



Multiple network organohydrogels with high strength and anti-swelling properties in different solvents

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Compared to traditional hydrogel materials, organohydrogels have wider applications due to their special properties such as abilities of self-adaptive, freeze-tolerant and mechanically stable over a wide range temperature. In this paper, we prepared Poly (vinyl alcohol)/Poly (butyl methacrylate)-co-Poly (lauryl methacrylate) multiple network organohydrogels (MN-OHGs) by multiple swelling polymerization method. By tuning the components of heterogeneous networks, the swelling behaviors and the surface wettability in different solvents of MN-OHGs could be controlled. When the ratio of oleophilic polymer network (OPN) content to hydrophilic polymer network (HPN) content was 1:1.4, the MN-OHGs showed the highest mechanical properties (the elastic modulus could reach 8 MPa, and the toughness could reach 12 MJ/m³). Moreover, when the OPN/HPN ratio was 2/1, the MN-OHGs could maintain a stable volume in artificial seawater with mechanical properties enhanced by 47.3%. These characteristics demonstrated that the MN-OHGs were ideal candidates for functional materials which could be applied in complex environments.

Introduction

Hydrogels, consisting of 3D cross-linked polymer networks and large amount of water, are proved to be promising candidates for designing as functional materials [1]. These soft and biocompatible materials are widely studied in biomedicine [2],

soft robotics [3], tissue engineering [4], bionics [5], and marine industry [6]. But, conventional hydrogels are difficult to be applied in complex environments. They are easily swelled or dehydrated in environments and damaged due to their poor mechanical properties. Many efforts have been carried out to control hydrogel's swelling behaviors and improve hydrogel's mechanical properties respectively, such as introducing nanomaterials [7], designing ideally homogeneous network structure [8], and utilizing dual network [9]. Due to the excellent performance of the heterogeneous network organohydrogels [10], the methods of designing and utilizing the heterogeneous networks attracted more and more attentions in recent years [11, 12].

With the integration of hydrophilic and oleophilic polymer networks, the heterogeneous network organohydrogels have possessed the merits of hydrogels and organogels within one

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material [13]. Unfortunately, due to the opposite solvent affinities of heterogeneous networks, the synthetic pathway of heterogeneous networks organohydrogels is a challenge. To control the accurate heterogeneous network ratio and pursue a good structurally-defined characteristics, current researchers usually adopt controlled polymerization methods [10]. Such as Atom Transfer Radical Polymerization (ATRP) [14], Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization [12], Group Transfer Polymerization [15]. However, the above-mentioned polymerization methods inevitably lead to the preparation process of heterogeneous network organohydrogels extremely complicated. Therefore, a simpler method that could introduce heterogeneous polymer networks and control the contents of the heterogeneous networks accurately still need to be developed.

In this work, we fabricated Poly (vinyl alcohol)/Poly (butyl methacrylate)-co-Poly (lauryl methacrylate)/N-methylpyrrolidone (NMP) multiple network organohydrogels (MN-OHGs) by multiple swelling polymerization method. We introduced lipophilic monomers into hydrophilic network through co-solvent NMP and then polymerized to obtain heterogeneous organohydrogels. This method could control the ratio of the hydrophilic polymer network (HPN) and the oleophilic polymer network (OPN) easily. When the ratio of OPN/HPN was 2:1, the MN-OHGs could maintain the same swelling ratio in different solvents (water and n-dodecane), and the surface wettability of MN-OHGs could switch between oleophobic in water and hydrophobic in oil. When the ratio of OPN/HPN was 1:1.4, the mechanical properties of MN-OHGs were optimal (the elastic modulus could reach 8 MPa, and the toughness could reach 12 MJ/m³). Also, the MN-OHGs (the OPN/HPN ratio was 2/1) could maintain a stable volume in artificial seawater with mechanical properties enhanced by 47.3%, which broaden the application of MN-OHGs in complex environments.

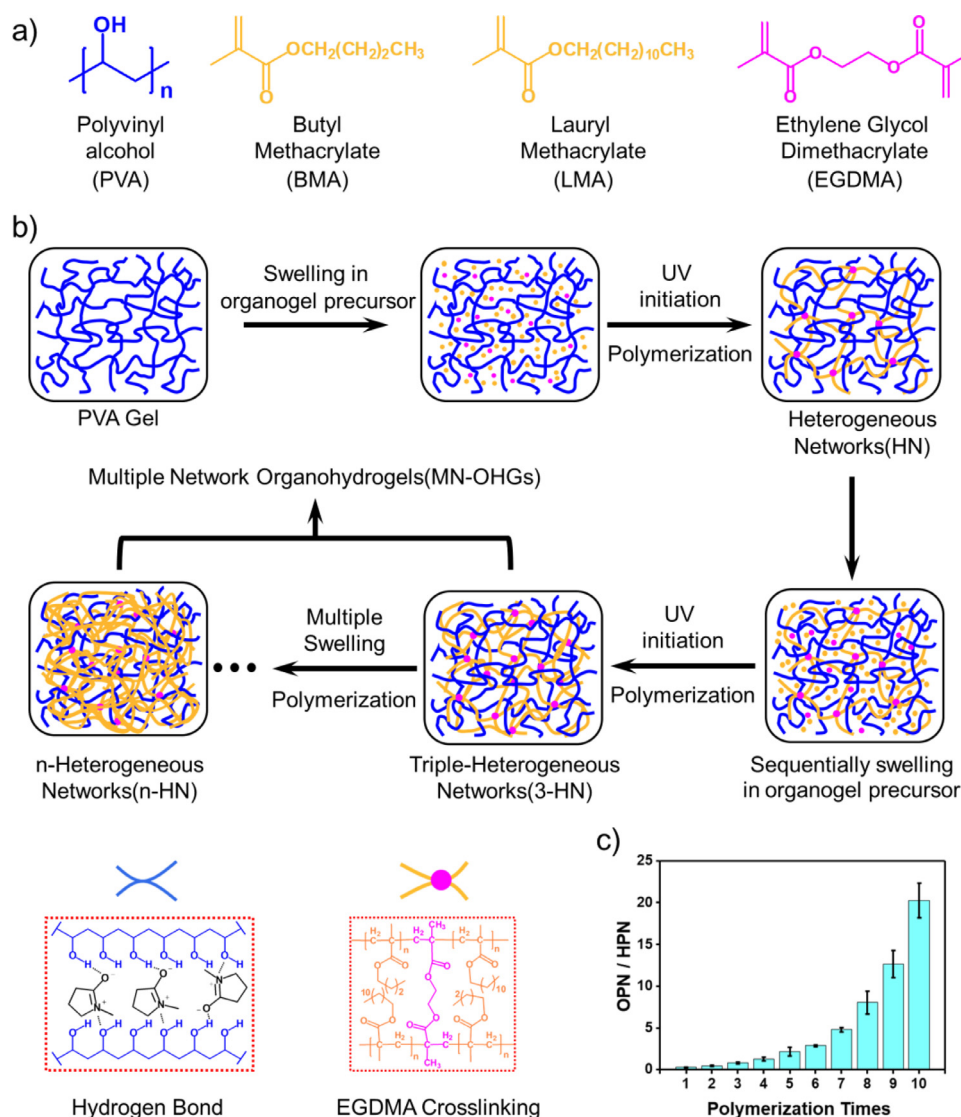
Results and discussion

Fabrication procedure of the multiple network organohydrogels (MN-OHGs) was shown in Fig. 1. The first hydrophilic polymer networks (HPNs), Polyvinyl alcohol (PVA) was dissolved in N-methylpyrrolidone (NMP) after heating for 4 h at 70 °C. Then, the homogeneous solution was cooled to -20 °C and kept for 12 h. This process could introduce physical crosslinking among PVA chains by hydrogen bonds and crystalline domains [16]. NMP as a typical dipolar aprotic solvent which could either be a strong electron donor or a hydrogen acceptor to form stable hydrogen bond with hydroxyl groups of PVA, and enhance the affinity between PVA and NMP (Fig. 1b) [17]. To further prepare the second oleophilic polymer networks (OPNs), the physical cross-linked PVA gels were swollen in NMP solution with oleophilic precursor (Fig. 1a). The details of the precursor solution for the preparation of oleophilic polymer networks were shown in supporting materials. Then, the swollen PVA gels were in situ polymerized with OPNs under the irradiation of 405 nm ultraviolet light. The samples with only one heterogeneous network were named as "HN-OHGs". Later, by repeating swelling and polymerization process as described above with controlled times, we could

synthesize a series of multiple network organohydrogels (named "MN-OHGs", see Supporting Information for detailed synthesis descriptions). As shown in Fig. 1c, the ratio of OPN/HPN could be tuned in a wide range from 1/5 to 20/1, and the OPN/HPN ratio of MN-OHGs increased exponentially when the polymerization times increased. This trend illustrated the MN-OHGs became more and more oleophilic as the OPNs gradually accumulated, and demonstrated that the ratio of heterogeneous networks could be tuned precisely by using the multiple swelling and polymerization method.

The swelling behavior of conventional hydrogels would weaken their desired properties, which limited their practical applications in nature environments [18]. Therefore, we investigated the swelling properties of the MN-OHGs first. A series of MN-OHGs samples were prepared with different OPN/HPN ratios, and swelled in different solvents to study the swelling behaviors respectively. As shown in Fig. 2b, the equilibrated swelling ratio (Q_v) of the MN-OHGs in water gradually decreased when the content of the OPNs increased. When the ratio of OPN/HPN increased over 2/1, the MN-OHGs would maintain at a constant volume in water. In contrast, when the MN-OHGs were exposed in n-dodecane, the equilibrated swelling ratio of the MN-OHGs gradually increased as the OPN/HPN ratio increased. When the ratio of OPN/HPN ratio was less than 3/1, the volume of MN-OHGs hardly changed in n-dodecane. As a result, the anti-swelling behavior of MN-OHGs versus OPN/HPN ratio in the water and oil existed an intersection. When the OPN/HPN was between 2/1 and 3/1, the MN-OHGs could maintain similar volume in both water and oil (Fig. 2b). This result illustrated that the heterogeneous network could mutually restricted the swelling behavior of MN-OHGs. When the MN-OHGs were exposed to water environments, the hydrophilic polymers networks (HPNs) swollen but the oleophilic polymer networks (OPNs) shrunken. In contrast, the HPNs shrunken and the OPNs swollen in oil (n-dodecane). Therefore, the MN-OHGs always existed the shrunken polymer networks and the swollen networks, which led to the volume of MIPN-gel hardly change.

In addition, this reconfiguration of heterogeneous networks in different external environments could also lead to the change of their surface properties [13]. To study this relationship, we tested the contact angle (CA) of a series of MN-OHGs samples with different OPN/HPN ratios in different solvents. As shown in Fig. 2c, when the OPN/HPN ratios increased, the water CA under n-dodecane of the MN-OHGs increased from 30° to 152°, and the oil CA under water of the MN-OHGs decreased from 156° to 21°. It should be noted that when the OPN/HPN ratio was 2/1–5/1, the MN-OHGs showed amphiphilic, and the MN-OHGs' surface properties could be switched between oleophobic in water and hydrophobic in oil. This is due to that when the MN-OHGs were placed in water environments, the hydroxyl groups of HPNs would expose outward and the alkane side chains of OPNs would collapse inward, and when placed in oil environments, the heterogeneous networks would exchange accordingly [19]. In addition, we studied the CAs of the samples reswelled in water and oil for five cycles. The results in Fig. 2e showed that the MN-OHGs (the ratio of OPN/HPN was 3/1) could maintain constant surface properties after each cycle.

**Fig. 1**

Synthesis of the multiple network organohydrogels. (a) The monomers and crosslinkers of the hydrogel (blue) and organogel precursors (yellow). (b) Preparation of the multiple heterogeneous networks gels by multiple swelling and polymerization methods. (c) The relationship between polymerization times and OPN/HPN ratio.

Excellent mechanical properties were essential for the practical application of gel materials [20]. In order to achieve such goal, we adjusted a series of factors on organohydrogels. Before multiple swelling and polymerization process, we first explored the influence of the concentration of the organogel precursors and the components of the oleophilic networks on the mechanical properties of the heterogeneous networks organohydrogels (HN-OHGs). As shown in Fig. 3a, the elastic modulus and toughness of organohydrogels could be improved when the concentration of the organogel precursors increased. When the concentration of the organogel precursors was 70 wt%, the elastic modulus of the sample could reach to 5.69 MPa and the toughness could reach to 8 MJ/m³ (Fig. 3c). But the maximum elongation at break of sample was 360% when the organogel precursors was 60 wt% (Fig. 3b). Besides, the Fig. S1 showed that the volume of the samples shrunk

seriously when the organogel precursors' concentration improved up to 80%. And the OPN/HPN ratio would increase when the organogel precursors' concentration improved. But, when the concentration was over 80%, the OPN/HPN ratio would decrease (Fig. S2). Then we investigated the effect of different oleophilic networks on the HN-OHGs' mechanical properties. For the second oleophilic network, we chose butyl methacrylate (BMA) with a short alkane side chain and lauryl methacrylate (LMA) with long alkane side chains as oleophilic monomers (Fig. 1a). Previous study showed that poly(butyl methacrylate) (PMBA) was rather rigid and poly(lauryl methacrylate) (PLBA) was rather soft [21]. So, by tuning the ratio of BMA/LMA in precursors as shown in Fig. 3d, the mechanical properties of the HN-OHGs could be altered. When the ratio of BMA/LMA was 10:1, its elastic modulus could reach 8 MPa, but with less elongation abilities (Fig. 3e).

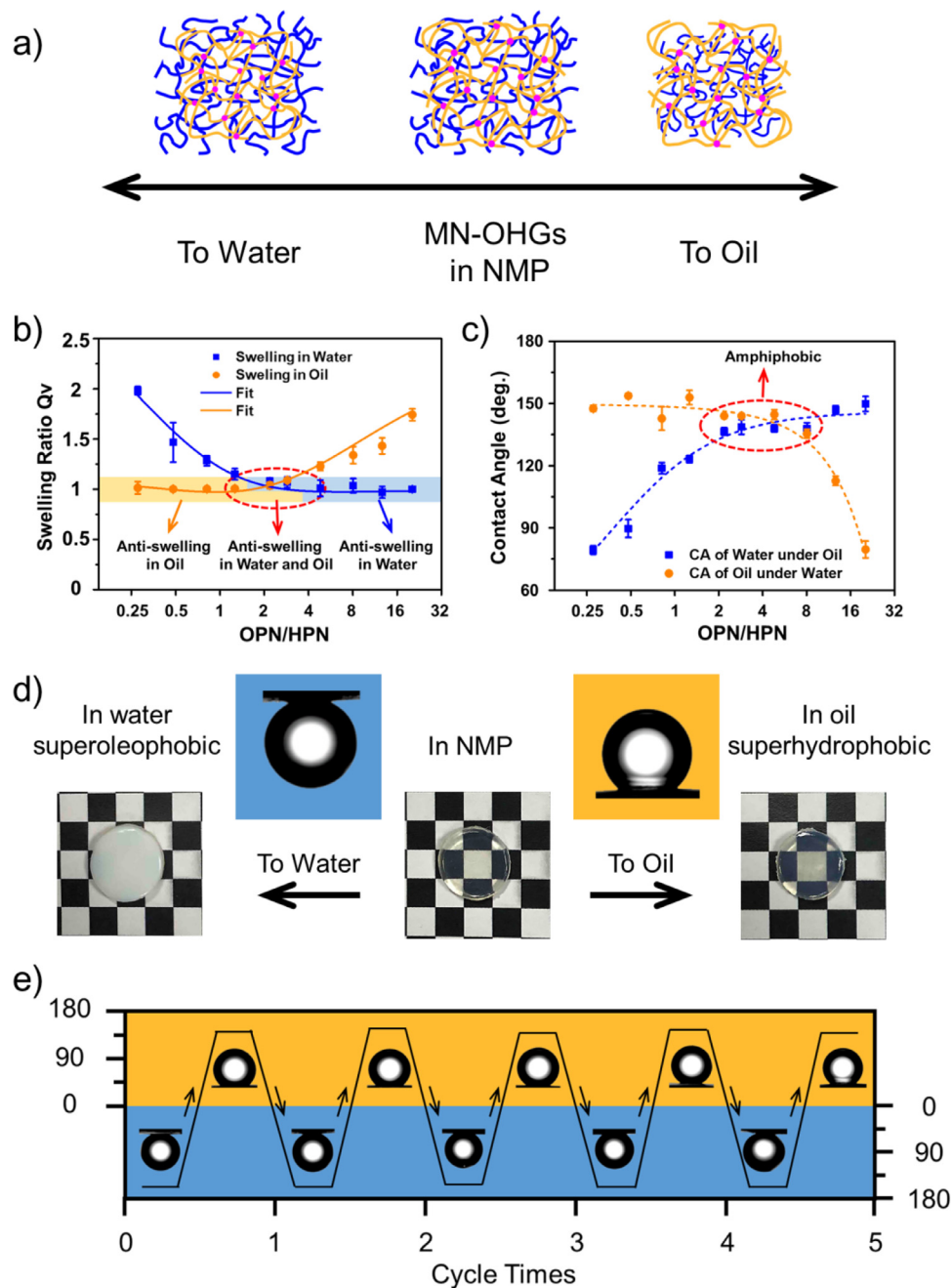


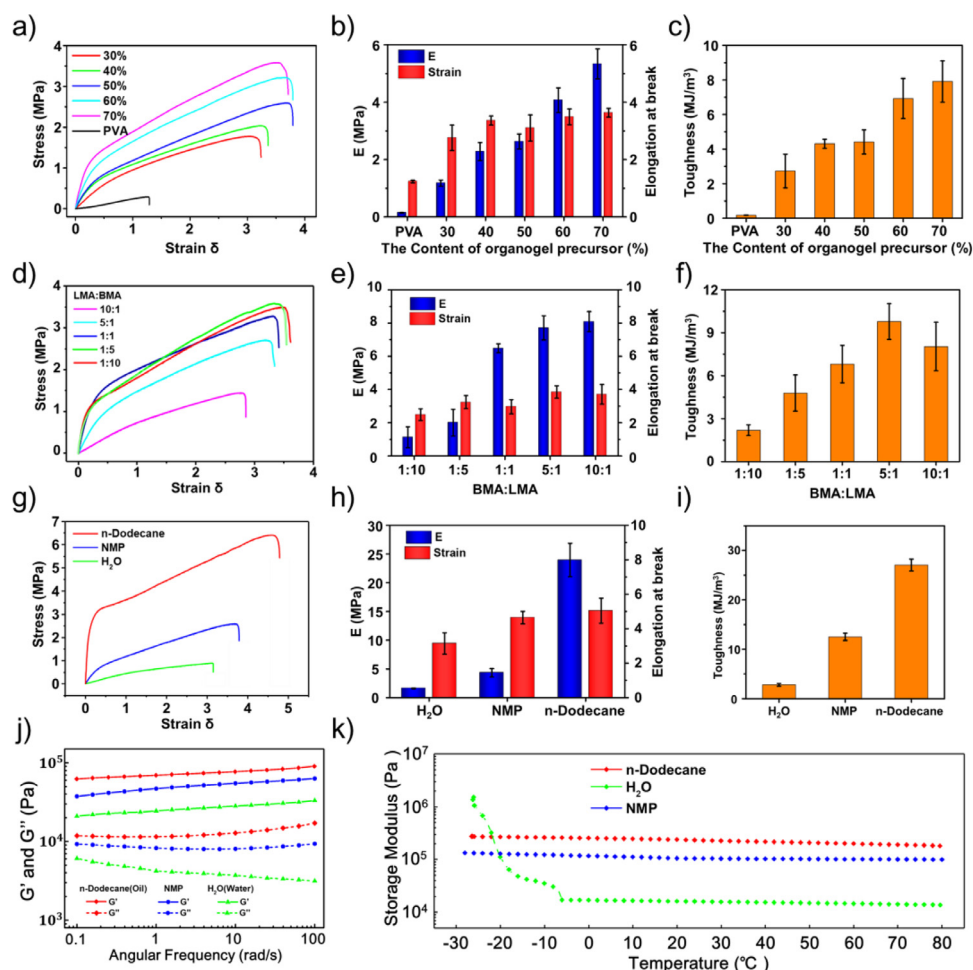
Fig. 2

Swelling properties and surface wettability of MN-OHG. (a) Reconfigurable structures of HPN and OPN in water and oil (n-dodecane) respectively. (b) The swelling ratio of MN-OHG in water and oil. The fit curve was obtained by the Doi's theory. The simulation details were described in Supporting Information. (c) The effect of the OPN/HPN ratio on the CA in different solvents. When the OPN/HPN ratio was in the range of 2/1–5/1, the reversible oleophobic and hydrophobic transitions could be achieved. (d) The surface properties of MN-OHG (OPN/HPN was 3/1) in different solvents. (e) The adaptive wetting transition showed good reversibility after alternately immersing the MN-OHG (OPN/HPN was 3/1) in water and oil.

Therefore, we decided to use the concentration of the organogel precursors at 70 wt% and the BMA/LMA ratio at 5:1 to prepare MN-OHG.

The rheological properties of the HN-OHG in different solvents (water, NMP and n-dodecane) were studied. Linear viscoelastic spectra of the samples at 25 °C were shown in Fig. 3j. The storage modulus (G') of the HN-OHG in oil were higher than of in water or NMP due to the volume shrunk seriously.

Besides, owing to the different freezing point of each solvents, the temperature would also have a great influence on the elasticity of different samples. As shown in Fig. 3k, the storage modulus of the HN-OHG in water abruptly increased from 10^4 Pa to 10^6 Pa (green) when temperature decreased from 0 to –20 °C. When under the freezing point of water, the HN-OHG swelled in water turned into ice-like solid that could be easily broken. In contrast, when the HN-OHG were swelled in oil or NMP, the storage

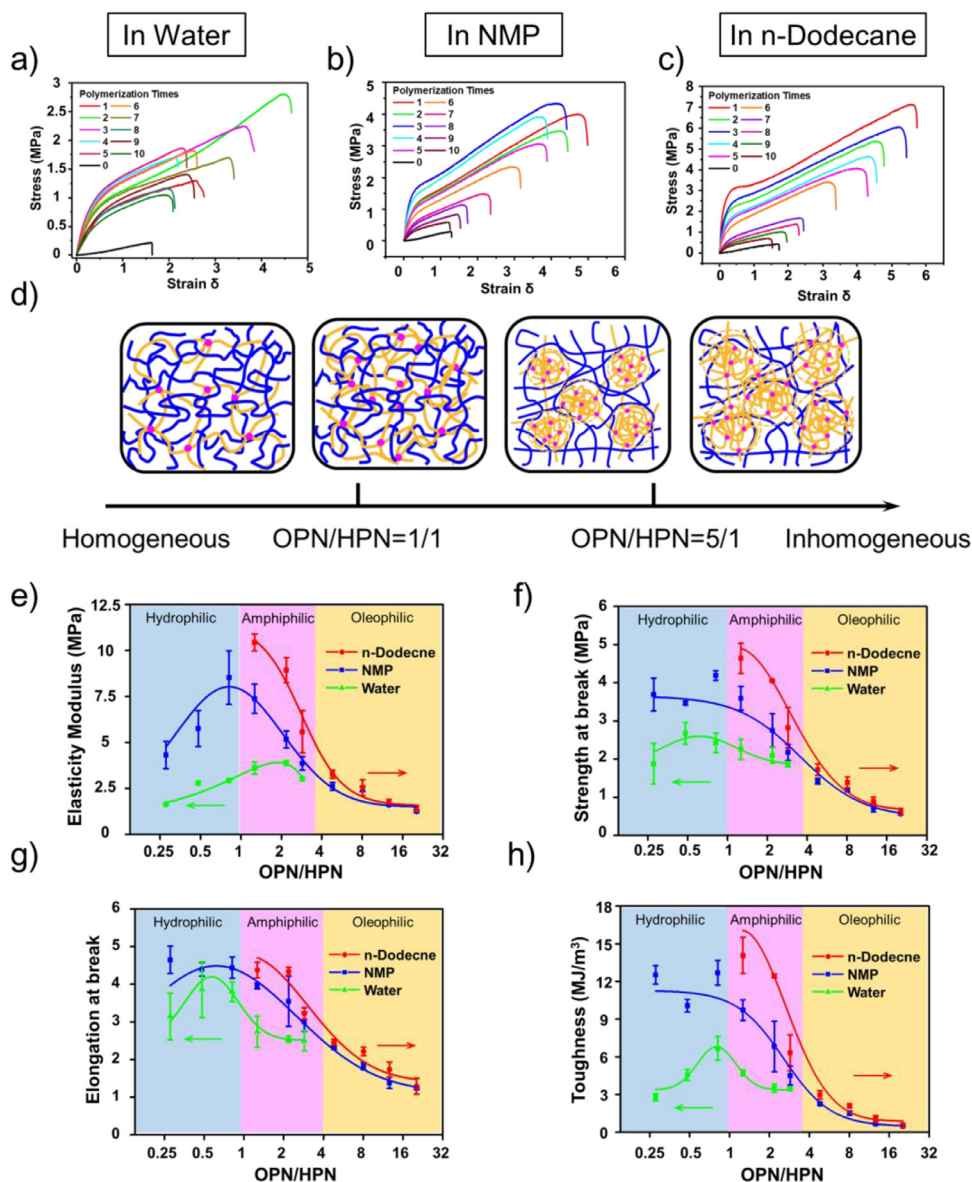
**Fig. 3**

Mechanical properties of heterogeneous network organohydrogels (HN-OHGs). (a) The strain–stress curve of HN-OHGs in different concentration of organogel precursors. (b) The elasticity modulus and elongation at break of HN-OHGs in different concentration of organogel precursors. (c) The toughness of HN-OHGs in different concentration of organogel precursors. (d) The strain–stress curve of HN-OHGs with different proportion of the second oleophilic networks. (e) The elasticity modulus and elongation at break of HN-OHGs with different proportion of the second oleophilic networks. (f) The toughness of HN-OHGs with different proportion of the second oleophilic networks. (g) The strain–stress curve of HN-OHGs in different solvents. (h) The elasticity modulus and elongation at break of HN-OHGs in different solvents. (i) The toughness of HN-OHGs in different solvents. (j) The rheological properties of HN-OHGs in water (green), NMP (blue) and n-dodecane (red). (k) The storage modulus of the HN-OHGs in water (green), NMP (blue) and n-dodecane (red) on a temperature sweep in the range of -20 to 80 °C at a constant shear strain of 0.1% and frequency of 10 rad s^{-1} .

modulus could maintain stable in much lower temperature. It was reasonable to speculate that the MN-OHGs would have similar behaviors.

In order to study the mechanical properties of the MN-OHGs, we prepared a series of MN-OHGs samples with different contents of OPNs and swelled in different solvents respectively. The strain and stress curve of MN-OHGs in water (hydrophilic), NMP (amphiphilic) and n-dodecane (oleophilic) were shown in Fig. 4a–c. When the MN-OHGs were exposed to NMP, the mechanical properties improved first and then decreased as the OPNs content increased. As shown in Fig. 4e, when the ratio of OPN/HPN was $1/1.4$, the elastic modulus of MN-OHGs was the highest which could reach 8 MPa , with 4 MPa of breaking strength, 450% of breaking elongation, and 12 MJ/m^3 of the toughness. We considered that the heterogeneous networks distribution was a determined factor for the MN-OHGs' mechanical properties.

As shown in schematic Fig. 4d. When the OPN/HPN ratio was less than $1/1$, the heterogeneous network distribution of the MN-OHGs was relatively homogeneous. The entire MN-OHGs were similar to the double network gel and the chemically cross-linked OPNs as the sacrificial bonds for energy dissipation [22]. Therefore, as the OPNs content increased in this stage, the mechanical properties were improved accordingly. Later when the OPN/HPN ratio was increased from $1/1$ to $5/1$, the accumulation of the OPNs became gradually inhomogeneous due to the sample preparation method. When the MN-OHGs were stretched under this stage, the inhomogeneous network distribution could lead to the arising of local stress inside the MN-OHGs, and weaken their toughness gradually. When the OPN/HPN ratio increased to over $5/1$, the inhomogeneous distribution further accumulated as internal defect and the mechanical properties of MN-OHGs dropped dramatically.

**Fig. 4**

Mechanical properties of MN-OHG networks in different solvents. The strain–stress curve of MN-OHG networks in water (a), NMP (b) and n-dodecane (c), respectively. (d) The network distribution of MN-OHG networks with different OPN/HPN ratio. The elasticity modulus (e), strength at break (f), elongation at break (g) and toughness (h) of MN-OHG networks in water (green), NMP (blue) and n-dodecane (red), respectively.

When replacing the solvent of MN-OHG networks to water, the MN-OHG networks became opaque (Fig. 2d). This indicated that the phase separation occurred inside the MN-OHG networks as OPNs collapsed [23]. Besides, the trend of mechanical properties was consistent with that swelled in NMP as in water, and the optimal OPN/HPN ratio was changed to 2/1. Due to that the NMP was a co-solvent to both networks, the mechanism of energy dissipation also changed. The collapsed OPNs would fill the voids of MN-OHG networks when the phase separation occurred. The OPNs in the voids effectively absorbed the crack energy either by viscous dissipation or by large deformation of the OPNs chains, preventing the crack to grow into macroscopic level [24]. Therefore, the optimal OPN/HPN ratio in water (~2/1) was larger than in NMP (~1/1.4).

But when the content of collapsed OPNs were too much, the MN-OHG networks became brittle. That was due to the size of collapsed OPNs domain generated by phase separation became too large which would exacerbate inhomogeneous distribution and cause the generation of internal defects (Fig. 4d, S3). As the OPNs contents continued to increase (OPN/HPN over 5/1), the MN-OHG networks became hydrophobic and could not absorb water as gel-like. In contrast, when the MN-OHG networks were exposed to n-dodecane, the HPNs collapsed and OPNs swelled. Similarly, when the OPNs contents were lower (OPN/HPN less than 1/1), the MN-OHG networks became hydrophilic and could not absorb oil. The MN-OHG networks materials became pure polymer networks in these stages. The oleophilic solvent was a good solvent for OPNs, which

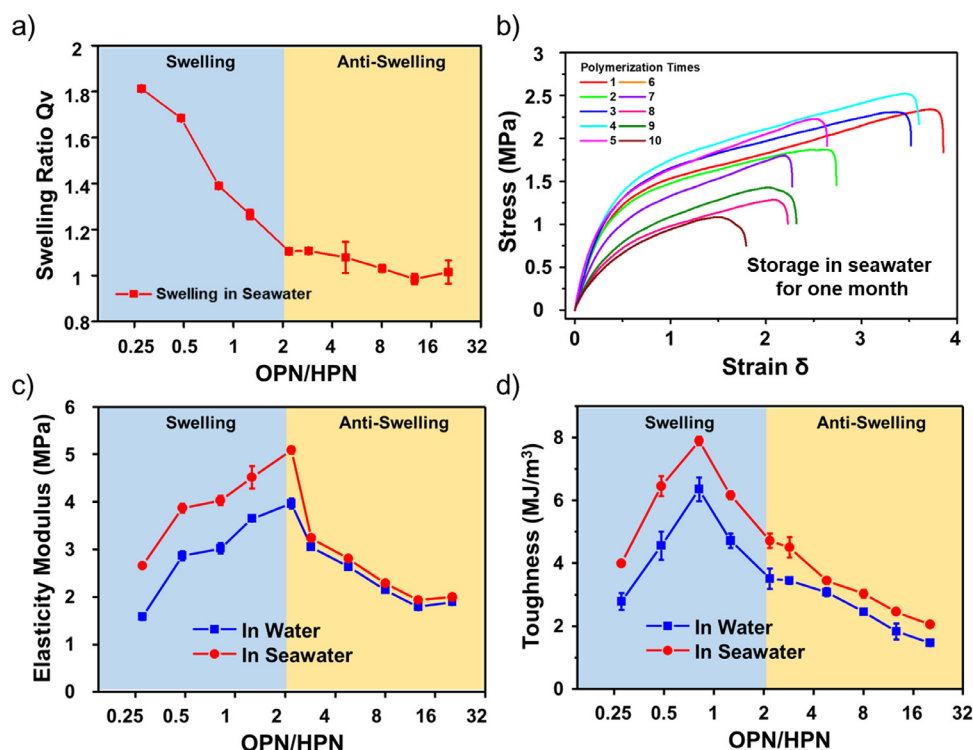


Fig. 5

Seawater mechanical enhancement of MN-OHG. (a) The swelling ratio of MN-OHG under seawater. (b) The strain–stress curve of MN-OHG in seawater for one month. The Elasticity modulus (c) and toughness (d) of the MN-OHG in water (blue) and seawater (red) for one month.

caused the OPNs to swell. Therefore, the swelled OPNs would increase the volume of the organohydrogels, which weakened their mechanical properties.

Seawater contained a large amount of ions, which would cause dehydration to conventional hydrogels [25]. Therefore, it was necessary to develop a gel material that could resist to seawater environment. The MN-OHG could maintain a constant volume due to the spatial restriction between hydrophilic and oleophilic polymer networks. We studied a series of MN-OHG samples which were stored in artificial seawater for one month. The swelling properties and surface wettability of MN-OHG were shown in Fig. 5a. When the ratio of OPN/HPN was over 2/1, the swelling behavior of MN-OHG were obviously controlled in artificial seawater. The mechanical behavior of the MN-OHG stored in artificial seawater were shown in the Fig. 5b. The elastic modulus and toughness of MN-OHG in artificial seawater were stronger than the samples in water before the OPN/HPN ratio of 3/1 (Fig. 5c, d). This could be explained that the sample had smaller swelling ratio in sea water than pure water due to different osmotic pressure [26]. When the OPN/HPN ratio was over 3/1, the MN-OHG showed low swelling ratio both in sea water and in pure water, which lead to similar mechanical properties.

Conclusions

In conclusion, we successfully fabricated multiple network organohydrogels by multiple swelling polymerization methods. These MN-OHG could absorb water, N-methylpyrrolidone (NMP) or oil (n-dodecane) due to the existing of heterogeneous networks.

The swelling behaviors of MN-OHG could also be tuned in water or oil with different ratio of heterogeneous polymer networks. When the ratio of OPN/HPN was 2/1, the MN-OHG could maintain the same swelling ratio in water and n-dodecane. And the surface properties of MN-OHG could switch between hydrophobic under oil and oleophobic under water. When the ratio of OPN/HPN was 1/1.4, the elastic modulus of MN-OHG was the highest which could reach 8 MPa, with 4 MPa of breaking strength, 450% of breaking elongation, and 12 MJ/m³ of the toughness. Besides, the mechanical properties of HN-OHG were enhanced when swelling in n-dodecane (the elastic modulus could reach 23 MPa, and toughness could reach 26 MJ/m³). And the storage modulus of HN-OHG could maintain stable over a wide range temperature when swelled in NMP or dodecane (the range was from −20 to 80 °C). Furthermore, MN-OHG could maintain long-term stability and further mechanical enhanced in artificial seawater, which broadened the application of gels materials in complex environments.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.giant.2021.100058](https://doi.org/10.1016/j.giant.2021.100058).

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