Investigation of MXene-modified agar/polyurethane hydrogel elastomeric repair materials with tunable water absorption

Abstract: The study of repairing materials is of paramount importance, considering that damage during usage can significantly impact performance and bring inconvenience during maintenance work. One highly sought-after material is water-swellable elastomers, known for their effect in sealing and repairing damaged materials. In this study, agar/polyurethane dual-network hydrogel elastomers were prepared, which were further modified by MXene. The material exhibits a uniform and flat surface, along with a rich pore-filled internal structure. It showcases excellent thermal stability, good tensile strength retention, and a controllable low swelling rate (SR) upon water absorption. The performance of the material can be regulated by the MXene content. In addition, the “water absorption–drying–water absorption” cycle effectively controls the reduction of the SR and gradually increases the tensile strength. All samples demonstrated exceptional photothermal conversion efficiency, stability, and durability, with the maximum conversion temperature increasing with the MXene content. The scratch repair experiments demonstrated the remarkable potential of these materials for photothermal conversion-assisted repair. These materials can be adapted as auxiliary restoration materials in water bodies and various application environments, making them ideal for repair and restoration purposes.

Keywords: MXene-modified, hydrogel elastomer, repair material, photothermal conversion, dual-network

1 Introduction

Water-swellable elastomers were first introduced in the 1970s as a distinct product from traditional hydrophobic rubber. These elastomers consist of two components: the elastic component, which imparts essential properties such as strength, toughness, and glass transition temperature, and the hydrophilic component, which enhances the overall hydrophilicity of the material. Water-swellable elastomers can both seal elastically and expand with water. This combination makes it suitable for sealing damaged areas. As a result, they have become increasingly popular for use in crack prevention and initial repairs. Water-swellable elastomers are widely used in various underwater or underground engineering applications (1,2), specifically in construction, oil fields (3,4), and mining. These applications include road construction joints, pipeline joint sealing, dams, and embedded joints in buildings. Moreover, they are applied in critical closures of waterproofing projects as well as in dikes, reservoirs, and rapid emergency leak plugging treatment projects. With advancements in technology, water-swellable elastomers are now used in cutting-edge fields such as agriculture and environmental protection, biomedicine (5,6), flexible sensing (7,8), and intelligent robotics (9,10).

The preparation of water-swellable elastomers involves the use of elastic components such as natural rubber, ethylene propylene rubber, neoprene, chlorinated polyethylene, styrene–butadiene rubber, nitrile rubber, silicone rubber and thermoplastic polyurethane; and hydrophilic components such as acrylic acid, acrylamide, polyvinyl alcohol, amphoteric polymers, and bentonite (11–16). The methods used for preparing water-swellable elastomers usually involve physical blending and chemical grafting. However, these methods have some drawbacks in terms of product performance, service life, and production process (17). The distinct characteristics of the elastic and hydrophilic components may cause agglomeration and water being unevenly absorbed and expanded. Consequently, the product’s mechanical properties, water absorption, long-term water retention, and durability
may decrease. Additionally, synthetic processes can be complex and not practical for mass production.

The fast-paced advancement of technology demands multi-functional materials. Numerous new functional materials have emerged in response, particularly MXene (18–20), which are highly promising. These materials are obtained by etching the MAX phase in an acidic environment, resulting in a general formula of $M_nX_nTX$, where M represents the transition metal, X is the element of carbon or nitrogen, T denotes the surface termination unit formed during the preparation process, and n usually ranges from 1 to 3 (21,22). MXene materials offer a variety of advantages, such as excellent thermal stability, high mechanical strength (23), low optical attenuation (24), efficient photothermal conversion (25–28), compatibility with both water and organic solvents, and ease of modification (19,29) and doping, making them highly attractive for various applications.

This study aims to create a dual-network hydrogel elastomer that possesses water absorption and dual repair properties. To achieve this, agar (30–32) and aqueous polyurethane (33) are chosen as the main raw materials, and a varying amount of polyisocyanate cross-linking agent is used as a controlling factor to prepare a series of agar/polyurethane dual-network hydrogel elastomers with tunable water absorption. The MXene-modified agar/polyurethane dual-network hydrogel elastomer was further developed on this basis. Adding MXene to the material gives it the photothermal conversion effect, which displays both the performance of photothermal conversion-assisted repair and the physical repair performance of traditional water-absorbent swelling elastomers. The agar/polyurethane dual-network hydrogel elastomer is characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and field emission scanning electron microscopy (FE-SEM) to identify its chemical composition and condensed structure. Thermal stability, water swelling, mechanical properties, and photothermal conversion properties are also investigated. Finally, the material’s ability to repair scratches on the surface of the polydimethylsiloxane (PDMS) adhesive layer is tested.

### 2 Materials and methods

#### 2.1 Materials

The agar powder was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. The water-based polyurethane dispersion was purchased from Guangzhou Guanzhi New Material Technology Co., Ltd. The polyisocyanate was purchased from Wanhua Chemical Group Co., Ltd. Aluminum titanium carbide and hydrochloric acid were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Lithium fluoride was also purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Finally, the PDMS was provided by Hangzhou Weisichuang Technology Co., Ltd.

#### 2.2 Preparation of agar/polyurethane dual-network hydrogel elastomer with tunable water absorption

A 5% agar solution was prepared for the experiment by mixing 3.5 g of agar powder and 66.5 g of deionized water in a 100 mL single-mouth flask. The mixture was heated to 90°C over approximately 20 min in an oil bath before being maintained at that temperature until the agar was completely dissolved. Once dissolved, the solution was placed in a 50°C environment until required. In a separate 50 mL beaker, 10 g of water-based polyurethane dispersion was combined with varying amounts of polyisocyanate crosslinker (0.5–2.5% of the weight of water-based polyurethane) and stirred for 3 min. The resulting mixture was added to the warm agar solution, stirred vigorously for 2 min, and then immediately poured into round Al molds with a diameter of 10 cm and a height of 0.5 cm. The samples were defoamed and left at room temperature overnight and then moved to a 60°C oven for further drying. Once the water mass was significantly reduced, the samples were transferred to a 105°C oven for complete drying.

#### 2.3 Preparation of MXene colloidal solution

To prepare the MXene colloidal solution, 3.2 g of lithium fluoride was dissolved in 40 mL of 30 wt% hydrochloric acid solution in a 100 mL single-mouth flask. The mixture was stirred using an electromagnetic stirrer at a speed of 400 rpm and heated to 40°C in a water bath. Next, 2 g of aluminum titanium carbide was slowly added to the mixture, and the reaction conditions were maintained for 48 h. After the reaction, the mixture was centrifuged, and the upper liquid layer was removed. The wet precipitate at the bottom was washed three times with 1 mol·L$^{-1}$ hydrochloric acid solution and then rinsed several times with deionized water until the pH was close to neutral.

To obtain the MXene colloidal solution, the washed product was transferred to a wide-mouth flask with 60 mL of deionized water, sonicated in an ice water bath for 90 min, and protected with nitrogen gas. After sonication, the product
was centrifuged at 3,500 rpm for 60 min, and the upper layer was collected.

### 2.4 Preparation of MXene-modified agar/polyurethane dual-network hydrogel elastomer with tunable water absorption

The method used for preparing the MXene-modified agar/polyurethane hydrogel elastomers with tunable water absorption was similar to the method used for preparing the agar/polyurethane hydrogel elastomers. The weight of the MXene colloid solution was varied as follows: 1%, 5%, 10%, and 15% of the total weight.

### 2.5 Characterization method

Several characterization methods, including FT-IR, XPS, XRD, and FE-SEM, were used to analyze the chemical composition and morphological structure of agar/polyurethane dual-network hydrogel elastomer. The FT-IR test was conducted using a scan range of 4,000–400 cm\(^{-1}\) and a resolution of 4 cm\(^{-1}\). The XPS test utilized a monochromatic Al K\(\alpha\) radiation source (\(h\nu = 1,486.6\) eV, 10.0 kV). For the XRD test, both conventional wide-angle and small-angle tests were conducted. The wide-angle test encompassed a range of 5–90° at a scan rate of 10°·min\(^{-1}\), while the small-angle test covered a range of 3–5° at the same scan rate. Additionally, before the FE-SEM test, the sample was freeze-dried and sprayed with gold, after which its morphology was observed at various magnifications.

### 2.6 Thermal stability testing

Thermal stability tests were performed on the samples using a TA Instruments Q600 simultaneous thermal analyzer under a nitrogen atmosphere. The samples were heated from 30°C to 800°C at a ramp-up rate of 10°C·min\(^{-1}\).

### 2.7 Water swelling performance testing

The water swelling performance of the samples was evaluated by cutting them into uniformly sized rectangles and recording their initial weight (\(W_0\)). The samples were then immersed in deionized water at room temperature and periodically removed, wiped dry, and weighed until a constant weight (\(W_f\)) was obtained. The swelling rate (SR) was calculated using Eq. 1. The samples were then dried in an oven at 105°C, and the earlier procedure was repeated for the second and third water absorption and swelling experiments.

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SR = \frac{W_f - W_0}{W_0} \times 100\%.
\]

### 2.8 Mechanical performance testing

The mechanical performance of the samples was evaluated using a PJ-101 type double-column tensile assembly with a tensile speed of 100 mm·min\(^{-1}\).

### 2.9 Photothermal effect testing

The study designed a test setup to conduct photothermal conversion testing, consisting of a near-infrared (NIR) light emitter with a power of 1 W and a thermal imaging component. The dried double-network hydrogel elastomer was cut into a rectangular sample measuring 1 cm \(\times\) 1 cm, positioned 30 cm away from an infrared laser emitter with a wavelength of 808 nm. After turning on the light source, a rectangular light spot was observed on the sample. In real-time, throughout the testing process, we used a mobile phone thermal imager to capture thermal images of the sample, allowing us to monitor any temperature changes caused by the photothermal conversion process.

### 2.10 Auxiliary repair performance testing

The auxiliary repair performance of the samples was evaluated by coating a PDMS glue mixture (consisting of components A and B stirred evenly at a 10:1 ratio) onto the surface of the MXene-modified agar/polyurethane double-network hydrogel elastomer substrate. The sample was then cured in a 100°C oven and subsequently scratched using an art knife. The scratch repair test was conducted under the 808 nm laser irradiation to observe the repair condition of the sample.

### 3 Results and discussion

#### 3.1 Characterization and testing of agar/polyurethane dual-network hydrogel elastomer with tunable water absorption

We developed agar/polyurethane dual-network hydrogel elastomers with tunable water absorption by utilizing
completely non-toxic agar and water-based polyurethane as the core materials and polyisocyanate as a cross-linking agent. By varying the amount of polyisocyanate from 0.5% to 2.5%, we adjusted the properties of the dual-network hydrogel elastomers, thus determining the ideal formulation for subsequent MXene modification.

3.1.1 FT-IR analysis

The chemical structures of the raw materials and samples were characterized using the FT-IR technique, as shown in Figure 1a. The agar polysaccharides exhibited characteristic peaks at 768.93, 890.68, and 929.33 cm\(^{-1}\), which were attributed to the bending vibrations of the galactose backbone in the agar structure. Due to the high hydrogen and oxygen content in agar, its intermolecular hydrogen bonding density is high, resulting in a broad and strong hydroxyl stretching vibration peak at 3,287.01 cm\(^{-1}\). The presence of trace amounts of sulfate groups and incompletely separated protein-like impurities in the agar was indicated by weak absorption peaks at 1,251.05 and 1,644.24 cm\(^{-1}\), respectively.

In the FT-IR spectrum of the water-based polyurethane dispersion, the absorption peak at 3,348.90 cm\(^{-1}\) corresponded to the stretching vibration of N–H in the carbamate. The absorption peak at 1,730.09 cm\(^{-1}\), typical of polyurethanes, represented the stretching vibration of the carbon–oxygen double bond in the ester carbonyl group.

The dual-network hydrogel elastomer exhibited absorption peaks from both agar and water-based polyurethane, albeit with changes in position and intensity. The interaction between the hydroxyl group in the agar molecule and the secondary amine group in the water-based polyurethane resulted in a broad absorption band at 3,328.63 cm\(^{-1}\), indicating the formation of three types of hydrogen bonds in the sample. These bonds were formed between the secondary...
amino groups in the polyurethane molecule, the hydroxyl groups in the agar molecule, and the secondary amino groups in the polyurethane and hydroxyl groups in the agar molecule. The intensity of the methylene antisymmetric and asymmetric tensile vibration absorption peak is higher in the sample compared to agar, indicating the successful preparation of the hydrogel elastomer.

### 3.1.2 Thermal stability analysis

In this study, the thermal stability of all dual-network hydrogel elastomers was found to be excellent, as shown in Figure 1b. To perform a detailed analysis of the thermal degradation process, a sample containing a 1.5% cross-linking agent was chosen. Due to their hydrophilic nature, double-network hydrogel elastomers can absorb moisture from the air, leading to weight loss in the initial zone. Removing free water, which is thermodynamically similar to pure water, causes a weight loss of approximately 1.21% below 100°C. Since higher temperatures are required to disrupt the interactions of the bound water in the system, weight loss continues at temperatures above 100°C, resulting in a weight loss of approximately 3.41%.

In the range of 190–300°C, the polysaccharide network of the agar begins to cleave, resulting in a second zone of weight loss. Here, the glycosidic bonds of agar decompose to form dehydrated pyranogalactose and pyranogalactose. Subsequent ring opening, dehydration, and hydrogen transfer reactions produced small organic molecules such as aldehydes, ketones, acids, esters, and furans, resulting in significant weight reduction. These processes cause the cross-link density within the system to decrease, leading to a decrease in the thermal stability of the polymer and an increase in the rate of weight loss.

The samples primarily undergo polyurethane hard segment degradation in the 200–380°C range, which is a complex process with multiple decomposition modes. The 260–500°C range showed the greatest weight change throughout the process due to polyurethane soft segment degradation, resulting in approximately 40.11% weight loss. The weight loss in the range of 380–500°C reflects complete degradation of the agar and polyurethane, while the third weight loss zone, which showed the least amount of weight change, occurred after 500°C.

The results of this study showed that the initial degradation temperature of the agar/polyurethane dual-network hydrogel elastomer increased by approximately 9.1°C with an increase in the polyisocyanate dosage. Moreover, the temperature at which the weight loss plateau was reached was delayed by about 9.2°C. This is because the increased cross-link density of the polyurethane led to a denser network structure, resulting in higher initial degradation temperatures and improved heat resistance.

### 3.1.3 Water swelling performance analysis

Figure 1c shows the SR of a double-network hydrogel elastomer. Its water absorption and expansion are one multimodal process. When agar molecules form an interpenetrating network with polyurethane, free water enters the system through adsorption, capillary action, and permeation. The hydroxyl groups in agar form strong hydrogen bonds with water molecules, accelerating water uptake. As water content increases, the agar molecular chains partially loosen and untangle, and the double-helix structure partially deconvolutes, leading to increased free volume in the system and expansion of sample volume. The agar molecular chains also act as water pathways, allowing water to penetrate deeper. As water absorption continues, the spacing between the network chains of the dual-network hydrogel elastomer increases, thereby increasing the elastic retraction force against deformation. When the anti-deformation force equals the osmotic pressure, water absorption reaches equilibrium, resulting in maximum water absorption and expansion rate. As the amount of polyisocyanate cross-linking agent increases, the cross-linking density of the polyurethane network increases, making the double-network hydrogel elastomer more compact and more difficult to penetrate. In the first water absorption and swelling experiment, the SR decreased with increasing cross-linker content, ranging from 72.84% to 53.49%. The cross-linkers also tighten the internal network structure of the dual-network hydrogel elastomer, resulting in better water retention properties.

The drying temperature in the “water absorption–drying–absorption” cycle process is above the melting temperature of agar and the softening temperature of polyurethane, which promotes the densification of agar/polyurethane double-network hydrogel elastomer. The gradient variation of cross-linker dosage caused different cross-link densities within the double-network hydrogel elastomer. Samples with a low dosage of cross-linker released more oligomers and small molecules, resulting in less water absorption due to weaker polymer–water interaction. The escape of oligomers and small molecules creates voids, which usually become denser during heating, making the water absorption process more difficult and reducing the SR. This effect is less pronounced in samples with higher amounts of cross-linking agents. As a result, the SR of all samples decreased, with a maximum value of 53.94% at a cross-linking agent dosage...
of 1.5%. The aforementioned effect decreased significantly in subsequent experiments, with a slight change of less than 3.8% in the second and third water absorption SRs.

### 3.1.4 Mechanical performance analysis

The agar/polyurethane dual-network hydrogel elastomer is a rigid, transparent material that appears light yellow when completely dry. Upon exposure to moisture, the material slowly absorbs water and softens. In water, it can absorb a significant amount of water, losing its transparency and becoming soft and resilient; however, upon drying, the material regains its transparency. The tensile strength of each sample was measured after reaching water absorption equilibrium (Figure 1d). Compared to agar, a raw material with a strength of only 800 g·cm$^{-2}$, the agar/polyurethane dual-network hydrogel elastomer has substantially higher mechanical strength. Increasing the dosage of cross-linking agents leads to a gradual increase in tensile strength, with the highest value of 4.98 MPa achieved at a 2.5% dosage of cross-linking agent. Compared to agar, a raw material with a strength of only 800 g·cm$^{-2}$, the agar/polyurethane dual-network hydrogel elastomer has substantially higher mechanical strength. Increasing the dosage of cross-linking agents leads to a gradual increase in tensile strength, with the highest value of 4.98 MPa achieved at a 2.5% dosage of cross-linking agent. In comparison, the tensile strength of water-swellable rubber prepared by Zhang et al. using chlorohydrin rubber, polyacrylate, and poly(vinyl alcohol)-g-poly(butyl acrylate) was less than 0.5 MPa after water absorption (34). Similarly, Ji et al. found that the mechanical properties of water-swellable composites made with sodium acrylate, neoprene, starch, and dicumyl peroxide significantly decreased to 1.7 MPa after water absorption (35). Adair and colleagues utilized composites of epoxidized natural rubber and superabsorbent polymer to produce water-swellable materials that demonstrate water absorption rates below 35%. Additionally, the tensile strength of the composite exhibiting the highest level of water absorption did not exceed 2 MPa (16). Overall, the agar/polyurethane dual-network hydrogel elastomer has good mechanical strength even after water immersion when compared to similar materials previously studied.

Through the “water absorption–drying–absorption” cycle process, the agar in the system melts and reconfigures, leading to the shrinkage and collapse of the double-network hydrogel elastomer's three-dimensional network structure and a denser system. This results in a decrease in sample size and an increase in mechanical strength. After the third water absorption cycle, the sample's tensile strength increases by more than 128% compared to the first cycle. Additionally, the tensile strength increases and then decreases with the amount of cross-linker, and the maximum tensile strengths for samples with 2.0% and 2.5% of the cross-linking agent were 6.98 and 6.96 MPa, respectively.

### 3.2 Characterization of MXene

Figure 2a presents the results of the elemental analysis of MXene using the XPS technique. The analysis revealed the presence of C, Ti, O, Cl, and F elements. Notably, the absence of any Al peaks in the spectrum indicates that the acidic environment efficiently etched away the Al layer and produced MXene. The surface of MXene contains O, Cl, and F terminal groups derived from lithium fluoride, hydrochloric acid, and water. The presence of these groups makes the surface of the MXene more hydrophilic and chemically active.

The structure and composition of MXene were investigated through further analysis using the XRD technique.
As depicted in Figure 2b, the XRD spectrum of MXene displayed five diffraction peaks located at 6.70°, 14.04°, 28.54°, 35.82°, and 43.08°. The successful etching process was confirmed by the non-appearance of the (104) strong diffraction peak located at 38.68°, which indicates that the Al element in the initial Ti₃AlC₂ MAX phase had been removed. Furthermore, the layer spacing of MXene was found to have increased compared to the previous phase, as evidenced by the (002) peak initially situated at 9.46° that shifted toward a smaller angle located at 6.70°. This result was achieved by the removal of the Al layer during the etching process and the effective peeling of accordion-like multi-layer MXenes during the sonication. The aforementioned results demonstrate the successful preparation of MXene.

3.3 Characterization and testing of MXene-modified agar/polyurethane dual-network hydrogel elastomer with tunable water absorption

To determine the optimal formulation for MXene modification, a comparison was made among a series of agar/polyurethane dual-network hydrogel elastomers with tunable water absorption. The sample with the best SR, using a cross-linker dosage of 1.5%, was selected for the modification process. Chemical structure and elemental analysis were carried out on the MXene-modified agar/polyurethane hydrogel elastomer.

Figure 3: EDS analysis of MXene-modified agar/polyurethane dual-network hydrogel elastomer with tunable water absorption: (a) EDS spectrum of sample with 1% MXene content, (b) EDS spectrum of sample with 5% MXene content, (c) EDS spectrum of sample with 10% MXene content, and (d) EDS spectrum of sample with 15% MXene content.
3.3.1 Chemical structure and elemental analysis

Figure 3 illustrates the energy dispersive spectrum (EDS) analysis results of the surface chemical elements. The Ti elements were present along with small amounts of F, Cl, and O, indicating the uniform dispersion of MXene in the double-network hydrogel elastomer. After removing the Al layer in the MAX phase, the surface was terminated with hydroxyl, fluorine, and superoxide anions, resulting in a new active surface that enhances reactivity. As a result, the Ti, F, and Cl contents increased with the addition of MXene. However, the presence of hydroxyl and carbamate content in the double-network hydrogel elastomer made it difficult to observe the variation of O element in the EDS energy spectrum.

Figure 4 shows the XRD of a double-network hydrogel elastomer with different MXene content to study its composition and cohesive structure. All samples showed mild peaks at around 19° and 41°, which is typical for polyurethane structures attributed to soft segment phase orientation. This is due to the high flexibility and ease of movement of the soft chain segments, which are composed of long aliphatic chains. The hard segment phase lacks structural regularity and flexibility, rendering it relatively amorphous and present only in short-range order. These characteristics cannot be reflected in X-ray diffraction. The stronger and broader diffraction peak at around 19° is also contributed by agar, which has molecular chains rich in hydroxyl groups that enable hydrogen bonding, ultimately leading to the formation of double-helix structures. These structures are accumulated in an orderly manner, and agar is considered a semi-crystalline macromolecule. The hydrogel elastomer used in this study was co-prepared with water-based polyurethane and agar, and the addition of polyurethane may have disrupted the interactions between the molecular chains of agar, leading to the formation of a broader hump peak instead of a crystalline peak at 19°. The comparison of spectra from four samples showed no significant changes in angle and intensity, indicating that the addition of MXene materials did not significantly affect the macromolecular aggregation in the system.

Additional small-angle tests were performed, but due to the limitations of the equipment, only spectra in the range of 2θ from 3 to 5 degrees were obtained. The peaks of Ti₃C₂ (002) at 4.34° and 4.16° were observed in samples with 15% and 10% MXene content, respectively, with the sample containing 15% MXene showing sharper diffraction peaks. Unfortunately, the diffraction peaks for samples with 5% and 1% MXene content were still at smaller positions and did not appear in the spectra. Overall, the intensity of diffraction peaks increased significantly with increasing MXene content. However, for samples with smaller MXene content, θ shifted more toward the small angle direction. This phenomenon is attributed to the MXene colloidal aqueous solution mixing with other components, leading to MXene dilution, and the embedding of water molecules intensifying the peeling of a few MXene layers, which increases the layer spacing of MXene. The polymer molecules may also encapsulate MXene, causing the lattice to be distorted.

3.3.2 Morphological analysis

Figure 5 shows the microstructures of the agar/polyurethane hydrogel elastomers with different MXene contents. The surface morphology of all the dual-network hydrogel elastomers appeared flat and smooth, indicating good compatibility among the constituents and uniform dispersion of MXene sheets throughout the matrix without any

Figure 4: XRD analysis of MXene-modified agar/polyurethane dual-network hydrogel elastomer with tunable water absorption: (a) small-angle X-ray diffraction pattern and (b) conventional X-ray diffraction pattern.
aggregation. There was no noticeable effect of MXene content on the surface features.

Figure 6 presents the cross-sectional SEM images of the agar/polyurethane hydrogel elastomers with varying MXene contents. The double-network hydrogel elastomer exhibited a layered structure with numerous pores throughout the system. The comparison of the cross-sectional structures shows that the density of the system increases and the

Figure 5: Top-view SEM images of the surface of MXene-modified agar/polyurethane dual-network hydrogel elastomer with tunable water absorption: (a–d) samples with MXene content of 1%, 5%, 10%, and 15%, respectively.
pore size decreases with increasing MXene content. This result can be attributed to the uniform and random dispersion of MXene sheet layers that occupied the original pore positions. Higher MXene content led to more occupied pores, resulting in reduced layer spacing and pore size.

3.3.3 Thermal stability analysis

Figure 7 shows the thermal degradation of MXene-modified agar/polyurethane hydrogel elastomer under a nitrogen atmosphere. MXene, known for its exceptional thermal

Figure 6: Cross-sectional SEM images of MXene-modified agar/polyurethane dual-network hydrogel elastomer with tunable water absorption: (a–d) samples with MXene contents of 1%, 5%, 10%, and 15%, respectively.
stability, experiences a slow and stable thermal degradation process, with a mass loss of less than 10% at 800°C. However, in this study, we focus on the degradation of the polymer component and the influence of MXene on polymer degradation. By detecting, we can improve our comprehension of the thermal properties of the composite material.

The random and uniform distribution of MXene within the agar/polyurethane hydrogel elastomer generates layers of barriers that act as a hindrance to moisture penetration, thereby reducing the hydrogel elastomer’s hygroscopic properties when exposed to air. This effect is particularly noticeable in the early stages of thermal decomposition.

Figure 7: (a) Thermogravimetric analysis (TG) of MXene-modified agar/polyurethane dual-network hydrogel elastomer with tunable water absorption. (b–f) Thermogravimetric analysis–derivative thermogravimetry curves of the samples with MXene content from 1% to 5%, 10%, and 15% in order.
when free and bound water is volatilized. A significant difference was observed between the weight loss process of unmodified and MXene-modified hydrogel elastomers. This difference was noticeable in the temperature range where the agar macromolecular chain breaks. Without modification, the weight loss of the double-network hydrogel elastomer was relatively gentle in the early stage of this stage, and the weight loss process accelerated suddenly after about 240°C. During the early stage of agar thermal degradation, only large molecular chains break into smaller ones without significant mass loss. As the temperature rises, the degradation of the already cleaved molecular chains into small molecules leads to a significant increase in weight loss. The destruction of the chain structure reduces the thermal stability of the polymer, further accelerating weight loss. The surface of the MXene contains highly reactive groups such as fluorine, chlorine, hydroxyl, and superoxide anions, which makes it catalytic in agar degradation. At the beginning of this stage, weight loss is more significant, while the degradation process becomes smoother throughout.

However, in the later stages of the degradation process, the MXene material plays an active role in the dehydration and carbonization of the polymer, promoting the formation of a more stable structure of the residual carbon. This allows the MXene to improve the polymer’s stability in the later stages of degradation. Furthermore, MXene has increased the degradation temperature and complete degradation temperature of polyurethane soft segments to varying degrees.

### 3.3.4 Water swelling performance analysis

Figure 8 illustrates the water absorption and swelling performance of MXene-modified agar/polyurethane hydrogel elastomers. The SR of hydrogel elastomers modified with MXene, ranging from 50.70% to 53.83%, was found to be lower than that of unmodified agar/polyurethane dual-network hydrogel elastomers, which had an SR of 66.05%. The effect of MXene on water absorption is multifaceted, showing both advantageous and disadvantageous impacts. First, MXene contains polar groups such as hydroxyl, fluorine atoms, and superoxide anion radicals that are hydrophilic and can promote water absorption. Second, the loose interfacial structure between MXene, agar, and polyurethane due to the absence of chemical bonding can favor water penetration. However, despite the hydrophilic nature of MXene, it inhibits water absorption and swelling more than it facilitates it. The random distribution of MXene flakes throughout the double-network hydrogel elastomer impedes water infiltration. Furthermore, during water absorption and swelling, MXene “pins” the system, dissipating some stresses but also limiting polymer chain segment movement, restricting volume expansion and hindering water absorption. Increasing MXene content results in a fluctuation in the SR change by less than 3.13%. The “water absorption–drying–absorption” cycle process led to a gradual decrease in the SR, and the elastomer containing 15% MXene exhibited the lowest SR of 35.87%.

![Figure 8](image)

**Figure 8**: SR of MXene-modified agar/polyurethane dual-network hydrogel elastomer with tunable water absorption. The numbers 1, 2, and 3 indicate how many times the material reaches water absorption equilibrium during the test.

### 3.3.5 Mechanical performance analysis

Figure 9 shows the stress–strain curves of MXene-modified agar/polyurethane hydrogel elastomer. MXene modification increased the tensile strength of the agar/polyurethane double-network hydrogel elastomer compared to the unmodified version. The tensile strength increases initially and then decreases with increasing MXene content. The maximum tensile strength of 6.59 MPa is obtained at 10% MXene content. MXene is a 2D sheet material that is randomly and uniformly dispersed in the system. When the material is subjected to external stress, the force is transmitted along the macromolecular chains within the system to the interface between MXene and the substrate, which can generate a lot of cracks and dissipate some of the stress. Additionally, due to the different deformation capacities of the MXene sheet and double-network hydrogel elastomer matrix, the detachment of the MXene sheet and...
the plastic deformation of the matrix occur during the force, which also dissipates part of the stress. These effects contribute to the improved strength of the MXene-modified agar/polyurethane hydrogel elastomer. However, when the MXene sheet layer content is too high, the strength decreases, and the tensile strength of the sample with 15% MXene content is only 4.72 MPa.

The "water absorption–drying–absorption" cycle process can promote the increase of tensile strength to 122–153% of the original value, where the maximum tensile strength of the sample with 10% MXene content is 9.69 MPa. During the drying process of the double-network hydrogel elastomer at high temperatures, the internal structure changes, and the material becomes denser, which leads to an increase in tensile strength.

3.3.6 Photothermal performance analysis

MXene’s unique Ti–C structure enables it to have both ceramic and metallic properties, allowing it to perform photothermal conversion through localized surface plasmon resonance just like metals. Its excellent electromagnetic wave absorption capability also makes it efficient in photothermal conversion. The MXene-modified hydrogel elastomer showed strong photothermal conversion performance under 808 nm irradiation. Figure 10 illustrates the variation of material temperature with time under irradiation. The temperature of the MXene-modified hydrogel elastomer increased by more than 27.5°C in 30 s, 32.3°C in 1 min, and 45.3°C in 10 min. Conversely, the temperature of the unmodified hydrogel elastomer increased by only 8°C after 1 h of irradiation. Therefore, the

![Stress-strain curves](image)

*Figure 9: Stress–strain curves of MXene-modified agar/polyurethane dual-network hydrogel elastomers with tunable water absorption. Subfigures (a–d) represent samples with MXene contents of 1%, 5%, 10%, and 15%, respectively. The numbers 1, 2, and 3 refer to the water absorption and expansion experiments.*
MXene-modified hydrogel elastomer demonstrates excellent photothermal conversion efficiency. The MXene-modified hydrogel elastomer was cooled to room temperature within 15 min after turning off the light source. It was discovered from the four sets of experiments that the impact of MXene content on the rate of temperature change in the material was insignificant. Moreover, the maximum transition temperature increased with increasing MXene content over the study range, leading to maximum transition temperatures of 74°C, 77.8°C, 81.4°C, and 83.4°C for MXene contents of 1%, 5%, 10%, and 15%, respectively. This is due to the uniform dispersion of MXene in the matrix, which utilizes the heat generated by the photothermal conversion effect to transfer to the matrix through thermal conduction, thereby increasing the temperature of the matrix. The higher the content of MXene in composite materials, the higher the maximum transformation temperature of the composite material. The agar/polyurethane hydrogel elastomer modified with MXene exhibits excellent photothermal stability and durability as the maximum transition temperature varied by no more than 4°C after five testing cycles.

### 3.3.7 Auxiliary repair performance analysis

For repairing a scratch on a substrate, a substrate made of agar/polyurethane double-network hydrogel elastomer with 1% MXene material content was selected. A PDMS adhesive was applied on the substrate, forming a 2–3 mm thick PDMS layer that could only be used for scratch repair at a temperature higher than 60°C. A 1 cm long scratch was then

![Figure 10](image1.png)

**Figure 10:** (a) Temperature change curve during the photothermal conversion process of the agar/polyurethane dual-network hydrogel elastomer with tunable water absorption and modified with MXene. (b–e) Photothermal conversion cycle experiments of samples with MXene contents of 1%, 5%, 10%, and 15%, respectively, in ascending order.

![Figure 11](image2.png)

**Figure 11:** (a) Images showing the changes before and after the repair of scratches on the surface of the PDMS layer using the agar/polyurethane dual-network hydrogel elastomer substrate doped with MXene. (b) Optical microscope image of the PDMS layer peeled off from the substrate after repair. (c) Stress–strain curves of the initial PDMS and the repaired PDMSs.
made on the surface of the PDMS layer. The scratch was repaired within 30 min using the efficient photothermal conversion of MXene-modified agar/polyurethane hydrogel elastomer under 808 nm NIR light irradiation (Figure 11). To observe the repair results better, the PDMS adhesive layer was peeled off from the agar/polyurethane dual-network hydrogel elastomer sheet, and an optical microscope examination revealed no scratches. To better observe its repair performance, the mechanical properties of the initial and repaired PDMS layers were tested, and the results showed that the tensile strength of the fixed PDMS layer could be restored to the initial 92.96%. This indicates that the agar/polyurethane dual-network hydrogel elastomer successfully repaired the PDMS adhesive surface using photothermal conversion.

4 Conclusions

In this study, we prepared agar/polyurethane dual-network hydrogel elastomers with tunable water absorption and MXene-modified agar/polyurethane hydrogel elastomers with photothermal properties through multiple raw material screening and careful experimental design. The main conclusions are as follows:

1. We have prepared a series of agar/polyurethane dual-network hydrogel elastomers with tunable water absorption. They exhibit good thermal stability, adjustable swelling properties, and satisfactory mechanical properties. The amount of polyisocyanate is a crucial factor in regulating their properties.

2. We have developed a series of MXene-modified agar/polyurethane hydrogel elastomers with flat and uniform surfaces and porous internal structures. They exhibit good thermal stability, adjustable water absorption, excellent mechanical properties, superior photothermal conversion performance, and photothermal stability. The MXene content has a modulating effect on their performance.

3. The “water absorption–drying–absorption” cycle used in the study results in a gradual increase in tensile strength and an adjustable decrease in SR by densifying the structure.

4. The experiments on scratch repair have shown that MXene-modified agar/polyurethane hydrogel elastomers have the potential for photothermal-assisted repair due to their photothermal properties.

Agar/polyurethane double-network hydrogel elastomers were prepared in mild reaction conditions without organic solvents, compatibilizer, and other additives, providing a new idea for the preparation of materials with similar properties to water-swellable elastomers. And further research is necessary to investigate the performance of the materials in complex water bodies with different sources and compositions, such as domestic sewage and groundwater, and extended restoration.

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References


