Optimization Analysis of Mechanical Properties in PEO/PAA Hydrogels

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Abstract: Hydrogels play a pivotal role in numerous advanced applications. Due to their structural and functional similarities to natural extracellular matrices, they serve as cellular scaffolds that promote cell growth, proliferation, and differentiation, thereby enabling tissue repair and regeneration. However, their mechanical properties often limit their practical applications. Enhancing the mechanical properties of hydrogels is a key issue in unlocking their practical application potential. Simulating and analyzing the mechanical properties of hydrogels facilitates the synthesis of hydrogels with superior mechanical performance. This study selected polyethylene oxide/polyacrylic acid (PEO/PAA) dual-network hydrogels as the research subject, performing theoretical calculations on the PEO/PAA ratio during synthesis to optimize the mechanical properties of this dual-network hydrogel. Specifically, this study systematically investigated the optimization of mechanical properties in PEO/PAA dual-network hydrogels by adjusting two key molecular parameters—degree of polymerization and molecular ratio. Stress-strain behavior under uniaxial tensile conditions was evaluated through molecular dynamics simulations and mechanical analysis based on the virial theorem. Results indicate that optimal mechanical properties are achieved when PEO polymerization degree is 30 and PAA polymerization degree is 70, yielding a peak stress of 0.92 GPa at 300% strain. Furthermore, a PEO:PAA molar ratio of 5:9 was identified as the most effective formulation, exhibiting superior strength and toughness compared to other formulations due to ideal interpenetrating networks and energy dissipation mechanisms. These findings provide key insights and practical guidelines for the rational design of high-performance dual-network hydrogels, advancing their application in load-bearing environments such as tissue engineering and soft robotics.

1. Introduction

As a polymeric material, the mechanical properties of hydrogels are critical for their end applications. Zhang et al. proposed a highly sensitive, self-adhesive, biocompatible organic hydrogel printed via DLP 3D printing [1]. By integrating entanglement-dominated crosslinking with chemical and physical crosslinking, this hydrogel achieves high elasticity, mechanical strength, and durability. These enhanced mechanical properties enable sustained adhesion and structural integrity, making it suitable for prolonged wear. Optimal grafting of methacrylic acid onto κ-carrageenan as the main network enhances tensile properties and strain regulation capabilities. The copolymer network of MA-kappa-CA and ACMO improves swelling integrity and long-term stability through steric hindrance effects. In practical applications, it holds promise for cervical spine monitoring and sports rehabilitation, and can be integrated into wearable smart devices to provide highly sensitive flexible sensors for health monitoring and injury prevention. Li et al. proposed a polyethyleneimine-polyacrylic acid (PEI-PAA, PEA) dual-network polyelectrolyte hydrogel [2]. Through one-step UV-initiated polymerization and regulation via electrostatic interactions and microphase separation induced by polymer chain entanglement, it exhibits tunable mechanical properties. The hydrogel modulus increased from 0.4 MPa to 106 MPa, while toughness rose from 1479 kJ/m^3 to 7641 kJ/m^3. Furthermore, the PEA hydrogel exhibits remarkable resistance to swelling in saline, TBS buffer, and blood, maintains stable adhesion to various moist tissues, promotes rat skin wound healing in vivo,

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and effectively stops arterial bleeding. This provides new insights for developing bioadhesives that meet diverse mechanical requirements. Yao et al. proposed a novel tough hydrogel scaffold termed GelMA hydrogel [3]. Through a universal manufacturing method—cyclic stretching training combined with UV curing—its mechanical properties were significantly enhanced, achieving a strength of 6.66 MPa. The mechanically enhanced hydrogel scaffold features functional surface structures that effectively promote cell-guided growth and in vivo muscle tissue regeneration. In practical applications, this mechanical enhancement represents a significant advancement in tissue engineering, particularly by enabling the development of robust, biocompatible tissue repair materials. This holds promise for accelerating the repair and regeneration of damaged muscle tissue. Hydrogels typically need to withstand certain external forces, such as tension, compression, and bending. Sufficient mechanical strength prevents hydrogels from fracturing or deforming during use, thereby ensuring structural integrity [4]. Good toughness and fatigue resistance extend the service life of hydrogels. Especially in applications requiring repeated deformation or sustained loading, such as biosensors and soft actuators, superior mechanical properties are fundamental to ensuring long-term stable operation [5].

Numerous factors influence the mechanical properties of hydrogels, such as polymer type and network structure. Different polymers exhibit distinct chemical structures and physical properties. Wang et al. constructed protein fibrils with distinct morphologies—rigid rod-like, flexible branched, and networked coiled structures—by varying ethanol concentration [6]. These fibrils were incorporated into transglutaminase (TG)-gelatin hydrogel systems, demonstrating that they significantly influenced the gelation behavior and mechanical properties of the resulting hydrogels, with each type exhibiting distinct effects. Beyond chemical modifications, physical structural adjustments also substantially enhance hydrogels. Xie et al. dehydrated the polymer chains of a double-network (DN) hydrogel by folding them in ethanol, a poor solvent [7]. This chain folding, combined with the DN network, significantly enhanced the hydrogel's stress buffering and energy dissipation capabilities during unfolding/stretching. This approach endowed the hydrogel with ultra-high strength (1.06 MPa), exceptional extensibility (15,400%), and outstanding toughness (88 MJ/m^3), substantially elevating its overall mechanical properties. Among various factors, polymerization degree and molecular ratio are two particularly crucial aspects. Polymerization degree refers to the number of repeating units in polymer chains, directly influencing hydrogel molecular weight and network structure. By controlling polymerization degree, the internal structure of hydrogels can be finely tuned, thereby affecting their mechanical properties. For instance, regulating polymerization degree can adjust hydrogel pore size and porosity, consequently influencing swelling behavior and permeability. Dolmat et al. demonstrated that selecting low- or high-molecular-weight poly(N-vinylpyrrolidone) (PVPON) enables control over the swelling degree, number of hydration water molecules, and water density in spin-assisted (SA) PMAA hydrogels [8]. The enhanced swelling of SA-PMAA hydrogels resulted in softening and reduced Young's modulus at pH>5. This indicates a direct correlation between the degree of hydrogel swelling and its mechanical stiffness. Additionally, controlling the degree of polymerization can modulate the surface morphology and properties of hydrogels, thereby influencing their biocompatibility and cell adhesion performance [9]. Molecular ratio refers to the proportion of different components within the hydrogel, such as monomers, crosslinkers, and initiators. Varying molecular ratios can significantly affect the network structure and mechanical properties of hydrogel. When hydrogels are copolymerized from two or more monomers, the monomer ratio directly affects the chemical composition and physical properties of hydrogel.

Hydrogels prepared using composite strategies based on binary materials have garnered increasing attention, as the combination of these materials can significantly enhance the mechanical properties of hydrogels through modifications in synthesis approaches. With growing demand for environmentally friendly materials, developing more sustainable raw materials has become increasingly important. Polyethylene oxide (PEO) and polyacrylic acid (PAA), two synthetic materials, are widely used in hydrogel preparation due to their low toxicity and hydrophilicity [10]. Fu et al. developed a PAA-PEO-NaCl ionic hydrogel [11]. This hydrogel exhibits outstanding mechanical strength (breaking stress>1.3 MPa), high extensibility (>1100%), and high toughness (up to 7.34 MJ/m^3). Due to reversible hydrogen bonding interactions and chain entanglement, the hydrogel exhibits outstanding mechanical resilience, adhesion, and self-healing capability. Under ambient conditions, its electrochemical and thermoelectric properties recover immediately after physical damage (e.g., cutting), with mechanical repair fully restoring the hydrogel's superior mechanical properties within 24 hours. The hydrogel's exceptional mechanical performance and self-healing capability may significantly extend the lifespan of wearable devices. PEO/PAA hydrogels can serve as scaffold materials for tissue engineering to construct artificial tissues. Demeter et al. successfully prepared a collagen-polyvinylpyrrolidone (PVP)-PAA-PEO quaternary copolymer hydrogel via electron beam crosslinking [12]. This hydrogel exhibits high elasticity and exceptional water absorption capacity. Its water absorption rate reaches 1600% in deionized water and a remarkable 4000% in simulated biological buffers. Rheological studies confirm that this collagen/PVP/PAA/PEO hydrogel demonstrates solid behavior similar to human soft tissues, such as abdominal fat, skin, dermis, and even breast, brain, and liver tissues. Due to its excellent elasticity, rheological behavior similar to natural soft tissues, and good biocompatibility, this hydrogel is highly suitable for soft tissue engineering, such as serving as a tissue scaffold or filler material.

However, in diverse application environments, PEO/PAA hydrogels still face mechanical challenges, including susceptibility to tensile fracture, plastic deformation, and fatigue failure, which severely limits their application scope. Therefore, continuous enhancement of hydrogel mechanical properties is necessary to adapt to varying working conditions. This paper will analyze the maximum stress of prepared PEO/PAA dual-network hydrogels by optimizing the polymerization degree and molecular ratio of PEO and PAA. It is anticipated to provide new insights for subsequent experiments aimed at achieving mechanical optimization of dual-network hydrogels.

2. Methods

2.1 Degree of Polymerization calculation

To evaluate the mechanical properties of the PEO/PAA dual-network hydrogel, the stress was calculated using the Virial formula.

$$\sigma_{zz} = \frac{1}{v}\sum_{i=1}^{N-1}\sum_{j=i+1}^{N} r_{z,ij} f_{z,ij}$$

Here, v, $r_{z,ij}$ and $f_{z,ij}$ denote the volume of the PEO/PAA dual-network hydrogel, the interatomic distance between atoms i and j, and the force acting on atom i along the z-axis, respectively. This study calculates the mechanical properties for each atom and sums them to compute the stress across the entire sample (Table 1).

Table 1 Peo/Paa Dual-Network Hydrogel Formulations with Different Polymerization Degrees

Number	**Polymerization Degree of PEO Monomer**	**Polymerization Degree of PAA Monomer**
1	**10**	**70**
2	**20**	**70**
3	**30**	**70**
4	**40**	**70**
5	**50**	**70**

2.2 Molar Ratio Calculation

Similarly, multiple sets of PEO/PAA dual-network hydrogel samples with different molecular ratios were prepared using the above method for comparative analysis. The composition of the sample systems is shown in Table 2.

Table 2 PEO/PAA Dual-Network Hydrogel Formulations with Different Molecular Weights

Number	PEO monomer count	PAA monomer count	Molar ratio
1	30	90	3:9
2	40	90	4:9
3	50	90	5:9
4	60	90	6:9
5	70	90	7:9

3. Results and Discussion

3.1 Degree of Polymerization Optimization Analysis

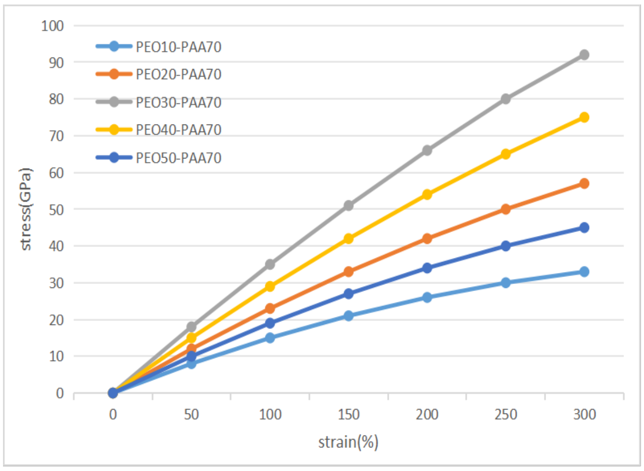

Fig. 1 Stress-strain curves at different degrees of polymerization

As shown in Fig 1, the sample with a PEO polymerization degree of 30 (PEO30-PAA70) exhibited the most outstanding comprehensive mechanical properties. Its stress-strain curve consistently remained at the top, reaching a peak stress of 0.92 GPa at 300% strain. Both samples with lower polymerization degrees (PEO10, PEO20) and higher ones (PEO40, PEO50) exhibited significantly reduced load-bearing capacity. This indicates the existence of an optimal polymerization degree ratio (approximately 30:70 here) that enables the dual-network structure to achieve peak mechanical performance.

This trend likely correlates closely with the toughening mechanism of dual-network hydrogels. PEO, functioning as the flexible primary network, primarily dissipates energy. When PEO polymerization is too low, molecular chains become too short to form an effective network structure for stress dispersion and dissipation, leading to material failure at lower strains. Conversely, excessively high PEO polymerization degrees result in overly long chains prone to entanglement, potentially inhibiting the effective fracture and energy dissipation of the rigid PAA second network. This diminishes the material's reinforcement effect. The PEO30-PAA70 combination precisely achieves the optimal balance between ideal energy dissipation in the first network and effective fracture in the second network.

3.2 Molar Ratio Optimization Analysis

As shown in Fig 2, all curves exhibit the typical deformation characteristics of dual-network hydrogels. Among them, the PEO50:PAA90 (molecular ratio 5:9) sample demonstrates the absolute optimal performance, with its curve being the highest and most rightward. Both excessively low (3:9) and high (7:9) molecular ratios lead to significant performance degradation, confirming the existence of an optimal ratio. At low ratios, insufficient PEO network chains result in too few crosslinks in the primary network—the primary energy dissipation source—creating a sparse network incapable of effectively bearing and distributing stress, thus yielding the lowest strength. An excessively high ratio introduces too many PEO chains, potentially overcrowding the network structure. This excessive entanglement restricts polymer chain mobility and adaptability while also hindering the uniform formation of the secondary PAA network. Consequently, stress concentration occurs, leading to diminished performance. At the 5:9 ratio, however, the two networks interpenetrate to form the most ideal dual-network topology. The primary network (PEO) provides optimal energy dissipation capabilities, while the secondary network (PAA) contributes a robust rigid backbone. Their synergistic interaction achieves a perfect balance of strength and toughness.

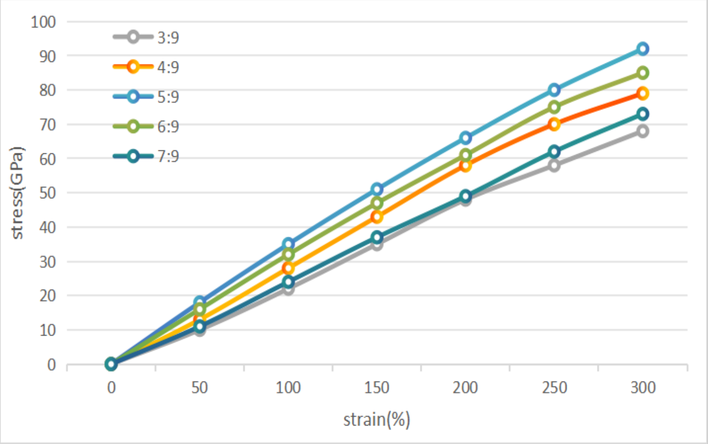

Fig. 2 Stress-strain curves for different molecular weights

3.3 Analysis of Other Factors Affecting the Mechanical Properties of Dual-Network Hydrogels

For preparing dual-network hydrogels with high mechanical properties, factors beyond raw material ratios also influence mechanical performance. Dual-network hydrogels typically consist of two distinct polymer networks: the primary network is generally rigid and brittle, while the secondary network is flexible and stretchable. The crosslink density of the primary network influences the hydrogel's strength and stiffness, while the secondary network primarily affects its toughness and stretchability. For instance, by regulating the crosslink density of polyacrylamide (PAM) and copper alginate (Cu-alg) dual-network hydrogels, their mechanical properties can be effectively controlled [13]. Interactions between the two networks, such as hydrogen bonding, hydrophobic interactions, or ionic interactions, also significantly influence the mechanical properties of hydrogels. Research by Wang et al. has revealed that modulating single amino acid variations in self-assembling peptides can transform the assembly structure from nanofibers to nanoribbons [14]. This microstructural change markedly enhances the Young's modulus, fracture stress, and toughness of polymer-supramolecular dual-network hydrogels (PS-DN hydrogels), while slightly accelerating their recovery rate. This mechanism stems from the impact of individual peptide breakage events on overall network connectivity, thereby enhancing the hydrogel's mechanical strength and rapid recovery capability. Since interactions between nanoparticles and polymer networks can strengthen hydrogel strength and toughness, incorporating nanoparticles into dual-network hydrogels can further improve their mechanical properties. Zhang et al. significantly enhanced the tensile and compressive strength of hydrogels by incorporating MXene nanosheets into a gelatin/polyacrylamide double-network hydrogel [15]. The mechanism involves the synergistic effect of the double network structure and the uniform hydrogen bonding between MXene, gelatin, and polyacrylamide polymers, leading to enhanced tensile and compressive strength. The topological structure of hydrogels also significantly influences their mechanical properties . For instance, designs such as slip rings, densely entangled regions, and force-triggered ring reversal reactions can all enhance the toughness of hydrogels.

After understanding these factors, theoretical simulations can be conducted to analyze which factor primarily influences the mechanical properties of dual-network hydrogels. This approach facilitates the synthesis of hydrogels with enhanced mechanical performance.

4. Conclusion

Simulations were conducted on PEO and PAA with varying degrees of polymerization and molecular ratios during the preparation of the PEO/PAA hydrogel in this study, identifying the optimal conditions for achieving maximum stress values. The mechanical properties of the PEO/PAA dual-network hydrogel were strongest when the monomer chain lengths of PEO and PAA were approximately 30 and 70, respectively, reaching a peak stress of 0.92 GPa at 300% strain. Furthermore, the tensile test results demonstrated optimal performance when the monomer ratio of PEO to PAA was 5:9. Simulation calculations of polymerization degree reveal that the polymerization degree of single chains is one of the key molecular parameters regulating the mechanical properties of hydrogels. By precisely controlling the polymerization degree of each component, it is possible to directionally optimize strength, toughness, and extensibility much like designing materials. This provides crucial theoretical foundations and design principles for preparing high-performance hydrogel materials suitable for specific load-bearing environments. Simultaneously, the ratio of molecular quantities between the two polymer networks represents an independent and critical design dimension. This ratio determines the microscopic topology of the dual-network structure, thereby governing macroscopic mechanical properties. This research provides essential formulation guidance for the controlled preparation and standardized production of dual-network hydrogels.

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