



Triple Network Hydrogels with Enhanced Robustness and Low Friction: Synergistic Design Strategies

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ABSTRACT

Hydrogels, three-dimensional polymeric networks capable of absorbing large amounts of water, have garnered significant attention for their potential applications in diverse fields, including tissue engineering, drug delivery, soft robotics, and artificial joints [1, 2, 5]. However, achieving a combination of high mechanical strength, toughness, and low friction, particularly under load-bearing conditions, remains a significant challenge for conventional single-network hydrogels. Triple network (TN) hydrogels, which combine three interpenetrating polymer networks with different properties, have emerged as a promising strategy to overcome these limitations by incorporating multiple energy dissipation mechanisms and synergistic interactions between the networks [35, 42, 43]. This article reviews the design strategies and underlying synergistic enhancement mechanisms responsible for the robust mechanical properties and low friction of triple network hydrogels. We discuss the role of different network components (e.g., brittle, ductile, and reinforcing networks), crosslinking methods (chemical and physical), and the interplay between network structure and macroscopic properties. The analysis highlights how the synergistic effects of multiple networks contribute to enhanced toughness, fatigue resistance, and lubrication, making TN hydrogels promising candidates for applications requiring high mechanical performance and low friction, such as artificial cartilage.

KEYWORDS

Robustness, Low friction, Synergistic enhancement, Mechanical properties, Lubricity, Artificial cartilage, Biomaterials.

INTRODUCTION

Hydrogels are soft, wet, and often biocompatible materials that mimic the properties of biological tissues. Their high water content and tunable mechanical properties make them attractive for various biomedical and engineering applications [1, 2, 5]. However, traditional hydrogels, typically formed by a single crosslinked polymer network, often suffer from poor mechanical strength and toughness, limiting their use in applications requiring significant load-bearing capacity or resistance to wear and fatigue [6, 9].

To address these limitations, significant research effort has been directed towards developing hydrogels with improved mechanical properties. Strategies include increasing polymer concentration, optimizing crosslinking density, incorporating reinforcing fillers (e.g., nanoparticles, fibers), and designing multi-network structures [6, 5]. Among these approaches, multi-network hydrogels, such as double network (DN) hydrogels, have demonstrated remarkable toughness compared to their single-network counterparts [8, 10]. DN hydrogels typically consist of a brittle, highly crosslinked first network and a ductile, loosely crosslinked second network. Under stress, the brittle

network fractures first, dissipating energy and protecting the ductile network from catastrophic failure, leading to high toughness [10].

Building upon the success of DN hydrogels, triple network (TN) hydrogels have been developed by introducing a third polymer network. This additional network provides further opportunities for synergistic interactions and energy dissipation mechanisms, potentially leading to even greater mechanical robustness and unique functional properties, such as enhanced low friction behavior [35, 42, 43]. The design of TN hydrogels involves carefully selecting the polymer components and crosslinking strategies for each network to achieve desired synergistic effects [35, 42, 43].

Achieving low friction, particularly under high loads and repeated cycles, is crucial for applications like artificial joints, where hydrogels can serve as potential cartilage replacements [17, 18, 19]. Articular cartilage in natural joints exhibits remarkably low friction due to its unique biphasic structure and lubrication mechanisms [19]. Designing synthetic hydrogels that can replicate this low-friction behavior while possessing sufficient mechanical robustness is a key challenge. TN hydrogels, with their complex network structures and potential for incorporating lubricating components, offer a promising avenue in this regard.

This article provides a systematic review of the design principles and synergistic enhancement mechanisms that contribute to the robust mechanical properties and low friction characteristics of triple network hydrogels. By analyzing recent advancements, we aim to elucidate how the interplay between multiple networks leads to superior performance and highlight the potential of TN hydrogels for demanding applications.

METHODS

This review was conducted by systematically searching and analyzing peer-reviewed scientific literature focusing on triple network (TN) hydrogels, their mechanical properties, and friction behavior. Academic databases were the primary source of information, using search terms such as "triple network hydrogel," "TN hydrogel," "mechanical properties," "toughness," "strength," "friction," "lubricity," "synergistic enhancement," "artificial cartilage," and related keywords.

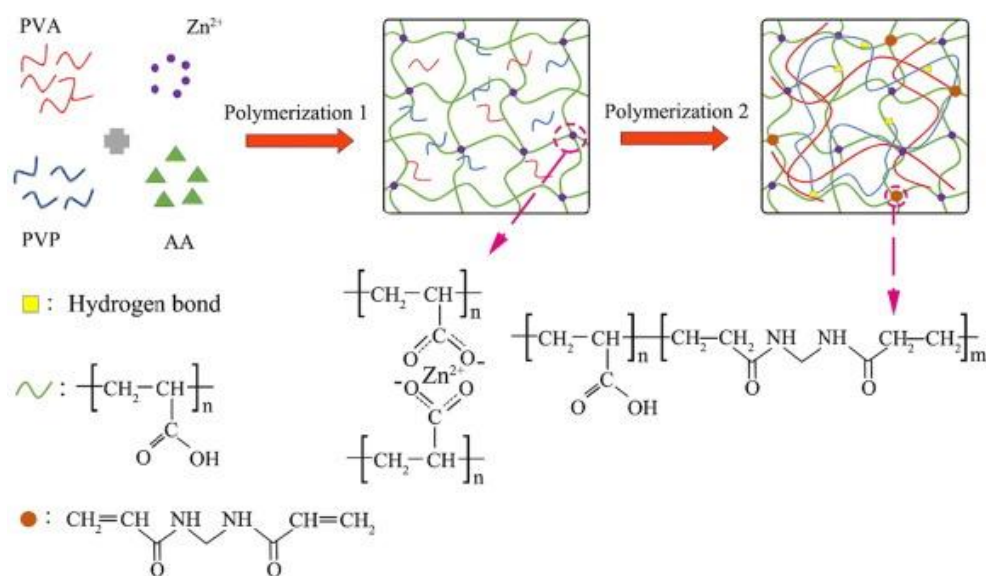


Fig. Triple-network hydrogels with high strength, low friction and self-healing

The identified studies were screened based on their relevance to TN hydrogels and the investigation of their mechanical and/or tribological properties. Articles focusing solely on single or double network hydrogels were included if they provided foundational knowledge or comparative data relevant to understanding the advantages

of TN structures. Review articles on hydrogel mechanics, multi-network hydrogels, and hydrogels for artificial cartilage were also consulted to provide broader context [1, 6, 8, 13, 19].

Thematic analysis was employed to synthesize the findings from the selected literature. Key themes identified and analyzed include:

1. **Design Principles of Triple Network Hydrogels:** Strategies for constructing TN hydrogels, including the selection of polymer components for each network (e.g., polyacrylamide (PAAm), poly(vinyl alcohol) (PVA), chitosan, alginate), the sequence of network formation, and the types of crosslinking (chemical, physical, or a combination) [35, 42, 43].
2. **Synergistic Enhancement Mechanisms for Mechanical Properties:** The underlying mechanisms by which the three interpenetrating networks interact to improve strength, toughness, stretchability, and fatigue resistance. This includes energy dissipation through network fracture, crack bridging, and stress redistribution among the networks [35, 42, 43, 10, 22, 23, 24, 26, 27, 28, 29, 30, 31].
3. **Mechanisms for Low Friction:** How the TN structure and incorporated components contribute to low friction and wear resistance under various loading conditions. This involves considering factors like surface hydration, boundary lubrication, and the load-bearing capacity of the network structure [17, 18, 19, 21, 44, 45].
4. **Role of Network Structure and Composition:** The influence of the properties of individual networks (e.g., crosslinking density, polymer concentration, charge) and their spatial arrangement on the overall mechanical and tribological performance of the TN hydrogel [35, 42, 43, 36, 37, 38, 39, 40, 41].
5. **Applications Requiring Robustness and Low Friction:** Identification of potential applications where TN hydrogels with these combined properties are particularly advantageous, with a focus on artificial cartilage [17, 18, 19].

The findings related to each theme were synthesized and are presented in the Results section. The Discussion section provides a comprehensive analysis, integrates the findings across themes, discusses the current limitations, and outlines future research directions.

RESULTS

The review of the literature on triple network hydrogels reveals that their superior mechanical properties and low friction behavior are a result of carefully designed synergistic interactions between the constituent networks.

Design Principles of Triple Network Hydrogels

Triple network hydrogels are typically fabricated by sequentially forming three interpenetrating polymer networks. A common strategy involves creating a brittle first network, followed by a ductile second network, and finally introducing a third network that can be either brittle, ductile, or contribute specific functionalities like physical crosslinking or lubrication [35, 42, 43]. Various polymer combinations have been explored, including PAAm, PVA, alginate, chitosan, and zwitterionic polymers [35, 42, 43, 36, 39, 40, 41].

Crosslinking strategies play a crucial role in defining the network properties and interactions. Chemical crosslinking, often achieved using crosslinking agents like N,N'-methylenebis(acrylamide) (BIS), provides permanent junctions and contributes to network integrity [35, 39]. Physical crosslinking, such as hydrogen bonding (common in PVA networks) or ionic interactions (in alginate or chitosan networks), provides reversible junctions that can break and reform under stress, contributing to energy dissipation and self-healing capabilities [34, 35, 30, 33]. The combination of chemical and physical crosslinking in TN hydrogels allows for a balance between mechanical strength and energy dissipation [35, 42, 30, 31]. For instance, TN hydrogels combining chemically crosslinked PAAm

with physically crosslinked PVA and a third network have shown enhanced properties [35, 36].

Synergistic Enhancement Mechanisms for Mechanical Properties

The enhanced mechanical properties of TN hydrogels arise from the synergistic interplay between the three distinct networks under deformation. When subjected to stress, the brittle first network fractures, dissipating energy and preventing premature failure of the entire structure, similar to the mechanism in DN hydrogels [10]. The ductile second network can undergo large deformations and absorb significant energy after the first network breaks [10]. The third network contributes additional energy dissipation pathways and can reinforce the overall structure.

Multiple synergistic mechanisms contribute to the robustness:

- **Hierarchical Energy Dissipation:** The sequential failure of networks with different mechanical properties provides a hierarchical energy dissipation system, allowing the hydrogel to withstand higher stresses and strains before complete fracture [24, 35, 42].
- **Crack Bridging and Deflection:** The intact ductile and third networks can bridge cracks initiated in the brittle network, preventing their propagation and increasing toughness [29, 30, 31].
- **Stress Redistribution:** Load can be effectively transferred between the networks, preventing stress concentration and distributing the applied force more evenly throughout the material [35, 42].
- **Reversible Crosslinking:** The presence of physical crosslinks in one or more networks allows for reversible bond breaking and reformation under stress, which dissipates energy and can contribute to self-recovery and fatigue resistance [30, 31, 33, 22, 23, 25, 26, 27, 29]. Muscle-like fatigue resistance has been achieved through mechanical training of hydrogels with reversible bonds [26].
- **Interpenetrating Network Effects:** The interpenetrating nature of the three networks leads to physical entanglement and topological constraints that further enhance mechanical strength and toughness [35, 42, 43, 11].

These synergistic effects result in TN hydrogels exhibiting remarkable combinations of high strength (comparable to or exceeding single and double network hydrogels), high stretchability, and superior toughness and fatigue resistance [35, 42, 43, 22, 23, 26, 27, 28, 29, 31].

Mechanisms for Low Friction

Achieving low friction in hydrogels, particularly under load, is crucial for applications like artificial cartilage. TN hydrogels offer advantages in this regard through several mechanisms:

- **Hydration Lubrication:** The high water content of hydrogels provides a hydration layer at the surface that can reduce friction by separating the sliding surfaces [44]. The stable network structure of TN hydrogels helps retain water even under pressure [36].
- **Boundary Lubrication:** Incorporating specific molecules or polymers with lubricating properties into one or more networks can provide boundary lubrication, reducing direct contact between the sliding surfaces [21]. Zwitterionic hydrogels, known for their excellent lubrication, have been combined with reinforcing elements like graphene oxide to improve both strength and lubricity [21].
- **Load-Bearing Capacity:** The robust mechanical properties of TN hydrogels, particularly their stiffness and resistance to deformation under load, help maintain a sufficient fluid film between the sliding surfaces, contributing to hydrodynamic or elastohydrodynamic lubrication [17, 19]. A biphasic structure, mimicking natural cartilage, can also contribute to load-bearing and lubrication [19, 17, 18].
- **Wear Resistance:** The toughness and fatigue resistance of TN hydrogels contribute to their ability to

withstand repeated loading cycles without significant material degradation, leading to sustained low friction over time [22, 23, 25, 26].

Studies have shown that TN hydrogels can achieve extremely low coefficients of friction, comparable to or even lower than natural cartilage, especially when designed with specific network compositions and structures [44, 45, 17, 18]. For example, PVA-based hydrogels, commonly used in TN structures, have demonstrated low friction against materials like titanium alloy, relevant for artificial joint components [45, 36].

Role of Network Structure and Composition

The specific polymers used for each network, their relative concentrations, crosslinking densities, and the sequence of network formation significantly influence the final properties of the TN hydrogel [35, 42, 43]. The first network often provides stiffness and initial energy dissipation. The second network contributes to ductility and toughness. The third network can be designed to enhance specific properties, such as increasing overall strength, introducing reversible crosslinks for self-healing and fatigue resistance, or incorporating lubricating components [35, 42, 43, 30, 31, 21].

For example, incorporating PVA, which can form physical crosslinks through crystallization, into a TN structure can enhance toughness and contribute to low friction [34, 35, 36]. The use of ionic or zwitterionic polymers can improve lubrication and introduce additional physical crosslinking mechanisms [40, 21]. The spatial arrangement and interpenetration of the networks also play a critical role in determining the stress distribution and energy dissipation pathways [35, 42]. Hierarchically crosslinked structures have been explored to improve mechanical properties [12].

Applications Requiring Robustness and Low Friction

The combination of high mechanical strength, toughness, and low friction makes triple network hydrogels ideal candidates for applications that demand these properties simultaneously. The most prominent application is in the field of artificial joints, particularly as a replacement for damaged articular cartilage [17, 18, 19]. The ability of TN hydrogels to mimic the mechanical behavior and lubrication of natural cartilage is a significant advantage [17, 18, 19].

Beyond artificial cartilage, TN hydrogels could also find applications in:

- Soft Robotics: As robust and flexible components for actuators and grippers [2].
- Wearable Electronics and Sensors: As durable and flexible substrates or components [39].
- Biomedical Implants: In load-bearing implants where both mechanical integrity and biocompatibility are required.
- Industrial Lubrication: As durable and environmentally friendly lubricants in various mechanical systems.

The development of TN hydrogels with tunable properties through synergistic design opens up a wide range of possibilities for these and other demanding applications.

DISCUSSION

The systematic review of triple network hydrogels highlights that their remarkable robustness and low friction are not merely additive properties of the individual networks but arise from complex synergistic interactions and hierarchical energy dissipation mechanisms. The strategic combination of networks with different mechanical properties and crosslinking types allows for efficient stress redistribution, crack bridging, and energy dissipation under load, leading to significantly enhanced strength, toughness, and fatigue resistance compared to single or double network hydrogels.

The low friction behavior of TN hydrogels is intrinsically linked to their mechanical robustness and water retention capabilities. The ability to maintain a stable hydration layer and resist deformation under pressure is crucial for effective lubrication. Furthermore, the incorporation of specific lubricating components or the design of network structures that promote boundary lubrication can further reduce friction and wear, making them highly suitable for articular cartilage replacement.

Despite the significant progress, several challenges remain in the field of TN hydrogels. Achieving precise control over the structure and properties of each network and their interpenetration is crucial for optimizing performance. Scalability of synthesis methods for large-scale production is also a consideration. Furthermore, comprehensive long-term in vivo studies are needed to evaluate the biocompatibility, stability, and durability of TN hydrogels for biomedical applications like artificial joints. The potential for degradation and wear over extended periods under physiological conditions requires thorough investigation.

Future research should focus on developing new polymer combinations and crosslinking strategies to further enhance the synergistic effects and tailor the properties for specific applications. Exploring novel methods for incorporating lubricating agents and designing hierarchical structures that mimic the complexity of natural tissues could lead to even better performance. The integration of computational modeling and advanced characterization techniques will be essential for gaining a deeper understanding of the structure-property relationships in these complex materials and guiding the rational design of next-generation triple network hydrogels.

CONCLUSION

In conclusion, triple network hydrogels represent a significant advancement in the design of robust and low-friction soft materials. By leveraging multiple synergistic enhancement mechanisms, these hydrogels overcome the limitations of traditional hydrogels and hold immense potential for a wide range of demanding applications, particularly in the field of artificial cartilage and other areas requiring high mechanical performance and low friction. Continued research and development in this area are crucial for translating these promising materials into practical solutions.

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