with a polysaccharide based network, offers an effective strategy to overcome these limitations. In such systems, the polysaccharide network provides excellent biocompatibility, ionic crosslinking capability, and efficient energy dissipation through reversible interactions, while the synthetic polymer network imparts structural integrity, elasticity, and mechanical robustness. This synergistic combination enables the development of hydrogels with significantly enhanced strength, toughness, and durability compared to single-network counterparts.

The current research work focuses on the development of interpenetrating polymer network (IPN) hydrogels comprising a synthetic polymer, polyacrylamide (PAAm), and natural polymers such as pectin and gellan gum. Pectin and gellan gum were selected due to their biocompatibility, biodegradability, and ability to form strong hydrogen bonding and ionic crosslinking interactions, which improve the mechanical strength and self-recovery behaviour of organogels. Their renew-

able nature also makes them suitable for sustainable material development. Moreover, only limited studies are available on pectin- and gellan gum-based organogels, highlighting the need for further investigation and the novelty of the present work. In these systems, the incorporation of calcium ions serves a dual function by forming ionic crosslinks within the polysaccharide network and simultaneously providing ionic conductivity. Furthermore, the incorporation of organic solvents such as glycerol and ethylene glycol is employed to enhance environmental tolerance, imparting anti-freezing and anti-drying properties while maintaining mechanical flexibility and conductive performance.

The objectives of the present research work are as follows:

1. To fabricate PAAm–pectin and PAAm–gellan gum (PAAm–GG) hydrogels and their corresponding organogels.
 2. To perform structural and morphological characterization of the prepared hydrogels and organogels.
 3. To investigate the effect of biopolymer content, calcium ion concentration, and organic solvent incorporation on the mechanical properties of the hydrogels.
 4. To evaluate the viscoelastic behaviour of the gels using rheological studies.
 5. To study the anti-freezing and anti-drying properties of the organogels under different environmental conditions.
 6. To examine the influence of biopolymer type, calcium ion concentration, and organic solvent content on the ionic conductivity of the gels.
 7. To understand the low-temperature ionic conductivity behaviour of the developed organogels.
-

Chapter 2

Materials and Methodologies

This chapter provides a concise overview of the materials, synthesis routes, and characterisation protocols used throughout the study.

2.1 Materials

The materials used in this study included Acrylamide (AAm), Pectin, Gellan gum (GG), Ammonium persulfate (APS), N, N'-Methylenebisacrylamide (MBAAm), N, N, N', N'-Tetramethylethylenediamine (TEMED), Calcium chloride (CaCl_2), Ethylene glycol and Glycerol. All reagents were of high-purity analytical grade and were procured from Merck Life Science Pvt. Ltd., Mumbai, India. Acrylamide, pectin, gellan gum, ammonium persulfate, MBAAm, and TEMED were used as the primary reagents for hydrogel synthesis. Calcium chloride was employed as the ionic crosslinking agent, while ethylene glycol and glycerol were used for solvent replacement during organogel formation. Deionised water, obtained from a Milli-Q water purification system, was used as the solvent throughout all experiments.

2.2 Preparation of PAAm hydrogel

The polyacrylamide hydrogel was synthesised via free-radical polymerisation of acrylamide monomers in an aqueous medium. Acrylamide (4 g) was dissolved in 40 mL of deionised water under continuous magnetic stirring at 500 rpm for 2

h at room temperature ($25 \pm 2^\circ\text{C}$) to obtain a clear and homogeneous precursor solution. N, N'-Methylenebisacrylamide (0.02 mol% relative to acrylamide) was incorporated as the crosslinking agent, while ammonium persulfate (0.1 mol% relative to acrylamide) served as the radical initiator, and N, N, N', N'-Tetramethylethylenediamine (40 μL) was added as the accelerator. The precursor solution was subsequently transferred into petri dishes (90 mm diameter), and polymerisation was carried out in a thermostatically controlled oven at 50°C for 12 h. Upon completion of polymerisation, the formed transparent hydrogels were carefully demoulded and thoroughly washed with deionised water to remove unreacted monomers and residual reagents. The purified PAAm hydrogels were stored at ambient temperature in airtight containers filled with distilled water to prevent dehydration prior to characterisation.

2.3 Preparation of PAAm-pectin hydrogel

The PAAm-pectin double-network (DN) hydrogel was synthesised through a two-step sequential polymerisation and crosslinking strategy to obtain a robust interpenetrating network structure. In the first step, acrylamide (4 g) and pectin were dissolved in 40 mL of deionised water at different weight ratios, corresponding to pectin-to-acrylamide contents of 0%, 5%, 10%, 15%, and 20%. The resulting solution was stirred at 500 rpm for 2 h at room temperature ($25 \pm 2^\circ\text{C}$) to ensure complete dissolution and homogeneity. Subsequently, N, N'-methylenebisacrylamide (0.02 mol% relative to acrylamide), ammonium persulfate (0.1 mol% relative to acrylamide), and N, N, N', N'-tetramethylethylenediamine (40 μL) were added as the chemical crosslinking agent, free-radical initiator, and accelerator, respectively. The precursor solution was further stirred and then poured into petri dishes (90 mm diameter). Polymerisation was carried out in a thermostatically controlled oven at 50°C for 12 h, resulting in the formation of a covalently crosslinked PAAm-pectin hydrogel (mono-crosslinked network).

In the second step, the mono-crosslinked hydrogel was immersed in a 0.1 M CaCl_2 solution for 4 h at room temperature to promote ionic crosslinking of the pectin network via coordination with Ca^{2+} ions, thereby yielding the PAAm-pectin- Ca^{2+} double-network hydrogel. Following ionic crosslinking, the hydrogels were thoroughly rinsed with deionised water to remove excess ions and residual species and subsequently stored in sealed containers to prevent dehydration before characterisation.

2.4 Preparation of PAAm-GG hydrogel

A dual-network hydrogel system was synthesised using a sequential chemical and ionic crosslinking strategy to obtain a robust interpenetrating network. Initially, acrylamide (4 g) and sodium gellan gum were dissolved in 40 mL of deionised water at varying weight ratios, corresponding to gellan gum-to acrylamide contents of 0%, 2.5%, 5%, 7.5%, and 10%. The mixture was stirred continuously to obtain a clear and homogeneous precursor solution. Subsequently, N, N'-methylenebisacrylamide (0.02 mol% relative to AAm) was added as the covalent crosslinking agent, followed by ammonium persulfate (0.1 mol% relative to AAm) and N, N, N', N'-tetramethylethylenediamine (40 μL) as the free-radical initiator and accelerator, respectively.

The resulting solution was poured into petri dishes and subjected to polymerisation in a thermostatically controlled oven at 50 °C for 10 h, yielding a covalently crosslinked PAAm-GG hydrogel (mono-crosslinked network). In the subsequent step, the mono-crosslinked hydrogel was immersed in a 0.1 M CaCl_2 solution for 3 h to introduce ionic crosslinks via coordination between Ca^{2+} ions and the carboxylate groups of the gellan gum backbone, resulting in the formation of a dual-crosslinked PAAm-GG- Ca^{2+} hydrogel.

2.5 Preparation of PAAm-pectin-EG organogel

The PAAm-pectin-EG organogel was fabricated using a solvent displacement approach, in which water within the hydrogel network was progressively replaced with ethylene glycol. The mono-crosslinked PAAm-pectin hydrogel, prepared as described in Section 2.3, was immersed in a 0.1 M CaCl_2 solution containing a binary solvent system of ethylene glycol and deionised water. The ethylene glycol content was systematically varied to obtain volume fractions of 0%, 10%, 25%, 50%, and 75% (v/v). The samples were maintained under these conditions for 12 h at 25 °C, allowing diffusion of ethylene glycol into the hydrogel matrix while maintaining ionic crosslinking of the pectin network through coordination with Ca^{2+} ions.

2.6 Preparation of PAAm-pectin-GL organogel

The PAAm-pectin-GL organogel was fabricated via the solvent displacement method, in which water was gradually replaced by glycerol. The monocrosslinked PAAm-pectin hydrogel, prepared as described in Section 2.3, was immersed in a 0.1 M CaCl_2 solution containing a binary solvent mixture of glycerol and deionized water (The volume ratio of glycerol to water was varied to obtain concentrations of 0%, 10%, 25%, 50%, and 75% (v/v) glycerol) for 12 hours at 25 °C. This process facilitated the diffusion of glycerol into the hydrogel matrix while maintaining ionic crosslinking with Ca^{2+} ions.

2.7 Preparation of PAAm-GG-EG organogel

The mono-crosslinked PAAm-GG hydrogel was immersed in a binary solvent mixture containing 0.1 M CaCl_2 and ethylene glycol (EG) in deionized water. The volume ratio of ethylene glycol to water was adjusted to obtain concentrations of 0%, 10%, 25%, 50%, and 75% (v/v). The immersion was carried out at room

temperature for 12 hours to enable sufficient solvent exchange. After the immersion period, the organogels were removed, gently blotted to remove surface liquid, and stored in sealed containers prior to further characterisation.

2.8 Preparation of PAAm-GG-GL organogel

The mono-crosslinked PAAm–GG hydrogel, prepared as described in Section 2.4, was immersed in a binary solvent mixture of 0.1 M CaCl₂ and glycerol in deionized water. The glycerol content was varied to achieve concentrations of 0%, 10%, 25%, 50%, and 75% (v/v). The hydrogel samples were kept in the solvent mixture at room temperature for 12 hours to allow partial replacement of water with glycerol. After the exchange period, the organogels were removed from the solution, lightly blotted to remove excess surface liquid, and stored in sealed containers for further analysis.

2.9 Swelling characterisation

The swelling behaviour of the hydrogels was evaluated by measuring the mass of the samples in both the dry and swollen states. Dried PAAm–pectin and PAAm–GG hydrogels were initially weighed and then immersed in 50 mL of deionised (DI) water. At predetermined time intervals, the samples were removed from the swelling medium, gently blotted with absorbent filter paper to remove excess surface water, and subsequently weighed using an analytical balance. The swelling ratio was calculated using the following equation.

$$\text{SR (\%)} = \frac{(W_e - W_d)}{W_d} \times 100 \quad (2.1)$$

Where W_e is the weight of the hydrogel at its equilibrium swollen state, and W_d is the weight of the dried hydrogel.

The swelling behavior of the hydrogels in water–glycerol and water–ethylene

glycol binary solvent systems was evaluated using the gravimetric method. Hydrogel samples of known initial weight (W_d) were immersed in binary mixtures of deionized water with either glycerol or ethylene glycol at predetermined volume ratios (0%, 10%, 25%, 50%, and 75% v/v). The samples were allowed to swell at room temperature until equilibrium was reached, which was determined by monitoring the weight of the hydrogels at regular time intervals. After equilibrium, the excess surface solvent was gently removed using filter paper, and the swollen weight (W_e) of each sample was recorded. The swelling ratio (SR) was then calculated using the above equation. All measurements were performed in triplicate, and the average values were reported.

2.10 SEM analysis

The surface morphology of the samples was examined using field emission scanning electron microscopy (FESEM, Hitachi SU6600, Japan). Before imaging, each sample was sputter-coated with a thin layer of gold using an Edwards S150B sputter coater to minimize surface charging. The obtained micrographs were subsequently analyzed with 'ImageJ' software for morphological evaluation.

In SEM, images are generated through the interaction of a focused primary electron beam with the specimen surface, leading to the emission of secondary electrons produced by the ionization of surface atoms with low energies (approximately 3–5 eV). These secondary electrons originate from a region within a few nanometers of the surface, providing detailed topographical information corresponding to the position of the scanning beam. The high spatial resolution of SEM is achieved because the primary electron beam can be focused to a spot size of less than 10 nm. Furthermore, imaging at lower accelerating voltages (~ 1 kV) reveals finer surface details compared to images acquired at higher voltages (~ 20 kV).

The hydrogel samples were lyophilized using a freeze-dryer (Lyophilizer; Make: Lark Innovative Fine Teknowledge, Model: Penguin Classic) prior to SEM analysis

to preserve their structural integrity.

2.11 Fourier Transform Infrared (FTIR) Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy is a widely used analytical technique for the characterisation of samples in various physical forms, including solids, liquids, powders, and films. The principle of infrared spectroscopy lies in the interaction of infrared radiation with the vibrational modes of atoms or molecules in the sample, where the absorbed or transmitted radiation at specific energies provides information about molecular structure and bonding. Attenuated Total Reflectance (ATR) is a versatile sampling method that enables direct analysis of samples in their native solid or liquid states. In this technique, an infrared beam is directed onto an internal reflection element, typically an optically dense crystal such as diamond, zinc selenide, or germanium, which generates an evanescent wave penetrating a few micrometers into the sample surface. The resulting reflected signal is then detected to obtain the infrared spectrum. In this study, the spectra of the synthesized samples were recorded using a Thermo Nicolet iS50 FTIR spectrometer equipped with an ATR accessory. Measurements were performed in the range of 400–4000 cm^{-1} , with a spectral resolution of 4 cm^{-1} , an aperture of 6 mm, and a scanner velocity of 2.2 kHz. Each spectrum was obtained from 100 scans with a background scan time of 32 seconds. Analysis of the stretching and bending vibration bands in the recorded spectra provided insights into the functional groups present in the material and their possible molecular interactions.

2.12 Anti-freezing studies

The PAAm–GG and PAAm–pectin hydrogels were converted into organogels by immersing them in 0.1 M CaCl_2 solutions containing varying ratios of organic solvents and water. The solvent mixtures were prepared with solvent (glycerol or

ethylene glycol) to water volume ratios of 10:90, 25:75, 50:50, and 75:25 (v/v), corresponding to solvent concentrations of 10%, 25%, 50%, and 75%, respectively. The hydrogels were immersed in the respective solvent mixtures for 12 hours. The equilibrium swollen hydrogels and organogels were then stored in a refrigerator at $-15\text{ }^{\circ}\text{C}$ for 6 h, to evaluate their anti-freezing performance. After freezing treatment, the samples were removed and visually inspected for changes in transparency. The mechanical flexibility was then assessed by manual bending and compression of the samples.

2.13 DSC analysis

The anti-freezing performance of the hydrogels and organogels was analysed using differential scanning calorimetry (DSC; DSC 204 F1, NETZSCH). Measurements were performed under a nitrogen atmosphere at a heating rate of $5\text{ }^{\circ}\text{C}/\text{min}$. The samples were initially cooled from room temperature to $-70\text{ }^{\circ}\text{C}$, held for 30 min to allow thermal equilibration, and then heated to $50\text{ }^{\circ}\text{C}$ to evaluate their thermal behavior and resistance to freezing.

2.14 Anti-drying and water retention

The long-term stability of the hydrogels and organogels was assessed by storing the samples at room temperature under controlled conditions of 70% relative humidity for a period of 20 days. The weight of each sample was periodically measured to evaluate changes arising from solvent evaporation. The solvent retention percentage was calculated using the following equation:

$$W\% = \frac{W_t}{W_0} \times 100 \quad (2.2)$$

where W_t is the weight of the hydrogel or organogel at a given time, and W_0 is the initial weight of the fully swollen hydrogel or organogel.

The thermal stability of the hydrogels and organogels was evaluated using thermogravimetric analysis (TGA). Measurements were performed with a TGA-DTA Hitachi STA7000 instrument. Approximately 3 mg of each sample was used for the study. Each sample was heated from ambient temperature to 400°C at a constant rate of 10°C/min. The weight loss and decomposition behavior under thermal stress were recorded to assess the thermal stability and decomposition profiles of the hydrogels and organogels.

2.15 Mechanical characterisation

The tensile properties of the hydrogels and organogels were evaluated using a universal testing machine (Shimadzu Autograph AG-X Plus Series) under uniaxial tension. Dumbbell-shaped samples with dimensions of 40 mm $\times$ 6 mm $\times$ 0.25 mm were prepared for the tests. The measurements were conducted at ambient temperature with a crosshead speed of 100 mm/min. Tensile strength, Young's modulus, and elongation at break were determined from the stress-strain curves. For each composition, three samples were tested, and the average of the three measurements was reported to ensure reproducibility and reliability of the results. The effects of biopolymer content and calcium concentration on the mechanical properties of hydrogels, as well as the influence of organic solvents on the mechanical properties of organogels, were systematically studied.

2.16 Rheological characterisation

The rheological properties of the hydrogels and organogels were analyzed using a modular compact rheometer (Anton Paar MCR 302) equipped with a parallel plate geometry of 25 mm diameter and a 0.5 mm gap. Disc-shaped samples with a diameter of 25 mm and a thickness of 0.5 mm were prepared and carefully placed between the plates to ensure uniform contact. All rheological measurements were performed at 25 °C, and the temperature was maintained with an accuracy of

± 0.1 °C.

To determine the linear viscoelastic region (LVER), strain sweep tests were carried out over a strain range of 0.01–100% at a fixed frequency of 1 Hz. The nonlinear behavior of the gels was also evaluated based on these measurements. Frequency sweep tests were then performed in the range of 0.1–100 Hz at a constant strain of 1%, which lies within the LVER, to obtain the storage modulus (G') and loss modulus (G''). During all tests, a solvent trap was used to minimize solvent evaporation and maintain sample integrity.

2.17 Conductivity studies

The electrochemical properties of the hydrogels and organogels were systematically investigated using a broadband dielectric spectrometer (Concept 80, NOVO-CONTROL Technologies, Germany). Dielectric spectroscopy, also known as impedance spectroscopy, measures the dielectric properties of a material as a function of frequency. The technique is based on the interaction of an external electric field with the electric dipole moments within the sample, typically expressed in terms of permittivity. Broadband dielectric spectroscopy covers an exceptionally wide frequency range, from 10^{-6} to 10^{12} Hz, allowing the investigation of both molecular and collective dipolar fluctuations, charge transport, and polarization effects at internal and external boundaries. This technique provides detailed insights into the dynamics of bound dipoles as well as mobile charge carriers, enabling a comprehensive understanding of the dielectric behavior and molecular dynamics of the system under study. Circular-shaped samples with a diameter of 15 mm and a thickness of 1 mm were used for all measurements. The measurements were performed at room temperature and under ambient pressure, covering a frequency range from 1 Hz to 20 MHz. The electrical conductivity (σ , S/cm) of the hydrogels

was calculated using the following equation:

$$\sigma = \frac{L}{R \times A} \quad (2.3)$$

where L represents the sample thickness (cm), A is the cross-sectional area of the sample (cm²), and R denotes the resistance (Ω) of the hydrogel. The temperature-dependent electrochemical behavior of the hydrogels and organogels was investigated using a Quatro Cryo System to control the temperature, allowing measurements over a range from -180°C to 400°C .

Chapter 3

Development and Characterisation of PAAm–Pectin Interpenetrating Polymer Network Hydrogels and Organogels

3.1 Introduction

The development of flexible, conductive, and temperature-tolerant soft materials has gained significant attention because of their potential applications in flexible electronics (Dang et al., 2025; Zhao, Yao, Shen, Chen, Zhu, Chen, Wang, Li, Liu and Zhao, 2025; Dutta et al., 2024). Due to their water-rich environment, softness, and biocompatibility, hydrogels have emerged as promising materials for such applications (Zhao, Yan, Lin, Zhao and Song, 2025; Yuan et al., 2025; Hua et al., 2023). However, conventional hydrogels often suffer from dehydration, freezing at low temperatures, and loss of functional integrity under environmental stress, which limits their long-term practical use (Chen, Wang, Fang, Guo, Liu, Li, Li, Wang, Li and Lei, 2023; Li, Cheng, Deng, Zhang, Luo, Huang, Wang, Wang and Zhao, 2024; Chen, He and Rong, 2023). To overcome these limitations, this work focuses on the preparation and characterisation of polyacrylamide-pectin (PAAm–pectin) organogels designed to exhibit improved thermal, mechanical, and conductive stability across a wide range of temperatures.

An interpenetrating polymer network (IPN) hydrogel was synthesized by com-

binning synthetic polyacrylamide (PAAm) and natural pectin. Pectin is an anionic polysaccharide rich in carboxyl groups capable of forming ionic crosslinks with divalent calcium ions (Ca^{2+}). The covalently crosslinked PAAm network contributes to mechanical robustness and flexibility. Meanwhile, the pectin network, crosslinked through ionic interactions, enhances biocompatibility, promotes water retention, and improves ionic conductivity. The hydrogels were subsequently transformed into organogels by solvent replacement using polyols such as ethylene glycol (EG) and glycerol (GL). The introduction of these organic solvents enhances the anti-freezing and anti-drying properties of the hydrogels and ensures flexibility and conductivity even at sub-zero temperatures.

A comprehensive characterisation was performed to understand the structure-property relationships of the prepared gels. The structural interactions and morphological characteristics of the polymer networks were investigated by FTIR spectroscopy and SEM analysis. Swelling studies were conducted to study the effects of pectin concentration and organic solvent content on the swelling ratio of hydrogels. Mechanical characterisation was performed to study the influence of pectin, Ca^{2+} concentration, and solvent content on the mechanical properties of the hydrogels. The rheological analysis provided insights into the viscoelastic properties under varying glycerol and ethylene glycol concentrations.

The anti-freezing and solvent retention studies were conducted to optimise the polyol concentration required for maintaining flexibility and stability under different environmental conditions. The conductivity measurements were carried out to study the effects of pectin and Ca^{2+} content on the ionic conductivity of hydrogels and organogels. The ionic conductivity of the gels was evaluated across a range of temperatures to determine the temperature-dependent conductivity behaviour of both hydrogels and organogels.

Thus, the chapter presents a systematic investigation into the design, preparation, characterisation, and optimisation of PAAm–pectin organogels, offering

a pathway toward multifunctional, environmentally tolerant, and mechanically robust soft materials suitable for next-generation flexible devices.

3.2 Results and Discussion

3.2.1 Mechanism of PAAm-pectin hydrogel and organogel formation

Preparation of PAAm hydrogel:- Polyacrylamide (PAAm) hydrogel was synthesized via free radical polymerisation of acrylamide using *N*, *N*'-Methylenebisacrylamide (MBAAm) as a crosslinker, ammonium persulfate (APS) as an initiator, and *N*, *N*, *N*', *N*'-tetramethylethylenediamine (TEMED) as an accelerator under aqueous conditions. Polyacrylamide (PAAm) is formed from acrylamide monomers through a free radical polymerisation process, in which radical species initiate the chain growth polymerisation of vinyl groups present in the acrylamide molecules. In this reaction, *N,N*'-Methylenebisacrylamide (MBAAm) is employed as a bifunctional crosslinking agent to establish covalent bridges between polymer chains, leading to the formation of a three-dimensional hydrogel network. The polymerisation is initiated by redox initiator, ammonium persulfate (APS), which decomposes under heating or in the presence of an accelerator (*N,N,N,N*'-tetramethylethylenediamine, TEMED) to generate sulfate radical anions. These radical species attack the carbon-carbon double bonds of acrylamide monomers, forming reactive carbon-centered radicals that propagate by successive addition of monomer units. Concurrently, MBAAm molecules participate in the polymerization by reacting with two growing polyacrylamide chains at their vinyl groups, thereby introducing covalent crosslinks that interconnect linear chains into a gel-like network (Wang et al., 2019; Sikdar et al., 2021; Li et al., 2025).

Preparation of pectin hydrogel:- The preparation of pectin hydrogel was carried out using a calcium ion-mediated crosslinking method. To begin with, a 2% (w/v) pectin solution was prepared by dissolving pectin powder, comprising 74% galacturonic acid, in deionized water under continuous stirring at ambient

temperature. The galacturonic acid units present in the pectin backbone provide carboxylic acid groups ($-\text{COOH}$), which, upon ionisation, are essential for ionic crosslinking with divalent metal ions like calcium. The divalent ions Ca^{2+} interact with the ionized carboxylate groups ($-\text{COO}^-$) on the galacturonic acid units, forming ionic bridges between adjacent polymer chains. This mechanism is often described by the “egg-box” model, where Ca^{2+} ions act as crosslinkers that stabilise the three dimensional polymer network (Said et al., 2023; Martínez-Sabando et al., 2023; Abualsoud et al., 2026).

Preparation of PAAm-pectin hydrogel and organogel:- The schematic representation of the formation of PAAm-pectin hydrogel and organogels is depicted in Fig. 3.1. The polyacrylamide–pectin (PAAm–pectin) double network (DN) hydrogel is prepared through a sequential two-step process. At first, a chemically crosslinked polyacrylamide network is synthesised, followed by the ionic crosslinking of pectin within the existing polyacrylamide matrix. This approach enables the integration of a ductile covalent network with a physically crosslinked network, resulting in an interpenetrating structure with enhanced mechanical properties (León-Campos et al., 2024).

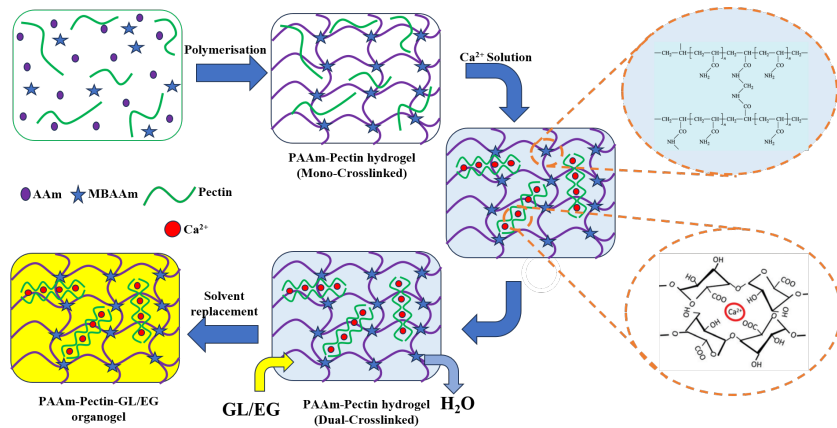


Figure 3.1: Schematic illustration of the preparation of PAAm-pectin organogel.

The integration of polyacrylamide (PAAm) and pectin into a hydrogel system results in the formation of an interpenetrating double network hydrogel, in which the two networks coexist without covalent crosslinking between them. The

polyacrylamide forms a flexible, elastic network through covalent crosslinking, whereas pectin forms a brittle, physically crosslinked network through ionic interactions and hydrogen bonding. The physical interaction between PAAm and pectin is primarily governed by hydrogen bonding. The amide groups ($-\text{CONH}_2$) in polyacrylamide can form hydrogen bonds with the hydroxyl ($-\text{OH}$) and carboxyl ($-\text{COOH}$) groups present in the pectin network. This non-covalent interaction facilitates inter-network adhesion and structural integration, contributing to the mechanical stability of the hydrogel. In addition, interpenetrating entanglements between polymer chains further reinforce the composite structure by physically restricting the mobility of the polymer chain under stress (Cona et al., 2024).

The PAAm–pectin hydrogel was subjected to a solvent replacement process to convert it into an organogel with enhanced properties. This was carried out by immersing the hydrogel in a binary solvent mixture composed of either glycerol or ethylene glycol and water. During the exchange process, water molecules within the hydrogel network were replaced by glycerol or ethylene glycol, thereby modifying the internal solvent environment without disturbing the integrity of the polymeric network. The ethylene glycol and glycerol molecules are capable of forming extensive hydrogen bonds with the amide groups of polyacrylamide ($-\text{CONH}_2$) and the hydroxyl and carboxyl groups ($-\text{OH}$ and $-\text{COOH}$) of pectin. These multiple hydrogen-bonding interactions create strong interfacial associations between the polymer chains and the incorporated solvent molecules, which facilitate uniform dispersion of polyols within the network. Such interactions effectively reinforce the polymer matrix, enhance molecular compatibility, and contribute to improved mechanical integrity of the resulting organogels (Lee et al., 2025; Nikam et al., 2024).

3.2.2 FTIR analysis

The FTIR spectra of pectin, PAAm hydrogel, PAAm-pectin hydrogel, and PAAm-pectin-EG organogels are presented in Figure 3.2. The spectrum of the PAAm hydrogel shows characteristic absorption bands at 3342 cm^{-1} and 3190 cm^{-1} , which are assigned to the symmetric and asymmetric stretching vibrations of N-H groups, respectively. The band at 1660 cm^{-1} is attributed to the C=O stretching vibration of primary amide groups, while the peak at 1596 cm^{-1} corresponds to N-H deformation vibrations of the primary amide. In addition, the band observed at 1415 cm^{-1} is assigned to C-N stretching associated with the primary amide group (Zhu et al., 2020; El-Diehy et al., 2025; Zhu, Wang, Ren, AlMasoud, El-Bahy, S. Alomar, Zhang, Zhang, Zhou, Li et al., 2023). The pectin hydrogel exhibited a broad absorption band at 3343 cm^{-1} , corresponding to O-H stretching vibrations, and characteristic peaks at 1739 cm^{-1} and 1629 cm^{-1} , which are attributed to the C=O stretching vibrations of the methyl ester and carboxylic acid groups, respectively (Costanza et al., 2019; Tong et al., 2023; Santos et al., 2020).

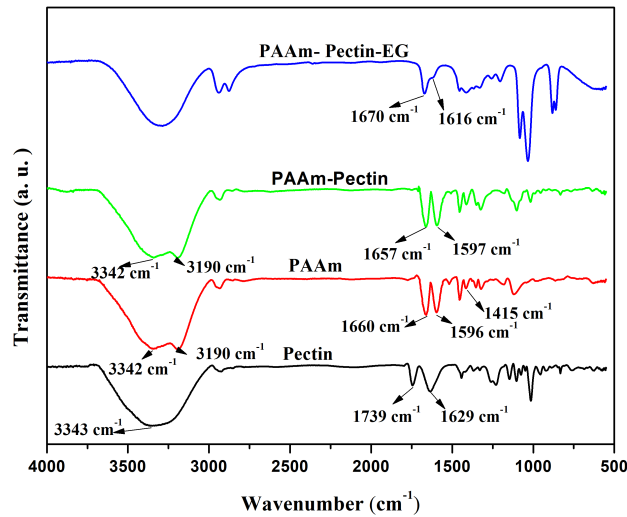


Figure 3.2: FTIR spectra of pectin, PAAm, PAAm-pectin and PAAm-pectin-EG hydrogels.

The FTIR spectrum of PAAm-pectin hydrogel exhibited no additional absorption bands compared to the spectra of the individual pectin and PAAm hydrogels. The absence of new characteristic peaks indicates that no covalent linkages were formed during hydrogel formation, confirming that the interaction between pectin and PAAm occurred through physical blending rather than chemical reaction (Niua et al., n.d.; Darnell et al., 2013). The hydrogel formation is therefore attributed to non-covalent interactions, primarily hydrogen bonding and electrostatic attractions between the functional groups of the two polymers. This observation confirms that the structural framework of both pectin and PAAm was preserved in the composite hydrogel, with molecular association achieved mainly through secondary interactions. However, slight shifts in the peak positions corresponding to the carbonyl and N-H vibrations were observed, which indicate the presence of intermolecular hydrogen bonding between the functional groups of pectin and PAAm (Fan et al., 2020; Yu et al., 2021).

Upon the addition of ethylene glycol, the characteristic C=O stretching and N-H bending peaks of the PAAm-pectin hydrogel shifted to 1670 cm^{-1} and 1616 cm^{-1} , respectively. These spectral shifts indicate the formation of hydrogen bonding interactions between the hydroxyl groups of ethylene glycol and the C=O and -NH_2 groups of the hydrogel (Zhang et al., 2018; Wang, Riaz, Ali, Gu, Zhong and Hu, 2023). Such interactions suggest strong molecular association and enhanced compatibility between the polymer chains and the incorporated solvent molecules.

A distinct shift in the characteristic absorption bands was observed in the FTIR spectra of the PAAm-pectin hydrogel following the incorporation of glycerol (Fig. 3.3). Upon glycerol addition, the C=O stretching peak of the PAAm-pectin hydrogel shifted from 1657 to 1668 cm^{-1} , while the N-H bending peak shifted from 1597 to 1617 cm^{-1} . These shifts indicate the formation of intermolecular hydrogen bonds between the hydroxyl groups of glycerol and the C=O and -NH_2 groups within the hydrogel network. This suggests strong molecular interactions and ef-

fective physical blending between the polymer matrix and the incorporated solvent (Yu et al., 2021; Yin et al., 2021). The FTIR peak positions with corresponding functional group assignments are summarized in Table 3.1

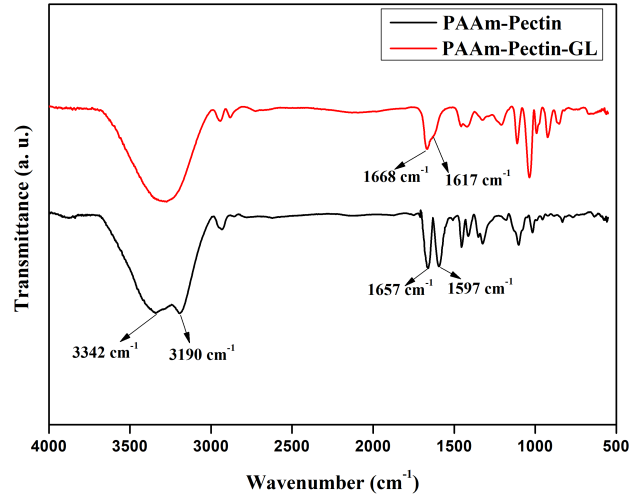


Figure 3.3: FTIR spectra of PAAm-pectin, and PAAm-pectin-GL hydrogels.

Table 3.1: FTIR peak assignments of pectin, PAAm, PAAm-pectin hydrogels and organogels.

Sample	Peak Position (cm^{-1})	Vibration	Assignment
Pectin	3343	O-H stretching	Hydroxyl groups
	1739	C=O stretching	Methyl ester groups
	1629	C=O stretching	Carboxylic acid groups
PAAm	3342	N-H stretching (symmetric)	Primary amide group
	3190	N-H stretching (asymmetric)	Primary amide group
	1660	C=O stretching	Amide I vibration
	1596	N-H bending	Amide II vibration
	1415	C-N stretching	Primary amide group
PAAm-Pectin	1657	C=O stretching	Intermolecular hydrogen bonding interaction
	1597	N-H bending	Hydrogen-bonded amide group
PAAm-Pectin-EG	1670	C=O stretching	Hydrogen bonding interaction with EG
	1616	N-H bending	Interaction between EG and polymer network
PAAm-Pectin-GL	1668	C=O stretching	Hydrogen bonding interaction with glycerol
	1617	N-H bending	Interaction between glycerol and polymer network

3.2.3 SEM analysis

The SEM image of the pure PAAm hydrogel (Figure 3.4 a) reveals a highly porous and interconnected network structure characterized by regular, sponge-like pores. These pores are uniformly distributed, with thin pore walls and small voids, indicative of a loosely crosslinked polymeric matrix. This morphology facilitates significant water uptake and diffusion through the network, which corresponds well with the observed high swelling behavior in aqueous environments.

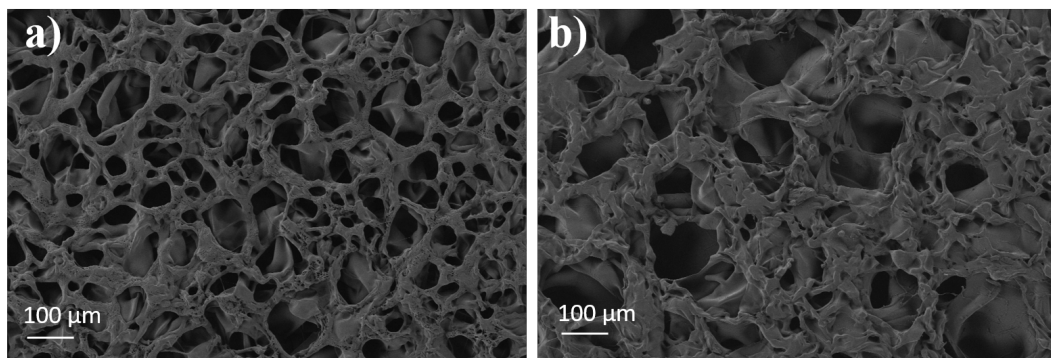


Figure 3.4: SEM images of a) PAAm hydrogel and b) PAAm-pectin hydrogel.

In contrast, the PAAm-pectin hydrogel (Figure 3.4 b) demonstrates a markedly different microstructure, with thicker pore walls and visibly denser architecture. The incorporation of pectin introduces an ionically crosslinked second network within the PAAm scaffold, resulting in fewer but larger pores with non-uniform distribution. The reduction in the number of pores in PAAm-pectin hydrogels compared to PAAm results in a higher crosslinking density and enhanced structural densification. Moreover, the PAAm-Pectin hydrogel walls appear more heterogeneous, with areas of folded and collapsed structures, potentially due to the formation of microphase-separated regions between the synthetic (PAAm) and natural (pectin) components. These features point to complex interactions within the interpenetrating network, where hydrogen bonding, electrostatic forces, and polymer entanglement collectively define the final architecture. The more dense morphology also implies enhanced mechanical stability, a desired attribute for

applications involving load-bearing or structural support.

3.2.4 Swelling studies

Figure 3.5 shows the variation in the swelling ratio of the PAAm-pectin hydrogel as a function of pectin content. The swelling ratio (SR) of polyacrylamide-pectin (PAAm-pectin) hydrogels is significantly influenced by the concentration of pectin incorporated into the hydrogel matrix, due to its impact on both hydrophilicity and network density. At lower pectin concentrations, the hydrogel exhibits a relatively loose polymer network with lower crosslinking density, facilitating greater water uptake and retention. The presence of hydrophilic carboxyl and hydroxyl functional groups in pectin enhances water absorption through hydrogen bonding thereby enhancing the swelling ratio (Panchev et al., 2010). As the pectin concentration increases, the hydrogel network becomes denser due to increased physical entanglement and ionic interactions between polymer networks. This denser network architecture reduces the effective pore size and limits the diffusion and accommodation of water molecules within the hydrogel. Consequently, hydrogels with higher pectin content generally exhibit a lower swelling ratio, as the compact network hinders further swelling despite the hydrophilic nature of pectin (Kowalski et al., 2019).

The addition of ethylene glycol into PAAm-pectin hydrogels affects the swelling ratio (Fig. 3.6) by altering the polymer-solvent interactions, network hydration, and osmotic driving forces. When the hydrogel is soaked in a binary solvent system composed of ethylene glycol and water, the uptake of EG molecules into the hydrogel matrix leads to a partial replacement of water in the polymer network. Since ethylene glycol has a lower dielectric constant and higher viscosity than water, its presence reduces the overall osmotic pressure driving water uptake, resulting in a decrease in the swelling ratio compared to hydrogels swollen in pure water (Han et al., 2008).

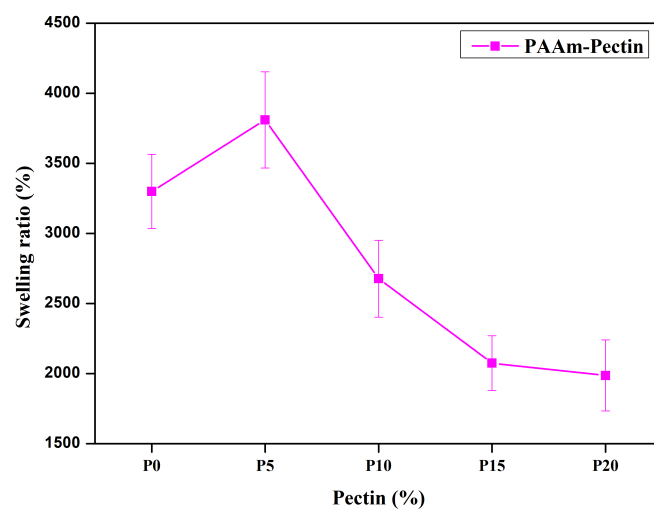


Figure 3.5: Effect of pectin concentration on swelling ratio of PAAm-pectin hydrogels.

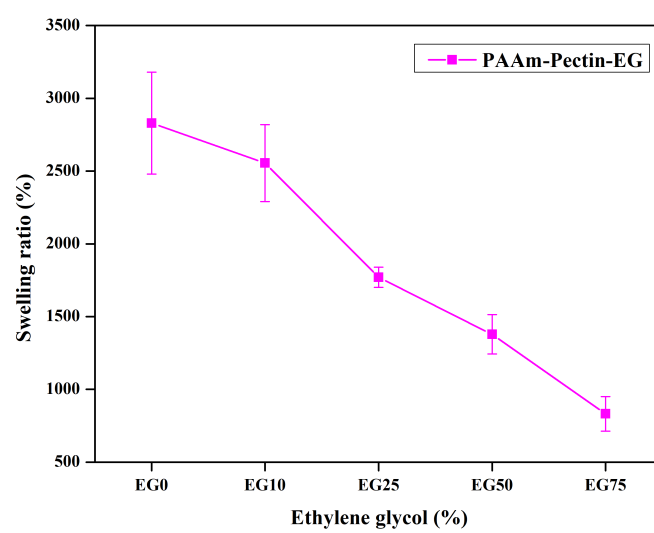


Figure 3.6: Effect of ethylene glycol concentration on swelling ratio of PAAm-pectin hydrogels.

Moreover, ethylene glycol acts as a plasticising agent that interacts with the polymer chains through hydrogen bonding with the carboxyl and amide groups of pectin and polyacrylamide, respectively (Cheng et al., 2019). These additional interactions increase physical crosslinking, leading to a more compact and stabilized network structure that resists further expansion (Ge et al., 2025). The presence of ethylene glycol also reduces the hydrophilic nature of the swelling medium, further limiting the ability of the network to absorb and retain water. Overall, increasing the ethylene glycol content in the solvent system leads to a progressive decrease in the swelling ratio of PAAm–pectin organogels due to reduced osmotic swelling forces, enhanced polymer–solvent interactions, and increased network compactness.

Figure 3.7 depicts the effect of glycerol concentration on the swelling ratio of the PAAm–pectin hydrogel, revealing that variations in glycerol content during the solvent-replacement process markedly influence the swelling behavior of PAAm–pectin organogels by altering polymer–solvent interactions and the structural integrity of the network. At low glycerol concentrations, the swelling ratio of PAAm–pectin organogels initially increases because small amounts of glycerol can disrupt the strong intermolecular hydrogen bonding within the polymer network, causing slight swelling or loosening of the network structure. This effect causes an increase in water absorption due to enhanced polymer chain mobility and increased free volume. Furthermore, the hygroscopic nature of glycerol attracts and retains water molecules, contributing to swelling at these lower concentrations (Kumar and Sharma, n.d.).

However, as the glycerol concentration continues to increase beyond a certain threshold, the swelling ratio begins to decrease. At higher glycerol levels, the organic solvent increasingly replaces water within the hydrogel matrix, reducing the overall hydrophilicity of the network. Glycerol molecules form strong hydrogen bonds with polymer chains, which effectively “lock” the network structure and

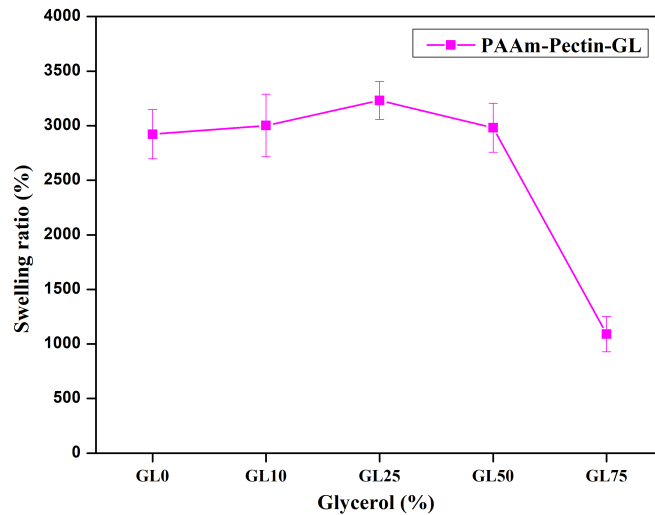


Figure 3.7: Effect of glycerol concentration on the swelling ratio of PAAm-pectin hydrogels.

limit chain mobility (Jian et al., 2019; Zhang, Jiang, Zhao, Diao, Liu, Chen, Liu and Yang, 2024). This increased interaction restricts polymer network expansion and reduces free volume available for water absorption. Moreover, the viscous nature of glycerol hinders water diffusion into the gel. Collectively, these effects lead to a decrease in swelling ratio at higher glycerol concentrations.

3.2.5 Mechanical characterisation

The mechanical properties of the synthesized hydrogels and organogels were systematically investigated to quantify the influence of pectin concentration, calcium ion content, and organic solvent composition (ethylene glycol and glycerol). All hydrogel samples were pre-dried at 40 °C for 24 h before testing to eliminate solvent-induced weakening effects. In contrast, the organogels were tested in their equilibrium swollen state to accurately represent their functional conditions and to preserve the integrity of solvent–polymer interactions within the network.

The mechanical performance of PAAm–pectin– Ca^{2+} hydrogels was evaluated as a function of calcium ion concentration (Fig. 3.8). The corresponding mechan-

ical parameters are listed in Table 3.2. Monocrosslinked PAAm–pectin hydrogels were immersed in CaCl_2 solutions of varying concentrations (0, 0.01, 0.05, 0.1, and 0.3 M) to introduce ionic crosslinking, and the resulting samples were subsequently analysed for their mechanical performance. An increase in Ca^{2+} concentration resulted in a progressive enhancement of the tensile strength and Young's modulus of the hydrogels. However, at concentrations above 0.1 M CaCl_2 , both parameters exhibited a slight decline.

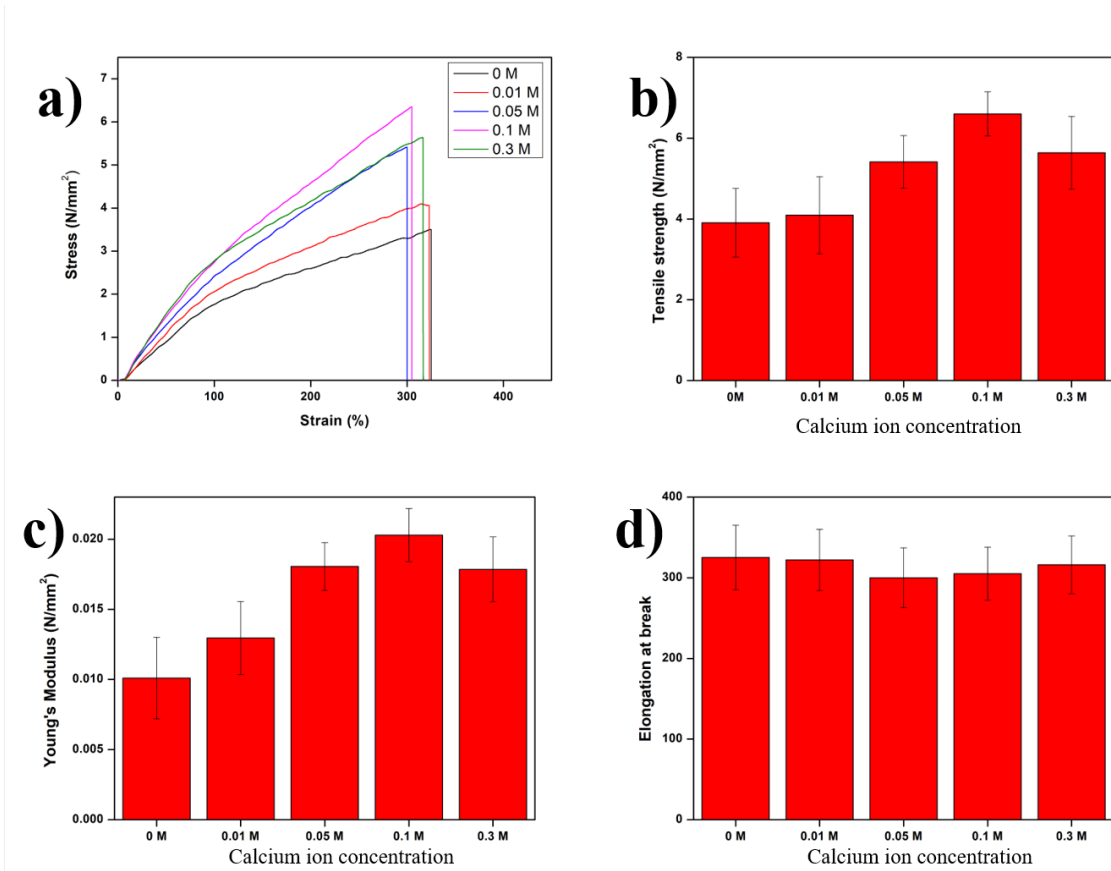


Figure 3.8: Effect of Ca^{2+} ion concentration on the mechanical strength of PAAm-pectin hydrogels.

Table 3.2: Mechanical properties of PAAm-pectin hydrogels at different Ca^{2+} concentrations.

$[\text{Ca}^{2+}]$ (M)	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation (%)
0	3.90	1.01×10^{-2}	325
0.01	4.09	1.30×10^{-2}	322
0.05	5.41	1.81×10^{-2}	300
0.10	6.60	2.03×10^{-2}	305
0.30	5.63	1.78×10^{-2}	316

At low calcium ion concentrations, only a limited number of ionic crosslinks are formed between pectin chains, resulting in a loosely crosslinked secondary network with insufficient load-bearing capacity. Consequently, the hydrogel exhibits low compressive strength, reduced stiffness, and poor resistance to deformation, as the polyacrylamide network is only sparsely reinforced by pectin. With increasing calcium ion concentration, more carboxylate groups of pectin participate in ionic coordination, producing a denser and stronger secondary network. These ionic crosslinks enhance the mechanical strength of the hydrogel by enabling energy dissipation through the reversible breaking and reformation of ionic bonds under deformation (Popov et al., 2022). The formation of more egg-box junctions reinforces the networks and leads to the formation of a more resilient hydrogel (Braccini and Pérez, 2001).

However, beyond the optimal calcium ion concentration, a reduction in the mechanical properties of the hydrogel was observed. This occurs because excess Ca^{2+} ions form a mixture of mono and bidentate complexes with the carboxyl groups of pectin, leading to partial unzipping and structural rearrangement of the pectin chains. This reorganization disrupts the uniformity of the cross-linked network and decreases the effective crosslinking density, resulting in a decrease in the overall mechanical performance of the hydrogel. (Wang et al., 2019; Lin et al., 2015).

Figure 3.9 illustrates the effect of pectin content on the mechanical properties of PAAm–pectin hydrogels. The corresponding mechanical properties of hydrogels with varying pectin concentrations are summarised in Table 3.3. The mechanical strength of the hydrogels increased progressively with increasing pectin concentration; however, a noticeable reduction in flexibility was observed at higher pectin levels, indicating the formation of a denser and less deformable network structure. Physical bonds found in natural polymers are typically weaker than covalent bonds. By breaking themselves rather than the material’s main framework,

these physical bonds may create an energy dissipation mechanism that makes the entire material extremely tough (Liu and Li, 2016). Cation-mediated (Ca^{2+}) ionic crosslinks between anionic polysaccharide helices function as sacrificial bonds in DN hydrogels, increasing their stiffness and toughness through energy dissipation (Lu et al., 2014; Sun et al., 2012).

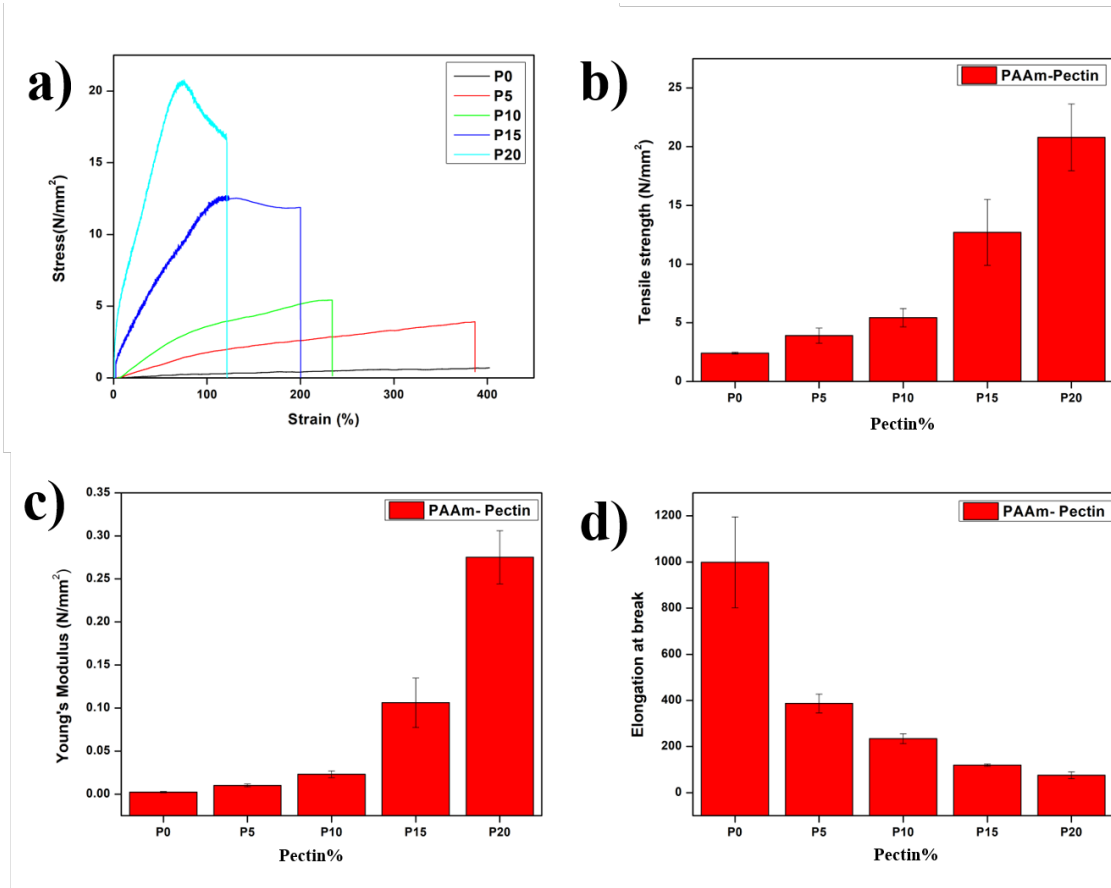


Figure 3.9: Effect of pectin concentration on mechanical properties of PAAm-pectin hydrogel.

Table 3.3: Mechanical properties of PAAm-pectin hydrogels with varying pectin content.

Hydrogel	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation (%)
PAAm-Pectin0	2.42	2.42×10^{-3}	998.71
PAAm-Pectin5	3.91	1.01×10^{-2}	386.78
PAAm-Pectin10	5.43	2.32×10^{-2}	233.91
PAAm-Pectin15	12.71	1.06×10^{-1}	119.65
PAAm-Pectin20	20.79	2.75×10^{-1}	75.58

At low pectin concentrations, the hydrogel contains fewer polymer chains capable of forming ionic crosslinks with calcium ions, resulting in a weak secondary network that provides limited reinforcement to the polyacrylamide framework. Consequently, the hydrogel exhibits lower compressive strength, reduced modulus, and poorer resistance to mechanical deformation due to insufficient load distribution and stress dissipation. As the pectin content increases, more functional groups are available to participate in calcium-mediated crosslinking, leading to a denser, more interconnected secondary network interpenetrated within the polyacrylamide matrix. This enhanced network density improves mechanical strength and stiffness by enabling better stress transfer and providing additional crosslinking points that restrict chain mobility. Furthermore, the formation of reversible ionic crosslinks within the pectin network allows energy dissipation through sacrificial bond rupture under stress, contributing to higher toughness and resistance to fracture.

Figure 3.10 displays the mechanical performance of PAAm-pectin organogels with varying ethylene glycol concentrations. The corresponding mechanical characteristics are summarised in Table 3.4. The mechanical strength of PAAm-pectin organogels was found to increase with the incorporation of higher EG content. This improvement in mechanical strength is due to the formation of hydrogen bonds between the hydroxyl groups of EG and the functional groups present in both the pectin and PAAm networks. These interactions create additional physical crosslinks that strengthen and stabilise the polymer matrix (Han, Zhou and Duan, 2020; Niu et al., 2021). Moreover, the progressive replacement of water with EG reduces the overall water content, leading to a denser and more compact polymer network with restricted chain mobility, thereby improving the stiffness and mechanical integrity of the hydrogel.

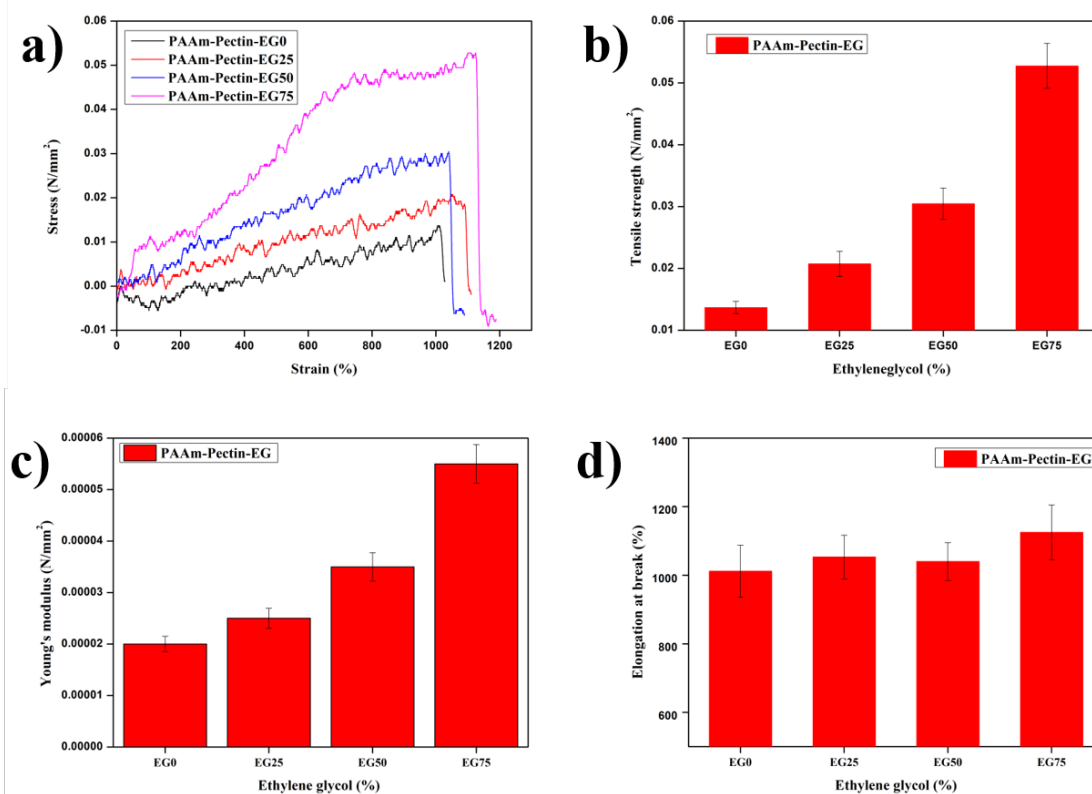


Figure 3.10: Effect of ethylene glycol content on the mechanical performance of PAAm-pectin-EG organogels.

Table 3.4: Mechanical properties of PAAm-pectin-EG organogels with varying ethylene glycol content.

Hydrogel	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation (%)
PAAm-pectin-EG0	1.37×10^{-2}	2.00×10^{-5}	1011.64
PAAm-pectin-EG25	2.08×10^{-2}	2.50×10^{-5}	1052.89
PAAm-pectin-EG50	3.05×10^{-2}	3.50×10^{-5}	1039.89
PAAm-pectin-EG75	5.28×10^{-2}	5.50×10^{-5}	1124.97

The figure 3.11 shows the mechanical properties of PAAm-pectin-GL organogels with varying concentrations of glycerol. The corresponding mechanical data are listed in Table 3.5. The mechanical properties of PAAm-pectin-glycerol organogels, including tensile strength, Young's modulus, and percentage elongation, exhibit a progressive increase with rising glycerol content, with the most significant enhancement observed at 75 % glycerol concentration. As glycerol is introduced into the hydrogel matrix via solvent replacement, it gradually replaces water molecules within the network. At low concentrations, glycerol contributes moderately to hydrogen bonding interactions with the amide groups of polyacrylamide and the carboxyl groups of pectin (Li, Deng and Zhou, 2020). However, as the concentration increases, these interactions become more pronounced and extensive, resulting in stronger intermolecular bonding within the gel matrix. These glycerol mediated hydrogen bonds act as additional physical crosslinking along with the existing covalent and ionic crosslinking (Mohsin et al., 2011). As a result, they strengthen the polymer network and enhance its ability to withstand mechanical loads.

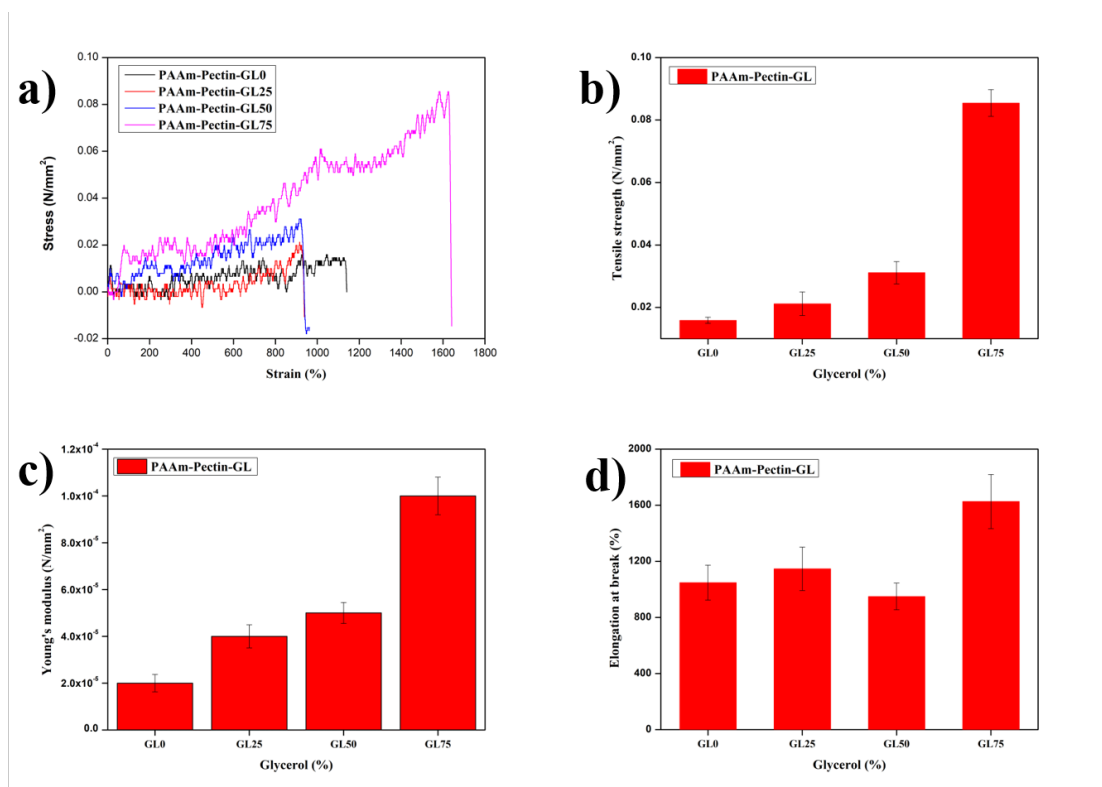


Figure 3.11: Effect of glycerol content on the mechanical performance of PAAm-pectin-GL organogels.

Table 3.5: Mechanical properties of PAAm-pectin-GL organogels with varying glycerol content.

Hydrogel	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation (%)
PAAm-pectin-GL0	1.59×10^{-2}	2.00×10^{-5}	1047.89
PAAm-pectin-GL25	2.12×10^{-2}	4.00×10^{-5}	1146.64
PAAm-pectin-GL50	3.11×10^{-2}	5.00×10^{-5}	950.00
PAAm-pectin-GL75	8.54×10^{-2}	1.00×10^{-4}	1626.56

3.2.6 Rheological Characterization

Figures 3.12 a and 3.12 b illustrate the variation in storage modulus (G') as a function of the angular frequency (ω) for PAAm–pectin organogels incorporating different concentrations (0%, 25%, 50%, and 75%) of glycerol and ethylene glycol, respectively.

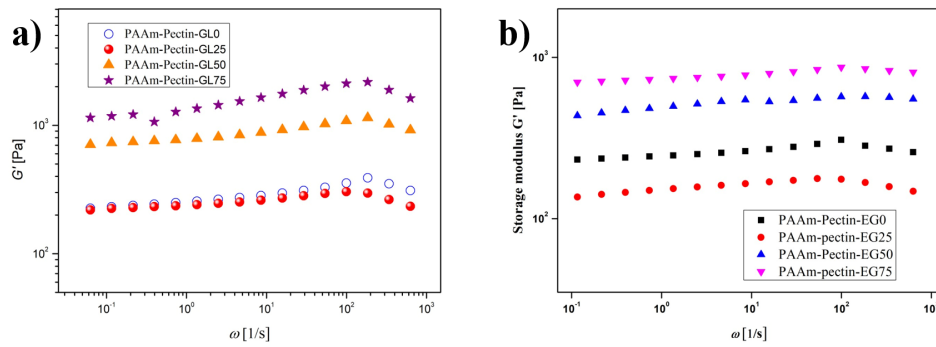


Figure 3.12: Variation of storage modulus (G') as a function of angular frequency (ω) for PAAm–pectin (a) Glycerol (b) Ethylene glycol organogels.

The storage modulus, which represents the elastic or solid component of the viscoelastic response, provides valuable information on the rigidity and structural integrity of the polymer network. In both systems, G' increases progressively with polyol concentration, reflecting the crucial role of solvent composition in modulating network elasticity. At lower concentrations (0% and 25%), the G' values remain relatively low and nearly frequency independent, suggesting a soft, weakly crosslinked network governed by limited physical interactions and the plasticising effect of the incorporated polyols. In contrast, organogels containing 50% and 75% glycerol and ethylene glycol exhibit a pronounced rise in G' and a slight frequency-dependent increase, indicative of enhanced crosslinking density and the development of a more compact and entangled polymeric matrix. Between the two systems, glycerol-modified organogels display slightly higher G' values than their ethylene glycol counterparts, implying that glycerol's tri-hydroxyl structure facilitates stronger hydrogen bonding and more extensive polymer–polymer associ-

ations. Overall, the observed trends confirm that both glycerol and ethylene glycol effectively reinforce the PAAm–pectin network, with glycerol imparting superior elasticity and structural stability through stronger intermolecular interactions and tighter network packing (Said et al., 2023; Li, Deng and Zhou, 2020).

Figures 3.13 a and 3.13 b present the variation of loss modulus (G'') as a function of angular frequency (ω) for PAAm–pectin organogels containing different concentrations (0%, 25%, 50%, and 75%) of glycerol and ethylene glycol, respectively.

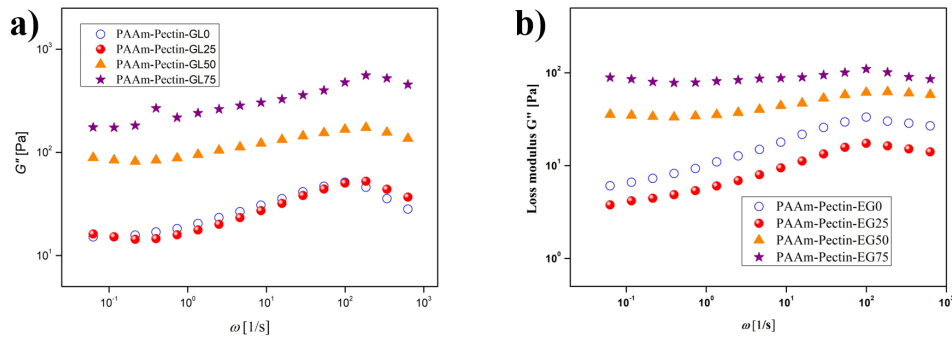


Figure 3.13: Variation of loss modulus (G'') as a function of angular frequency (ω) for PAAm–pectin (a) Glycerol (b) ethylene glycol organogels.

The loss modulus represents the viscous or liquid-like component of the viscoelastic response, providing insight into molecular mobility, internal friction, and energy dissipation within the polymer network. In both systems, G'' increases progressively with polyol concentration, following a trend comparable to that observed for the storage modulus (G'), but with greater sensitivity to frequency. At lower concentrations (0% and 25%), G'' remains comparatively low and nearly frequency independent, indicative of limited energy dissipation and a weakly viscous system. However, at higher polyol contents (50% and 75%), a substantial rise in G'' is observed, accompanied by a steeper frequency response. This indicates enhanced viscous flow and more dynamic molecular rearrangements, which can be attributed to the plasticizing role of glycerol and ethylene glycol. The increased internal friction and molecular motion result from greater chain flexi-

bility, reinforcing the conclusion that polyols facilitate a transition toward a more viscoelastic and adaptable gel structure (Feng et al., 2021).

Between the two systems, glycerol-based organogels exhibit slightly higher G'' values and more pronounced frequency dispersion than their ethylene glycol counterparts, indicating superior damping characteristics. This behaviour can be attributed to the higher viscosity of glycerol, and its tri-hydroxyl functionality enables stronger hydrogen bonding and greater structural flexibility. Overall, the increase in G'' with polyol loading demonstrates that both glycerol and ethylene glycol induce a transition from a predominantly elastic to a more viscoelastic regime, thereby improving energy dissipation and structural adaptability under oscillatory deformation.

Collectively, the observed trends in storage and loss moduli for both glycerol and ethylene glycol-based PAAm-pectin organogels reveal a systematic evolution in rheological behavior with increasing polyol concentration. At lower contents (0 % and 25 %), the organogels exhibit the characteristics of soft, weakly elastic materials with limited energy dissipation, functioning as lightly crosslinked or loosely entangled systems. In this state, the modest G' and G'' values reflect minimal physical interactions and restricted molecular mobility within the polymer matrix. As the polyol concentration increases to 50 % and 75 %, the systems undergo a distinct transition toward more structurally integrated viscoelastic solids. In these formulations, the storage modulus (G') consistently exceeds the loss modulus (G'') across the entire frequency range, signifying the dominance of elastic behavior and the establishment of a robust, percolated network (Wang, Du, Hashmi, Cui, Li, Handschuh-Wang, Zhou and Stadler, 2023). This enhancement in mechanical resilience and energy absorption is attributed to intensified polymer-polymer and polymer-polyol hydrogen bonding interactions, which reinforce the network junctions and promote dynamic responsiveness under stress (Shi et al., 2017).

The ability to fine-tune viscoelastic properties through polyol incorporation thus provides an effective strategy for designing gels with tailored mechanical performance. Higher polyol loadings, particularly at 75 %, yield organogels with elevated G' and G'' values, indicative of superior elasticity and damping capacity, key attributes for applications requiring structural integrity and energy dissipation under deformation. Conversely, formulations with lower polyol levels may be advantageous in scenarios where reduced mechanical resistance, higher permeability, or enhanced degradability is preferred.

Fig. 3.14 a and Fig. 3.14 b present the variation of $\tan \delta$ (G''/G') as a function of angular frequency (ω) for organogels formulated with varying glycerol and ethylene glycol concentrations respectively. As a key indicator of viscoelastic character, $\tan \delta$ provides insight into the relative dominance of viscous versus elastic behaviour within the system. A higher $\tan \delta$ denotes a more energy-dissipative (viscous) response, while a lower value indicates predominant elasticity (Rolón-Garrido and Wagner, 2009; Murata, 2012). The plot reveals a systematic increase in $\tan \delta$ with both polyol concentration and frequency, suggesting that the incorporation of polyol enhances the viscous characteristics of the gel and that higher oscillatory stress further amplifies energy dissipation.

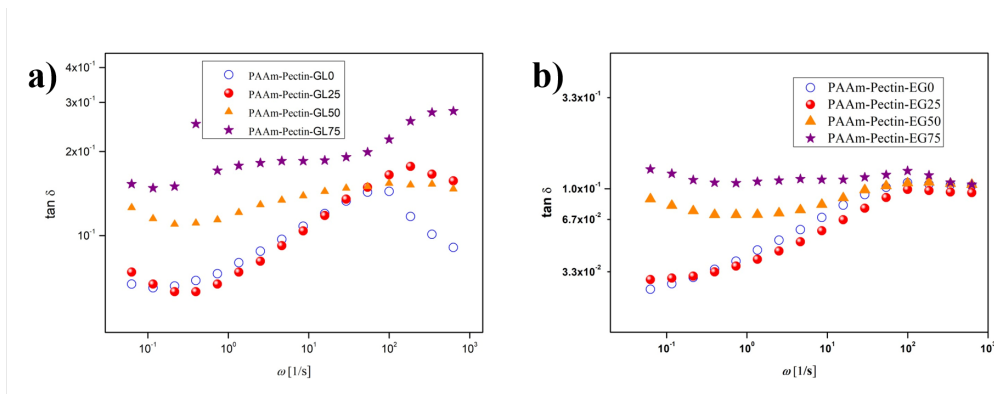


Figure 3.14: Variation of damping factor ($\tan \delta$) as a function of angular frequency (ω) for PAAm-pectin organogels formulated with (a) glycerol and (b) ethylene glycol at different concentrations.

At lower polyol levels (0% and 25%), $\tan \delta$ values remain relatively low across

most of the frequency spectrum. This trend reflects the formation of a highly elastic network with limited energy dissipation, attributes of a gel system dominated by strong physical or covalent crosslinks and reduced chain mobility. A modest rise in $\tan \delta$ at higher frequencies may indicate minor disruption of these interactions under dynamic conditions, leading to slight increases in viscous contributions. These formulations are better suited for applications requiring structural rigidity, minimal deformation, and consistent elastic recovery under stress.

In contrast, organogels containing 50% and 75% polyols exhibit significantly elevated and more frequency-sensitive $\tan \delta$ values. This indicates a more damping-capable and mechanically adaptable material, characteristic of soft viscoelastic systems where polyol enhances polymer chain mobility while still maintaining the gel framework ($G' > G''$). Such a profile is particularly advantageous in applications where the structural integrity and dynamic responsiveness is critical. The $\tan \delta$ plot thus confirms its utility as a design parameter for tuning the mechanical behaviour of PAAm–pectin organogels through precise modulation of polyol content (Li, Deng and Zhou, 2020; Cai et al., 2024).

Fig. 3.15 a and Fig. 3.15 b present a semi-logarithmic plot of shear stress versus shear strain (%) for PAAm–pectin organogels across varying glycerol and ethylene glycol concentrations (0%, 25%, 50%, and 75%) respectively. . The measurements were performed through amplitude sweep tests conducted at a fixed frequency of 1 Hz, with strain amplitudes ranging from 0.01 to 100% at 25 °C. At low strain amplitudes (10^{-2} –1%), all samples display a nearly constant stress response, representing the Linear Viscoelastic Region (LVER), where the gels deform reversibly without significant microstructural disruption.

Beyond the LVER threshold (1% strain), the stress rises nonlinearly, indicating the onset of structural rearrangements and yielding behavior. The magnitude of this nonlinear escalation strongly depends on polyol concentration, with GL50\EG50 and GL75\EG75 exhibiting the most pronounced increases. The en-

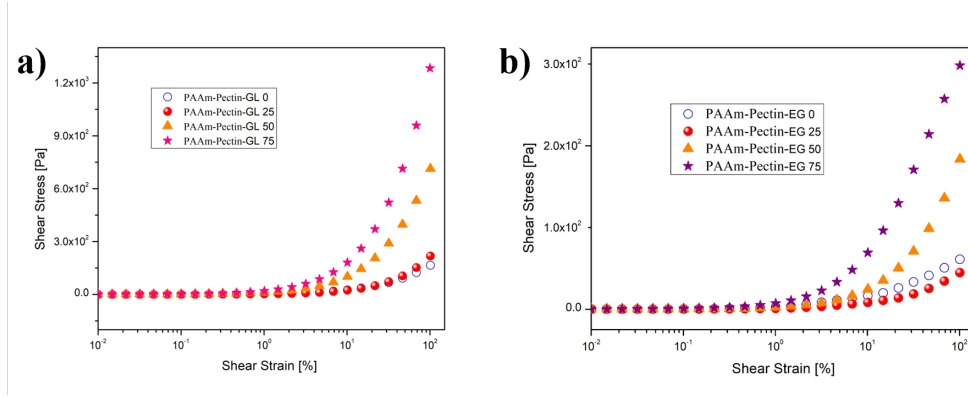


Figure 3.15: Plot of shear stress versus shear strain (%) for PAAm-pectin (a) glycerol and (b) ethylene glycol organogels at varying polyol concentrations.

hanced stress response of polyol-rich gels reflects the dual role of polyol in facilitating polymer mobility while simultaneously promoting intermolecular hydrogen bonding, which strengthens the network and distributes stress more effectively. These findings confirm that polyols significantly extend the strain tolerance of PAAm-pectin organogels, enabling them to resist higher stresses before yielding. Such tunable stress-strain behaviour is critical for applications where gels must endure large deformations while maintaining functional integrity.

Fig. 3.16 a and Fig. 3.16 b provides a comparative bar chart illustrating the storage modulus (G') and loss modulus (G'') at a frequency of 1 Hz for PAAm-pectin-GL and PAAm-pectin-EG organogels containing 0%, 25%, 50%, and 75% polyols, respectively. This representation clearly captures the evolving viscoelastic profile of the organogels as a function of polyol concentration. The storage modulus (G'), depicted in blue, signifies the elastic or solid-like component of the material, while the loss modulus (G''), shown in green, reflects its viscous or liquid-like characteristics. At lower polyol contents (0% and 25%), G' remains high, while G'' is considerably lower. This indicates a weakly crosslinked network exhibiting dominant elastic behaviour with limited viscous dissipation, characteristic of a soft gel with restricted molecular mobility.

As the polyol concentration increases to 50%, both G' and G'' exhibit a pronounced rise, with G' showing a substantial increase and G'' increasing propor-

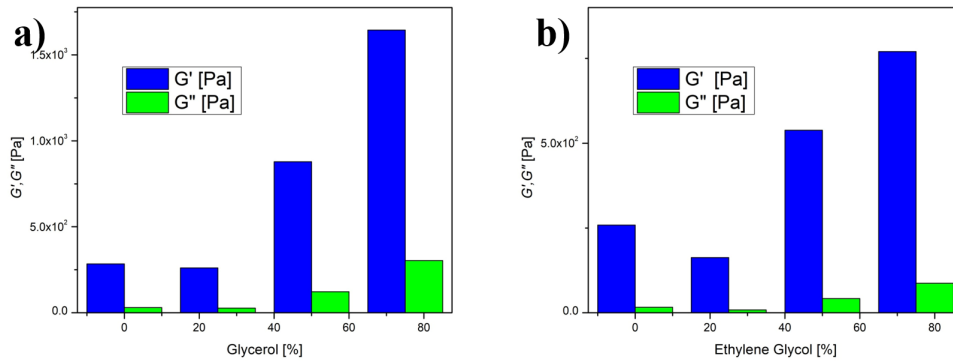


Figure 3.16: Storage modulus (G') and loss modulus (G'') at a frequency of 1 Hz for PAAm-pectin (a) glycerol and (b) ethylene glycol organogels containing 0%, 25%, 50%, and 75% polyols.

tionally. This substantial enhancement in moduli highlights the formation of a denser, more cohesive gel network facilitated by stronger intermolecular interactions. Polyols, in this context, function not only as a plasticiser but also as a network-modifying agent, promoting hydrogen bonding, increasing chain entanglement, and improving load transfer throughout the matrix. The result is a material with improved rigidity and energy dissipation capacity, ideal for applications demanding a balance of structural strength and viscoelastic responsiveness. At 75% polyol content, the organogels exhibit their highest mechanical performance, with G' reaching markedly elevated values and G'' increasing correspondingly. The dominance of G' over G'' is retained, confirming the gel's solid-like behavior, yet the elevated G'' underscores its enhanced ability to dissipate energy. This balance of elasticity and damping suggests a highly optimized viscoelastic material, capable of absorbing and recovering from deformation efficiently. Overall, the bar graph highlights the polyol-dependent tunability of the organogel's mechanical properties, reinforcing its potential for a broad range of soft material applications.

3.2.7 Evaluation of Anti-freezing Behaviour

After storage at $-15\text{ }^{\circ}\text{C}$ for 6 h, both the PAAm-pectin hydrogel and the PAAm-pectin-EG10 organogel were completely frozen, exhibiting an opaque appearance and brittle mechanical behaviour. This freezing process reduced their flexibility and transparency at sub-zero temperatures. In contrast, the PAAm-pectin-EG25 and PAAm-pectin-EG50 organogels remained transparent and mechanically flexible under identical conditions, indicating that the water confined within these networks did not undergo freezing (Figs. 3.17). Their ability to retain both mechanical integrity and optical transparency demonstrates the superior anti-freezing capability of organogels with higher ethylene glycol content. Ethylene glycol depresses the freezing point of water through colligative effects and forms strong hydrogen-bonding interactions with water molecules, thereby inhibiting ice formation.

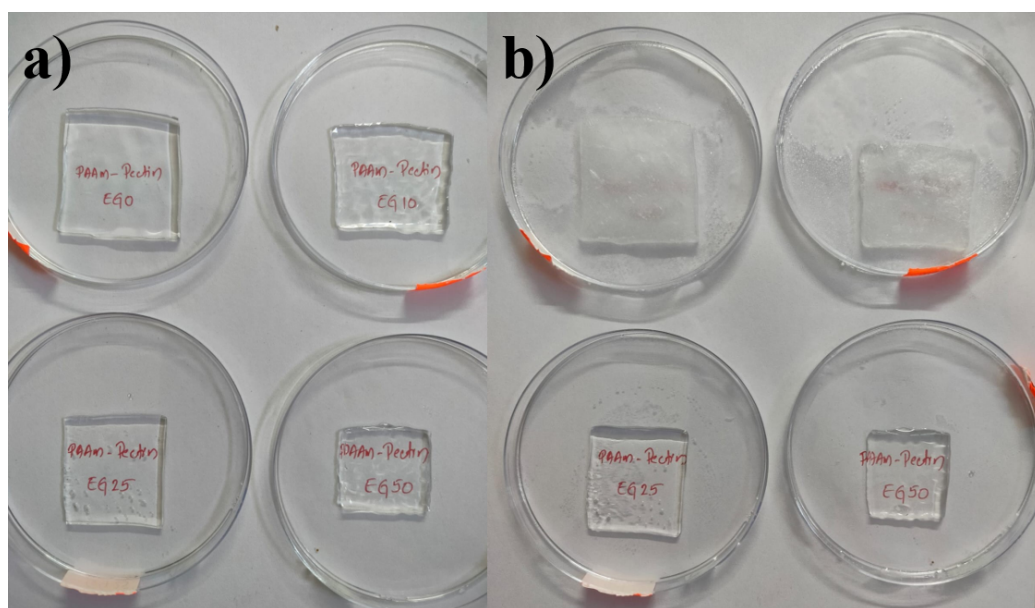


Figure 3.17: Photographs of the PAAm-pectin hydrogel and PAAm-pectin-EG organogels taken a) before and b) after refrigeration.

A similar trend was observed in the case of glycerol-based organogels, where higher glycerol content effectively suppressed ice crystallization and maintained flexibility and transparency even at sub-zero temperatures (Fig. 3.18).

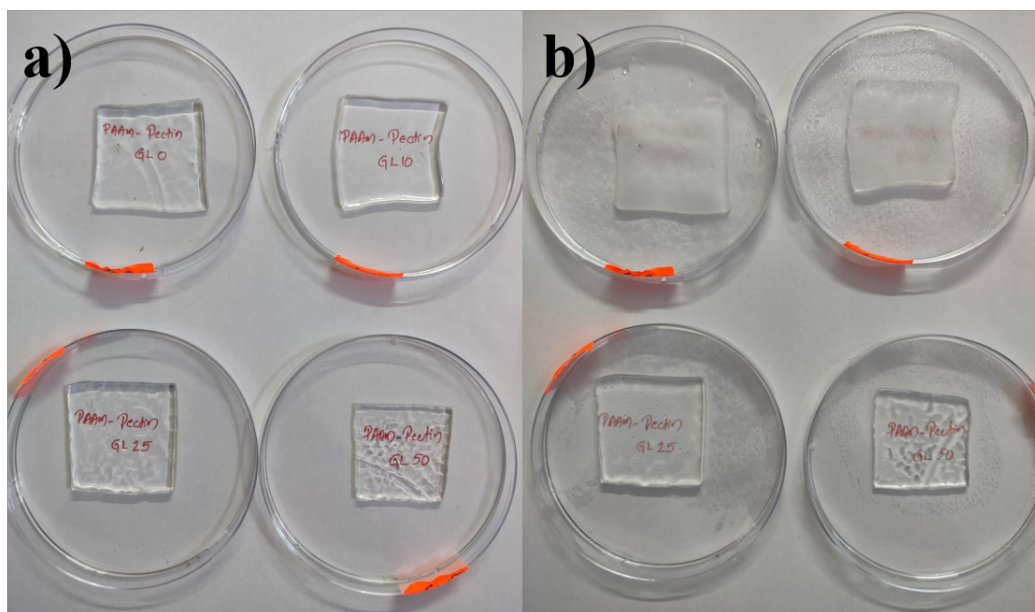


Figure 3.18: Photographs of the PAAm-pectin hydrogel and PAAm-pectin-GL organogels taken a) before and b) after refrigeration.

Differential Scanning Calorimetry (DSC) analysis further supported these observations. The PAAm-pectin hydrogel exhibited a sharp exothermic peak in the DSC spectrum, corresponding to the freezing of water within the hydrogel matrix. In contrast, the DSC spectra of the PAAm-pectin-EG (Fig. 3.19) and PAAm-pectin-GL (Fig. 3.20) organogels showed a progressive shift of the exothermic peaks towards lower temperatures with increasing ethylene glycol and glycerol content, respectively. This shift indicates a depression of the freezing point of the organogels induced by the presence of ethylene glycol or glycerol. The onset and peak freezing temperatures of the PAAm-pectin organogels containing different ethylene glycol concentrations are presented in Table 3.6, while the corresponding values for the PAAm-pectin-GL organogels with varying glycerol contents are summarised in Table 3.7.

EG and GL form extensive hydrogen bonds with water molecules, effectively inhibiting ice crystal formation at low temperatures (Mo et al., 2019). The anti-freezing efficacy of the organogels increased with higher polyol content, as the enhanced concentration disrupted the hydrogen bonding network among water

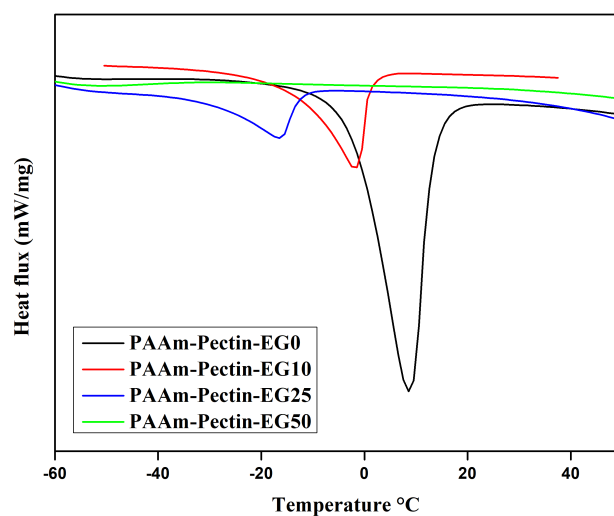


Figure 3.19: The DSC spectra of PAAm-pectin hydrogel and the PAAm-pectin-EG organogels.

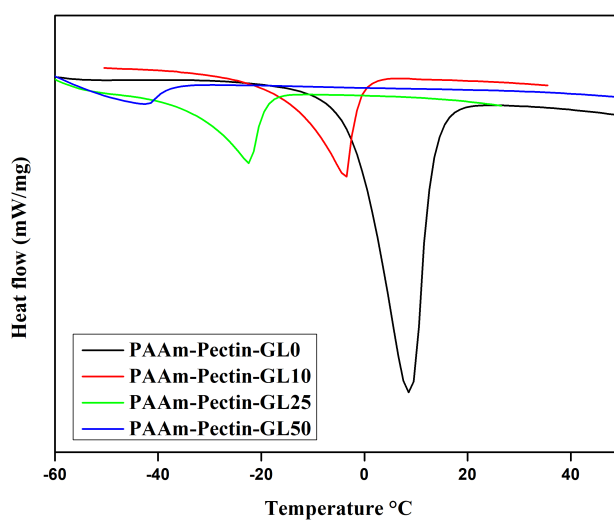


Figure 3.20: The DSC spectra of PAAm-pectin hydrogel and the PAAm-pectin-GL organogels.

Table 3.6: Onset and peak freezing temperatures of PAAm–pectin–EG organogels with varying EG contents.

Organogel	Peak Freezing Temp (°C)	Onset Freezing Temp (°C)
PAAm–pectin–EG0	8.6	-1.5
PAAm–pectin–EG10	-1.8	-10.3
PAAm–pectin–EG25	-16.4	-27.0
PAAm–pectin–EG50	Not observed	Not observed

Table 3.7: Onset and peak freezing temperatures of PAAm–pectin–GL organogels with varying GL contents.

Organogel	Peak Freezing Temp (°C)	Onset Freezing Temp (°C)
PAAm–pectin–GL0	8.6	-1.5
PAAm–pectin–GL10	-1.6	-8.9
PAAm–pectin–GL25	-12.3	-21.8
PAAm–pectin–GL50	-42.3	-55.6

molecules more effectively, thereby lowering the freezing point and improving the flexibility and transparency of the gels under sub-zero conditions (Gao, Wang, Wu, Xue, Yan, Zhang, Wang, Zhang, Jiang and Zhao, 2024; Bisht et al., 2024). Moreover, the hydroxyl groups of glycerol and EG interact not only with water molecules but also with polar functional groups (carboxylates in pectin, amides in polyacrylamide) within the polymer network, forming hydrogen bonding bridges between solvent and polymer chains. These interactions reduce the amount of “free” water available to form ice by preferentially associating water molecules within polymer-solvent-solvent complexes. Consequently, a higher proportion of water remains in a bound or non-crystallisable state as glycerol or EG content increases.

3.2.8 Solvent retention and stability analysis

The PAAm–pectin hydrogel became dry and brittle within one day of storage at room temperature, indicating its poor solvent-retention capability. In contrast, the corresponding organogels preserved their original state, maintaining optical transparency and mechanical flexibility. The time-dependent solvent-retention

behavior of the PAAm-pectin hydrogel and PAAm-pectin-EG10, PAAm-pectin-EG25, and PAAm-pectin-EG50 organogels is presented in Fig. 3.21. After one day of storage, the hydrogel retained only 4.67 % of its initial weight, whereas the organogels exhibited substantially enhanced solvent retention, which increased systematically with ethylene glycol content. As shown in Fig. 3.22, after 20 days of storage the hydrogel displayed significantly lower weight retention compared to the organogels, which demonstrated a progressive increase in retained weight with increasing ethylene glycol concentration. The quantitative solvent-retention values of the PAAm-pectin hydrogel and PAAm-pectin-EG organogels after 20 days are summarised in Table 3.8.

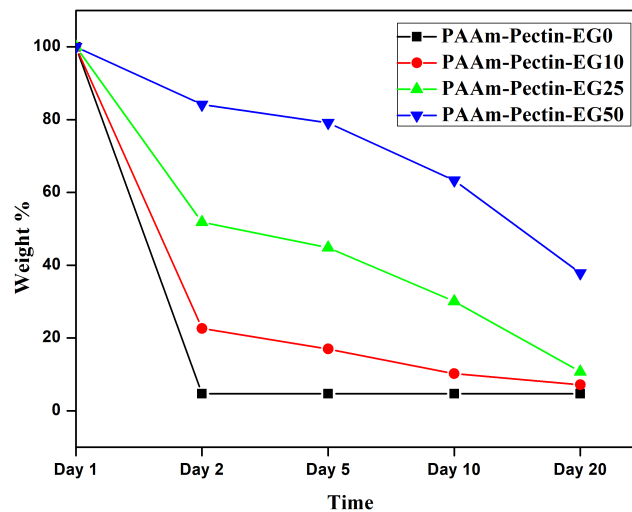


Figure 3.21: Solvent retention capacity of PAAm-pectin-EG organogels at different storage times.

Table 3.8: Weight retained by PAAm-pectin-EG organogels after 20 days.

Organogel	Weight Retained (%)
PAAm-pectin-EG0	4.67
PAAm-pectin-EG10	7.17
PAAm-pectin-EG25	10.70
PAAm-pectin-EG50	37.89

The solvent-retention behavior of PAAm-pectin hydrogels and PAAm-pectin-

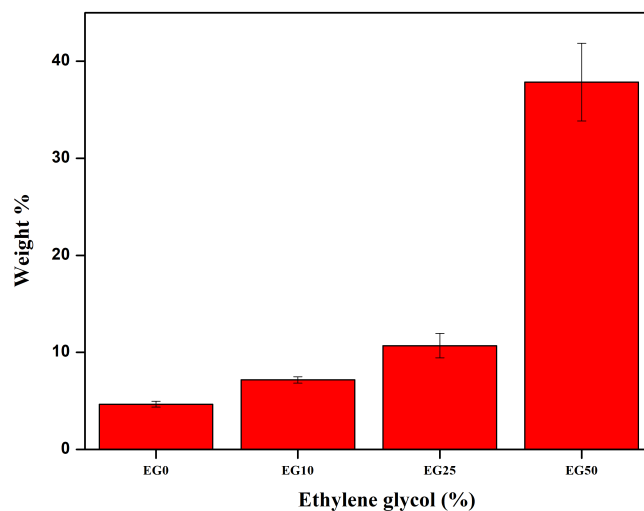


Figure 3.22: Solvent retention capacity of PAAm-pectin-EG organogels after 20 days.

GL10, PAAm-pectin-GL25, and PAAm-pectin-GL50 organogels over different storage durations is presented in Fig. 3.23. The hydrogel and organogels exhibited progressively enhanced solvent-retention capacity with increasing glycerol content. Figure 3.24 compares the solvent-retention capacities of the hydrogel and organogels after 20 days of storage at room temperature. The quantitative solvent-retention values for PAAm-pectin-glycerol organogels with varying glycerol concentrations are summarised in Table 3.9.

The solvent retention capacity of PAAm-pectin hydrogel and PAAm-pectin-GL10, PAAm-pectin-GL25, and PAAm-pectin-GL50 organogels at different storage times is shown in Fig. 3.23. The hydrogel exhibited a gradual enhancement in solvent-retention capacity with increasing glycerol content. The plot (Fig. 3.24) compares the solvent retention capacity of the hydrogel and organogels after being kept for 20 days at room temperature. Table 3.9 presents the solvent retention capacities of PAAm-pectin-glycerol organogels with different glycerol contents.

Thermogravimetric analysis (TGA) provided further insights into the thermal stability of the hydrogels and organogels (Fig. 3.25). A noticeable improvement in thermal stability and moisture retention was observed in PAAm-pectin-EG

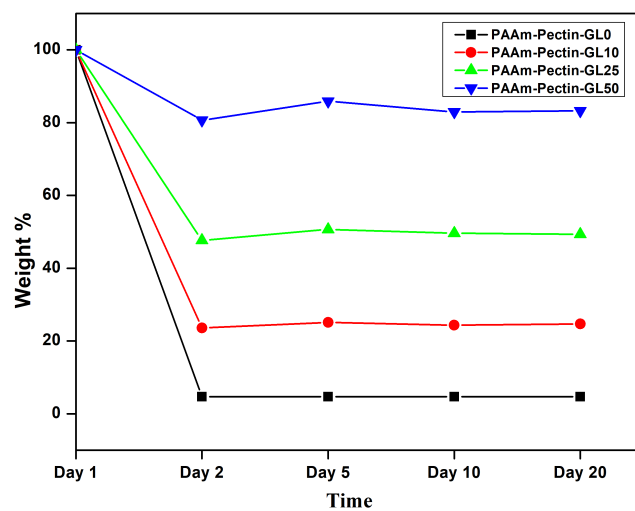


Figure 3.23: Solvent retention capacity of PAAm-pectin-GL organogels at different storage times.

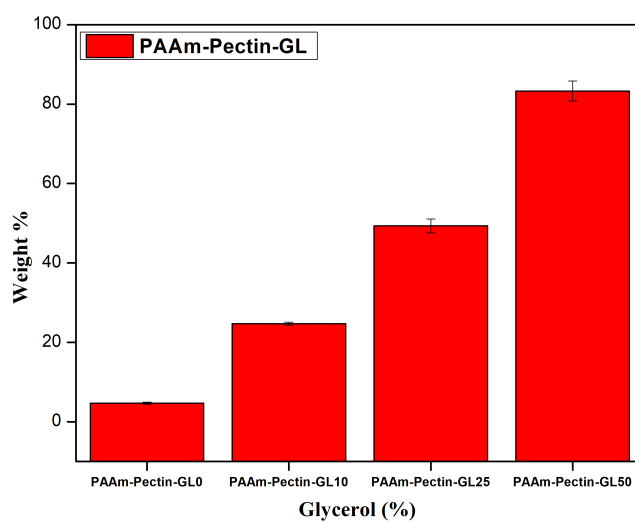
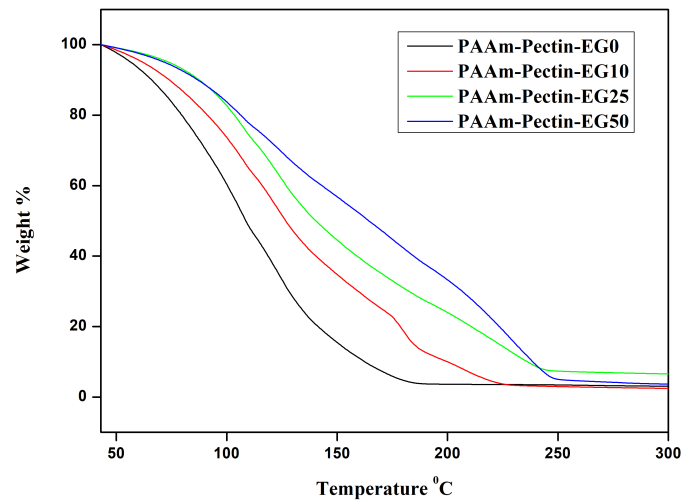


Figure 3.24: Solvent retention capacity of PAAm-pectin-GL organogels after 20 days.

Table 3.9: Weight retained by PAAm-pectin-GL organogels with varying glycerol contents after drying.

Organogel	Weight Retained (%)
PAAm-pectin-GL0	4.67
PAAm-pectin-GL10	24.71
PAAm-pectin-GL25	49.32
PAAm-pectin-GL50	83.28

organogels compared to that of the PAAm-pectin hydrogel. With the incorporation of ethylene glycol, the organogels exhibited enhanced resistance to thermal degradation and reduced solvent loss upon heating. The Table 3.10 shows the weight retained by PAAm-pectin hydrogels and PAAm-pectin-EG organogels at different temperatures.

**Figure 3.25:** The TGA thermograms of the PAAm-pectin hydrogel and PAAm-pectin-EG organogels.**Table 3.10:** Weight retained by PAAm-pectin-EG organogels at different temperatures.

Organogel	50°C	100°C	150°C	200°C
PAAm-pectin-EG0	97.62	60.25	15.18	3.63
PAAm-pectin-EG10	98.20	73.96	33.72	5.36
PAAm-pectin-EG25	97.47	71.68	34.01	8.27
PAAm-pectin-EG50	98.13	80.99	57.70	11.82

The TGA thermograms of PAAm-pectin hydrogel and PAAm-pectin-GL10,

PAAm-pectin-GL25, and PAAm-pectin-GL50 organogels are shown in Fig.3.26. The thermal behaviour and water retention properties of PAAm-pectin hydrogel were significantly influenced by the glycerol content. Compared to the pristine hydrogel, the PAAm-pectin-GL organogels demonstrated improved thermal stability and a stronger ability to retain solvent upon heating. This enhancement can be attributed to the hydrogen bonding interactions between glycerol and the polymer matrix, which restrict water evaporation and delay thermal degradation. The weight retention values of the PAAm-Pectin hydrogel and its glycerol-based organogels at different temperatures are presented in Table 3.11.

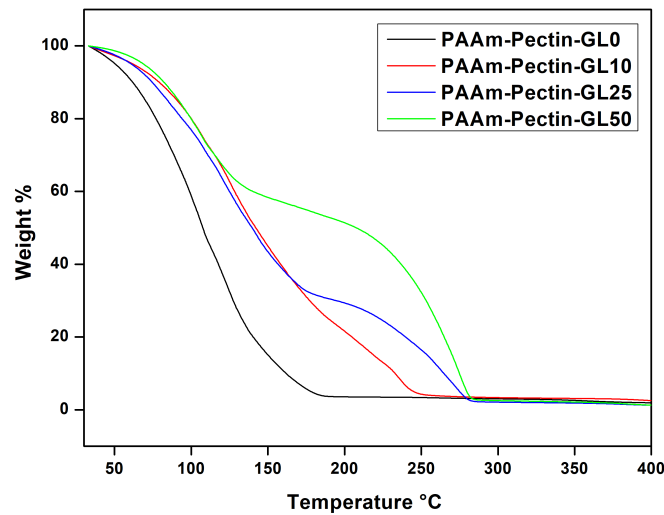


Figure 3.26: The TGA thermograms of the PAAm-pectin hydrogel and PAAm-pectin-GL organogels.

Table 3.11: Weight retention of PAAm-pectin-GL organogels at different temperatures.

Organogel	50°C	100°C	150°C	200°C
PAAm-pectin-GL0	94.51	58.34	14.92	3.53
PAAm-pectin-GL10	94.92	70.19	26.23	6.10
PAAm-pectin-GL25	97.32	79.06	48.90	29.17
PAAm-pectin-GL50	98.56	84.68	62.45	52.93

The water in a hydrogel can be found in three different states, namely free water, intermediate water, and bound water. The bound water is strongly attached

to the polymer chains or solvents by forming hydrogen bonds. The free water consists of water molecules that are not bound to the polymer networks or any solvents. The intermediate water weakly interacts with the polymer networks or solvents in the hydrogels. In a hydrogel, the free water content is more compared to bound water and intermediate water, and hence, its water retention capacity is poor. Glycerol and ethylene glycol are capable of forming hydrogen bonds with the water molecules and transforming the free water into bound or intermediate water. Hence, the introduction of these polyols into the hydrogel matrix improves its water retention capacity (Sekine and Ikeda-Fukazawa, 2009; Yu et al., 2021).

The increase in polyol content leads to the formation more and extensive hydrogen bonds with polymer networks. This restricts the movement of solvent molecules within the network, helping to prevent solvent loss through evaporation or leaching. Moreover, glycerol and ethylene glycol have much lower vapor pressures and higher boiling points than water. When water in the hydrogel matrix is replaced by these polyols, the volatility of the solvent system in the gel decreases. This reduction in volatility slows down evaporation when the material is exposed to air or heat. As a result, the organogel is able to retain its solvent for a longer time and avoid dehydration-induced shrinkage or stiffening.

3.2.9 Conductivity studies

The ionic conductivity of the gels was determined using AC impedance spectroscopy, where a thin film of the gel was placed between two stainless steel electrodes to form a parallel-plate configuration. This setup ensured uniform contact and minimised interfacial resistance during measurement. Impedance spectra were recorded over a broad frequency range, and the bulk resistance of the gel was obtained from the Nyquist plot.

The Nyquist plot (Fig: 3.27) compares the electrochemical performance of PAAm hydrogel and PAAm-pectin hydrogel with increasing concentrations of

pectin. The intercept at the real part in the Nyquist plot was taken as the resistance (Huang et al., 2019; Li, Lou, Wang, Sun, Li and Liu, 2020). The conductivity of the hydrogels was calculated using the formula $\sigma = L/R \times A$, where the thickness (cm) of the sample is L, the cross-sectional area (cm^2) of the sample is represented by A and R represents the resistance (Ω) of the hydrogel samples. The ionic conductivity of PAAm-pectin hydrogels with varying pectin contents is shown in Fig. 3.28. Compared to the PAAm hydrogel, the PAAm-Pectin hydrogels exhibited higher ionic conductivity. The incorporation of the anionic polysaccharide pectin enhances ion mobility by increasing the concentration of dissociable ionic groups within the polymer network, thereby facilitating more efficient ion diffusion and resulting in improved conductivity (Zhu et al., 2022). Moreover, a direct correlation was observed between pectin content and ionic conductivity, whereby higher pectin concentrations enhanced ion transport within the hydrogel network. The higher the pectin content in the hydrogels, the more Ca^{2+} ions are required for ionic crosslinking and generate more conductive ion paths; this in turn, enhances the ionic conductivity of the hydrogels. (Huang, Liu, Chi, Jiang, Xu, Qu, Zhao, Li, Chen, Chen et al., 2021)

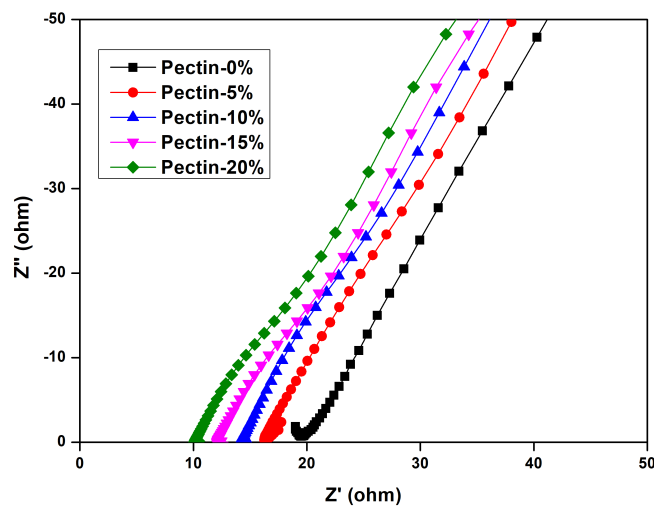


Figure 3.27: Nyquist plot to compare the electrochemical performances of PAAm-pectin hydrogel at different pectin content.

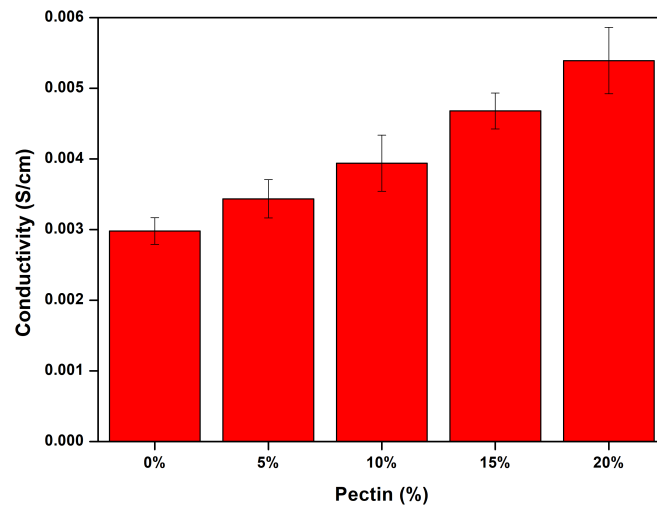


Figure 3.28: Ionic conductivity of PAAm-pectin-hydrogel at different pectin content.

The polyacrylamide–pectin (PAAm–pectin) hydrogel exhibits higher ionic conductivity than a pure polyacrylamide (PAAm) hydrogel due to the polyelectrolyte nature of pectin and the introduction of additional ionizable functional groups into the hydrogel matrix. Pectin networks consisting of a large number of carboxylate groups ($-\text{COO}^-$) along their backbone. These groups can attract and bind cations and thereby increase the amount of mobile ions within the hydrogel. The presence of these dissociated counterions enhances the ionic conductivity by increasing the number of charge carriers available for ion transport through the gel.

In contrast, polyacrylamide itself is a neutral polymer lacking ionisable groups in its backbone. A pure PAAm hydrogel primarily supports ionic conduction through the passive diffusion of ions dissolved in the water phase, without contributing additional fixed charges or ion-binding sites. Therefore, its ionic conductivity is limited by the ionic strength of the external medium and lacks the contribution of an internal polyelectrolyte mechanism. As a result, the synergistic effect of increased fixed charge density, enhanced ion-binding capacity, and a more ion-conducive network architecture leads to significantly higher ionic conductivity in PAAm–pectin hydrogels compared to their purely polyacrylamide counterparts.

This enhancement makes PAAm–pectin hydrogels particularly suitable for applications requiring ionic conductivity, such as bioelectronic interfaces, ionic skin sensors, and electrolyte membranes.

The ionic conductivity of hydrogels was found to be influenced by the concentration of Ca^{2+} ions. The AC conductivity vs. frequency plot of PAAm-pectin hydrogels with varying concentrations of calcium ions is shown in Fig. 3.29. The hydrogels with 0.1 M and 0.5 M calcium concentrations exhibited low conductivity, and the conductivity of the hydrogels increased with an increase in the calcium concentration. The hydrogels prepared by immersing them in 1 M and 2 M Calcium chloride solutions exhibited nearly identical ionic conductivities.

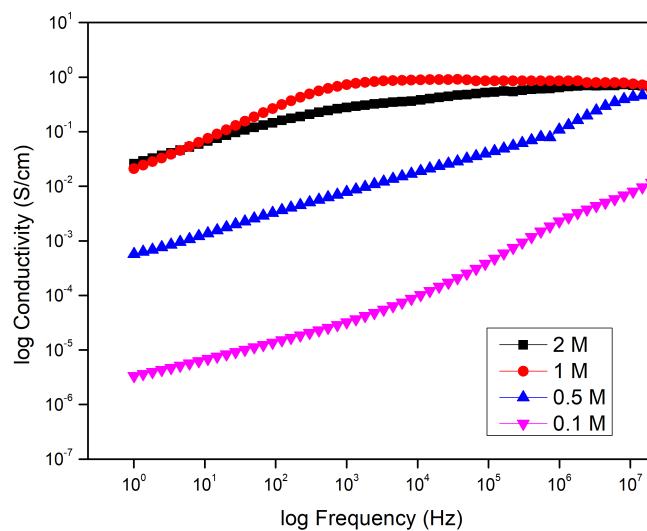


Figure 3.29: AC conductivity vs frequency plot of PAAm-pectin-hydrogel at different calcium concentrations.

The ionic conductivity of polyacrylamide–pectin (PAAm–pectin) hydrogels is significantly influenced by the concentration of calcium ions (Ca^{2+}) used during the crosslinking process. Calcium ions play a dual role: they act as ionic crosslinkers that form “egg-box” structures with the carboxylate groups of pectin, and they contribute to the population of mobile charge carriers within the hydrogel matrix. At low calcium ion concentrations, a limited number of Ca^{2+} ions are available

both for crosslinking and as free ions in the aqueous phase. Although some Ca^{2+} ions participate in the formation of ionic crosslinks with pectin, the remaining free ions contribute to the ionic conductivity. Within this range, ionic conductivity increases with increasing calcium concentration, as more mobile charge carriers are present in the hydrogel. At high calcium ion concentrations, the saturation of available binding sites can result in excessive crosslinking and network stiffening, which not only limits the number of free ions but also restricts ionic transport pathways by reducing polymer chain flexibility and network porosity. As a result, the ionic conductivity may decline or plateau at high calcium ion concentrations despite an abundance of calcium ions in the system.

Fig. 3.30 shows the AC conductivity vs. frequency plot of PAAm-pectin hydrogel at different temperatures. The conductivity of the hydrogels decreased with the decrease in temperature. The Nyquist plot of the electrochemical performances of PAAm-pectin hydrogel at different temperatures is shown in Fig. 3.31 and Fig. 3.32. The ionic conductivity of the PAAm-pectin hydrogels at 233 K, 253 K, 273 K, and 298 K was quantitatively obtained from the corresponding Nyquist plot, and the resulting values are provided in Table 3.12.

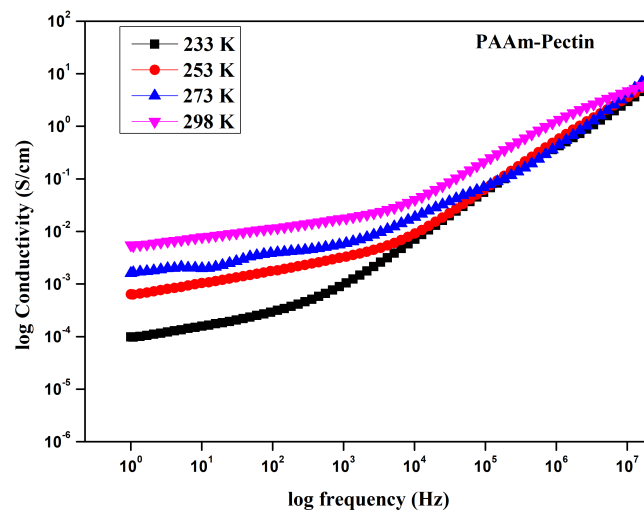


Figure 3.30: AC conductivity vs frequency plot of PAAm-pectin-hydrogel at different temperatures.

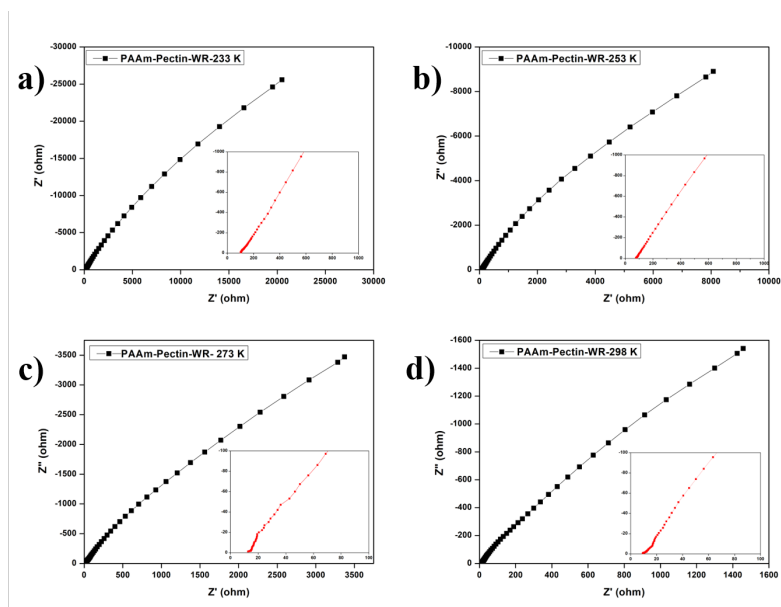


Figure 3.31: Nyquist plot of the electrochemical performances of PAAm-pectin hydrogel at different temperatures.

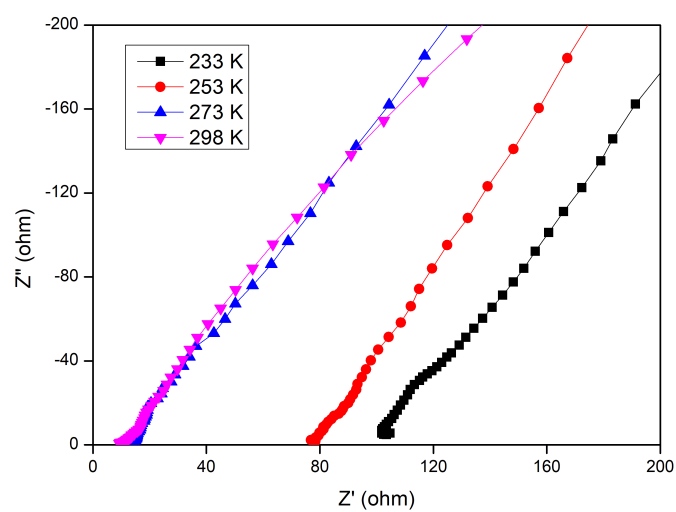


Figure 3.32: Nyquist plot to compare the electrochemical performances of PAAm-pectin hydrogel at different temperatures.

Table 3.12: Temperature-dependent ionic conductivity of PAAm-pectin hydrogel and PAAm-pectin-EG organogel.

Temperature (°C)	PAAm-pectin Hydrogel ($S\text{ cm}^{-1}$)	PAAm-pectin-EG Organogel ($S\text{ cm}^{-1}$)
-40	5.40×10^{-4}	1.31×10^{-3}
-20	7.37×10^{-4}	1.90×10^{-3}
0	4.47×10^{-3}	2.29×10^{-3}
25	5.45×10^{-3}	3.05×10^{-3}

In the PAAm-pectin hydrogel system, a pronounced decline in ionic conductivity is observed at subzero temperatures due to the phase transition of water within the polymer network. As the temperature decreases below 0°C, a large fraction of the free water present in the PAAm-pectin matrix crystallises into ice, thereby reducing the availability of liquid water that facilitates the transport of ions. Because ionic conduction in these hydrogels depends on the movement of solvated ions through continuous aqueous domains, the formation of ice disrupts these conductive pathways and severely restricts ion mobility (Zhu et al., 2022).

Fig. 3.33 shows the ac impedance spectra of the PAAm-pectin-EG organogel at different temperatures. The Nyquist plots of the electrochemical performance of PAAm-pectin-EG organogel at different temperatures are shown in Fig. 3.34 and Fig. 3.35. Table 3.12 compares the ionic conductivity of PAAm-Pectin hydrogels and PAAm-pectin-EG organogels measured at different temperatures. In contrast to the PAAm-pectin hydrogel, temperature drops had minimal impact on the ionic conductivity of the PAAm-pectin-EG organogel.

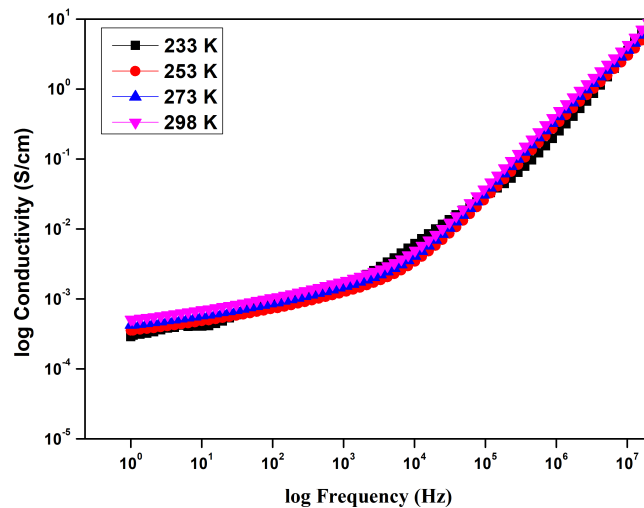


Figure 3.33: AC conductivity vs frequency plot of PAAm-pectin-EG organogels at different temperatures.

The ionic conductivities of PAAm-pectin hydrogels and PAAm-pectin-EG organogels at various temperatures are presented in Fig. 3.36. At room temper-

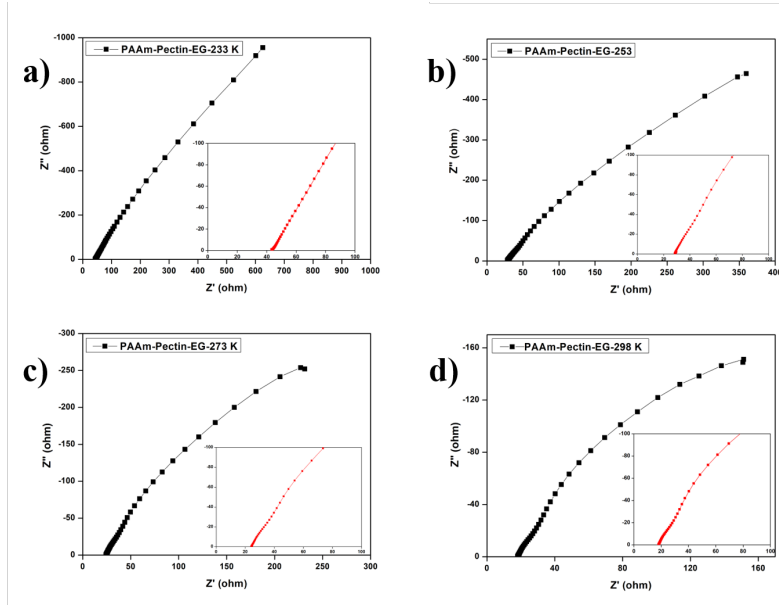


Figure 3.34: Nyquist plot of the electrochemical performances of PAAm-pectin-EG organogels at different temperatures.

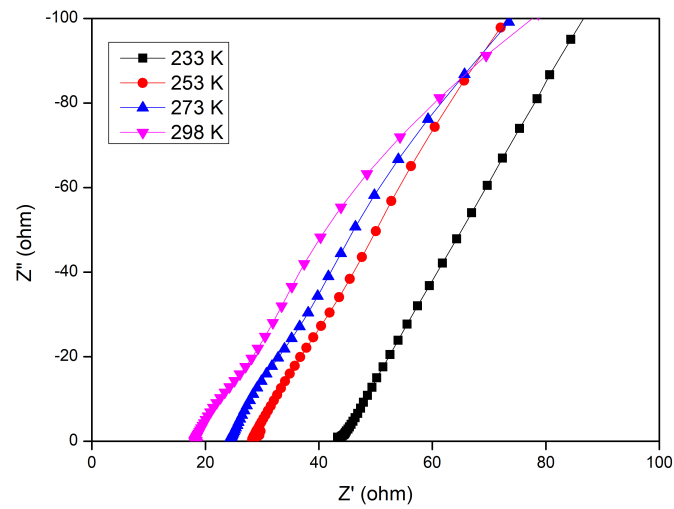


Figure 3.35: Nyquist plot of the electrochemical performances of PAAm-pectin-EG organogel at different temperatures.

ature and 273 K, the PAAm-pectin hydrogel demonstrated higher ionic conductivity compared to the PAAm-pectin-EG organogel. This reduced conductivity in the organogel is attributed to its lower water content and the presence of ethylene glycol, a high-viscosity solvent that restricts ion mobility (Liao et al., 2019; Lu et al., 2020). However, at subzero temperatures (253 K and 233 K), the PAAm-pectin-EG organogel outperformed the PAAm-pectin hydrogel in conductivity, highlighting its superior anti-freezing capabilities. This ability to maintain significant ionic conductivity at subzero temperatures establishes the PAAm-pectin-EG organogel as a promising material for the development of flexible, anti-freezing electronic devices.

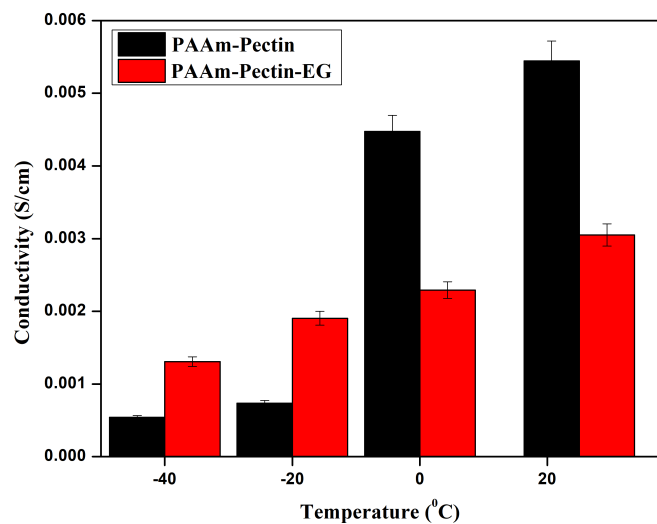


Figure 3.36: Ionic conductivity of PAAm-pectin-hydrogel and PAAm-pectin-EG organogel at different temperatures.

Fig. 3.37 shows the ac impedance spectra of PAAm-pectin-GL organogel at various temperatures. Unlike the PAAm-pectin hydrogel, the PAAm-pectin-GL organogel exhibited minimal changes in ionic conductivity with decreasing temperature, indicating its enhanced temperature resilience. The Fig. 3.38 and 3.39 compare Nyquist plot of the electrochemical performance of PAAm-pectin-GL organogel at different temperatures. A comparison of the ionic conductivities of

PAAm-pectin hydrogels and PAAm-pectin-GL organogels is provided in Table 3.13.

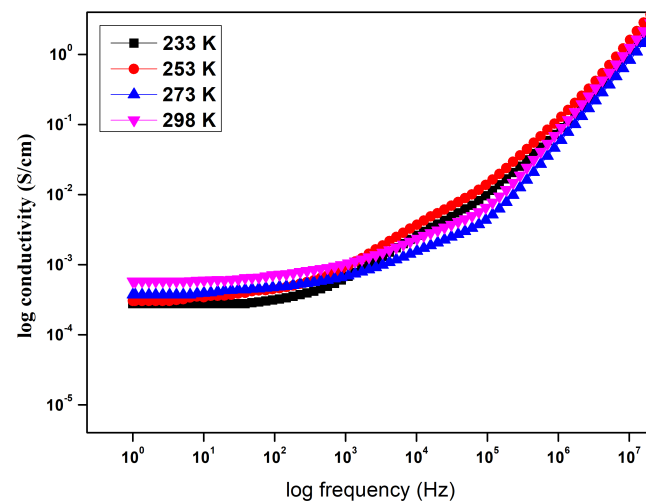


Figure 3.37: AC conductivity vs frequency plot of PAAm-pectin-GL organogels at different temperatures.

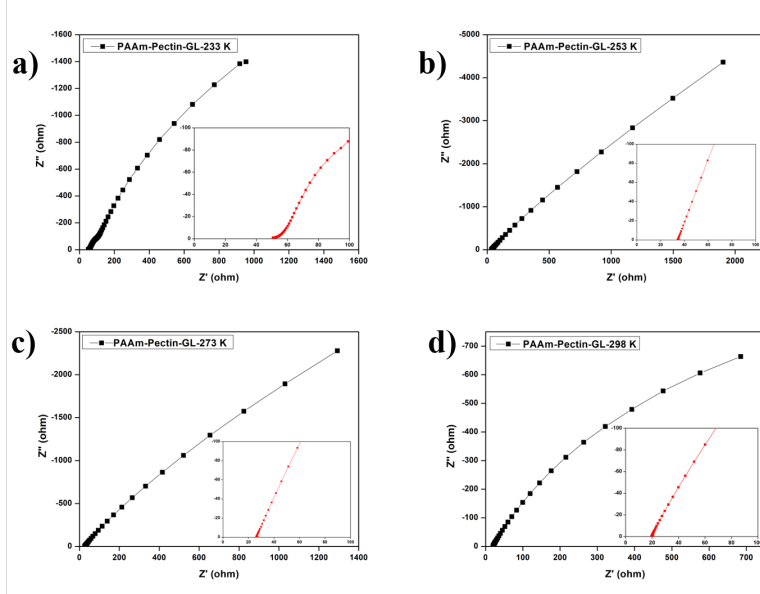


Figure 3.38: Nyquist plot of the electrochemical performances of PAAm-pectin-GL organogels at different temperatures.

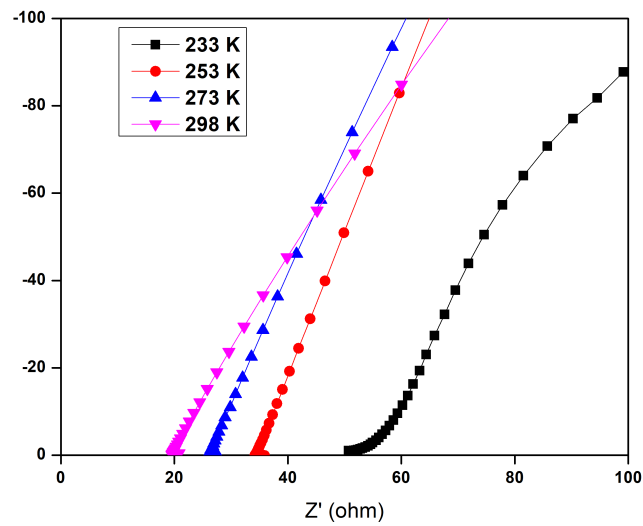


Figure 3.39: Nyquist plot of the electrochemical performances of PAAm-pectin-GL organogel at different temperatures.

Table 3.13: Temperature-dependent ionic conductivity of PAAm-pectin hydrogel and PAAm-pectin-GL organogel.

Temperature (°C)	PAAm-pectin Hydrogel (S cm ⁻¹)	PAAm-pectin-GL Organogel (S cm ⁻¹)
-40	5.40 × 10 ⁻⁴	1.12 × 10 ⁻³
-20	7.37 × 10 ⁻⁴	1.58 × 10 ⁻³
0	4.47 × 10 ⁻³	2.04 × 10 ⁻³
25	5.45 × 10 ⁻³	2.72 × 10 ⁻³

The Fig. 3.40 shows the ionic conductivity exhibited by the PAAm-pectin hydrogels and PAAm-pectin-GL organogels at various temperatures. At room temperature and 273 K, the PAAm-pectin hydrogel exhibited more ionic conductivity than PAAm-pectin-GL organogel. The organogel has less conductivity than the hydrogel due to its decreased water content (Liao et al., 2019). Solvents with high viscosity, such as glycerol, naturally restrict ion migration, explaining why organogel has lower conductivity than hydrogel (Lu et al., 2020). However, at sub-zero temperatures (253 K and 233 K), the PAAm-pectin-GL hydrogel exhibited higher conductivity in comparison to the PAAm-pectin hydrogel.

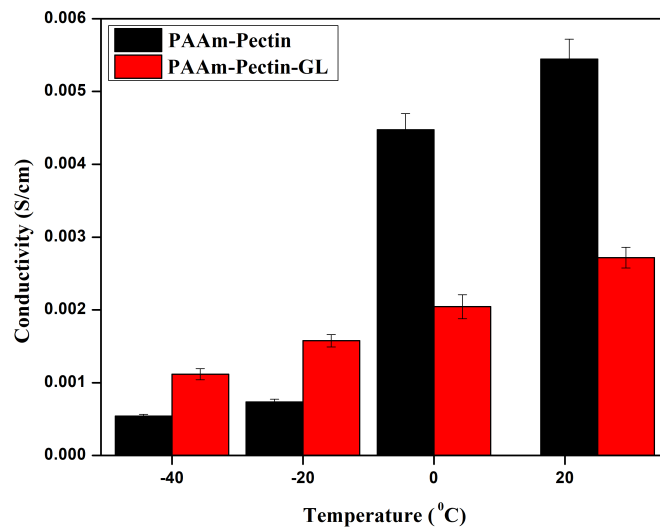


Figure 3.40: Ionic conductivity of PAAm-pectin-hydrogel and PAAm-pectin-GL organogel at different temperatures.

Organogels exhibit lower ionic conductivity than hydrogels because of key differences in their solvent environment, ion mobility, and dielectric properties. In hydrogels, the solvent water provides a highly polar, low-viscosity medium that supports the easy dissociation and rapid movement of ions through the polymer network. Its high dielectric constant stabilizes solvated ions, reduces ion pairing, and greatly enhances ionic mobility, resulting in higher conductivity. In contrast, organogels contain organic solvents ethylene glycol or glycerol, which replace or

partially substitute water within the gel structure. These solvents typically have lower dielectric constants and higher viscosities than water. As a result, ions are less likely to fully dissociate and tend to form ion pairs or aggregates, reducing the number of free charge carriers available for conduction. The higher viscosity also slows down ion movement, which further limits ionic conductivity.

Organogels show better ionic conductivity than hydrogels at sub-zero temperatures because they resist freezing and are able to maintain ion mobility in the presence of organic solvents. In hydrogels, water forms the main continuous phase that allows ions to move freely. However, when the temperature drops below 0°C, the water inside the network freezes and turns into a rigid crystalline structure. This restricts ion movement and disrupts the pathways needed for ionic conduction, causing a sharp drop in conductivity. The polyols in the organogel prevent ice formation even at sub-zero temperatures. As a result, the organogels keep a liquid environment that allows ions to move easily, helping to maintain good conductivity even at low temperatures.

3.3 Conclusion

This chapter presented the design, fabrication, and systematic characterisation of PAAm-pectin hydrogels and their corresponding organogels prepared via solvent replacement using ethylene glycol and glycerol. A double-network structure was successfully developed by combining a covalently crosslinked PAAm network with a pectin network ionically crosslinked through Ca^{2+} coordination. FTIR analysis confirmed that the polymers interact through non-covalent intermolecular interactions rather than covalent bonding, with additional hydrogen-bonding associations occurring upon polyol incorporation, indicating improved polymer-solvent compatibility. Swelling studies demonstrated that increasing pectin content, as well as the introduction of EG or GL, reduced the swelling ratio due to increased network density and decreased solvent affinity. Mechanical testing revealed that reinforcing

ionic crosslinks and polyol-induced secondary interactions substantially enhanced tensile strength, stiffness, and ductility, particularly at higher EG and GL concentrations. Rheological measurements further confirmed an increase in both storage (G') and loss (G'') moduli with polyol content, indicating a transition from a soft, weakly connected network to a more elastic and viscoelastic structure capable of improved energy dissipation.

Anti-freezing evaluations revealed that organogels with higher ethylene glycol (EG) or glycerol (GL) contents retained flexibility and transparency at sub-zero temperatures. Consistent with this observation, DSC analysis demonstrated a pronounced depression of both the onset and peak freezing temperatures with increasing polyol concentration, confirming the enhanced anti-freezing capability of the organogels. Solvent retention and thermal stability studies revealed markedly improved moisture preservation and resistance to thermal degradation in organogels compared to hydrogels, attributable to strong polyol-mediated hydrogen bonding and reduced solvent volatility.

The conductivity measurements confirmed that the incorporation of pectin increased ionic conductivity due to its polyelectrolyte nature, and that organogels sustained effective charge transport even at sub-zero temperatures, unlike the frozen hydrogels. The preservation of conductivity in cold environments highlights their suitability for cryo-tolerant electroactive applications. Overall, the findings of this chapter demonstrate that PAAM–pectin organogels modified with EG and GL successfully integrate mechanical robustness, thermal resilience, antifreezing performance, solvent retention stability, and ionic conductivity. Their tunable physicochemical properties position them as promising candidates for flexible electronics, wearable sensors, bioelectronic interfaces, and other low-temperature operational devices.

Table 3.14: Summary of the key findings

Characterisation	Key Findings
FTIR analysis	FTIR spectra confirmed intermolecular hydrogen bonding interactions between PAAm, pectin, and polyols through characteristic peak shifts without the formation of new covalent bonds.
SEM analysis	SEM images showed that pectin incorporation produced a denser and more compact porous structure with improved network integrity.
Swelling studies	Swelling behaviour depended on pectin and polyol concentration, with higher contents reducing swelling due to increased crosslinking density and reduced free volume.
Mechanical properties	Mechanical strength and Young's modulus increased significantly with Ca^{2+} , EG, and GL incorporation due to enhanced ionic and hydrogen-bonding interactions.
Rheological behaviour	Storage modulus (G'), loss modulus (G''), and $\tan \delta$ increased with polyol concentration, indicating improved structural stability and energy dissipation.
Anti-freezing studies	EG and GL organogels retained flexibility and transparency at sub-zero temperatures, while DSC analysis confirmed depression of freezing temperatures with increasing polyol concentration.
Solvent retention and thermal stability	Organogels exhibited enhanced solvent retention and thermal stability compared to pristine hydrogels, especially at higher polyol contents.
Conductivity studies	PAAm-pectin hydrogels showed improved ionic conductivity compared to pure PAAm hydrogels, while the organogels maintained good conductivity even at sub-zero temperatures.

Chapter 4

Fabrication and Comprehensive Physicochemical Characterisation of PAAm–Gellan Gum Hydrogels and Organogels

4.1 Introduction

Ionic conductive hydrogels have attracted considerable attention as flexible and stretchable materials for applications in sensors, soft actuators, and energy storage devices due to their excellent ionic transport capability and mechanical compliance (Wu, Luo, Cuthbert, Shokurov, Chu, Feng and Menon, 2022; Yuk et al., 2017; Li, Wang, Jiang, Fu, Liang, Zhang, Li, Zhao, Feng, Nie et al., 2018; Zhang et al., 2015; Liu et al., 2017; Hou et al., 2017). However, conventional hydrogels based on aqueous systems often suffer from severe limitations such as dehydration, freezing, and loss of conductivity under extreme environmental conditions (Han et al., 2018; Gao et al., 2017). These drawbacks significantly restrict their long-term stability and practical applicability. To overcome these challenges, this chapter focuses on the design and characterization of polyacrylamide-gellan gum (PAAm-GG) organogels, an advanced class of double-network ionic conductive materials that integrate the desirable properties of synthetic and natural polymers. The incorporation of organic solvents into the hydrogel matrix enhances flexibility, mechanical durability, and environmental tolerance, rendering these organogels

suitable for multifunctional applications (Dong et al., 2024; Wang, Yao, Hao, Pan, Zhuang, Guo and Wang, 2025).

The synthetic polymer, polyacrylamide (PAAm), provides mechanical robustness and elasticity, while gellan gum (GG), a natural anionic polysaccharide containing carboxylate groups ($-COO^-$), offers excellent hydrophilicity, biocompatibility, and ionic functionality. The PAAm–GG hydrogel was synthesized through free-radical copolymerization of acrylamide using *N,N'*-Methylenebisacrylamide (MBAAm) as a covalent crosslinker and ammonium persulfate (APS) as an initiator, followed by ionic crosslinking of gellan gum with calcium ions (Ca^{2+}). This dual crosslinking strategy produced an interpenetrating polymer network (IPN) exhibiting improved structural cohesion and load-bearing capability (Huang, Sun, Lu, Hu, Chen, Du, Shan and Zheng, 2025; Nonoyama and Gong, 2015).

To further enhance environmental stability, the hydrogels were converted into organogels by introducing low-volatile organic solvents ethylene glycol (EG) and glycerol (GL) into the network. The incorporation of these polyols effectively reduced water crystallization and evaporation, imparting anti-freezing and anti-drying properties (Long et al., 2023). The resulting PAAm-GG-EG and PAAm-GG-GL organogels retained flexibility and transparency even at sub-zero temperatures, demonstrating potential for applications in flexible and wearable devices operating under variable environmental conditions.

Comprehensive characterization was performed to elucidate the structure-property relationships of these gels. FTIR spectroscopy confirmed hydrogen bond formation among amide, hydroxyl, and carboxyl groups of PAAm, GG, and the organic solvents, indicating strong intermolecular interactions. SEM analysis revealed the morphological evolution of the network upon hydrogel formation. Swelling experiments quantified the effects of GG content and polyol composition (EG and GL) on solvent uptake, whereas uniaxial tensile testing elucidated the roles of GG loading and Ca^{2+} -mediated ionic crosslinking in governing ten-

sile strength, extensibility, and energy dissipation. Rheological studies provided insight into viscoelastic behaviour, and DSC and TGA analyses evaluated anti-freezing and thermal stability performance. Furthermore, ionic conductivity measurements were conducted to understand the impact of GG content, Ca^{2+} concentration, and temperature on charge transport within the network.

The objective of this chapter is to develop and optimize PAAm-gellan gum based organogels exhibiting high mechanical strength, enhanced solvent retention, antifreezing capability, and stable ionic conductivity across a broad temperature range. By systematically studying the effects of polymer composition and solvent modification, this work aims to establish structure-property correlations vital for designing environmentally resilient and mechanically stable soft ionic materials suitable for advanced bioelectronic applications.

4.2 Results and discussion

4.2.1 Mechanism of formation of PAAm-GG hydrogel/organogel

Preparation of gellan gum hydrogel:- In aqueous media, gellan gum exists as disordered single chains at elevated temperatures. Upon cooling, these chains adopt an ordered conformation and form double helices through intra- and inter-molecular hydrogen bonding. The subsequent aggregation of these helices gives rise to a three-dimensional network, resulting in gel formation (Osmalek et al., 2014; Picone and Cunha, 2013). Gellan gum is a linear anionic polysaccharide containing carboxylate ($-COO^-$) groups on its glucuronic acid residues, which impart a net negative charge along the polymer backbone. Divalent cations such as Ca^{2+} enhance intermolecular association by forming ionic bridges between adjacent $-COO^-$ sites. These $Ca^{2+}-COO^-$ interactions create junction zones that interconnect polymer chains and yield a stable, elastic network with improved rigidity and thermal stability (Coutinho et al., 2010; Chen, Li, Chen, Shao, Chen, Fan, Liu, Ding, Xu, Zhou et al., 2023; Wang, Luo, Xiao and Saleh, 2022).

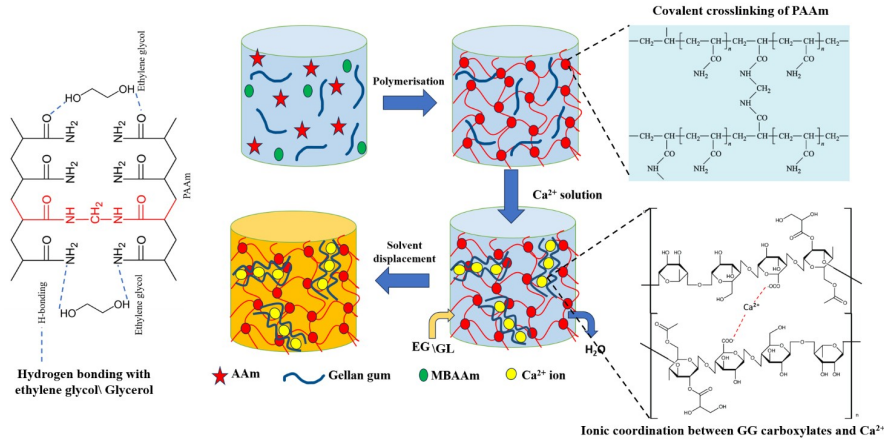


Figure 4.1: Schematic representation of the preparation of PAAm-GG organogels.

Preparation of PAAm-GG organogel:- The schematic representation of the formation of PAAm-GG hydrogel and organogels is depicted in Fig. 4.1. The polyacrylamide-gellan gum (PAAm-GG) double-network (DN) hydrogel was developed through a sequential synthesis approach. In the first stage, a chemically crosslinked polyacrylamide framework was prepared via free-radical polymerization, employing N,N'-Methylenebisacrylamide (MBAAm) as the covalent crosslinker and ammonium persulfate (APS) as the initiator. Subsequently, the gellan gum networks were introduced into the system and ionically crosslinked to form the secondary network within the preformed PAAm matrix. This was accomplished by immersing the hydrogel in a calcium chloride (CaCl_2) solution, wherein the divalent Ca^{2+} ions interacted with the carboxylate ($-\text{COO}^-$) groups present on the gellan gum backbone. The ionic crosslinking reinforced the secondary network and provided extra rigidity and elasticity to the overall structure. This dual crosslinking approach successfully combined a covalent backbone with a physically crosslinked ionic network, creating an interpenetrating polymer system with enhanced mechanical strength. (Haque et al., 2012; Yang et al., 2018). The intermolecular hydrogen bonds between the amide groups ($-\text{CONH}_2$) of polyacrylamide and the hydroxyl and carboxyl groups ($-\text{OH}$ and $-\text{COOH}$) of gellan gum further enhance the mechanical strength of the hydrogel. Together, these

interactions produce a mechanically robust and highly elastic double-network hydrogel that can withstand large strains without fracturing (Aldana et al., 2021; Xu, Zhang, Liu, Zhao, Geng, Wang and Xia, 2021; Wang et al., 2021).

The prepared PAAm–GG hydrogel was subsequently converted into an organogel through a solvent-exchange process (Wu, Chen, Xu and Zhang, 2022; Smith et al., 2019). The hydrogel samples were immersed in mixed water-organic solvent systems containing either ethylene glycol (EG) or glycerol (GL). During this immersion, water inside the hydrogel network was gradually replaced by the organic solvent through diffusion, resulting in PAAm–GG–EG and PAAm–GG–GL organogels. The introduced solvents formed multiple hydrogen bonds with the amide groups of PAAm and the hydroxyl and carboxyl groups of gellan gum, strengthening the polymer network. These additional interactions improved the mechanical strength and structural stability of the organogels (Shi et al., 2017; Li, Fang, Wang, Feng, Yu, Zhang, Liu and Guo, 2024).

4.2.2 FTIR analysis

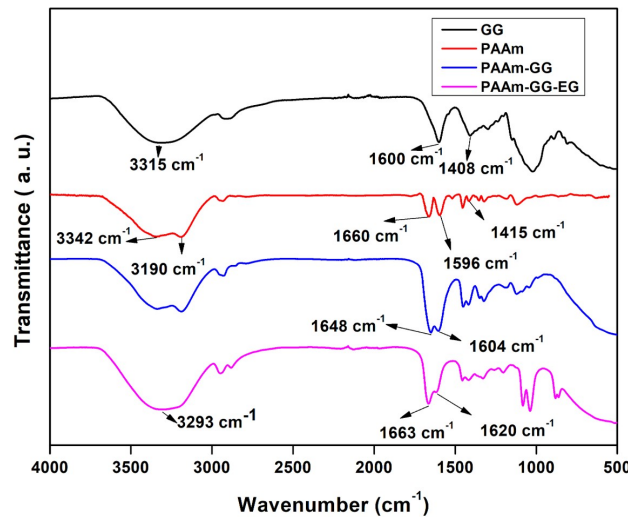


Figure 4.2: FTIR Spectra of Gellan gum, PAAm, PAAm-GG hydrogel, and PAAm-GG-EG organogel.

The chemical interactions and network structure of the individual components, hydrogel, and organogel were elucidated by Fourier-transform infrared (FTIR) spectroscopy, as presented in Figures 4.2 and 4.3. The FTIR spectrum of pure gellan gum (GG) exhibited a broad absorption band centered around 3315 cm^{-1} , corresponding to the O-H stretching vibrations, indicative of abundant hydroxyl groups in its structure (Sudhamani et al., 2003). A prominent band observed at 2915 cm^{-1} was attributed to the C-H stretching of aliphatic $-\text{CH}_2$ groups. Additionally, characteristic peaks at 1600 cm^{-1} and 1408 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of carboxylate ($-\text{COO}^-$) groups, respectively. Further, the bands at 1297 cm^{-1} and 1021 cm^{-1} were associated with C-O stretching vibrations from ether and hydroxyl groups, while the band near 891 cm^{-1} corresponded to the bending vibrations of the C-H bonds (Dixit et al., 2011; Silva-Correia et al., 2011; Arun Krishna and Vishalakshi, 2017).

The spectrum of pure polyacrylamide (PAAm) hydrogel displayed distinctive peaks at 3342 cm^{-1} and 3190 cm^{-1} , attributed to the symmetric and asymmetric N – H stretching vibrations, respectively. A strong absorption at 1660 cm^{-1} was observed, corresponding to the C = O stretching vibration of the amide I band, while the peak at 1596 cm^{-1} was assigned to N – H bending vibrations (amide II). The signal around 1400 cm^{-1} was associated with the C – N stretching vibration, characteristic of primary amides (Zhu et al., 2020; Krakovský et al., 2025).

The PAAm-GG hydrogel spectrum incorporated features from both GG and PAAm, without the appearance of any new peaks. This observation indicates the absence of covalent bonding between the two polymers (İsmaıl and Gökçe Kocabay, 2021), suggesting that the interaction between GG and PAAm is governed predominantly by noncovalent interactions, such as hydrogen bonding and physical entanglement (Jafari et al., 2021).

A slight shift of the carbonyl (C = O) stretching band from 1660 cm^{-1} (in PAAm) to 1648 cm^{-1} (in PAAm-GG hydrogel) was recorded, implying the estab-

lishment of hydrogen bonds between the -NH_2 groups of PAAm and the -OH groups present in gellan gum (Sun et al., 2019).

Upon the incorporation of ethylene glycol during organogel formation, notable spectral shifts were detected. The $\text{C}=\text{O}$ stretching vibration shifted to 1663 cm^{-1} , and the $\text{N}-\text{H}$ bending peak moved from 1604 cm^{-1} to 1620 cm^{-1} . These changes confirm the successful formation of additional hydrogen bonding between ethylene glycol molecules and the polymeric network, leading to enhanced network stability (Yu et al., 2021).

The formation of a hydrogen bond between glycerol and PAAm-GG was also confirmed by FTIR spectra. As shown in Fig. 4.3 after the addition of glycerol, the characteristic bands of $\text{C}=\text{O}$ stretching vibrations (1648 cm^{-1}) and $\text{N}-\text{H}$ bending of acrylamide (1604 cm^{-1}) in the PAAm-GG shifted to 1664 cm^{-1} and 1617 cm^{-1} , respectively, indicating the remarkable effects of hydrogen bonding interactions (Fornaro et al., 2015; Yu et al., 2021). Thus, FTIR analysis clearly supports the proposed mechanism of dual cross-linking and solvent modification, which contributes to the improved mechanical integrity of the developed organogel systems. The FTIR peak positions with corresponding functional group assignments are summarized in Table 4.1

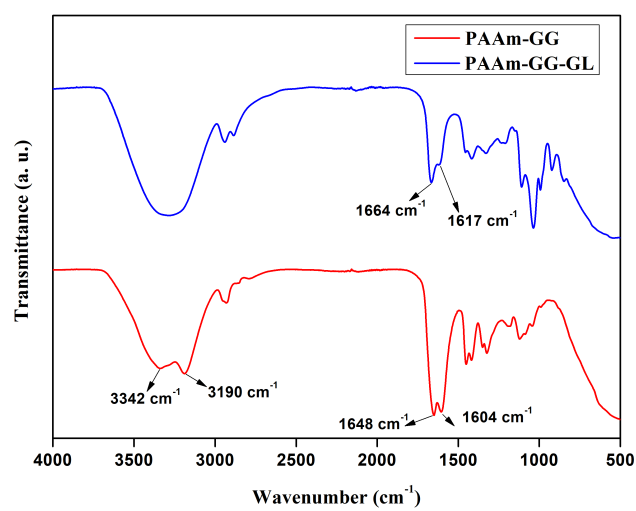


Figure 4.3: FTIR spectra of PAAM-GG hydrogel and PAAM-GG-GL organogel.

Table 4.1: FTIR peak assignments of Gellan Gum (GG), PAAm, PAAm-GG hydrogels and organogels.

Sample	Peak Position (cm^{-1})	Vibration	Assignment
GG	3315	O-H stretching	Hydroxyl groups
GG	2915	C-H stretching	Aliphatic $-\text{CH}_2$ groups
GG	1600	Asymmetric COO^- stretching	Carboxylate groups
GG	1408	Symmetric COO^- stretching	Carboxylate groups
GG	1297	C-O stretching	Ether groups
GG	1021	C-O stretching	Hydroxyl groups
GG	891	C-H bending	C-H vibration
PAAm	3342	N-H stretching (symmetric)	Primary amide group
PAAm	3190	N-H stretching (asymmetric)	Primary amide group
PAAm	1660	C=O stretching	Amide I vibration
PAAm	1596	N-H bending	Amide II vibration
PAAm	1415	C-N stretching	Primary amide group
PAAm-GG	1648	C=O stretching	Hydrogen bonding interaction between GG and PAAm
PAAm-GG	1604	N-H bending	Hydrogen-bonded amide group
PAAm-GG-EG	1663	C=O stretching	Hydrogen bonding interaction with EG
PAAm-GG-EG	1620	N-H bending	Interaction between EG and polymer network
PAAm-GG-GL	1664	C=O stretching	Hydrogen bonding interaction with glycerol
PAAm-GG-GL	1617	N-H bending	Interaction between glycerol and polymer network

4.2.3 SEM analysis

The Fig. 4.4 presents the SEM micrographs of freeze-dried PAAm and PAAm–GG hydrogels, highlighting the effect of gellan gum incorporation on the microstructure. Compared to the relatively open and porous morphology of the pure PAAm network, the PAAm–GG hydrogel exhibits a denser and more compact architecture with reduced pore size and connectivity. This reduction in porosity is attributed to the additional physical and ionic crosslinking interactions introduced by gellan gum, which enhance the crosslinking density, restrict polymer chain mobility, and promote the formation of a tighter three-dimensional network (Pourjalili et al., 2022; Wang, Jiang, Ji, Xing and Ma, 2024).

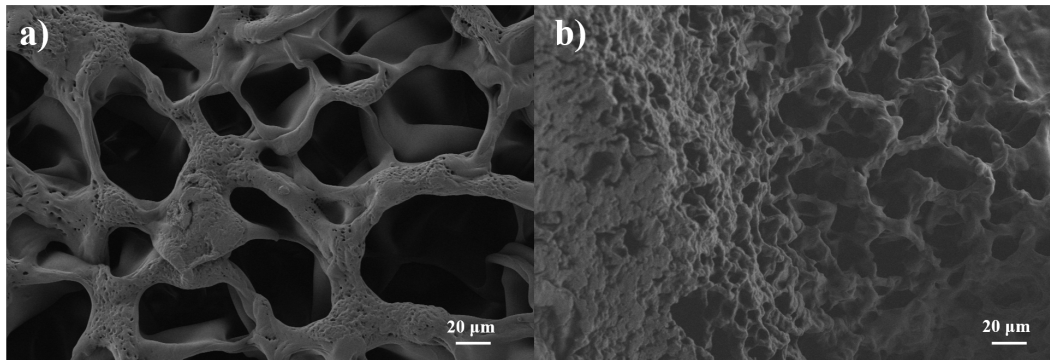


Figure 4.4: SEM images of (a) PAAm hydrogel and (b) PAAm–GG hydrogel.

4.2.4 Swelling studies

The swelling behavior of hydrogels is strongly affected by the composition and crosslinking density of the polymer network. For the polyacrylamide–gellan gum (PAAm–GG) hydrogels studied here, an inverse trend was observed between the swelling ratio and the amount of gellan gum added to the system. As the concentration of gellan gum increased, the swelling ratio decreased noticeably (Fig. 4.5). This reduction in swelling can be explained by changes in the network structure. When gellan gum is introduced into the PAAm matrix the hydrogel becomes more compact and tightly crosslinked. This, in turn, decreases the free volume

and consequently limits water uptake (Tomić et al., 2023; Nasution et al., 2022).

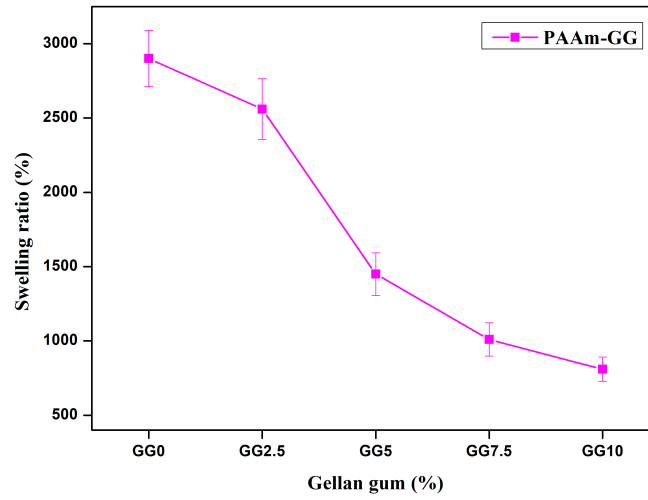


Figure 4.5: Effect of Gellan gum concentration on swelling ratio of PAAm-GG hydrogels.

The composition of the swelling medium strongly influences the swelling behavior of hydrogels. The swelling ratio of PAAm-GG hydrogels was found to decrease with increasing ethylene glycol concentration (Fig. 4.6). Ethylene glycol can form hydrogen bonds with the amide groups in PAAm as well as the carboxyl and hydroxyl groups present in gellan gum. These additional interactions result in a more compact and rigid network that further limits swelling. Moreover, the higher viscosity of EG-rich solutions slows down solvent diffusion into the hydrogel matrix, reducing both the rate of swelling and the overall solvent uptake (Ge et al., 2025; Niu et al., 2021).

Figure 4.7 illustrates the effect of glycerol concentration on the swelling behavior of PAAm-GG hydrogels. At lower glycerol contents, an increase in the swelling ratio is observed. This effect is explained by the hygroscopic nature of glycerol, which readily attracts and holds water molecules, helping the polymer network retain more water (Chen et al., 2022; Pipart et al., 2025). At higher glycerol concentrations, a decrease in the swelling ratio was observed. At higher levels,

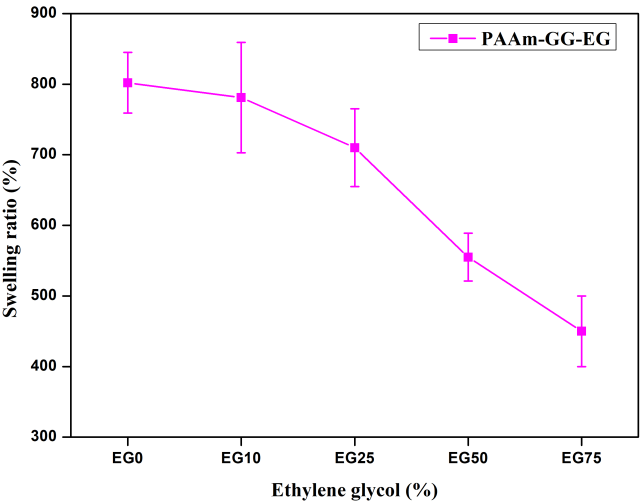


Figure 4.6: Effect of Ethylene glycol concentration on swelling ratio of PAAm-GG hydrogels.

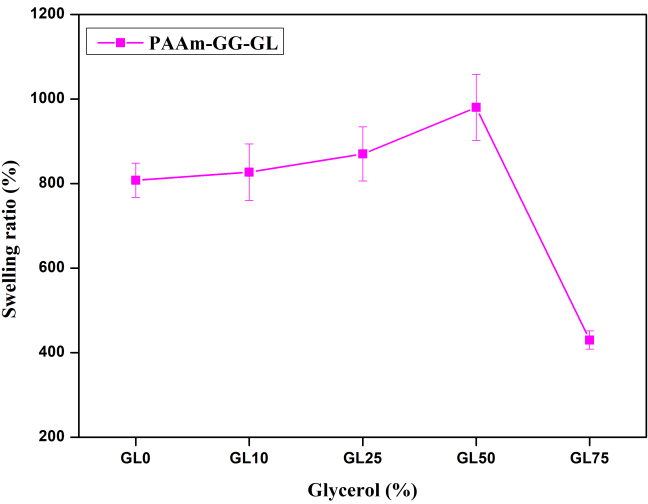


Figure 4.7: Effect of glycerol concentration on swelling ratio of PAAm-GG hydrogels.

glycerol strongly competes with the hydrogel for water molecules, reducing the amount of free water that the network can absorb. This competition disrupts the hydration balance and weakens the osmotic driving force required for swelling. Moreover, the high glycerol concentration increases the viscosity of the solvent system and slows down the diffusion of water into the gel. At the same time, glycerol forms extensive hydrogen bonds with functional groups in both PAAm and gellan gum, creating reversible physical crosslinks that tighten the polymer structure. This denser network has reduced free volume and porosity, limiting its ability to expand (Li, Deng and Zhou, 2020; He et al., 2022).

4.2.5 Mechanical characterisation

The mechanical properties of the developed hydrogels and organogels were systematically evaluated to understand the effects of gellan gum concentration, calcium ion crosslinking, ethylene glycol, and glycerol content. All hydrogel samples were pre-dried at 40°C for 24 hours prior to the test to eliminate solvent induced weakening effects, whereas the organogels were tested in their equilibrium swollen state to accurately represent their actual functional conditions and to preserve the integrity of the solvent–polymer interactions within the network.

The effect of calcium ion concentration on the mechanical performance of PAAm-GG hydrogels is shown in Fig. 4.8. The corresponding mechanical parameters are listed in Table 4.2. In the absence of calcium ions (0 M CaCl_2), the hydrogel structure relies solely on covalent crosslinks formed during polymerisation. Under these conditions, gellan gum remains largely uncrosslinked and behaves mainly as a passive filler, offering limited mechanical reinforcement. As a result, the hydrogel exhibits relatively low strength, elasticity, and structural stability. As the CaCl_2 concentration increased from 0 M to 0.1 M, both the tensile strength and Young’s modulus improved significantly. This enhancement is due to the increase in ionic crosslinks, which strengthen the polymer networks.

However, when the CaCl_2 concentration exceeded 0.1 M, the mechanical strength began to decrease due to over-crosslinking, where excessive Ca^{2+} ions disrupt the network structure and reduce crosslinking efficiency (Lin et al., 2015; Wang et al., 2019; Lin et al., 2015).

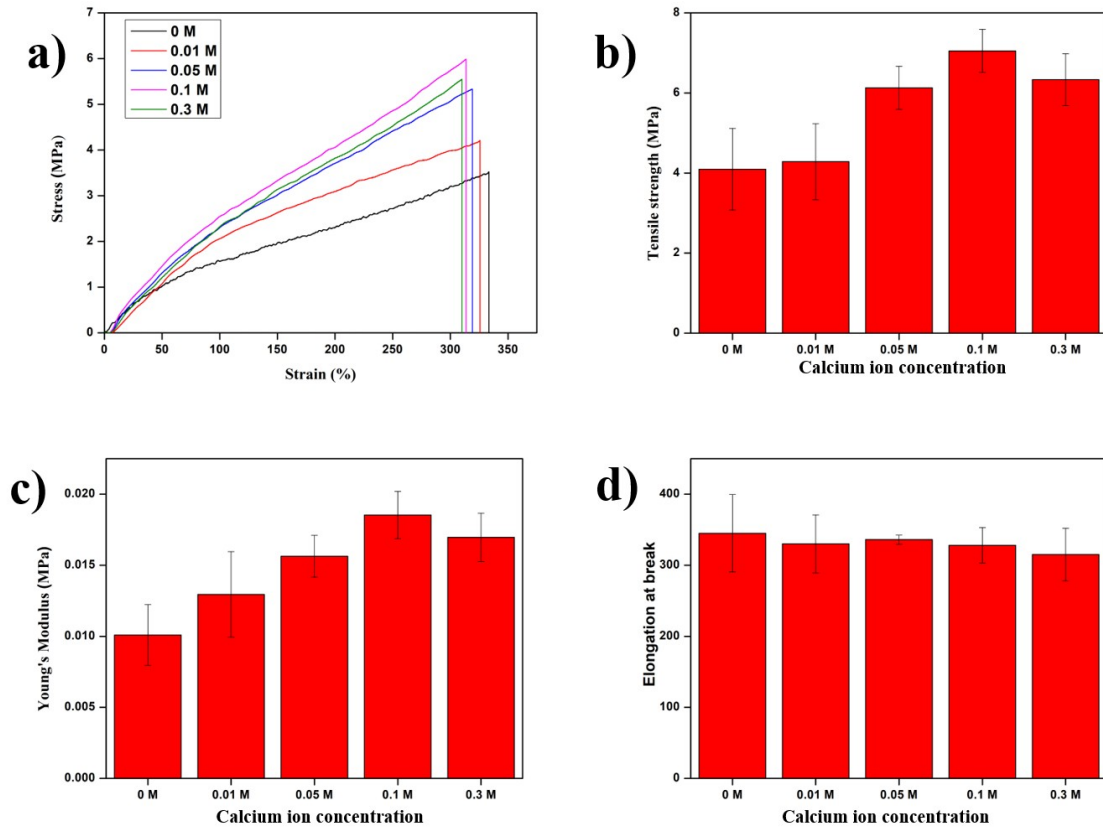


Figure 4.8: Effect of Ca^{2+} ion concentration on the mechanical strength of PAAm-GG hydrogels.

Table 4.2: Effect of calcium ion concentration on the mechanical properties of PAAm-GG hydrogels, showing tensile strength, Young’s modulus, and elongation percentage

Sl. No.	[Ca ²⁺] (M)	Tensile Strength (MPa)	Young’s Modulus (MPa)	Elongation (%)
1	0	4.09	1.01×10^{-2}	345
2	0.01	4.28	1.30×10^{-2}	330
3	0.05	6.12	1.56×10^{-2}	336
4	0.10	7.04	1.85×10^{-2}	328
5	0.30	6.33	1.69×10^{-1}	315

The effect of gellan gum concentration on the mechanical strength of PAAm-GG hydrogel was also investigated. Figure 4.9 shows the mechanical behaviour of PAAm-GG hydrogels with different gellan gum content. The incorporation of gellan gum into the PAAm network significantly enhanced the mechanical strength, evident from the increase in tensile stress, although a moderate reduction in flexibility was noted. It is observed that the mechanical strength of PAAm-GG gum hydrogel increases with the increase in the gellan gum content. The tensile strength and Young's modulus of the PAAm-GG hydrogels increased with increasing gellan gum concentration. This improvement is due to the formation of dynamic sacrificial bonds between Ca^{2+} and the carboxyl groups in gellan gum, which dissipate energy effectively when the material is stretched (Chen, Tang, Yan, Zhu, Wang, Ma, Mao, Yang and Ran, 2023; You et al., 2025). In contrast, the elongation at break decreased significantly, indicating that higher gellan gum content enhances mechanical strength but reduces flexibility.

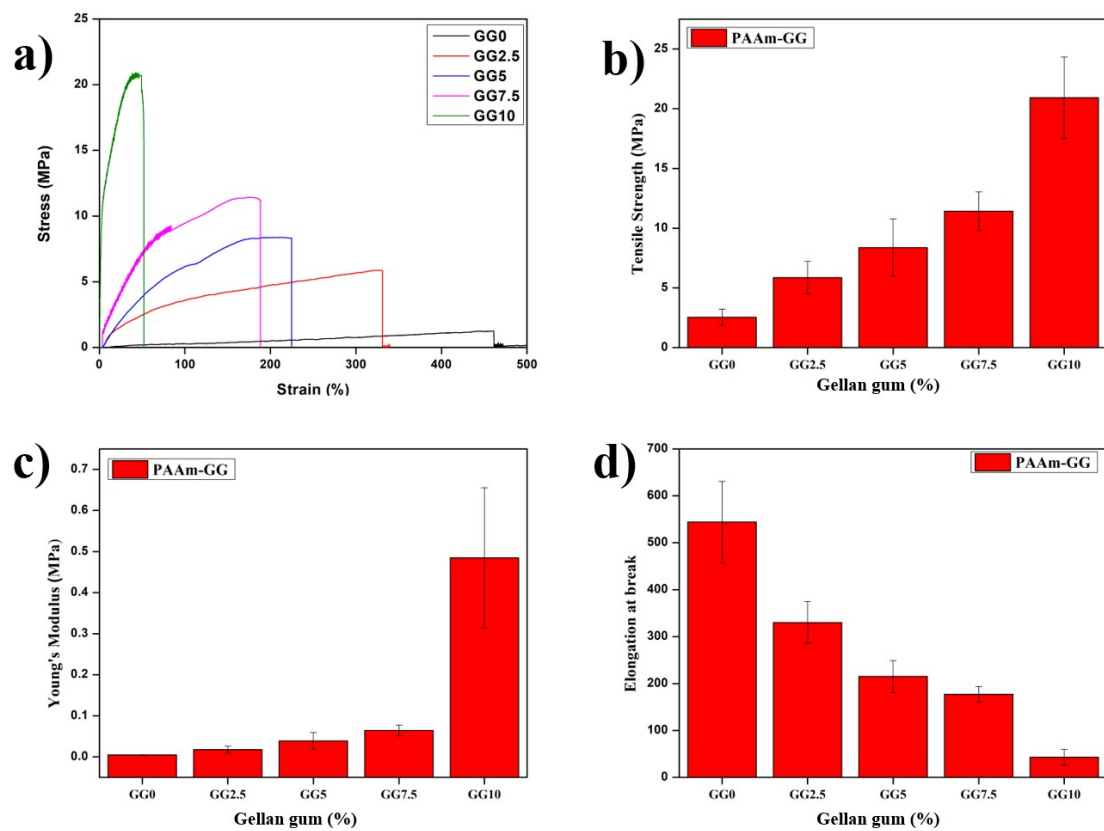


Figure 4.9: . Influence of gellan gum concentration on the tensile properties of PAAm-GG hydrogels.

Table 4.3: Mechanical properties of hydrogels with varying gellan gum (GG) concentrations.

Sl. No.	Hydrogel	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation (%)
1	PAAm-GG0	2.54	4.67×10^{-3}	544.11
2	PAAm-GG2.5	5.86	1.78×10^{-2}	330.11
3	PAAm-GG5	8.37	3.90×10^{-2}	215.02
4	PAAm-GG7.5	11.42	6.44×10^{-2}	177.23
5	PAAm-GG10	20.92	4.84×10^{-1}	43.15

The physical bonds commonly present in natural polymers are generally weaker than covalent linkages. When subjected to stress, these non-covalent interactions preferentially rupture instead of damaging the primary polymer backbone, thereby providing an effective energy-dissipation pathway that enhances the overall toughness of the material. In double-network (DN) hydrogels, Ca^{2+} -mediated ionic crosslinks between anionic polysaccharide helices act as sacrificial bonds, enabling efficient energy dissipation and significantly improving stiffness and mechanical resilience (Liu and Li, 2016; Lu et al., 2014; Sun et al., 2012).

Table 4.3 summarises the mechanical performance of PAAm–GG hydrogels prepared with different gellan gum (GG) concentrations. The availability of fewer crosslinking points at low GG concentrations results in a mechanically weaker hydrogel. As the GG content increases, more physical crosslinks form through stronger hydrogen bonding and ionic interactions. These increased crosslinking interactions enhance the mechanical properties of the hydrogel. Within an optimal concentration range, PAAm and GG create a well-integrated interpenetrating network capable of distributing applied stress more efficiently, producing a more durable and reliable hydrogel.

The effect of ethylene glycol on organogel mechanical properties is demonstrated in Figure 4.10. The mechanical properties of PAAm–GG organogels at different ethylene glycol concentrations are compared in the table 4.4. An increase in ethylene glycol (EG) concentration leads to a significant enhancement in the mechanical properties of PAAm-GG-EG organogels. Ethylene glycol forms strong hydrogen bonding interactions with the functional groups of PAAm and GG, thereby reinforcing the network and enhancing its mechanical strength (Niu et al., 2021; Zhu, Rong, Wang, Bao, An, Huang and Huang, 2023).

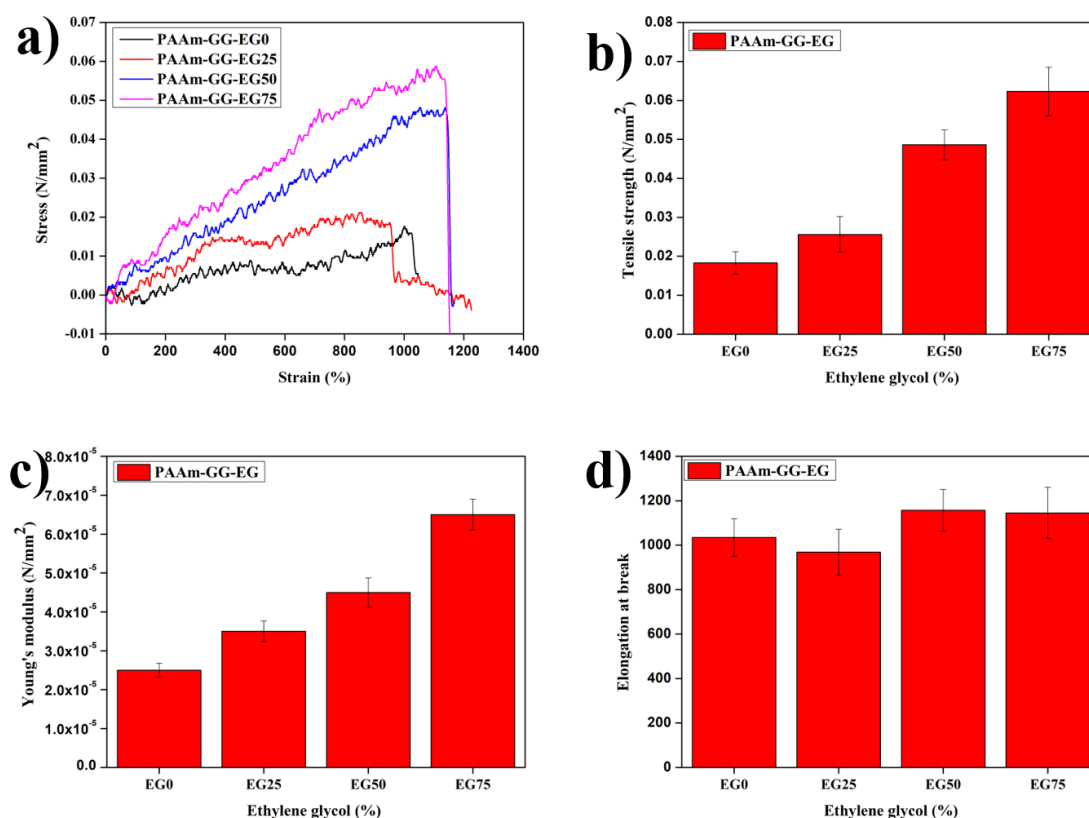


Figure 4.10: Effect of ethylene glycol content on the mechanical performance of PAAm-GG-EG organogels.

Table 4.4: Mechanical properties of PAAm-GG-EG organogels with varying EG content.

Sl. No.	Organogel	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation (%)
1	PAAm-GG-EG0	1.83×10^{-2}	2.46×10^{-5}	1035
2	PAAm-GG-EG25	2.56×10^{-2}	3.19×10^{-5}	969
3	PAAm-GG-EG50	4.86×10^{-2}	4.41×10^{-5}	1157
4	PAAm-GG-EG75	6.23×10^{-2}	6.88×10^{-5}	1145

The mechanical properties of PAAm–GG hydrogels improve significantly with increasing glycerol concentration (Fig. 4.11 and Table 4.5). The hydroxyl groups in glycerol form strong hydrogen bonds with the amide groups of polyacrylamide ($-\text{CONH}_2$) as well as the hydroxyl and carboxyl groups ($-\text{OH}$ and $-\text{COOH}$) present in gellan gum. As the glycerol content increases, a tighter network of reversible hydrogen bonds develops throughout the hydrogel. These interactions act as temporary physical crosslinks that complement the existing covalent and ionic bonds, thereby enhancing the structural stability of the network. When the material is stretched, these reversible bonds break and reform, allowing the network to dissipate energy and prevent disruption (Wang, Liu, Liu, Yan, Wu, Zhang, Li, Wang, Xue, Wang et al., 2024; Tang et al., 2023).

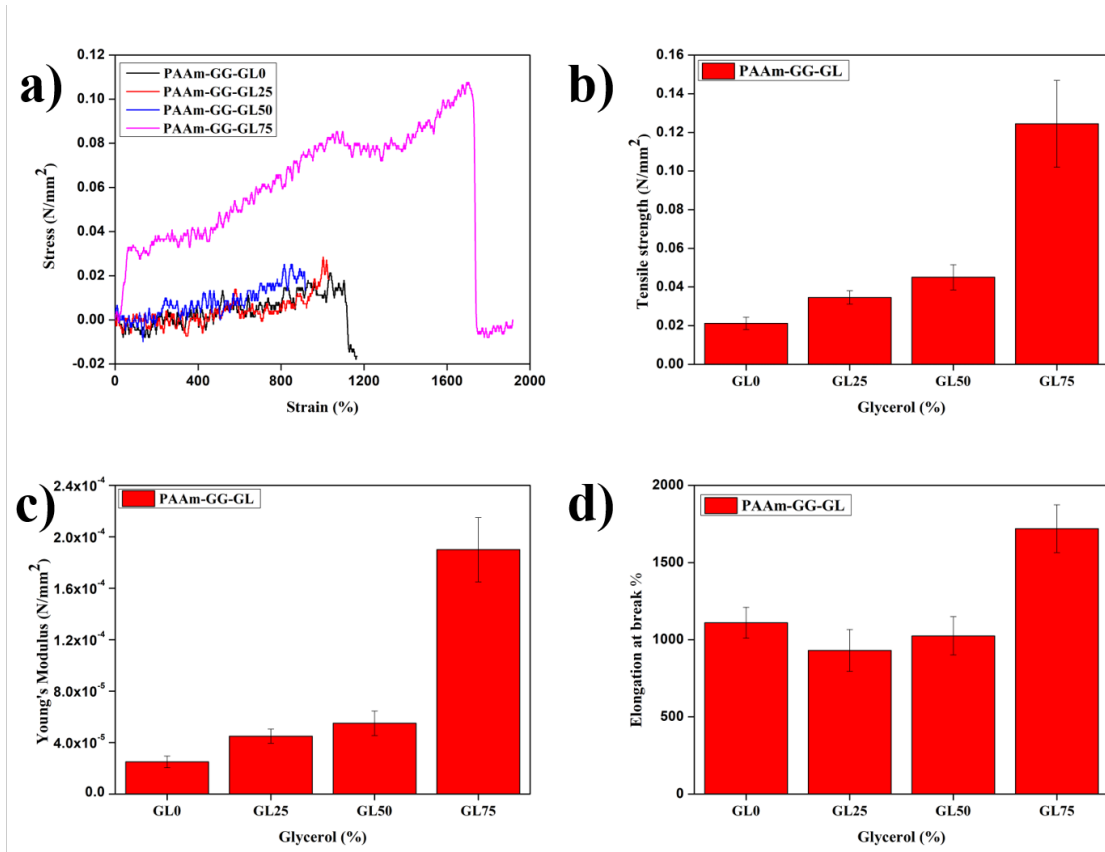


Figure 4.11: Effect of glycerol content on the mechanical performance of PAAm-GG-GL organogels.

Table 4.5: Mechanical properties of PAAm-GG-GL organogels with varying GL content.

Sl. No.	Organogel	Tensile Strength (MPa)	Young's Modulus (MPa)	Elongation (%)
1	PAAm-GG-GL0	2.12×10^{-2}	2.61×10^{-5}	1110
2	PAAm-GG-GL25	3.46×10^{-2}	4.53×10^{-5}	930
3	PAAm-GG-GL50	4.52×10^{-2}	5.49×10^{-5}	1026
4	PAAm-GG-GL75	12.44×10^{-2}	1.92×10^{-4}	1719

4.2.6 Rheological analysis

The storage modulus (G') profiles of PAAm–GG interpenetrating network (IPN) organogels modified with glycerol (Fig. 4.12 a) and ethylene glycol (Fig. 4.12 b) exhibit a characteristic solid-like response, with G' consistently exceeding G'' across all formulations. Both systems show nearly frequency independent G' values, forming a “rubbery plateau” indicative of a stable crosslinked network (Li, Deng and Zhou, 2020). This behaviour underscores the elastic dominance of the double-network architecture, a hallmark of robust hydrogel and organogel systems.

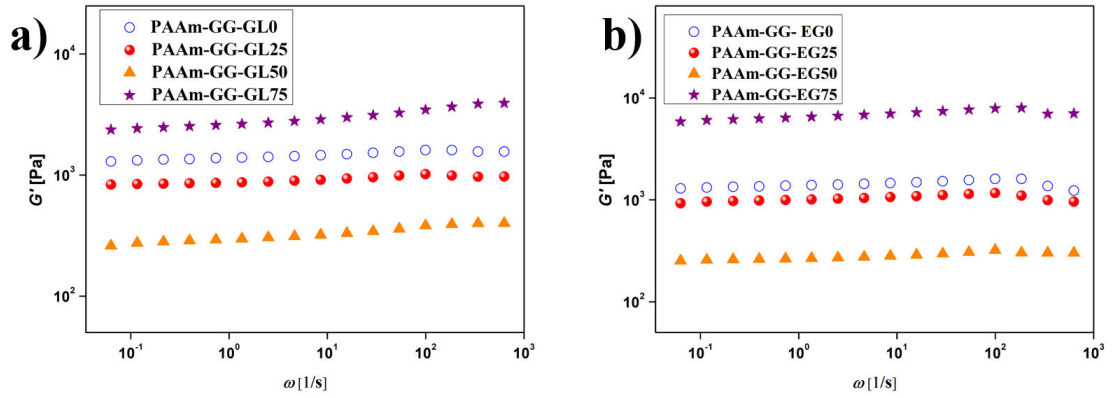


Figure 4.12: Variation of storage modulus (G') as a function of angular frequency (ω) for PAAm–GG (a) Glycerol (b) Ethylene glycol organogels.

For both glycerol and ethylene glycol series, the introduction of 25-50% polyol significantly reduces G' compared to pristine gels. This reduction reflects the plasticizing effect of polyols at intermediate concentrations, where water activity is lowered, and effective crosslink density is diminished, leading to enhanced chain mobility. Strikingly, at 75% polyol content, both systems display a pronounced recovery and enhancement of elasticity: G' rises to ~ 3 kPa for PAAm-GG-GL75 and ~ 6 kPa for PAAm-GG-EG75. This pronounced stiffening is attributed to polyol-induced deswelling, extensive hydrogen bonding, and network compression, which collectively transform the gels into highly reinforced elastic matrices (Li,

Deng and Zhou, 2020; Ye et al., 2023).

The comparative analysis highlights the dual functionality of polyols: as plasticizers at low-to-moderate levels, facilitating network softening, and as reinforcing agents at high concentrations, where hydrogen-bond-mediated secondary crosslinking dominates. While glycerol enhances toughness and maintains balanced ductility, ethylene glycol produces superior stiffening at 75%, yielding the highest modulus observed in this study. These findings validate earlier reports on binary solvent hydrogels, where sacrificial hydrogen-bond networks confer simultaneous resilience and toughness (Cheng et al., 2019; Wang, Du, Hashmi, Cui, Li, Handschuh-Wang, Zhou and Stadler, 2023). Overall, the results establish that polyol concentration critically governs the rheological performance of PAAm–GG IPN organogels, enabling tailored design strategies for load-bearing and flexible material applications.

The loss modulus (G'') profiles of PAAm–GG organogels modified with glycerol (Fig.4.13a) and ethylene glycol (Fig.4.13 b) highlight the influence of polyol concentration on viscous dissipation under oscillatory shear. In both systems, G'' increases with angular frequency (ω), consistent with enhanced molecular friction and energy loss at higher deformation rates, a typical feature of viscoelastic gels (Li, Deng and Zhou, 2020).

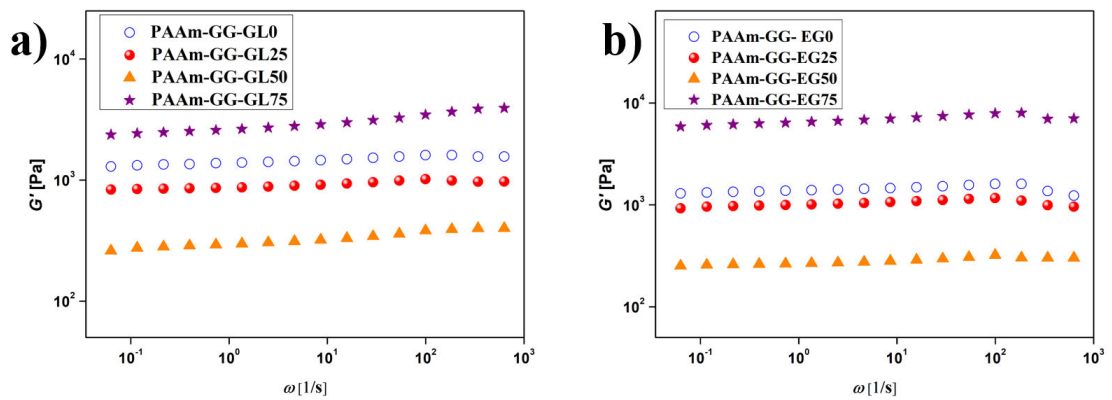


Figure 4.13: Variation of loss modulus (G'') as a function of angular frequency (ω) for PAAm–GG (a) Glycerol (b) ethylene glycol organogels.

In the glycerol-modified series, PAAm-GG-GL0 and PAAm-GG-GL25 display moderate G'' values with a steady frequency dependent increase, while PAAm-GG-GL50 shows a marked reduction, reflecting maximum plasticisation and reduced chain friction. At higher concentration (PAAm-GG-GL75), however, G'' rises sharply across all frequencies, surpassing other formulations. This recovery is attributed to glycerol induced network densification and hydrogen bond mediated restructuring, which enhance both elasticity and viscous damping. A similar but less pronounced trend is observed in the ethylene glycol system. PAAm-GG-EG0 and PAAm-GG-EG25 maintain comparable values, PAAm-GG-EG50 exhibits the lowest G'' due to plasticisation, and PAAm-GG-EG75 demonstrates a significant increase, reflecting the compact and highly crosslinked structure generated by extensive hydrogen bonding and solvent replacement (Stojkov et al., 2021).

Altogether, these results show that the viscous response of the system is strongly concentration dependent: at moderate polyol levels (25–50%), glycerol and ethylene glycol function as plasticizers, lowering viscous resistance by enhancing chain mobility; at higher concentrations (75%), they facilitate secondary crosslinking and network densification, thereby producing a marked increase in G'' . This behaviour aligns with earlier findings on polyol-modified organogels, where the balance between plasticisation and hydrogen bond reinforcement governs viscoelastic performance (Stojkov et al., 2021; Wang, Du, Hashmi, Cui, Li, Handschuh-Wang, Zhou and Stadler, 2023). The pronounced rise in G'' at PAAm-GG-GL75 and PAAm-GG-EG75 suggests their suitability for applications requiring enhanced damping capacity while maintaining structural resilience.

Figure 4.14 a and Figure 4.14 b present the nonlinear viscoelastic behavior of PAAm-GG interpenetrating network (IPN) organogels with varying glycerol (GL) and ethylene glycol (EG) contents. In both systems, the stress-strain profiles exhibit an initial linear region at small deformations, followed by a pronounced nonlinear increase at higher strains, characteristic of strain induced structural

rearrangements and network stiffening typical of double-network gels (Li, Deng and Zhou, 2020).

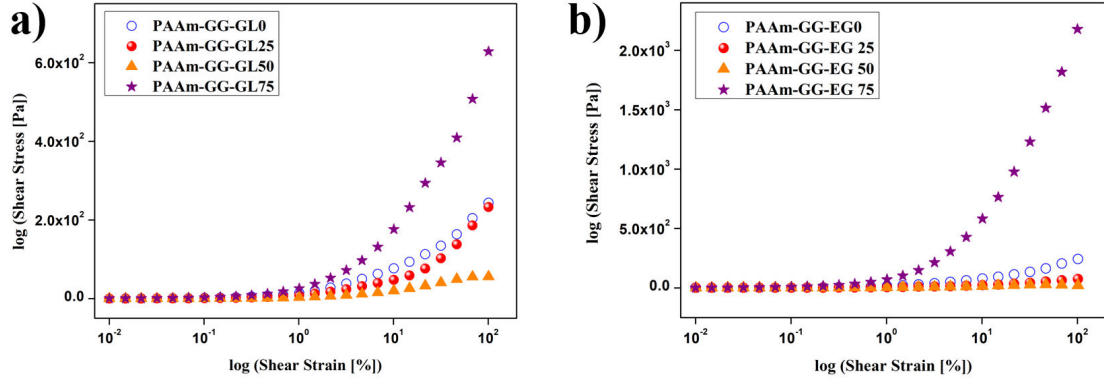


Figure 4.14: Plot of shear stress versus shear strain (%) for PAAm-GG (a) glycerol and (b) ethylene glycol organogels at varying polyol concentrations.

For the glycerol-modified system, PAAm-GG-GL0 and PAAm-GG-GL25 display comparable stress responses, whereas PAAm-GG-GL50 exhibits the lowest stress across the entire strain range, reflecting significant plasticisation and weakened network connectivity. In contrast, PAAm-GG-GL75 shows a steep rise in stress beyond $\sim 10\%$ strain, surpassing all other formulations. This recovery is attributed to network densification and secondary crosslinking, which reinforce the gel under large deformation (Li, Deng and Zhou, 2020; Wang, Du, Hashmi, Cui, Li, Handschuh-Wang, Zhou and Stadler, 2023). The ethylene glycol system demonstrates a similar non-monotonic pattern. PAAm-GG-EG0, PAAm-GG-EG25, and PAAm-GG-EG50 maintain relatively low stresses, consistent with reduced crosslinking efficiency and enhanced chain mobility. However, PAAm-GG-EG75 reveals a sharp increase in stress at higher strains, even exceeding the glycerol series, suggesting that EG at elevated concentrations induces compact network formation through extensive hydrogen bonding and solvent-mediated volume shrinkage (Feig et al., 2018).

Collectively, these stress-strain results confirm the dual role of polyols: at moderate concentrations (25-50%), both glycerol and ethylene glycol act as plas-

ticisers, lowering shear resistance and facilitating energy dissipation, while at high concentrations (75%) they trigger network reinforcement, producing pronounced nonlinear stiffening. This behaviour reflects the activation of sacrificial hydrogen bond networks that dissipate energy while preserving structural integrity, a defining characteristic of tough double-network gels (Wang, Du, Hashmi, Cui, Li, Handschuh-Wang, Zhou and Stadler, 2023). The pronounced stiffening observed at PAAm-GG-GL75 and PAAm-GG-EG75 highlights their suitability for applications demanding resilience under extreme deformation.

Figure 4.15 a and Figure 4.15 b compare the storage modulus (G') and loss modulus (G'') at a fixed frequency of 1 Hz for PAAm-GG organogels modified with different concentrations of glycerol (GL) and ethylene glycol (EG). In all cases, G' remains substantially higher than G'' , confirming that the systems are predominantly elastic in nature, consistent with the characteristics of robust dual-network gels (Wang, Du, Hashmi, Cui, Li, Handschuh-Wang, Zhou and Stadler, 2023).

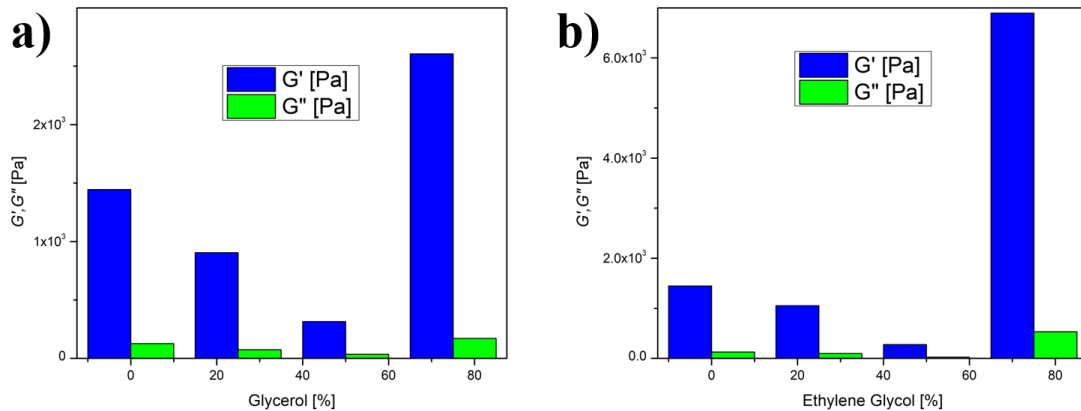


Figure 4.15: Storage modulus (G') and loss modulus (G'') at a frequency of 1 Hz for PAAm-GG (a) glycerol and (b) ethylene glycol organogels containing 0%, 25%, 50%, and 75% polyols.

In the glycerol-modified system, G' decreases when glycerol content changes from 0% to 50%, reflecting the plasticising action of glycerol, which enhances chain mobility and weakens effective crosslinking. However, at 75% glycerol con-

centration, a significant reinforcement is observed, with G' reaching its maximum, indicative of secondary crosslinking and network densification. The corresponding G'' values remain relatively low, although a modest increase at 75 % suggests that energy dissipation mechanisms coexist with enhanced elasticity (Grattoni et al., 2001).

The ethylene glycol series displays a similar non-monotonic response. PAAm-GG-EG0 and PAAm-GG-EG25 maintain moderately high G' values, but PAAm-GG-EG50 exhibits a distinct reduction, highlighting the maximal plasticisation effect. Notably, PAAm-GG-EG75 shows a substantial recovery, with G' surpassing that of the glycerol system, indicating that EG at high concentrations forms extensive networks and promotes solvent-mediated densification. While G'' values show only subtle variations across the series, a clear increase at 75 % EG concentration reflects additional viscous contributions associated with reinforced yet energy dissipative networks (Li, Deng and Zhou, 2020).

The damping factor ($\tan \delta$) profiles for PAAm-GG organogels containing glycerol and ethylene glycol (Fig. 4.16 a and 4.16 b) provide deeper insight into the balance between energy storage and dissipation across polyol concentrations. In both systems, $\tan \delta$ values remain well below unity, confirming the dominance of elastic behavior over viscous relaxation and aligning with the high storage moduli observed in earlier analyses (Li, Deng and Zhou, 2020). However, distinct concentration-dependent trends are evident. In the glycerol system, PAAm-GG-GL50 exhibits the highest $\tan \delta$ across the frequency spectrum, reflecting significant plasticisation and enhanced chain mobility that increase viscous contributions. By contrast, PAAm-GG-GL75 maintains consistently low damping values, indicative of a densified network that minimises energy loss while reinforcing elasticity (Wang, Du, Hashmi, Cui, Li, Handschuh-Wang, Zhou and Stadler, 2023).

In the ethylene glycol series, PAAm-GG-EG0 and PAAm-GG-EG25 display

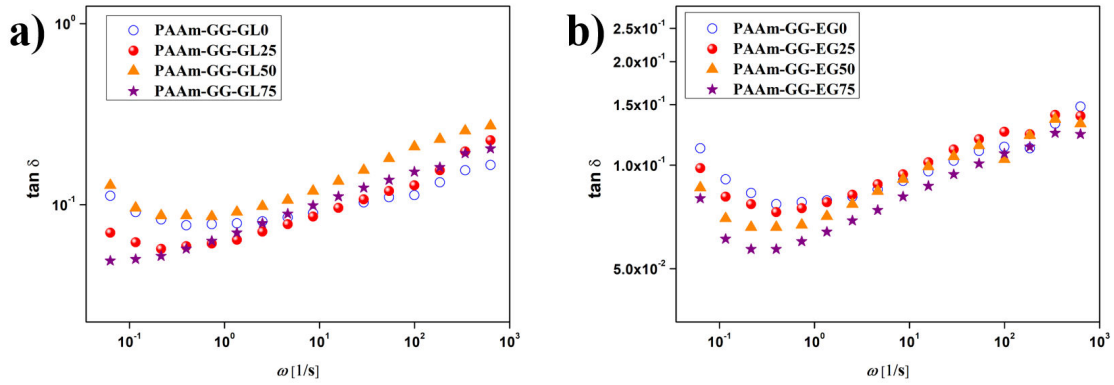


Figure 4.16: Variation of damping factor ($\tan \delta$) as a function of angular frequency (ω) for PAAm-GG organogels formulated with (a) glycerol and (b) ethylene glycol at different concentrations.

relatively higher $\tan \delta$ values at low frequencies, reflecting weaker network connectivity and greater molecular mobility. PAAm-GG-EG50 sustains slightly elevated damping across the frequency range, consistent with maximal plasticisation. However, at PAAm-GG-EG75, $\tan \delta$ decreases substantially, highlighting the formation of a compact and highly crosslinked network that favours energy storage over dissipation (Wang, Du, Hashmi, Cui, Li, Handschuh-Wang, Zhou and Stadler, 2023; Feig et al., 2018). This elastic dominance at high EG concentration underscores the role of hydrogen bond mediated reinforcement in stabilising the gel structure, even under dynamic deformation.

Taken together, these results reveal the non-monotonic damping response of PAAm-GG organogels modified with polyols. Moderate concentrations (25-50%) enhance viscous contributions via solvent-induced plasticisation, while high loadings (75%) suppress damping through hydrogen bond driven network densification. Such tunable viscoelastic behaviour, consistent with previous reports on polyol-modified dual-network hydrogels (Li, Deng and Zhou, 2020; Calvet et al., 2004), highlights the potential of glycerol and ethylene glycol to design organogels with tailored damping properties.

Beyond the individual contributions of glycerol and ethylene glycol, the com-

parative rheological behavior underscores the significance of polyol structure in dictating organogel performance. The tri-hydroxyl functionality of glycerol facilitates higher damping capacity and toughness, particularly at intermediate concentrations where energy dissipation is desirable. In contrast, the smaller di-hydroxyl structure of ethylene glycol favours tighter chain packing and stronger network densification at high loadings, leading to superior stiffness and reduced viscous relaxation. This distinction highlights a clear structure-property relationship, wherein glycerol optimises ductility and energy absorption, while ethylene glycol enhances rigidity and resilience under stress.

4.2.7 Evaluation of Anti-freezing behaviour

The anti-freezing properties of PAAm–GG hydrogels and their organogel counterparts containing ethylene glycol (EG) or glycerol (GL) were evaluated through visual observation and differential scanning calorimetry (DSC). After storage at -15°C for 6 hours, distinct differences in their physical states were observed. For the EG based systems (Figure 4.17), both the pristine PAAm–GG hydrogel and the PAAm–GG–EG10 organogel became completely opaque and brittle, indicating significant freezing of the water phase. In contrast, the PAAm–GG–EG25 and PAAm–GG–EG50 organogels retained excellent transparency and flexibility under the same subzero conditions, demonstrating superior anti-freezing performance. A similar trend was observed for the GL based systems (Figure 4.18). The PAAm–GG hydrogel and PAAm–GG–GL10 organogel showed severe opacity and brittleness after freezing, while the PAAm–GG–GL25 and PAAm–GG–GL50 organogels remained highly transparent and flexible, confirming that higher concentrations of glycerol effectively suppress ice formation. These results clearly demonstrate the role of both ethylene glycol and glycerol in depressing the freezing point and preserving the structural integrity of the organogels at subzero temperatures.

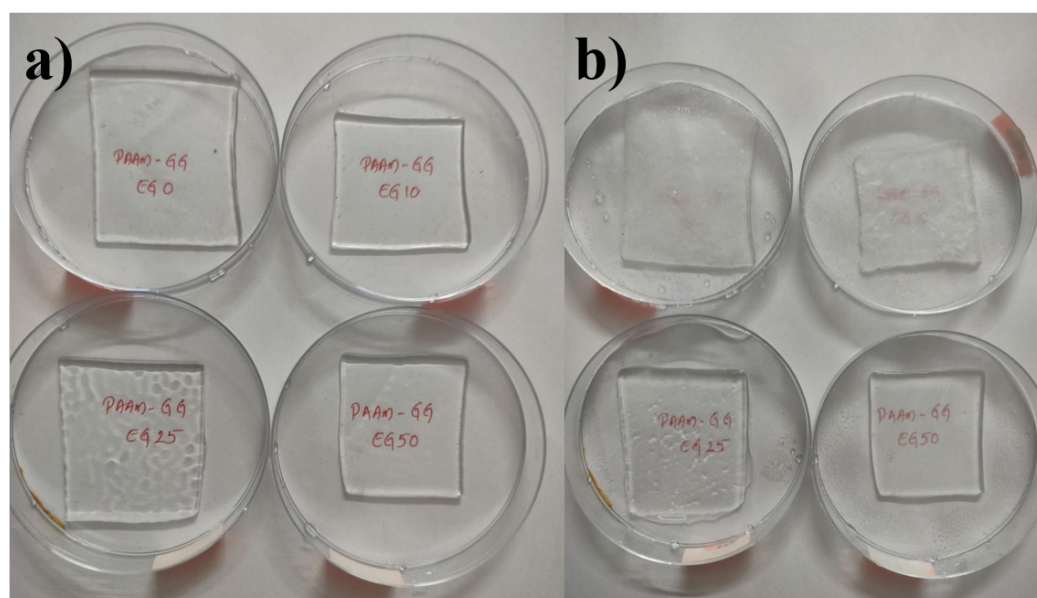


Figure 4.17: Photographs of the PAAm-GG hydrogel and PAAm-GG-EG organogels taken a) before and b) after refrigeration.

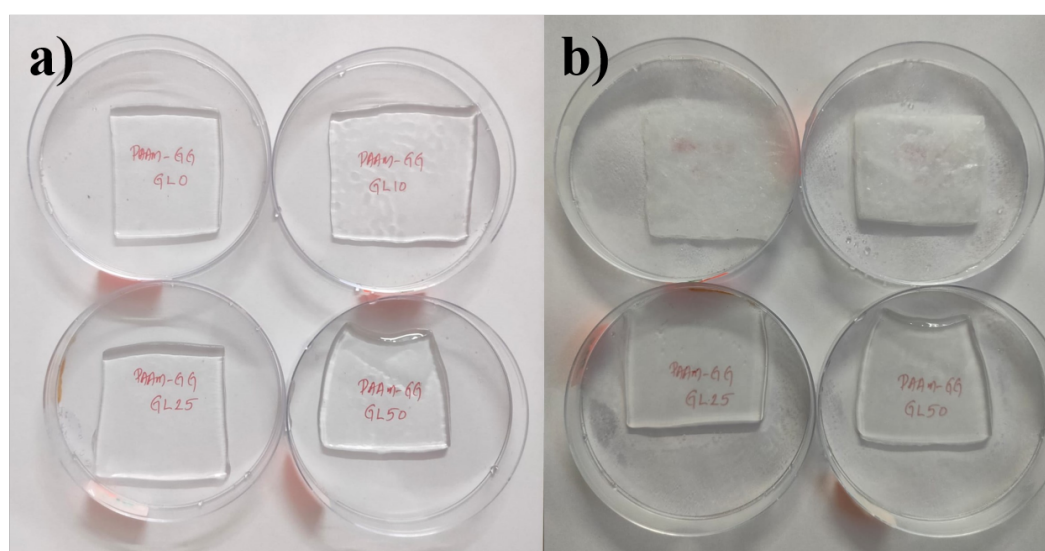


Figure 4.18: Photographs of the PAAm-GG hydrogel and PAAm-GG-GL organogels taken a) before and b) after refrigeration.

The DSC thermograms (Figure 4.19 and 4.20) further support the visual observations. The PAAm–GG hydrogel exhibited a sharp exothermic peak near 0°C, corresponding to the freezing of bulk water. In contrast, the DSC curves of the PAAm–GG–EG organogels (EG10, EG25, and EG50) and PAAm–GG–GL organogels (GL10, GL25, and GL50) showed a progressive shift of the freezing exotherm toward lower temperatures, with PAAm–GG–EG50 and PAAm–GG–GL50 demonstrating the most pronounced suppression of freezing transitions. The onset and peak freezing temperatures of the organogels with different concentrations of ethylene glycol and glycerol are summarized in Table 4.6 and 4.7. The absence of a sharp crystallization peak, along with the appearance of broad and less intense thermal transitions, indicates that water molecules predominantly exist in a bound or intermediate state within the organogel matrices. This restricted mobility inhibits the formation of large ice crystals, thereby enhancing the anti-freezing performance of both EG and GL based organogels.

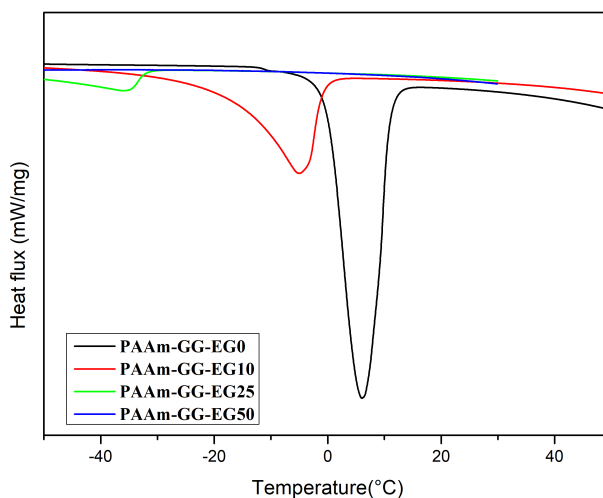
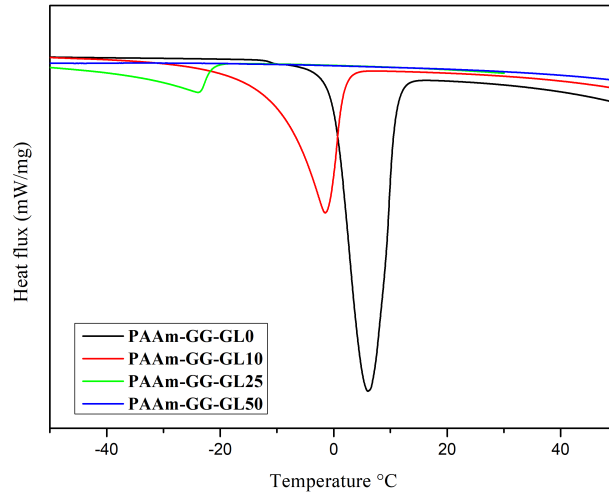


Figure 4.19: The DSC spectra of PAAm-GG hydrogel and the PAAm-GG-EG organogels.

The incorporation of ethylene glycol and glycerol into hydrogels significantly enhances their anti-freezing performance by modifying the thermodynamic and

Table 4.6: Freezing transition temperatures of PAAm–GG–EG organogels with varying EG content.

Organogel	Onset Freezing Temp (°C)	Peak Freezing Temp (°C)
PAAm-GG-EG0	0.1	6.0
PAAm-GG-EG10	−12.5	−5.1
PAAm-GG-EG25	−41.6	−35.2
PAAm-GG-EG50	<i>Not observed</i>	<i>Not observed</i>

**Figure 4.20:** The DSC spectra of PAAm-GG hydrogel and the PAAm-GG-GL organogels.

structural behaviour of water within the hydrogel matrix. Both ethylene glycol and glycerol are small, highly hydrophilic molecules capable of forming extensive hydrogen bonding networks with water molecules as well as with the functional groups present in the polymer chains, such as amide ($-\text{CONH}_2$), hydroxyl ($-\text{OH}$), and carboxyl ($-\text{COOH}$) groups (Long et al., 2023; Wu et al., 2019; Zhan et al., 2023). These polyols compete with water–water hydrogen bonding, thereby disrupting the ordered hydrogen-bonded network necessary for the nucleation and growth of ice crystals (Gao et al., 2025; Zhuo et al., 2021; Zhang, Wang, Wei, Li and Chen, 2024). This effect becomes more pronounced at higher polyol concentrations, where the enhanced interaction strength provides sufficient depression of the freezing point to prevent visible phase separation or freezing induced brittle-

Table 4.7: Onset and peak freezing temperatures of PAAm-GG-GL organogels with varying glycerol contents.

Organogel	Onset Freezing Temp (°C)	Peak Freezing Temp (°C)
PAAm-GG-GL0	0.1	6.0
PAAm-GG-GL10	-7.6	-1.1
PAAm-GG-GL25	-31.8	-23.5
PAAm-GG-GL50	Not observed	Not observed

ness (Mo et al., 2019).

4.2.8 Solvent retention and stability analysis

The long-term solvent retention behaviours and thermal stability of PAAm-GG hydrogel, PAAm-GG-EG and PAAm-GG-GL organogels were systematically evaluated under ambient conditions (25°C, 70 % relative humidity). Upon storage, the pristine PAAm-GG hydrogel exhibited rapid water loss, becoming dry and brittle within a day, with a drastic reduction to approximately 2.98 % of its original weight. In contrast, the PAAm-GG-EG and PAAm-GG-GL organogels demonstrated substantially enhanced solvent retention, with the degree of retention increasing proportionally to the ethylene glycol and glycerol content.

Table 4.8: Solvent retention of PAAm-GG-EG organogels after 20 days.

Organogel	Weight Retained (%)
PAAm-GG-EG0	2.98
PAAm-GG-EG10	4.18
PAAm-GG-EG25	6.30
PAAm-GG-EG50	38.11

Figures 4.21 and 4.23 illustrate the solvent retention behavior of the PAAm-GG hydrogel (EG0) together with the PAAm-GG-EG (EG10, EG25, EG50) and PAAm-GG-GL (GL10, GL25, GL50) organogels over a period of 20 days, highlighting the influence of ethylene glycol and glycerol incorporation on the long-term solvent retention capability of the network. In addition to these observations, Figures 4.22 and 4.24 present the final weight retained by PAAm-GG organogels containing varying amounts of EG and GL after 20 days of storage, further demon-

strating that polyol incorporation enhances solvent retention capacity and that retention increases progressively with increasing polyol content.

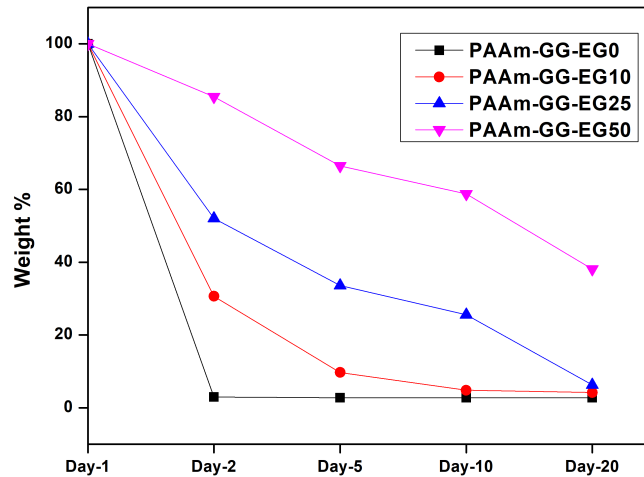


Figure 4.21: Solvent retention capacity of PAAm-GG-EG organogels at different storage times.

As shown in tables 4.8 and 4.9, the incorporation of polyols markedly enhanced the solvent retention capacity of the organogels compared to the hydrogel. While ethylene glycol improved retention by reducing solvent loss from the network, glycerol provided an even greater enhancement, reflecting its superior ability to minimize evaporation and maintain long-term structural stability.

Table 4.9: Solvent retention of PAAm-GG-GL organogels after 20 days.

Organogel	Weight Retained (%)
PAAm-GG-GL0	2.72
PAAm-GG-GL10	20.56
PAAm-GG-GL25	44.13
PAAm-GG-GL50	79.81

Thermogravimetric analysis (TGA) further corroborated the solvent retention results, as shown in Figures 4.25 and 4.26. Figure 4.25 presents the TGA thermograms of the PAAm-GG hydrogel and the corresponding EG-based organogels (PAAm-GG-EG10, -EG25, and -EG50). The data presented in table 4.10 sum-

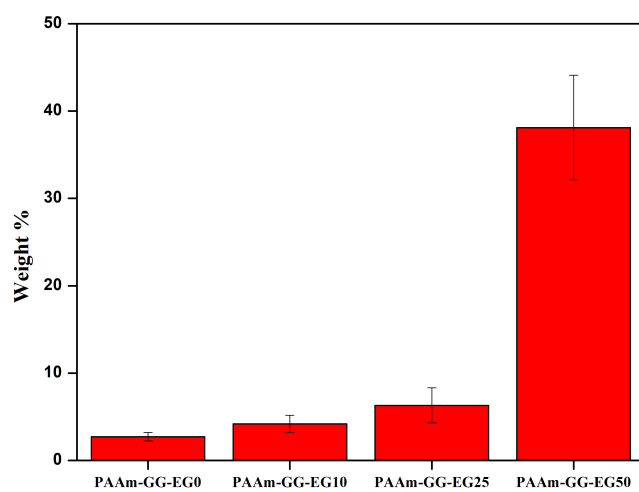


Figure 4.22: Solvent retention capacity of PAAm-GG-EG organogels after 20 days.

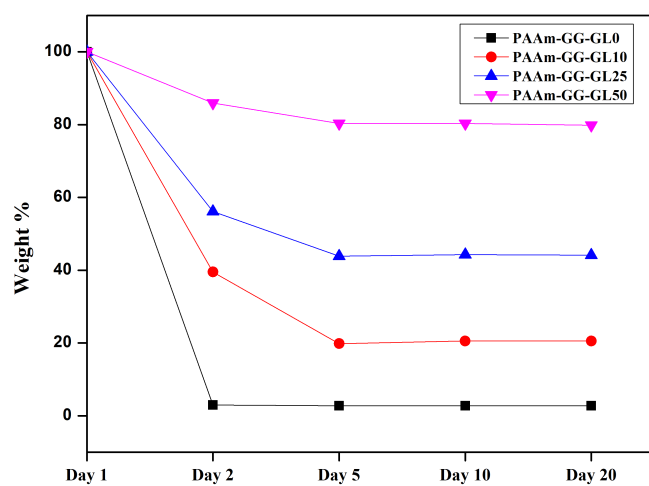


Figure 4.23: Solvent retention capacity of PAAm-GG-GL organogels at different storage times.

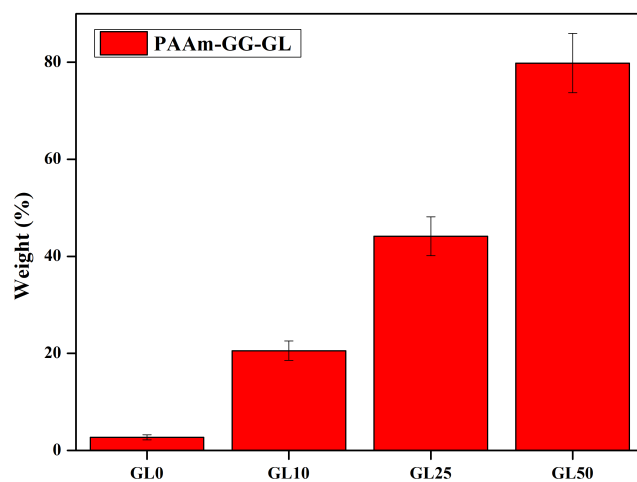


Figure 4.24: Solvent retention capacity of PAAm-GG-GL organogels after 20 days.

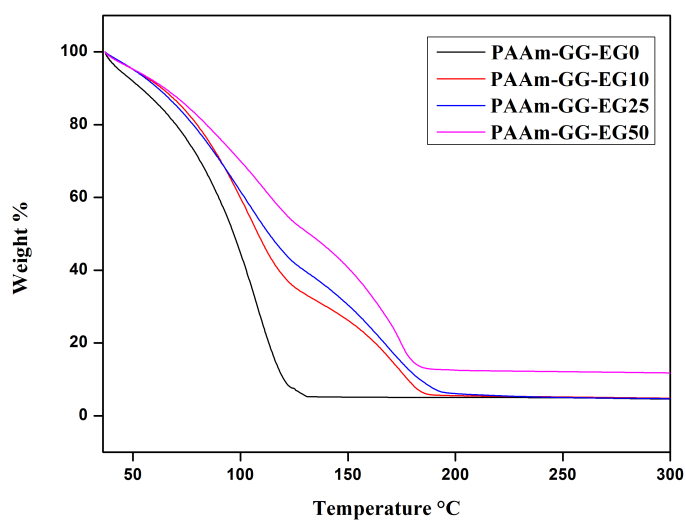


Figure 4.25: The TGA thermograms of the PAAm-GG hydrogel and PAAm-GG-EG organogels.

Table 4.10: Thermal stability of PAAm–GG hydrogel and organogels at different temperatures.

Sample	50 °C	100 °C	150 °C	200 °C
PAAm–GG hydrogel	91.90%	44.47%	5.12%	5.02%
PAAm–GG–EG10 organogel	95.18%	59.67%	26.01%	5.52%
PAAm–GG–EG25 organogel	95.19%	61.55%	30.21%	6.09%
PAAm–GG–EG50 organogel	95.27%	69.90%	40.40%	12.52%

marise the thermal stability of the PAAm–GG hydrogel and organogels containing different concentrations of ethylene glycol at various temperatures. The hydrogel exhibits a rapid decrease in weight with increasing temperature, indicating limited thermal stability. In contrast, the organogels retain a higher percentage of their initial mass at all temperature points, and this retention improves progressively with increasing ethylene glycol content. The PAAm–GG–EG50 organogel exhibits the highest thermal stability, indicating that ethylene glycol effectively enhances the thermal resistance of the polymer network by strengthening intermolecular interactions and mitigating thermal degradation.

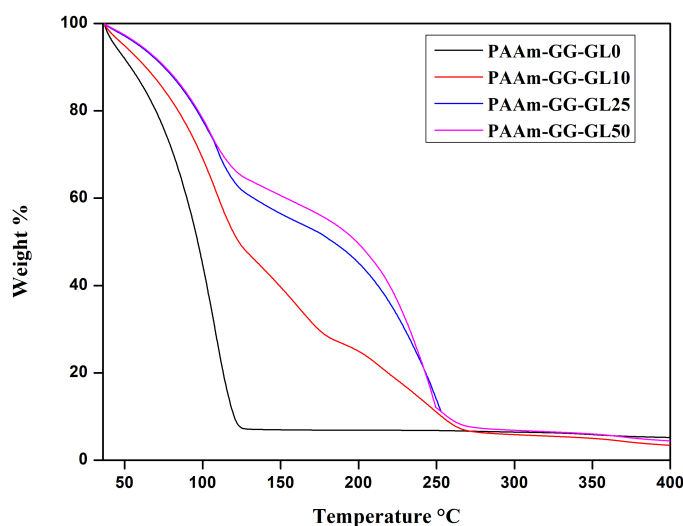
**Figure 4.26:** The TGA thermograms of the PAAm–GG hydrogel and PAAm–GG–GL organogels.

Figure 4.26 shows the thermal degradation profiles of the PAAm–GG hydrogel and the glycerol-based organogels. The hydrogel experienced rapid weight

Table 4.11: Thermal stability of PAAm–GG hydrogel and PAAm–GG–GL organogels at different temperatures.

Sample	50 °C	100 °C	150 °C	200 °C
PAAm–GG hydrogel	91.90%	44.47%	6.94%	6.85%
PAAm–GG–GL10 organogel	94.86%	68.97%	39.46%	24.92%
PAAm–GG–GL25 organogel	97.14%	77.69%	56.37%	45.14%
PAAm–GG–GL50 organogel	97.34%	78.15%	60.54%	49.55%

loss as temperature increased, indicating lower thermal stability. In contrast, the organogels containing glycerol showed slower degradation and retained a larger percentage of their original mass during heating. Thermal stability improved progressively with higher glycerol content, demonstrating that glycerol strengthens the polymer network and delays thermal decomposition.

Table 4.11 summarises the thermal stability of the PAAm–GG hydrogel and organogels with varying glycerol concentrations. The hydrogel displayed a rapid decrease in mass with temperature, confirming inferior thermal resistance. The organogels, however, maintained significantly higher weight retention across all tested temperatures, and the retention increased with glycerol loading. Among all samples, PAAm–GG–GL50 exhibited the highest thermal stability, further confirming the beneficial role of glycerol in enhancing structural integrity and delaying thermal degradation.

In hydrogels, water exists in three states: bound water, intermediate water, and free water. Bound water is strongly associated with the polymer matrix through hydrogen bonding to groups such as hydroxyl, carboxyl, or amide, and is largely immobile. Intermediate water is weakly associated, while free water behaves similarly to bulk water and can easily evaporate. The hydrogels contain a high proportion of free water, which contributes to poor water retention under drying or heating. The polyols introduced to the hydrogel matrix, readily form hydrogen bonds with free water molecules, converting them into intermediate or bound forms and reducing their mobility and volatility. This transformation improves long-term water retention and reduces moisture loss (Yu et al., 2021;

Sekine and Ikeda-Fukazawa, 2009; Naohara et al., 2022).

4.2.9 Conductivity studies

The Nyquist plots illustrating the electrochemical behaviour of the PAAm hydrogel and the PAAm–GG hydrogels containing varying amounts of gellan gum are presented in Fig. 4.27. The bulk resistance was obtained from the Nyquist plot, and the ionic conductivity of the hydrogels was subsequently calculated using this value. The corresponding ionic conductivity values for the PAAm–GG hydrogels with different gellan gum concentrations are summarised in Fig. 4.28. All PAAm–GG formulations exhibited higher ionic conductivity compared to the pure PAAm hydrogel. This confirms that the incorporation of gellan gum enhances ion transport within the network. The presence of negatively charged carboxylate groups ($-COO^-$) in gellan gum promotes the dissociation of ionic species and facilitates their mobility through the polymer matrix. As a result, the concentration of mobile charge carriers increases, enabling more efficient ion migration throughout the hydrogel network (Zhu et al., 2022; Ji et al., 2022).

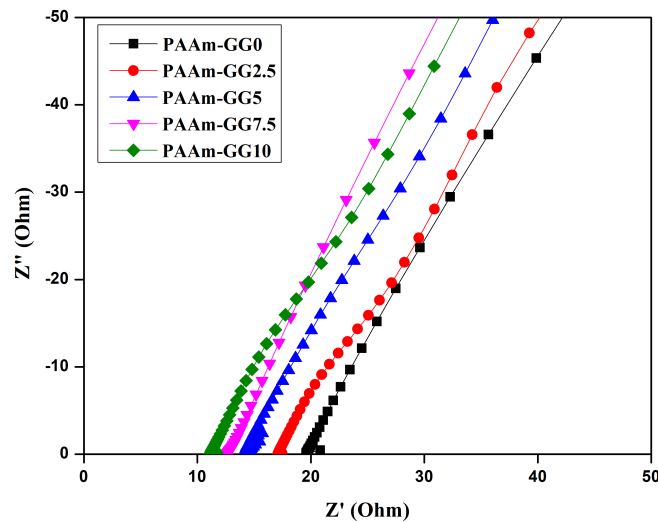


Figure 4.27: Nyquist plot to compare the electrochemical performances of PAAm-GG hydrogel at different gellan gum content.

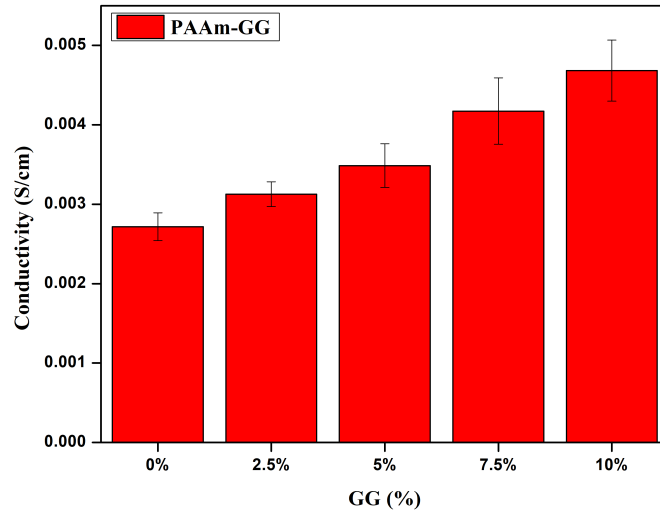


Figure 4.28: Ionic conductivity of PAAm-GG hydrogel at different gellan gum content.

The ionic conductivity of PAAm-GG hydrogels increased with gellan gum content. As the GG concentration increases, more ionic sites are readily available for interaction with the Ca^{2+} ions, resulting in greater ionic crosslinking. Higher GG levels improve carboxyl group availability, allowing more Ca^{2+} ions to bind and form ionic bridges between polymer chains. These ionic interactions promote long-range ion migration and enhance the hydrogel's overall conductivity (Huang, Liu, Chi, Jiang, Xu, Qu, Zhao, Li, Chen, Chen et al., 2021; Peng et al., 2022).

The ionic conductivity of PAAm-GG hydrogel is influenced by the concentration of Ca^{2+} ions. The AC conductivity vs frequency plot (Fig. 4.29) illustrates that hydrogels with lower calcium concentrations (0.1 M and 0.5 M $CaCl_2$) possess lower ionic conductivity. At lower calcium ion concentrations, the majority of Ca^{2+} ions are used to form ionic crosslinks within the polymer network. Consequently, only a small fraction of free ions remains available to contribute to charge transport, leading to reduced ionic conductivity.

As the Ca^{2+} concentration increases, the hydrogels exhibit a clear improvement in ionic conductivity. This enhancement results from a greater population of

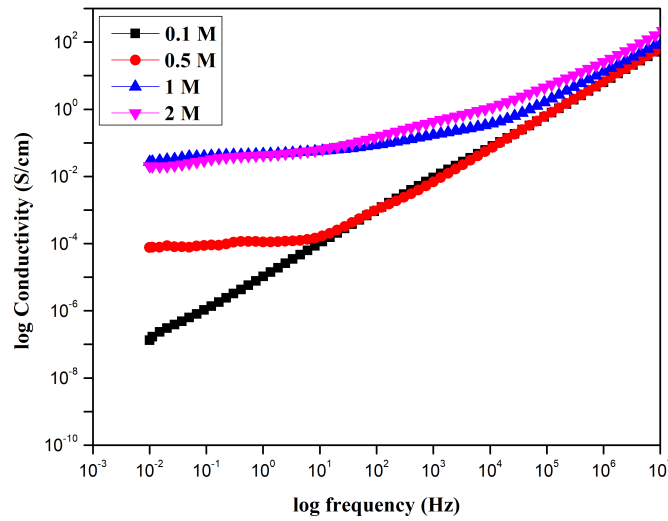


Figure 4.29: AC conductivity vs frequency plot of PAAm-GG hydrogel at different calcium concentrations.

mobile ions, which generates more continuous pathways for efficient ion migration (Li et al., 2016; Zhang, Wang, Hu, Zhang, Dai and Xia, 2020). However, when the CaCl_2 concentration is further increased to 2 M, the ionic conductivity does not exhibit a corresponding rise. Instead, it plateaus at a value comparable to that observed for 1 M. This behaviour suggests that the system approaches a saturation point in which most available carboxylate sites are already complexed with Ca^{2+} . Excess ions become immobilized within an overly crosslinked and tightly packed network, thereby limiting additional ionic mobility.

The AC conductivity vs. frequency plot of the PAAm-GG hydrogel at different temperatures (Fig. 4.30) illustrates that the conductivity decreases with decreasing temperature. The Nyquist plot of the electrochemical performances of PAAm-GG hydrogel at different temperatures are shown in Fig. 4.31 and 4.32. The ionic conductivity of the PAAm-GG hydrogels at 233 K, 253 K, 273 K, and 298 K was calculated from the corresponding Nyquist plots, and the obtained values are summarised in Table 4.12.

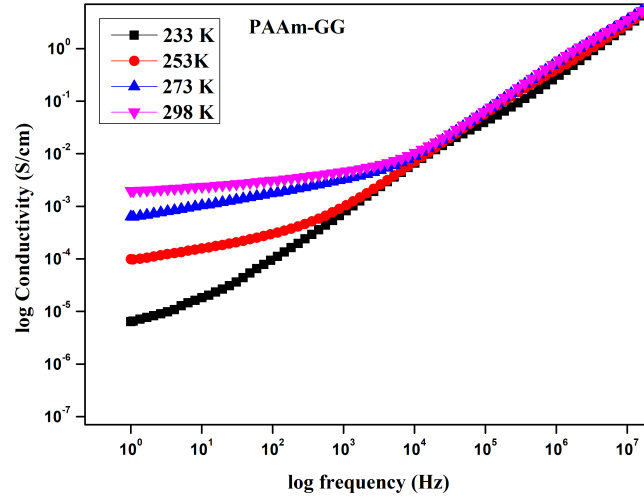


Figure 4.30: AC conductivity vs frequency plot of PAAm-GG hydrogel at different temperatures.

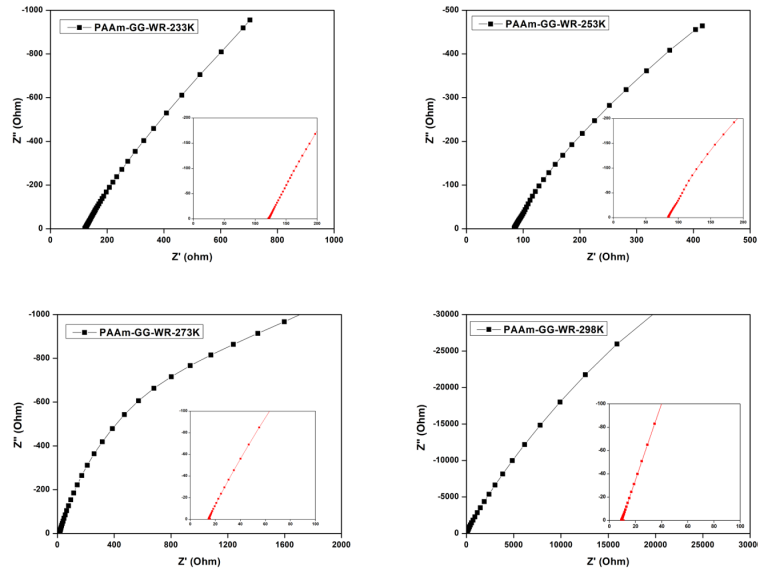


Figure 4.31: Nyquist plot of the electrochemical performances of PAAm-GG hydrogel at different temperatures.

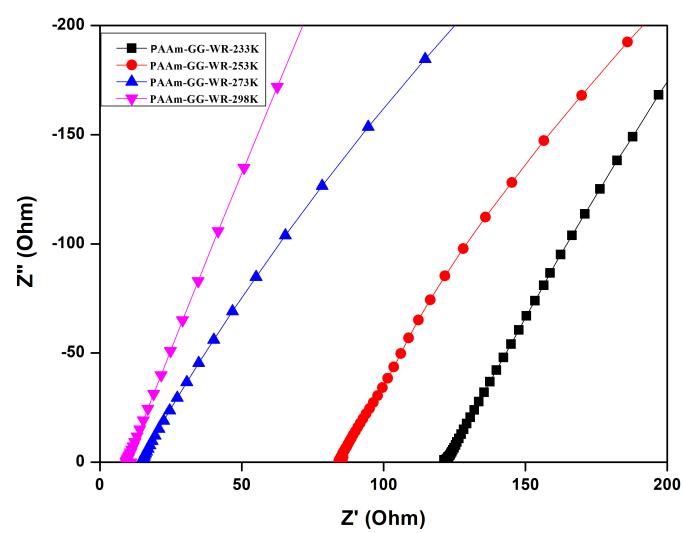


Figure 4.32: Nyquist plot to compare the electrochemical performances of PAAm-GG hydrogel at different temperatures.

Table 4.12: Ionic conductivity of PAAm-GG hydrogel and PAAm-GG-EG organogel at different temperatures.

Temperature (°C)	PAAm-GG Hydrogel (S cm ⁻¹)	PAAm-GG-EG Organogel (S cm ⁻¹)
-40	4.68×10^{-4}	1.12×10^{-3}
-20	6.66×10^{-4}	1.56×10^{-3}
0	3.57×10^{-3}	1.90×10^{-3}
25	5.18×10^{-3}	2.20×10^{-3}

At subzero temperatures, hydrogels experience a significant reduction in ionic conductivity primarily due to the phase transition of water within the polymer network. As the temperature drops below 0°C , a large portion of the free water content crystallises into ice, drastically reducing the amount of liquid water available to act as a solvent and medium for ion transport. Since ionic conduction in hydrogels relies on the mobility of solvated ions through interconnected aqueous domains, the formation of a solid ice phase interrupts these conduction pathways (Li, Charaya, Bernard, Elliott, Michaelis, Lee and Chung, 2018). Furthermore, the freezing process immobilises water molecules and disrupts the hydration shells surrounding the ions, thereby increasing ion-pairing or aggregation and further limiting their mobility. The polymer network itself may become more rigid at low temperatures, restricting segmental motion and reducing the dynamic flexibility necessary for coordinated ion movement. This combination of ice formation, reduced dielectric permittivity, and constrained polymer dynamics leads to a marked suppression of ionic conductivity in hydrogels under subzero conditions (Zhu et al., 2022; Huang, Zhong, Cai, Cao, Wang, Li, Lin and Zhang, 2025).

Fig. 4.33 shows the ac impedance spectra of PAAm-GG-EG organogel at different temperatures. In contrast to PAAm-GG hydrogel, temperature drops had minimal impact on the ionic conductivity of PAAm-GG-EG organogel. The Nyquist plot of the electrochemical performance of PAAm-GG-EG organogel at different temperatures are shown in Fig.4.34 and 4.35. The ionic conductivity values derived from the Nyquist plots have been compiled and compared with the corresponding PAAm-GG hydrogel data, as presented in Table 4.12.

The ionic conductivity exhibited by the hydrogels and organogels at different temperatures is shown in Fig. 4.36. The PAAm-GG hydrogel exhibits higher ionic conductivity than the PAAm-GG-EG organogel at room temperature and 273 K , attributable to the reduced water content of the organogel (Liao et al.,

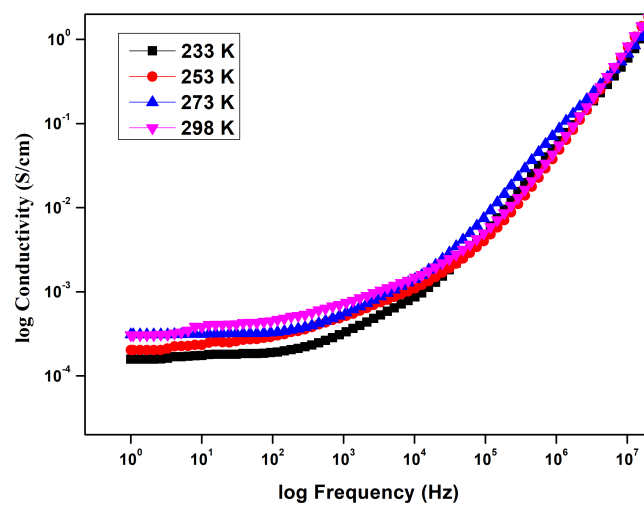


Figure 4.33: AC conductivity vs frequency plot of PAAm-GG-EG organogels at different temperatures.

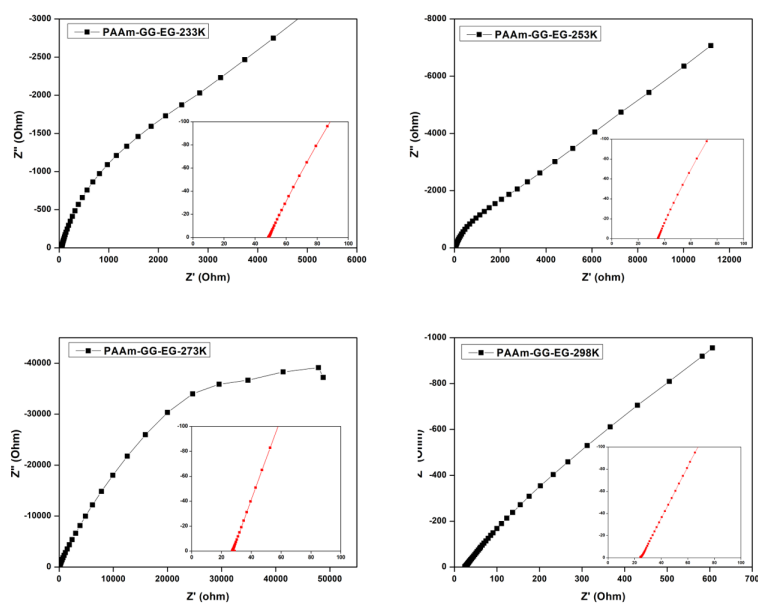


Figure 4.34: Nyquist plot of the electrochemical performances of PAAm-GG-EG organogels at different temperatures.

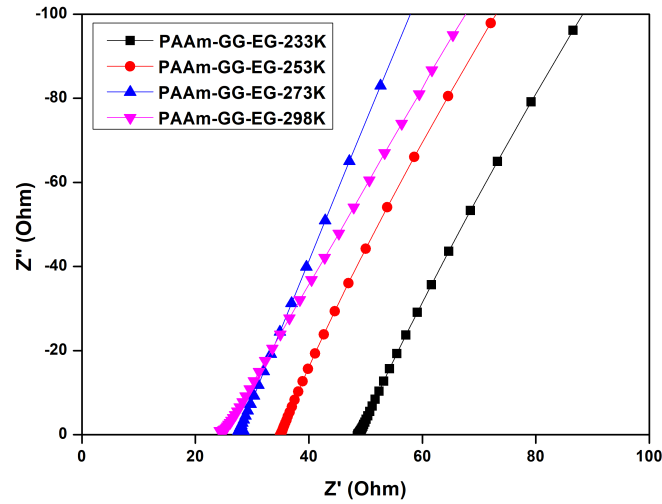


Figure 4.35: Nyquist plot of the electrochemical performances of PAAm-GG-EG organogel at different temperatures.

2019). Solvents with high viscosity, such as ethylene glycol, naturally restrict ion migration, explaining why organogels have lower conductivity than hydrogels (Lu et al., 2020). At 253 K and 233 K, the PAAm-GG-EG organogel outperformed the PAAm-GG hydrogel in ionic conductivity. Its ability to retain good ionic conductivity even at sub-zero temperatures makes PAAm-GG-EG organogel a promising material to fabricate flexible anti-freezing electronic devices.

Figures 4.38 and 4.39 compare the Nyquist plots representing the electrochemical performance of the PAAm-GG-GL organogel at different temperatures. The ionic conductivities of PAAm-GG-GL organogels across different temperatures were determined from the corresponding Nyquist plots and are summarised in Table 4.13. Figure 4.40 presents a comparison of the ionic conductivities exhibited by PAAm-GG hydrogels and PAAm-GG-GL organogels over a range of temperatures.

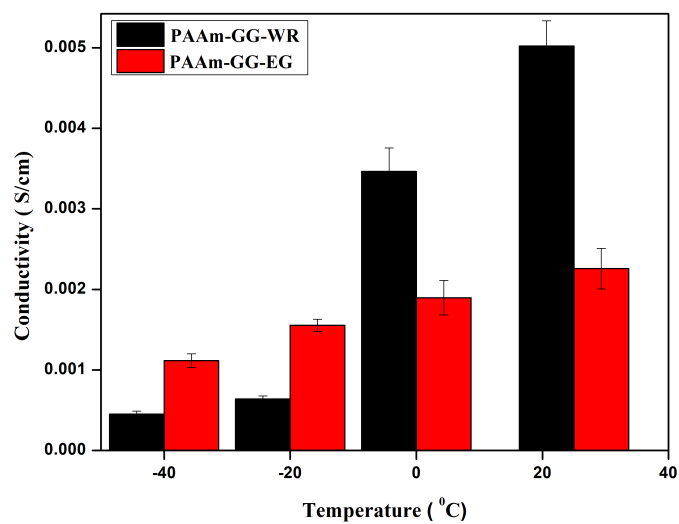


Figure 4.36: Ionic conductivity of PAAm-GG-hydrogel and PAAm-GG-EG organogel at different temperatures.

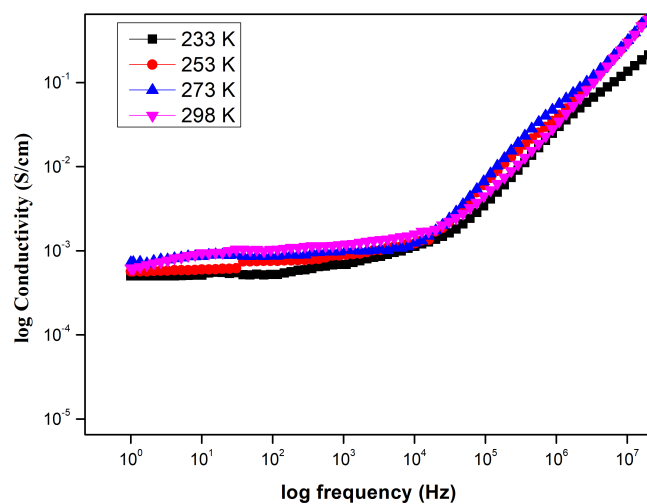


Figure 4.37: AC conductivity vs frequency plot of PAAm-GG-GL organogels at different temperatures.

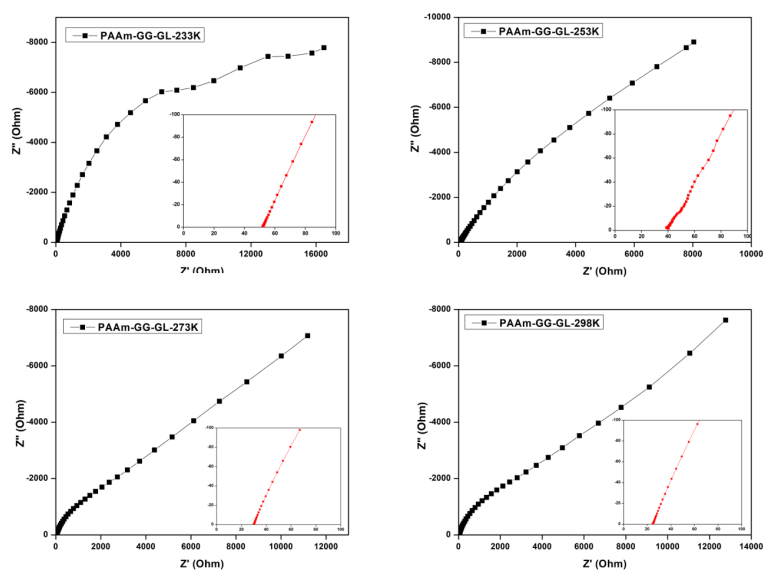


Figure 4.38: Nyquist plot of the electrochemical performances of PAAm-GG-GL organogels at different temperatures.

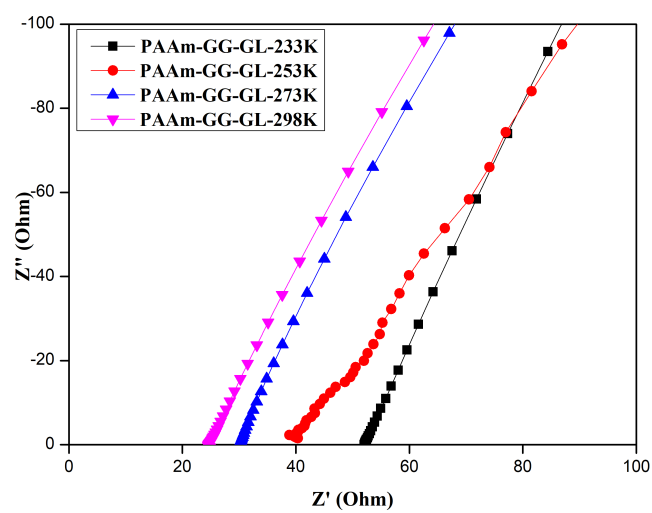


Figure 4.39: Nyquist plot of the electrochemical performances of PAAm-GG-GL organogel at different temperatures.

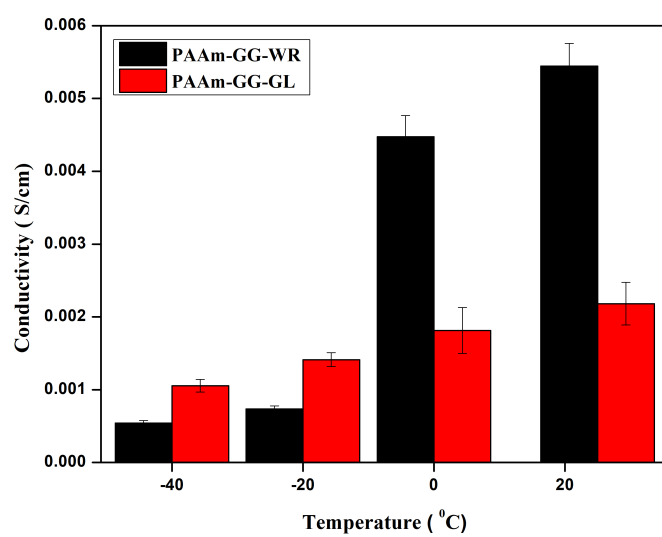


Figure 4.40: Ionic conductivity of PAAm-GG-hydrogel and PAAm-GG-GL organogel at different temperatures.

Table 4.13: Ionic conductivity of PAAm-GG hydrogel and PAAm-GG-GL organogel at different temperatures.

Temperature (°C)	PAAm-GG Hydrogel (S cm ⁻¹)	PAAm-GG-GL Organogel (S cm ⁻¹)
-40	4.68×10^{-4}	1.05×10^{-3}
-20	6.66×10^{-4}	1.41×10^{-3}
0	3.57×10^{-3}	1.81×10^{-3}
25	5.18×10^{-3}	2.18×10^{-3}

At room temperature and 273 K, the PAAm–GG hydrogel exhibits higher ionic conductivity than the PAAm–GG–GL organogel. This reduced conductivity in the organogel arises from its lower water content, which diminishes the number of effective ion-transport channels (Liao et al., 2019). In addition, the greater viscosity of glycerol significantly restricts ion mobility, further limiting charge transport within the organogel network (Lu et al., 2020). Conversely, under sub-zero conditions (253 K and 233 K), the PAAm–GG–GL organogel demonstrates enhanced conductivity relative to the PAAm–GG hydrogel, attributed to the cryoprotective and anti-freezing role of glycerol that prevents ice-induced immobilization of ions (Zhou et al., 2023).

Solvents like ethylene glycol and glycerol, which possess higher viscosities than water, impose physical restrictions on ion movement within organogel systems. When these polyols are introduced into the polymer matrix either partially or fully replacing water they significantly modify the surrounding environment through which ions travel. In hydrogels, ion mobility is supported by the high fluidity and polarity of water, which provides a low viscosity medium that enables rapid diffusion and effective dielectric screening, assisting in ion dissociation. In contrast, organogels containing ethylene glycol or glycerol behave quite differently. Both solvents form extensive hydrogen-bonding interactions with the PAAm and gellan gum polymer networks, as well as with residual water molecules. These interactions immobilise portions of the solvent phase and reduce the amount of free solvent available for solvating ions. Besides, their inherently high viscosity greatly slows the motion of ions. As a result, ion mobility throughout the gel network is substantially reduced.

Although organogels exhibit lower ionic conductivity than hydrogels at room temperature, the trend reverses at sub-zero temperatures. Under such conditions, organogels exhibit higher ionic conductivity than hydrogels, due to the superior anti-freezing properties of organic solvents. In hydrogels, when the temperature

drops below 0°C, the water within the network begins to crystallise and form ice. This phase transition immobilizes the solvent, disrupts ion hydration shells, and blocks ion-transport pathways, leading to a sharp decrease in conductivity. In contrast, organogels containing ethylene glycol or glycerol are able to resist freezing even at sub-zero temperatures. As a result, the network remains in a semi-liquid or amorphous state, allowing ions to retain mobility despite the low temperature (Hu et al., 2018). While the absolute ion mobility in organogels is lower than in water-rich systems at ambient temperatures, their relative conductivity becomes significantly higher than that of frozen hydrogels when water is no longer available for ion transport.

4.3 Conclusion

In this study, high-performance dual-crosslinked polyacrylamide-gellan gum (PAAm-GG) organogels were successfully fabricated through covalent and ionic crosslinking, followed by solvent displacement using hydrophilic polyols-ethylene glycol (EG) and glycerol (GL). The resulting PAAm-GG-EG and PAAm-GG-GL organogels demonstrated outstanding mechanical strength, enhanced thermal stability, improved ionic conductivity, and excellent anti-freezing performance. FTIR results demonstrated that PAAm and GG form an interpenetrating network stabilised by physical interactions rather than covalent bonds, while polyol incorporation introduced additional hydrogen bonding interactions within the network. Swelling studies revealed a decrease in swelling ratio for both EG and GL based organogels, attributed to increased network rigidity and reduced water affinity. Tensile studies established that dual crosslinking with Ca^{2+} and introduction of polyols substantially enhanced the mechanical properties of the hydrogels.

Anti-freezing evaluations showed that both PAAm-GG-EG and PAAm-GG-GL organogels preserved flexibility, transparency, and structural integrity at sub-zero temperatures, with DSC confirming a significant freezing-point depression

proportional to polyol content. Thermal and solvent-retention experiments further demonstrated improved long-term durability and dehydration resistance. Ionic conductivity measurements indicated that the organogels sustained effective ion transport under sub-zero conditions, highlighting their potential for low-temperature flexible electronics applications. Overall, the cryotolerant PAAm-GG-EG and PAAm-GG-GL organogels effectively integrate mechanical robustness, thermal resilience, and reliable ionic conductivity, positioning them as advanced candidates for next-generation soft functional materials.

Table 4.14: Summary of the key findings

Characterisation	Key Findings
FTIR analysis	FTIR spectra confirmed intermolecular hydrogen bonding interactions between PAAm, GG, and polyols through characteristic peak shifts without formation of new covalent bonds.
SEM analysis	SEM images showed that incorporation of GG produced a denser and more compact porous structure with enhanced network integrity.
Swelling studies	The swelling ratio decreased with increasing GG and EG concentration due to enhanced crosslinking density and reduced free volume, while lower GL concentrations slightly increased swelling.
Mechanical properties	Mechanical strength and Young's modulus increased significantly with Ca^{2+} , GG, EG, and GL incorporation due to enhanced ionic and hydrogen-bonding interactions.
Rheological behaviour	Storage modulus (G'), loss modulus (G''), and $\tan \delta$ increased with increasing polyol concentration, indicating improved structural stability and energy dissipation.
Anti-freezing studies	EG and GL organogels retained flexibility and transparency at sub-zero temperatures, while DSC analysis confirmed depression of freezing temperatures with increasing polyol concentration.
Solvent retention and thermal stability	Organogels exhibited enhanced solvent retention and thermal stability compared to pristine hydrogels, especially at higher EG and GL concentrations.
Conductivity studies	PAAm-GG hydrogels showed enhanced ionic conductivity with increasing GG concentration, while organogels maintained good conductivity under sub-zero conditions.

Chapter 5

Comparative Analysis of PAAm-Pectin and PAAm-Gellan Gum Hydrogels and Organogels

5.1 Introduction

This chapter presents a comparative evaluation of the Polyacrylamide-pectin (PAAm-pectin) and Polyacrylamide-gellan gum (PAAm-GG) systems, both developed as double-network hydrogels reinforced through covalent and ionic crosslinking and subsequently transformed into ethylene glycol (EG) and glycerol (GL) based organogels. Although both materials share similar fabrication routes and solvent modification strategies, variations in the chemical structures of the natural polysaccharides (pectin vs gellan gum) and the physicochemical properties of the organic solvents (EG vs GL) result in differences in network architecture, mechanical response, solvent retention, anti-freezing ability, and ionic conductivity.

Beyond structural characterization, this chapter also examines key functional attributes that govern the performance and stability of the hydrogels and their corresponding organogels. The anti-freezing and anti-drying behaviours of the EG and GL based organogels are systematically compared to elucidate how differences in polyol properties influence water retention, thermal resilience, and long-term stability.

The ionic conductivities of the PAAm-pectin and PAAm-GG hydrogels were

examined over a range of temperatures to understand how the chemical structure of the polysaccharides influences ion mobility within the hydrated matrices. Furthermore, a direct comparison between glycerol-based and ethylene glycol-based organogels is carried out to reveal how differences in solvent viscosity and hydrogen bonding behaviour affect charge transport characteristics.

Together, these evaluations provide a comprehensive understanding of how changes in polysaccharide composition and polyol environment influence the chemical, morphological, thermal, mechanical, and electrochemical behaviour of the PAAm–pectin and PAAm–GG organogel systems. These insights help to establish clear structure-property relationships and offer a practical framework for designing organogels with tailored functionalities suited to a wide range of application needs.

5.2 Structural and morphological characterisation

The FTIR analysis confirmed that, in both the PAAm–pectin and PAAm–gellan gum systems, no covalent bonds were formed between the constituent polymer networks. In both cases, the blending was governed by non-covalent interactions (Ohm et al., 2021), particularly hydrogen bonding between the polymer chains and also between the polymer network and the incorporated organic solvents (Yang et al., 2013). This confirms that the structural integrity of the organogels arises mainly from physical associations rather than chemical crosslinking. Observable peak shifts were detected for both the EG and GL based organogels compared to their corresponding hydrogels, indicating the occurrence of strong hydrogen bonding interactions (Zhang, Jiang, Zhao, Diao, Liu, Chen, Liu and Yang, 2024). These spectral changes confirm that the structural integrity of the organogels arises primarily from physical associations rather than chemical crosslinking.

The SEM images reveal distinct microstructural differences among the PAAm, PAAm–pectin, and PAAm–GG hydrogels (Fig. 5.1). The pure PAAm hydrogel

exhibits a highly porous and interconnected network with thin pore walls and uniformly distributed sponge-like pores, characteristic of a loosely crosslinked matrix that supports high water uptake (Zhou and Jin, 2020). Incorporation of pectin results in the PAAm–pectin hydrogel, which shows thicker pore walls and a denser architecture with fewer and larger, irregular pores. This morphological densification indicates increased crosslinking density due to hydrogen bonding interactions between PAAm and pectin, leading to reduced swelling and enhanced structural stability (Rodrigues et al., 2024). In contrast, the PAAm–GG hydrogel presents an even more compact and tightly crosslinked network with fine, interconnected pores, attributed to stronger intermolecular interactions between gellan gum and PAAm chains (Wang, Yu and Liu, 2022). The progressive transition from a loose (PAAm) to moderately dense (PAAm–pectin) and highly compact (PAAm–GG) microstructure clearly demonstrates the strengthening effect of biopolymer incorporation on the overall network morphology (Dou et al., 2017).

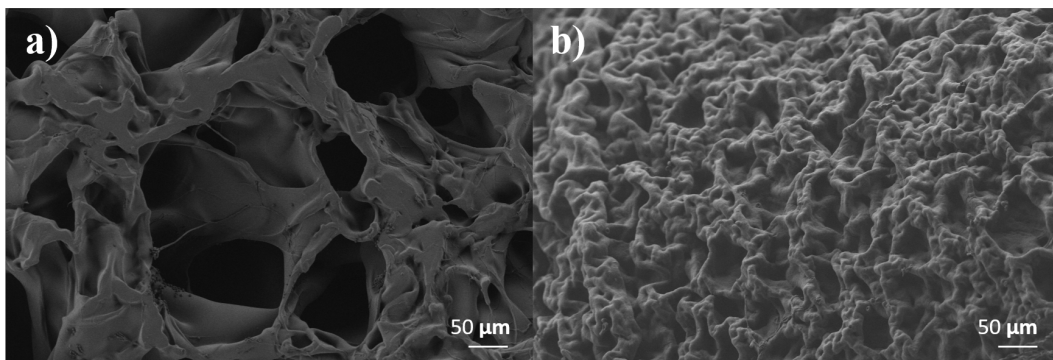


Figure 5.1: SEM images of a) PAAm-pectin hydrogel and b) PAAm-GG hydrogel.

5.3 Swelling studies

The swelling behavior of the PAAm–pectin and PAAm–GG hydrogels, prepared at two different biopolymer concentrations (5 % and 10 %), is compared in Fig. 5.2. At both concentrations, the PAAm–pectin hydrogels exhibited a markedly higher swelling ratio than the PAAm–GG hydrogels, indicating that the pectin-

based network possesses greater hydrophilicity and a lower crosslink density, which facilitates enhanced water uptake (Chen et al., 2010). This behavior can be attributed to the presence of abundant hydrophilic carboxyl and hydroxyl groups in pectin that promote hydrogen bonding with water molecules, as well as the moderate crosslinking between PAAm and pectin that allows greater chain mobility and network expansion upon hydration (Oh et al., 2022; Tomić et al., 2023). In contrast, the PAAm–gellan gum hydrogels exhibited a relatively lower swelling ratio, consistent with their denser and more rigid microstructure observed in SEM analysis. The strong intermolecular associations within the gellan gum network result in a compact structure that restricts solvent diffusion and limits volumetric expansion.

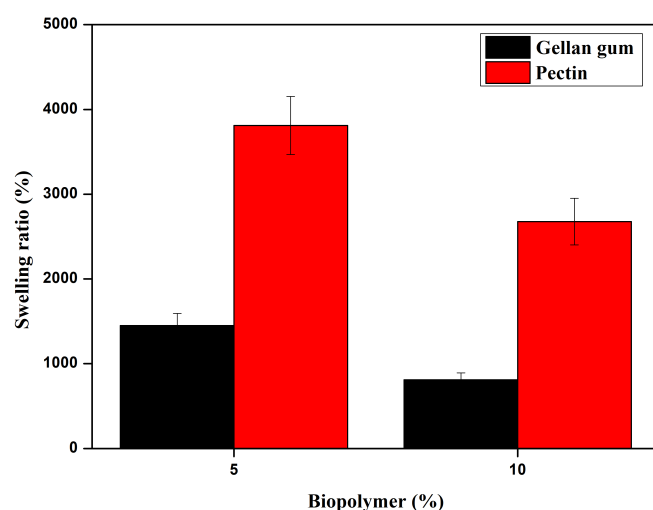


Figure 5.2: Comparison of the swelling ratio of PAAm-pectin and PAAm-GG hydrogels in aqueous medium.

The swelling behavior of ethylene glycol (EG) and glycerol (GL) based organogels differs significantly due to variations in solvent polarity, viscosity, and hydrogen-bonding tendencies, as shown in both PAAm–pectin and PAAm–GG systems (Fig. 5.3 and 5.4). In the PAAm–pectin hydrogels, the incorporation of ethylene glycol progressively decreased the swelling ratio. Ethylene glycol, with its lower dielectric

constant and higher viscosity compared to water, decreased osmotic pressure and limited water uptake. It also formed additional hydrogen bonds with the amide and carboxyl groups of PAAm and pectin, increasing physical crosslinking and network compactness, thereby suppressing swelling (Sundar et al., 2012). Conversely, at lower concentrations glycerol produced a biphasic effect. Its hygroscopic nature increased polymer chain mobility and enabled greater water absorption, leading to a slight rise in swelling (Jakubczyk et al., 2023). However, at higher concentrations, glycerol replaced water within the matrix, formed strong hydrogen bonds with polymer chains, and increased viscosity, all of which reduced swelling by restricting diffusion and network expansion (Li, Zhang, Jia, Ma and Hao, 2018).

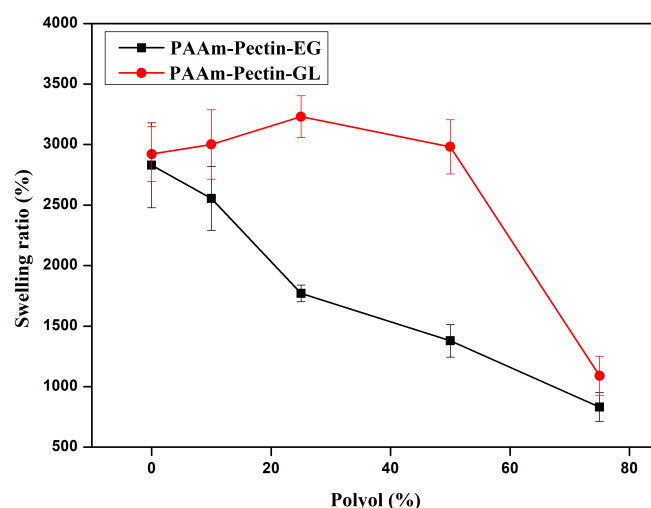


Figure 5.3: Comparison of the swelling ratio of PAAm-pectin in glycerol and ethylene glycol solvent systems.

A similar trend was observed in the PAAm-GG system, where increasing ethylene glycol concentration led to a pronounced decrease in swelling. EG reduced solvent polarity, decreased solvation of amide and hydroxyl groups, and promoted intra-network hydrogen bonding, resulting in a denser, less hydrophilic structure. Glycerol-based PAAm-GG organogels, on the other hand, exhibited a slight increase in swelling at low concentrations can be explained by the plasticizing and

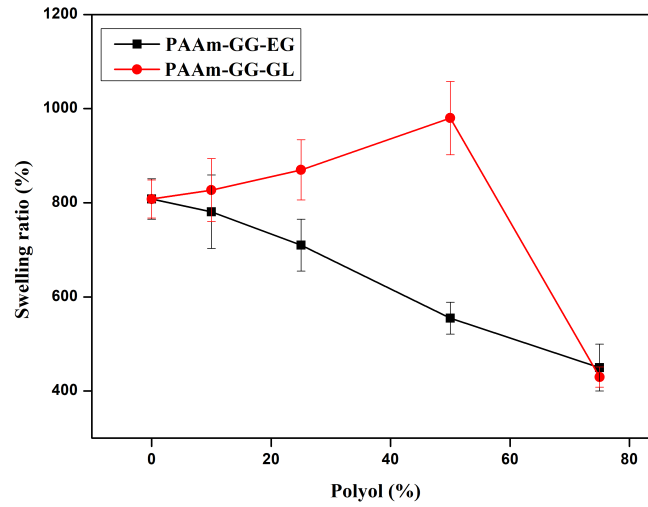


Figure 5.4: Comparison of the swelling ratio of PAAm–GG in glycerol and ethylene glycol solvent systems.

water-retaining effects of glycerol. The substantial decrease beyond 50% glycerol, due to reduced water availability, increased viscosity, and extensive hydrogen bonding within the network. Overall, ethylene glycol–based organogels exhibit lower swelling ratios and more compact structures due to stronger polymer–solvent interactions and reduced hydrophilicity, while glycerol-based organogels maintain moderate swelling and greater flexibility at low concentrations, transitioning to reduced swelling at higher levels (Ge et al., 2022; Mo et al., 2021). This comparative behaviour highlights the tunability of organogel swelling through solvent selection and composition.

5.4 Mechanical characterisation

The mechanical properties of ethylene glycol (EG) and glycerol (GL) based organogels exhibit distinct patterns due to differences in molecular structure, polarity, and hydrogen-bonding capacity of the incorporated solvents. Fig. 5.5 compares the tensile strength of PAAm–pectin organogels containing glycerol and ethylene glycol. The glycerol-based organogels exhibit superior mechanical strength compared

to their ethylene glycol counterparts, and the enhancement becomes more pronounced at higher glycerol concentrations. A similar trend was observed for the PAAm–GG organogels, where the glycerol containing formulations demonstrated higher tensile strength than their ethylene glycol counterparts, particularly at elevated glycerol concentrations (Fig. 5.6). The elongation at break at the highest polyol concentration (75%) is compared in Fig. 5.7. In both the PAAm–pectin and PAAm–GG systems, the glycerol incorporated organogels exhibited significantly higher elongation at break in comparison to their ethylene glycol-based counterparts. This comparison indicates that glycerol-based organogels exhibit enhanced mechanical performance, superior to ethylene glycol-based systems in both strength and flexibility. The greater hydrogen bonding capability of glycerol, containing three hydroxyl groups compared to the two in ethylene glycol, facilitates the formation of a denser network of reversible, glycerol-mediated physical crosslinks (Yan et al., 2021; Su et al., 2022). These dynamic interactions can break and reform more efficiently under applied stress, resulting in enhanced energy dissipation, improved toughness, and markedly greater extensibility in glycerol-based organogels (Cheng et al., 2024; Su et al., 2025).

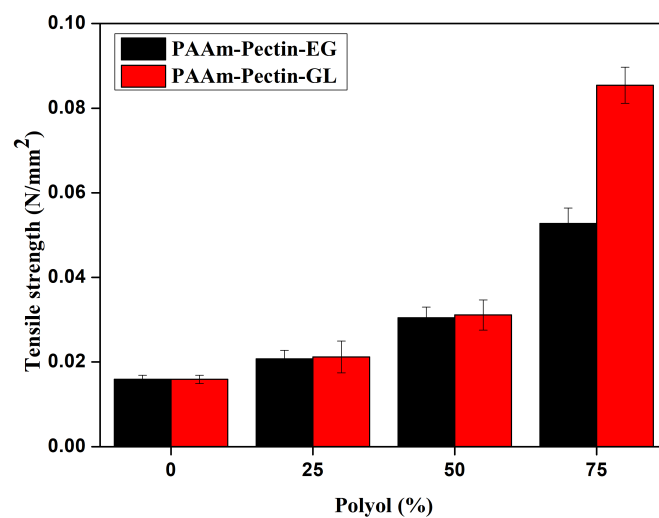


Figure 5.5: Comparison of tensile strength of PAAm-pectin-EG and PAAm-pectin-GL organogels.

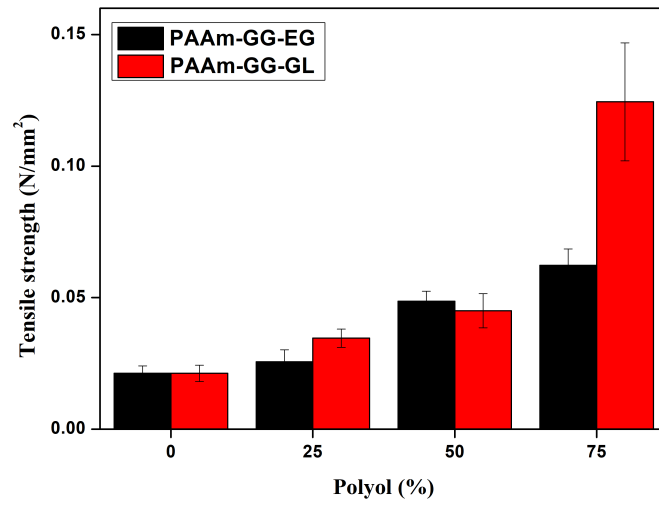


Figure 5.6: Comparison of tensile strength of PAAm-GG-EG and PAAm-GG-GL organogels.

The mechanical properties of the PAAm–pectin and PAAm–GG hydrogels exhibit clear differences arising from the nature of the incorporated biopolymer and the resulting network interactions. Fig. 5.8 compares the mechanical strength of the PAAm–pectin and PAAm–GG systems incorporating glycerol, while Fig. 5.9 presents the corresponding comparison for the ethylene glycol-containing systems. The data clearly demonstrate that, irrespective of the polyol type or its concentration, the gellan gum-based organogels always exhibited higher mechanical strength than the pectin-based systems.

Gellan gum-based organogels exhibit superior mechanical strength to pectin-based systems primarily due to their significantly higher crosslinking density and more ordered network architecture (Seo et al., 2023). In the presence of Ca^{2+} , gellan gum readily forms stable double helices and tightly packed ionic junction zones, establishing a dense and highly reinforced crosslinked network that greatly enhances load-bearing capacity (Vilela et al., 2024). This elevated crosslinking density is further complemented by strong hydrogen bonding interactions and efficient interpenetration with the PAAm chains, producing a more cohesive and homogeneous interpenetrating network (Pachaiyappan et al., 2025). In contrast,

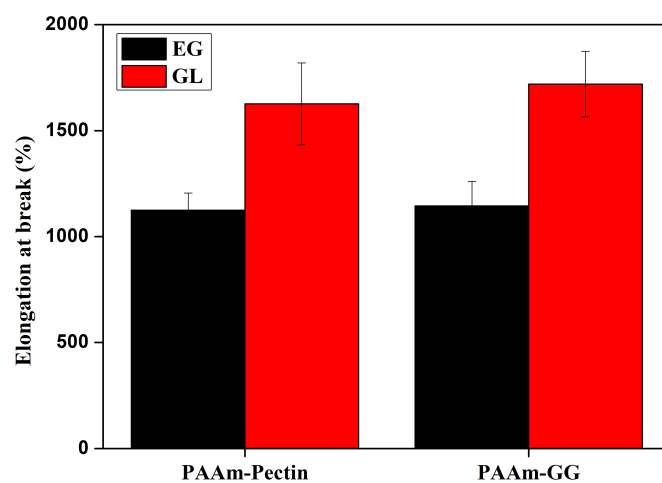


Figure 5.7: Comparison of elongation at break of EG and GL based organogels.

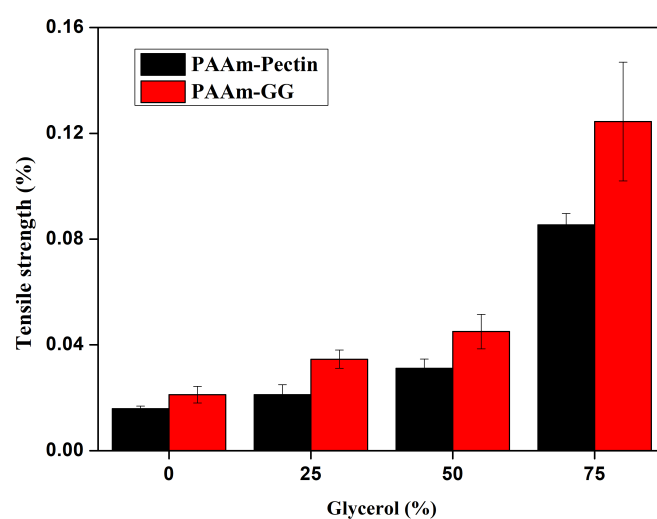


Figure 5.8: Comparison of tensile strength of glycerol-based PAAm-Pectin and PAAm-GG organogels

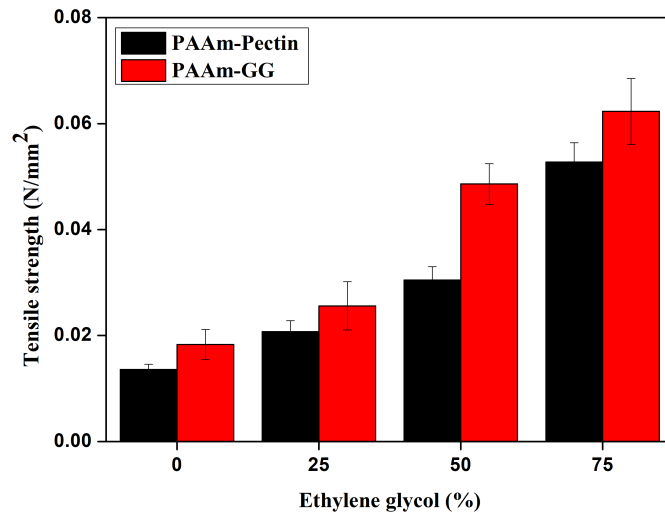


Figure 5.9: Comparison of tensile strength of ethylene glycol-based PAAm-pectin and PAAm-GG organogels.

pectin forms a comparatively looser “egg-box” structure, resulting in a lower overall crosslinking density, reduced network rigidity, and diminished mechanical resistance. Consequently, the higher crosslinking density and stronger network integrity of GG based organogels directly translate to their substantially improved tensile strength and overall mechanical robustness.

5.5 Rheological characterisation

Figure 5.10 compares the storage modulus (G') and loss modulus (G'') of the PAAm-pectin and PAAm-GG hydrogels. The storage modulus values of both PAAm-pectin and PAAm-GG are found to be greater than the loss modulus across the entire frequency range, indicating solid-like behavior and the elastic nature of the hydrogels. The PAAm-GG hydrogels exhibited a higher storage modulus (G') compared to the PAAm-pectin hydrogels, indicating that the GG-based networks possess a more pronounced solid-like and elastic character. This enhanced elastic response arises from the stronger Ca^{2+} mediated double-helix junction zones of gellan gum, which impart a higher crosslinking density and a more rigid IPN

architecture, leading to a distinctly more solid-like behaviour in the GG-based system (Tavagnacco et al., 2023). The PAAm-GG hydrogels exhibited a higher loss modulus than the PAAm-pectin hydrogels, showing that the material exhibits more damping and energy dissipation.

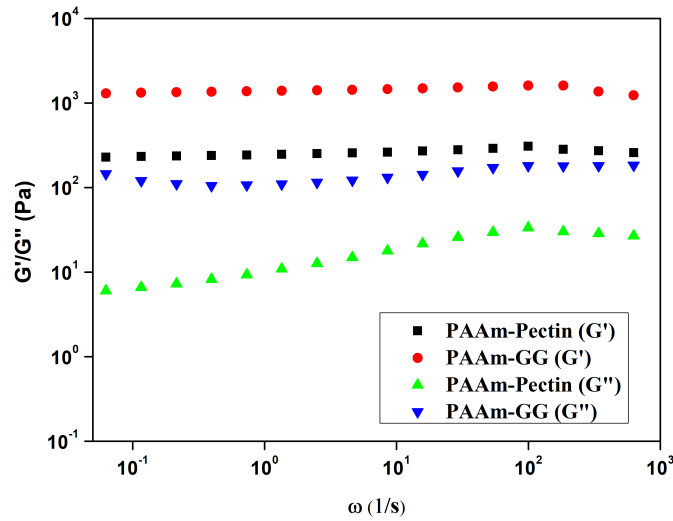


Figure 5.10: Comparison of Modulus (G' and G'') of PAAm-pectin and PAAm-GG hydrogels

The plot of the loss factor ($\tan \delta$) for the PAAm-pectin and PAAm-GG hydrogels as a function of frequency is shown in Fig. 5.11. The $\tan \delta$ values of both hydrogels were found to be less than 1, demonstrating that the materials are predominantly solid-like and behave more elastically than viscously. The comparison shows that the PAAm-GG hydrogels exhibit higher $\tan \delta$ values than the PAAm-Pectin hydrogels, indicating higher damping and a slightly greater viscous response in the GG-based network.

5.6 Evaluation of Anti-freezing behaviour

The anti-freezing ability of both ethylene glycol (EG) and glycerol (GL) based organogels was found to depend strongly on solvent concentration. At 0% and 10%, both systems became opaque and rigid when exposed to sub-zero temper-

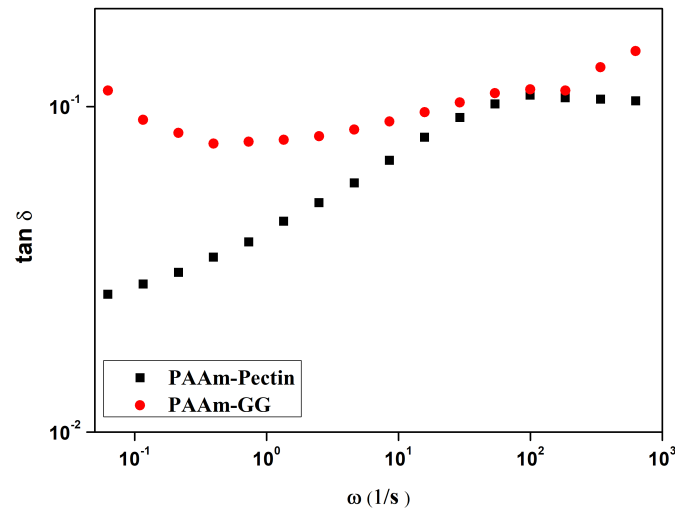


Figure 5.11: Comparison of loss factor ($\tan \delta$) of PAAm-pectin and PAAm-GG hydrogels.

atures, indicating ice formation within the polymer network. However, when the solvent content reached 25% or higher, the gels remained soft, transparent, and flexible, demonstrating effective anti-freezing behavior. This improvement results from the substitution of freezable water with EG or GL molecules that form strong hydrogen bonding interactions with the polymer chains and residual water, thereby disrupting ice crystallization (Khan et al., 2025; Gong et al., 2025).

Tables 5.1 and 5.2 present a comparative summary of the peak and onset freezing temperatures obtained from the DSC analysis of the PAAm-pectin-EG and PAAm-pectin-GL organogel systems. Similarly, the peak and onset freezing temperatures of the PAAm-GG organogels containing ethylene glycol and glycerol are provided in Tables 5.3 and 5.4, respectively. The DSC analysis of both PAAm-pectin and PAAm-gellan gum (GG) organogel systems revealed consistent anti-freezing trends for ethylene glycol (EG) and glycerol (GL) based formulations, though with varying degrees of freezing-point suppression. The freezing transition data presented in Tables 5.1 to 5.4 indicate that both ethylene glycol (EG) and glycerol (GL) effectively depress the freezing point of the PAAm-pectin

and PAAm–GG organogels compared to their corresponding hydrogels (Ge et al., 2022; Liu et al., 2021). However, the EG-based systems exhibit slightly better anti-freezing capability than the GL based systems, as evidenced by the lower onset and peak freezing temperatures across comparable compositions. The smaller molecular size and higher diffusivity of EG facilitate more efficient replacement of free water and the formation of extensive hydrogen-bonding interactions within the polymer network (Bhattarai et al., 2025). Consequently, EG more effectively disrupts ice nucleation and crystal growth, leading to enhanced freezing-point suppression in both hydrogel systems (Tessier et al., 2022; Fukusako and Yamada, 1989).

Table 5.1: Comparison of peak freezing temperatures of PAAm–pectin–EG and PAAm–pectin–GL organogels.

Organogel	PAAm–pectin–EG (°C)	PAAm–Pectin–GL (°C)
PAAm–pectin–0	8.6	8.6
PAAm–pectin–10	–1.8	–1.6
PAAm–pectin–25	–16.4	–12.3
PAAm–pectin–50	Not observed	–42.3

Table 5.2: Comparison of onset freezing temperatures of PAAm–pectin–EG and PAAm–pectin–GL organogels.

Organogel	PAAm–Pectin–EG (°C)	PAAm–Pectin–GL (°C)
PAAm–pectin–0	–1.5	–1.5
PAAm–pectin–10	–10.3	–8.9
PAAm–pectin–25	–27.0	–21.8
PAAm–pectin–50	Not observed	–55.6

Table 5.3: Comparison of peak freezing temperatures of PAAm–GG–EG and PAAm–GG–GL organogels.

Organogel	PAAm–GG–EG (°C)	PAAm–GG–GL (°C)
PAAm–GG–0	6.0	6.0
PAAm–GG–10	–5.1	–1.1
PAAm–GG–25	–35.2	–23.5
PAAm–GG–50	Not observed	Not observed

Table 5.4: Comparison of onset freezing temperatures of PAAm–GG–EG and PAAm–GG–GL organogels.

Organogel	PAAm–GG–EG (°C)	PAAm–GG–GL (°C)
PAAm–GG–0	0.1	0.1
PAAm–GG–10	–12.5	–7.6
PAAm–GG–25	–41.6	–31.8
PAAm–GG–50	Not observed	Not observed

5.7 Solvent retention and stability analysis

The solvent retention behaviour of both PAAm–pectin and PAAm–GG organogels improved markedly with increasing polyol concentration, with glycerol consistently exhibiting superior performance compared to ethylene glycol. Figure 5.12 compares the solvent retention capacity of PAAm–pectin organogels containing ethylene glycol (EG) and glycerol (GL), while Figure 5.13 presents the corresponding comparison for PAAm–GG organogels. In both systems, the glycerol-based organogels displayed higher solvent retention capacities than their ethylene glycol counterparts, due to the stronger water binding affinity and hygroscopic nature of glycerol molecules (Chen et al., 2022). Tables 5.5 and 5.6 further summarize the solvent retention capacities of PAAm–pectin and PAAm–GG organogels containing 25% and 50% of EG or GL after 20 days. Consistent with the graphical results, the glycerol-based organogels retained significantly more solvent at both concentrations, reaffirming the superior hydration retention capability of glycerol compared to ethylene glycol (Zha et al., 2023; Dong et al., 2022; Gao, Han, Wan, Fu, Yang, Guo, Ji, Chu, Tian and Lai, 2024).

Table 5.5: Comparison of solvent retention capacity of PAAm–pectin and PAAm–GG organogels containing 25% ethylene glycol and glycerol after 20 days.

Sample	Polyol Type	Retention after 20 days (%)
PAAm–pectin	Ethylene glycol (25%)	10.70
PAAm–GG	Ethylene glycol (25%)	6.30
PAAm–pectin	Glycerol (25%)	49.32
PAAm–GG	Glycerol (25%)	44.13

Thermogravimetric Analysis (TGA) was performed to evaluate the thermal

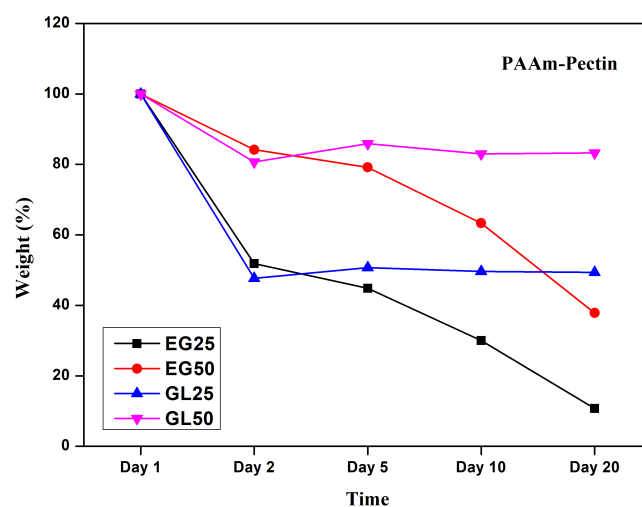


Figure 5.12: Comparison of the solvent retention capacity of PAAm-pectin organogels containing ethylene glycol (EG) and glycerol (GL).

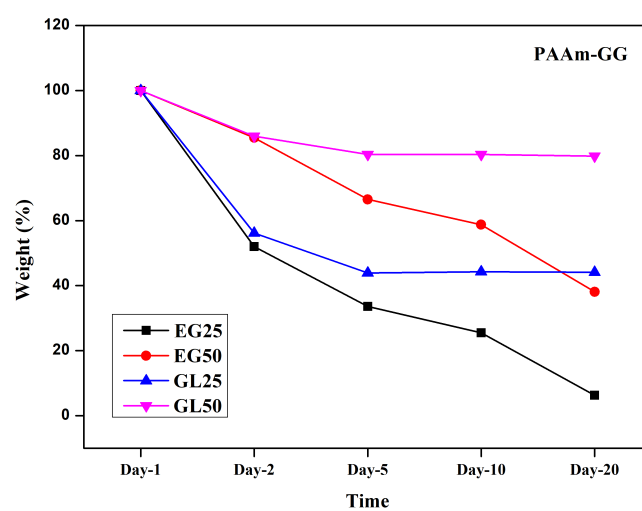


Figure 5.13: Comparison of the solvent retention capacity of PAAm-GG organogels containing ethylene glycol (EG) and glycerol (GL).

Table 5.6: Comparison of solvent retention capacity of PAAm–Pectin and PAAm–Gellan gum organogels containing 50% ethylene glycol and glycerol after 20 days.

Sample	Polyol Type	Retention after 20 days (%)
PAAm–Pectin	Ethylene glycol (50%)	37.84
PAAm–GG	Ethylene glycol (50%)	38.12
PAAm–Pectin	Glycerol (50%)	83.28
PAAm–GG	Glycerol (50%)	79.82

stability and solvent retention behavior of PAAm-pectin and PAAm-GG organogels containing 25% and 50% polyol. The results are summarized in Tables 5.7 and 5.8. At both 100°C and 200°C, the glycerol-based organogels (GL25 and GL50) retained a substantially higher percentage of their initial weight compared to the corresponding ethylene glycol-based systems (EG25 and EG50). This trend was consistent across both PAAm–pectin and PAAm–GG networks, indicating that glycerol imparts superior thermal stability and solvent retention capability at elevated temperatures. The enhanced performance of glycerol containing organogels can be attributed to its higher boiling point, stronger hydrogen bonding interactions with the polymeric network, and greater hygroscopicity, which collectively suppress solvent evaporation and thermal degradation (Castelló et al., 2009; Xue et al., 2019).

Table 5.7: Comparison of weight retention of PAAm–pectin and PAAm–GG organogels containing 25% ethylene glycol and glycerol at 100 °C and 200 °C.

Organogel	100 °C (%)	200 °C (%)
PAAm–pectin–EG25	71.68	8.27
PAAm–GG–EG25	61.55	6.09
PAAm–pectin–GL25	79.06	29.17
PAAm–GG–GL25	77.69	45.14

5.8 Ionic conductivity

Figure 5.14 illustrates the ionic conductivity of PAAm–pectin and PAAm–GG hydrogels measured at different temperatures, while Figures 5.15 and 5.16 present

Table 5.8: Comparison of weight retention of PAAm–pectin and PAAm–Gellan gum organogels containing 50% ethylene glycol and glycerol at 100°C and 200°C.

Organogel	100 °C (%)	200 °C (%)
PAAm–pectin–EG50	80.99	11.82
PAAm–GG–EG50	69.90	12.52
PAAm–pectin–GL50	84.68	52.93
PAAm–GG–GL50	78.15	49.55

the corresponding results for organogels containing ethylene glycol (EG) and glycerol (GL), respectively. Across all measurements, the PAAm–pectin system consistently demonstrated slightly superior ionic conductivity compared to the PAAm–GG system over the full temperature range. This marginal enhancement reflects a more favorable ionic environment and lower internal resistance within the pectin-based network. The superior conductivity of the PAAm–pectin hydrogel can be attributed to the higher density of hydrophilic carboxyl and hydroxyl groups in pectin, which promote efficient ion dissociation and the formation of continuous, water-mediated conduction pathways (Zdunek et al., 2021; Kumar et al., 2025). In contrast, the PAAm–GG hydrogel, though also ionically active, possesses a comparatively denser network that moderately restricts ionic migration. The PAAm–pectin hydrogel shows slightly higher ionic conductivity compared to the PAAm–GG system. This improvement is due to the more hydrated polymer matrix and the increased mobility of charge carriers within the network (Mohapatra et al., 2024).

Figures 5.17 and 5.18 compare the ionic conductivity of ethylene glycol and glycerol-based organogels at different temperatures. Across all temperatures, EG-based organogels showed slightly higher conductivity than GL-based ones in both PAAm–pectin and PAAm–GG systems. This improvement arises from the lower viscosity and higher dielectric constant of EG, allowing ions to dissociate more easily and move more efficiently through the network (Meredith et al., 2024; Gong et al., 2025). In contrast, the higher viscosity and stronger hydrogen-bonding interactions of glycerol (GL) slightly hinder ionic mobility, resulting in compara-

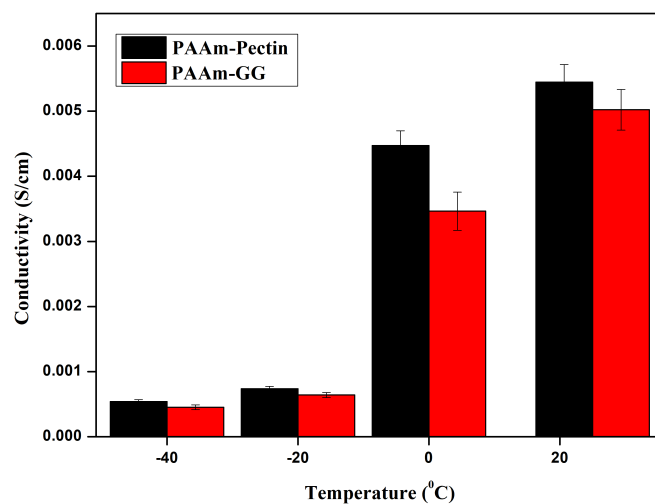


Figure 5.14: Comparison of ionic conductivity of PAAm-pectin and PAAm-GG hydrogels at different temperatures.

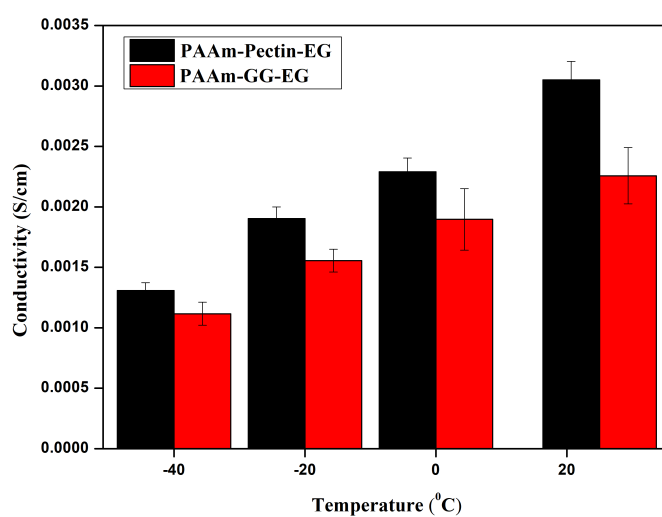


Figure 5.15: Comparison of ionic conductivity of PAAm-pectin-EG and PAAm-GG-EG organogels at different temperatures.

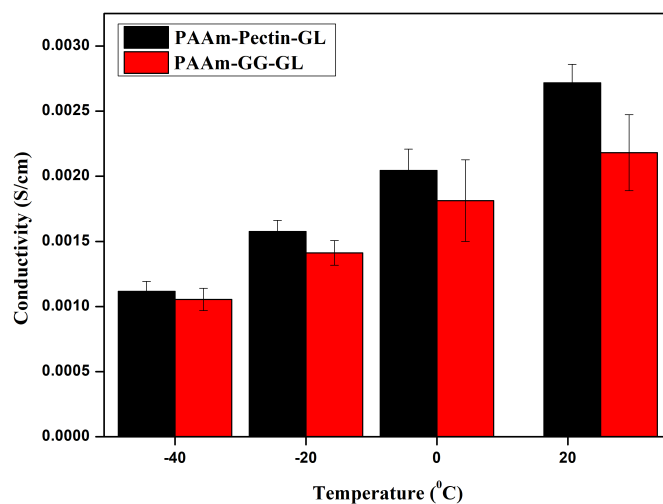


Figure 5.16: Comparison of ionic conductivity of PAAm-pectin-GL and PAAm-GG-GL organogels at different temperatures.

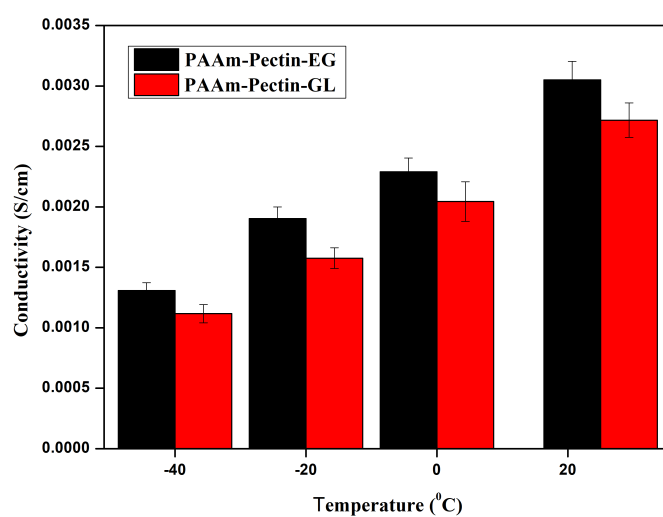


Figure 5.17: Comparison of ionic conductivity of PAAm-pectin-EG and PAAm-pectin-GL organogels at different temperatures.

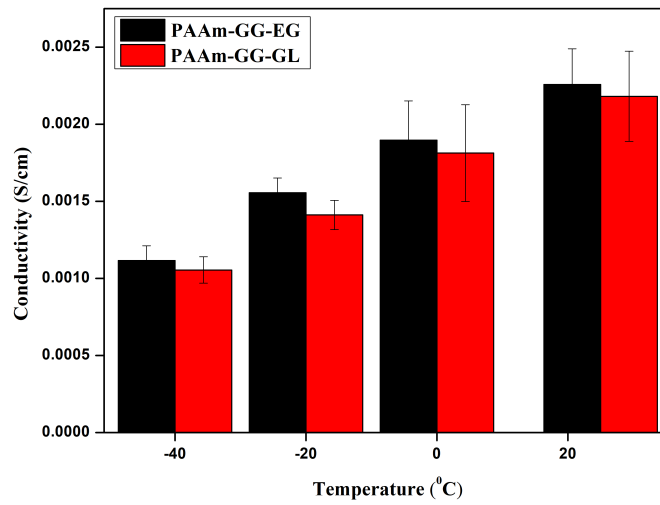


Figure 5.18: Comparison of ionic conductivity of PAAm-GG-EG and PAAm-GG-GL organogels at different temperatures.

tively lower conductivity (Ali and Kareem, 2022). Overall, both EG and GL effectively enhance the ionic conduction of the organogels at sub-zero temperatures, with EG-based systems exhibiting a slight advantage in conductivity performance.

5.9 Conclusion

This chapter presented a comparative study of PAAm–pectin and PAAm–GG hydrogels and their corresponding ethylene glycol (EG) and glycerol (GL) organogels. Both systems consist of a covalently crosslinked PAAm network and an ionically crosslinked biopolymer network. However, the type of biopolymer used and the organic solvent incorporated lead to differences in their overall behaviour. The PAAm–pectin network exhibited greater swelling capacity and higher ionic conductivity, whereas the PAAm–GG system demonstrated increased stiffness and a more compact network. The introduction of polyols enhanced the mechanical properties and environmental tolerance of the hydrogels. The organogels fabricated using ethylene glycol exhibited better anti-freezing properties and ionic conductivity. Whereas the glycerol incorporated organogels show enhanced ther-

mal stability, solvent retention, and mechanical performance. Overall, the findings highlight that careful selection of both biopolymer and solvent allows precise tuning of the structural, mechanical, and electrochemical properties of PAAm-based hydrogel-organogel systems.

Table 5.9: Comparison of PAAm–Pectin and PAAm–GG systems.

Property	PAAm–Pectin System	PAAm–GG System
Network structure	Loosely packed network with larger pores.	Compact and densely crosslinked network with fine pores.
Swelling behaviour	Higher swelling ratio due to greater hydrophilicity.	Lower swelling ratio due to a more compact structure.
Mechanical properties	Moderate mechanical strength and flexibility.	Higher tensile strength and Young’s modulus.
Rheological behaviour	Lower G’ and G’’ values.	Higher G’ and G’’ values, indicating enhanced structural integrity and greater energy dissipation.
Ionic conductivity	Higher ionic conductivity.	Lower conductivity due to a denser network.

Table 5.10: Comparison of EG and GL based organogel systems.

Property	EG Based Organogels	GL Based Organogels
Swelling behaviour	Significant reduction in swelling with increasing EG concentration.	Slight increase at lower concentration, followed by a reduction at higher concentration.
Mechanical properties	Improved strength and stiffness.	Enhanced mechanical performance with superior strength and flexibility.
Rheological behaviour	Lower G' and G'' values with moderate energy dissipation.	Higher G' and G'' values with enhanced structural integrity and greater energy dissipation.
Anti-freezing behaviour	Excellent anti-freezing behaviour with more effective suppression of ice crystal formation.	Good anti-freezing behaviour with moderate freezing point suppression.
Solvent retention and thermal stability	Moderate solvent retention with improved thermal stability.	Higher solvent retention along with superior thermal stability due to the stronger hygroscopic nature of glycerol.
Ionic conductivity	Slightly higher ionic conductivity due to lower viscosity.	Slightly lower conductivity because of stronger hydrogen bonding and higher viscosity.

Chapter 6

Conclusion and Future Outlook

This chapter provides a concise summary of the major findings of the present research and outlines prospective directions for future work. In this study, two distinct dual-crosslinked polyacrylamide-polysaccharide hydrogel and organogel systems were successfully developed, in which the covalently crosslinked polyacrylamide network was reinforced through ionic coordination between Ca^{2+} ions and the polysaccharide backbone, thereby generating a mechanically robust interpenetrating network architecture. The incorporation of polyols via solvent displacement introduced additional hydrogen bonding interactions, which significantly improved mechanical strength, anti-freezing capability, and solvent retention, along with substantially improved ionic conductivity under sub-zero temperatures.

Comprehensive characterization, including swelling studies, mechanical and rheological analysis, temperature tolerance studies, and electrochemical measurements, revealed a direct structure-property correlation that determines the functional performance of the developed materials. Mechanical studies demonstrated marked improvements in tensile strength, toughness, and elasticity, while rheological characterization confirmed a predominantly elastic response ($G' > G''$) with increased viscoelastic dissipation at higher polyol concentrations. The organogels retained flexibility and ionic conductivity even under sub-zero temperatures, demonstrating superior anti-freezing and anti-drying characteristics, while maintaining

effective ionic conductivity at low temperatures, underscoring their suitability for emerging wearable and soft electronic applications. The results of this study provide a strong foundation for further advancement of dual-network hydrogel and organogel systems toward practical applications of soft materials. The developed PAAm–pectin and PAAm–gellan gum organogels demonstrated excellent mechanical strength, anti-freezing behaviour, solvent retention, and ionic conductivity, confirming their suitability for advanced flexible electronic applications. Their stable electrochemical performance under sub-zero conditions highlights their strong potential for use in wearable sensors, electronic skin, flexible solid-state supercapacitors, soft actuators, and other next-generation low-temperature soft electronic devices. Among the developed systems, organogels containing higher concentrations of glycerol and ethylene glycol exhibited superior environmental stability and electrochemical performance, making them promising candidates for practical flexible energy storage and sensing applications.

Future work will primarily focus on device fabrication, cyclic durability evaluation, deformation-dependent conductivity studies, and the development of multifunctional soft electronic and energy-storage devices based on these organogel systems. Further investigations may focus on examining the dependence of ionic conductivity on temperature variation and mechanical deformation, which could enable the development of multifunctional sensing platforms. Their ability to translate thermal and mechanical stimuli into measurable electrical signals, enabling applications in next-generation soft electronic systems, including electronic skin, soft robotics, and human-motion monitoring platforms. Future research may focus on fabricating temperature-tolerant all-solid-state supercapacitors and batteries using these organogels as flexible solid-state electrolytes, where their anti-freezing capability and stable ionic conduction at low temperatures could provide significant advantages for energy-storage applications operating under extreme environmental conditions. Progress in this field may include the development of

hydrogels composed exclusively of natural biopolymers to enable fully biodegradable and environmentally sustainable soft materials. Further opportunities for improvement lie in the exploration of alternative anti-freezing agents beyond conventional cryoprotectants like glycerol and ethylene glycol, which may broaden the operational temperature window and enhance long-term stability. The incorporation of diverse multivalent cations capable of modulating both conductivity and crosslinking density may contribute additional tunability in mechanical and functional performance. The suitability of these hydrogel systems for biomedical engineering applications encourages future investigations into controlled or stimuli-responsive drug-delivery strategies, as well as their potential use in wound-healing applications. Enhancing durability through the design of dynamic and reversible bonding interactions to impart self-healing capability represents another important advancement, improving functional reliability under repeated mechanical deformation.

Detailed cyclic loading experiments and compression testing will provide further insight into fatigue resistance and structural resilience under practical conditions. Overall, this study establishes dual-network hydrogels and organogels as promising materials for next-generation flexible electronics. Further refinement of their composition and processing is essential to enable reliable integration into practical soft-interface technologies.

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Publications

Published Articles

1. Gokul, G. K.; Sudheesh Parathakkatt. *Design and Rheological Characterization of PAAm-Pectin-Glycerol Double-Network Organogels for Next-Generation Soft Materials*. **Polymer Engineering and Science** 2025, *65*(12), 6879–6889.
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