Double-Network Hydrogels with a Gradient Hydrophobic Coating that Prevents Water Evaporation and Allows Strong Adhesion to a Solid Substrate

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Gradient coating of tough double-network hydrogels

Key words

Hydrogel; Double Network; Coating; Gradient Structure; Adhesion; Water Evaporation

Abstract

Hydrogels are soft and wet polymeric materials containing large amounts of water. The high water content gives hydrogels their unique characteristics, such as biocompatibility. However, the water in the hydrogels easily evaporates under atmospheric conditions. In addition, since hydrogels consist of mostly water, adhering them to solid substrates with commercial glues is difficult. To overcome these problems, we developed a method to apply a robust gradient hydrophobic coating to tough double-network (DN) hydrogels. Liquid hydrophobic monomers were dropped onto the DN gel precursor (the first network gel containing the second network precursor) and spontaneously spread to cover the gel surface. This led to the simultaneous polymerization of the hydrophobic monomer near the gel–air interface and the second network precursor of the bulk gel to yield a gradient hydrophobic coating. The resulting hydrophobic coating effectively prevents water evaporation from the coated DN gel. Moreover, strong adhesion of the coated gel to various solid substrates was achieved with commercial glues.

Introduction

Hydrogels are soft and wet materials that contain water in a hydrophilic polymer network(s). The most representative structural characteristic of hydrogels is their large water content (typically 50–99%). Since hydrogels are mostly composed of water, they have become attractive as environmentally friendly materials. Furthermore, the water-rich nature of hydrogels leads to their unique functions, such as their ability to retain molecules, biocompatibility, and flame retardance.[1–3] Although conventional gels exhibit poor mechanical properties, which is the greatest concern for their real-world applications, recent advances in gel science have allowed the production of more robust hydrogels by introducing weak bonds inside the network(s),[4,5] homogenizing the network structures,[6,7] and hybridizing with nanoscale filler materials.[8] From the viewpoint of mechanical strength, these tough hydrogels have achieved mechanical performance that is sufficient for practical applications as structural materials.[9]

However, hydrogels are still not widely used. There are two important problems among the various issues that need to be solved before hydrogels can be universally applied. The first problem is water evaporation. When hydrogels are exposed to air, their water content and volume decrease over time. This is a critical problem for hydrogel application. Although solvent evaporation from hydrogels can be prevented by changing the solvent within the hydrogel from water to a nonvolatile solvent, such as an ionic liquid or glycerol,[10,11] the resulting ionic gels and glycerogels lose some of the important gel characteristics, i.e., being environmentally friendly, biocompatible, and responsive to external stimuli. The second problem is the difficulty with hydrogel–solid adhesion. Generally, materials (including gels) tend not to be used alone but rather as composites or assemblies with other materials. For example, gel-made artificial

cartilage, which has been studied by several researchers, needs bond strongly to bones.[12,13] To create bonding between different materials, numerous methods, including welding, mechanical anchoring, chemical bonding, adhesion, and glues, have been used depending on the material.[14] Here, we focus on the bonding of covalently crosslinked gels (chemical gels) to solid substrates. Chemical gels cannot be welded because they do not melt when heated. Furthermore, although strong mechanical anchoring of gels adhering to porous glass has been reported,[15] general methods for anchoring, such as the use of screws or rivets, are difficult to adopt for hydrogel–solid bonding because of the extreme softness of hydrogels. For chemical bonding, several researchers have reported strong hydrogel–solid bonding via the formation of covalent or noncovalent interactions,[16–18] but most of these methods require specific pretreatment of the surface of either the hydrogel or the solid. For adhesion, the rheological and chemical properties of hydrogels must be optimized to achieve strong adhesion to solid substrates.[19,20] Strong bonding of hydrogels to solids using glues is usually difficult because of the high water content of hydrogels. While many glues rely on adhesive–substrate interactions to achieve high adhesive strength, the interactions between gels and glues are much weaker than those between solids and glues owing to the low polymer contents of hydrogels. Overall, conventional gel–solid adhesion methods are only applicable to certain systems or require special pretreatment protocols.

To overcome these two problems, we conceived an approach involving robust gradient coating of double-network (DN) hydrogels with hydrophobic polymer layers. A hydrophobic surface layer constructed on a hydrogel would effectively prevent water evaporation from the hydrogel. Furthermore, the tough hydrophobic layer of the hydrogel would allow strong adhesion of the hydrogel to any solid substrate through the

use of commercial glues via conventional solid–solid adhesion. DN hydrogels are tough, interpenetrating hydrogels consisting of a brittle and weak first network and a stretchable second network.[21] Traditional DN hydrogels are synthesized via two-step polymerization. The first network is typically prepared by the free-radical copolymerization of monomers and crosslinkers. The prepared first network gel is then immersed in an aqueous second network precursor solution containing monomers, crosslinkers, and UV initiators to allow these precursors to diffuse into the first network; this first network gel containing the second network precursors is denoted the DN precursor gel. Finally, the second network precursors are polymerized in the DN precursor gel to form DN hydrogels with two networks.[21] To prepare a robust hydrophobic coating on a DN hydrogel, we adopted the strategy shown in Figure 1. First, the coating precursor, which is a mixture of the hydrophobic liquid vinyl monomer, crosslinker, and UV initiator, was dropped onto the surface of the DN precursor gel. No solvent was used to ensure the formation of a robust coating. Subsequently, the second network precursor in the bulk gel and the coating precursor near the surface of the gel simultaneously polymerized. The resulting second network and the coating layer are likely covalently bound, forming a robust hydrophobic coating.

Experimental

Materials

2-Acrylamido-2-methylpropanesulfonic acid (AMPS; Tokyo Kasei Co., Ltd.), acrylamide (AAm; Junsei Chemical Co., Ltd. (Junsei)), methyl methacrylate (MMA; Wako Pure Chemical Industries, Ltd. (Wako)), divinylbenzene (DVB; Wako), and 2-

oxoglutaric acid (Wako) were used as received. *N*,*N*'-Methylenebis(acrylamide) (MBAA; Wako) and azobisisobutyronitrile (AIBN; Junsei) were used after recrystallization from ethanol.

Synthesis of the double-network hydrogels

The DN hydrogels were synthesized via two-step free-radical polymerization as previously reported. First, the AMPS aqueous solution was prepared with 1 M AMPS as the monomer, 40 mM MBAA as the crosslinker, and 1 mM 2-oxoglutaric acid as the photoinitiator. After bubbling with argon gas for 30 min, the solution was poured into a mold made from two glass plates separated by a 5 mm silicone rubber spacer. Photopolymerization was carried out under an argon atmosphere with UV lamps (two 15 W black lights at 365 nm) for 7 h. After gelation, the PAMPS gel was immersed in a large amount of aqueous solution consisting of 2 M AAm as the monomer, 2 mM MBAA, and 2 mM 2-oxoglutaric acid for at least 2 days to obtain the DN precursor gels. After irradiation with a UV lamp for 7 h under an argon atmosphere, the PAAm network was synthesized in the presence of the PAMPS network. The synthesized DN gel was then immersed in pure water for 2 days.

Synthesis of the coated double-network hydrogels

The coated DN gel was synthesized by applying the same synthesis method as that for the DN gel. The PAMPS gel was prepared and then soaked in AAm solution via the abovementioned method to prepare the DN precursor gels. Then, the DN precursor gels were cut into 3 × 3 cm squares, placed into 70 mm diameter glass Petri dishes, and placed under an argon atmosphere. Next, 0–12 mL of the coating precursor was dropped

onto the cut PAMPS gel samples. The coating precursor was prepared from bulk liquid MMA with 0.1 mol% (with respect to the monomer) DVB as the crosslinker and 0.1 mol% AIBN as the photoinitiator without any additional solvent. The dropped coating precursor spontaneously spread onto and coated the entire surface of the PAMPS gels. Next, UV irradiation was immediately applied for 9 h, and the coating precursor and second network precursor polymerized simultaneously. Finally, the synthesized coated DN gel was immersed in pure water for 2 days.

Microscopy observations

Cross-sections of the coated DN gel were observed with a 3D laser scanning microscope (VK-9500, Keyence Co.). The gradient coating structure and the coating layer thickness were investigated from the optical microscopy images.

Peeling force measurements

The peeling test was performed with a tensile-compressive tester (TENSILON RTC-1150A, Orientec Co.). The top and bottom sides of the coated DN gel were bonded to two substrates, where an initial notch of ~1 mm was imposed on the top of the adhesion interface. One side of the top substrate was then lifted up at a velocity of 5 mm/min to induce peeling. The peeling force (N/m) was calculated as the average of the raw peak forces divided by the sample thickness.

Drying experiment

The drying experiment was carried out in a closed chamber. The humidity and temperature of the chamber were fixed at 25 ±1 °C and 40 ± 5%, respectively by

introducing dry N_2 gas into the chamber at a constant flow rate of 1 cm^3/min through a copper pipe in a 30 °C water bath. The initial weights of the gel samples were measured with an electronic balance. The samples were then moved into the chamber, and the weights of the dried samples were measured. The normalized weight of the sample was determined by dividing the weight of the sample of interest by its initial weight.

Results

The PAMPS/AAm DN precursor gel, consisting of the first PAMPS network containing a second network precursor aqueous solution composed of the monomer AAm, a crosslinker and an initiator, was prepared. Under an argon atmosphere, the desired amount of the coating precursor composed of the monomer methyl methacrylate (MMA), a crosslinker and an initiator was dropped onto the gel. The dropped coating precursor spontaneously spread over the surface of the PAMPS gel, including the gel–Petri dish interface, to block the gel from the argon atmosphere. The second network, PAAm (in the bulk gel), and the hydrophobic polymer layer (at the surface) were polymerized simultaneously upon UV irradiation to yield the PAMPS/PAAm DN hydrogel with a hydrophobic layer (coated DN hydrogel). The amount of coating precursor dropped onto the gel was fixed at 10 mL unless specifically mentioned. Notably, some of the added coating precursors remained on the Petri dish and thus were not incorporated into the coating, as schematically shown in Figure 1. Figure 2(a) shows a photograph of the coated DN hydrogel covered with a hydrophobic layer consisting mainly of PMMA. The transparent and relatively soft DN gel was completely covered by an opaque and stiff hydrophobic layer. A thin layer formed almost evenly on all sides of the DN hydrogel. The hydrophobic layer adhered so strongly to the gel that

they could not be separated by hand, and no degradation or decomposition of the coating layer was observed during the experiment. The addition of crosslinkers to the coating precursor, causes the effective molecular weight of the coating to be quasi-infinite, may play a role in the high toughness of the coating. Notably, the addition of the hydrophobic monomer and polymerization should be performed in an oxygen-free environment because oxygen in the air disturbs radical polymerization. Similar hydrophobic coating layers were obtained by using other hydrophobic liquid monomers, such as ethyl methacrylate, butyl methacrylate, vinyl acetate, and mixtures of these materials (Figure S1).

The chemical compositions of the hydrophobic layer and the bulk gel of the coated DN gel were analyzed by Fourier transform infrared (FT-IR) spectroscopy (Figure S2). The opaque layer at the surface of the coated DN gel consisted mainly of PMMA. Figure 2(b) shows an optical microscopy image of the cross-section of the coated gel, and Figure 2(c) shows a line profile of the corresponding grayscale image. These images demonstrate that the bulk DN gel and the hydrophobic coating had combined and were not obviously segregated. The dark region near the surface is the PMMA layer, and the white region far from the surface is the bulk DN gel. In addition, a color gradient was observed in the intermediate region. This means that the PMMA and the bulk DN gel formed a gradient structure near the surface. The formation of such a structure can be explained by considering the polymerization process. Despite their hydrophobicity, hydrophobic monomers dissolve slightly in aqueous solutions. For example, the solubility of MMA in water is 1.59 wt% at 20 °C. Thus, when the MMA coating precursor was dropped onto the DN gel precursor and spread, it diffused into the gel slightly. As a result, before polymerization, AAm and the hydrophobic monomers

coexisted in the intermediate region and were subsequently copolymerized upon UV irradiation. We observed complete wetting of the coating precursor in contact with the DN gel precursor, which might be attributed to a decrease in the interfacial free energy due to mixing at the interface. The concentration of PMMA would be close to 100% at the surface and decrease with depth. The resulting PMMA layer and the PAAm network were unified by the formation of covalent bonds, and these polymer chains are expected to be strongly entangled (via topological bonding) due to the high concentrations of AAm and MMA. We consider that such a gradient structure with two types of bonding interactions based on the DN structure results in a robust, tightly bonded coating. Notably, pure PMMA is highly transparent whereas the PMMA coating on the DN hydrogel was opaque, which is probably because of the polymerization-induced phase separation of PMMA and water.

We found that this hydrophobic PMMA coating remarkably prevents water evaporation from the DN hydrogels. The uncoated and coated DN hydrogels were left in a draft chamber in our laboratory for 7 days. Figure 3(a) shows photographs of the DN hydrogels before and after drying. The uncoated DN hydrogel clearly shrank because of water evaporation. In contrast, the volume of the coated DN hydrogel did not change much because the PMMA layer prevented water evaporation. To quantify the water retention of the coated DN hydrogel, a controlled drying test was performed. The coated gel samples were placed in a closed chamber where the temperature and humidity were fixed at 25 °C and 40% RH, respectively. While the uncoated DN hydrogel lost approximately 40% of its weight after drying for 2 days, the coated DN hydrogel showed better water retention. Furthermore, water retention improved with increasing dropped MMA amount. Cross-sections of the coated DN gels are shown in Figure S3. A

coating layer was observed on the top surface of the coated DN gels, and the thickness of this layer appeared to increase as the amount of coating precursor increased, although the gradient structure makes layer thickness quantification difficult. Figure 3(b) shows the normalized change in weight of the coated DN hydrogels with various amounts of the coating precursor. The optimally coated DN gel (coated with 12 mL of coating precursor) lost only 6% of its weight. Additionally, because moisture permeability generally decreases with film thickness (which is represented by the amount of MMA added), the water retention of the coated gel increased with increasing amounts of coating precursor.

Furthermore, we demonstrated the strong adhesion between the coated DN gel and the solid surfaces with commercial glues. Because the surface of the coated DN gel is a solid polymer (PMMA), the hydrogel can bond to solid substrates with common glues. A PMMA board and a cyanoacrylate-type adhesive (Aron Alpha (JP)/Krazy Glue (EN), Toa Gosei Co., Ltd.) were used as the solid substrate and glue, respectively. Figure 4(a) shows a photograph of the coated DN hydrogel adhered to the PMMA solid substrate. These materials bonded so strongly that the gel could not be removed from the PMMA board by hand. Additionally, the bonding was stable and did not dissociate after 30 days of immersion in water. To measure the adhesion force, a peeling test was performed with the DN gel–PMMA board interface, as shown in Figure 4(b). A photograph of the upper PMMA board after hydrogel removal is shown in Figure 4(c). The opaque coating layer remained on the transparent board, indicating that when the DN hydrogel is removed, debonding at the adhesion interface does not occur, but rather the bulk DN hydrogel is fractured, probably inside the gradient coating layer. Figure 4(d) shows the force–displacement curve from the peeling test. The calculated peeling force was 376

N/m, which is comparable to the bulk fracture force of the DN gel (approximately 100–4,000 N/m).[22,23] This means that strong adhesion at the hydrogel–solid interface was achieved at the coating layer upon commercial glue application. Like conventional solid materials, coated DN hydrogels can be bonded to various types of solid substrates when appropriate chemical agents are used. For example, PMMA/toluene and polycarbonate/cyanoacrylate (substrate/chemical agents for adhesion) systems also strongly adhered to the PMMA-coated DN hydrogel (Figure S4). This adhesion method can be applied to a variety of solid–hydrogel interfaces, such as bones/artificial cartilages[12] and ship bottoms/barnacle inhibitor gels.[24]

Conclusion

In conclusion, a robust gradient hydrophobic coating was applied to tough DN hydrogels by the spontaneous spreading of the hydrophobic monomer MMA on the surface of the DN precursor gel and the simultaneous polymerization of AAm (in the bulk gel) and MMA (near the gel surface) upon UV irradiation. The PMMA coating on the DN hydrogels effectively prevented water evaporation from the hydrogels and enabled strong adhesion of the hydrogel to a solid interface with the aid of commercial glues. One of the advantages of this gradient coating method over previous hydrogel hydrophobic coating methods is that the coating layer provides water retention and adhesion properties, and the second supportive network, which improves the mechanical strength, can be synthesized easily and simultaneously in/on the hydrogel.[25,26] This is particularly important from the viewpoint of obtaining hydrogels with high adhesive strength. The gradient between the coating layer and the DN hydrogel makes the interface ambiguous, increasing the adhesive strength but not

interfacial peeling.

Acknowledgments

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References

1. Peppas, N. A., Hilt, J. Z., Khademhosseini, A. & Langer, R. Hydrogels in Biology and Medicine: From Molecular Principles to Bionanotechnology. *Advanced Materials* **18,** 1345–1360 (2006).
2. Lin, C.-C. & Metters, A. T. Hydrogels in controlled release formulations: Network design and mathematical modeling. *Advanced Drug Delivery Reviews* **58,** 1379–1408 (2006).
3. Mastalska-Popławska, J., Wójcik, Ł. & Izak, P. Applications of hydrogels with fire retardant properties—a review. *J Sol-Gel Sci Technol* **105,** 608–624 (2023).
4. Zhao, X. Multi-scale multi-mechanism design of tough hydrogels: building dissipation into stretchy networks. *Soft Matter* **10,** 672–687 (2014).
5. Nakajima, T. Generalization of the sacrificial bond principle for gel and elastomer

toughening. *Polymer Journal* **49,** 477–485 (2017).

6. Ito, K. Novel Cross-Linking Concept of Polymer Network: Synthesis, Structure, and Properties of Slide-Ring Gels with Freely Movable Junctions. *Polymer Journal* **39,** 489–499 (2007).
7. Sakai, T., Matsunaga, T., Yamamoto, Y., Ito, C., Yoshida, R., Suzuki, S., Sasaki, N., Shibayama, M. & Chung, U. I. Design and fabrication of a high-strength hydrogel with ideally homogeneous network structure from tetrahedron-like macromonomers. *Macromolecules* **41,** 5379–5384 (2008).
8. Haraguchi, K. Synthesis and properties of soft nanocomposite materials with novel organic/inorganic network structures. *Polymer Journal* **43,** 223–241 (2011).
9. Li, X. & Gong, J. P. Design principles for strong and tough hydrogels. *Nat Rev Mater* **9,** 380–398 (2024).
10. Ueki, T. & Watanabe, M. Macromolecules in Ionic Liquids: Progress, Challenges, and Opportunities. *Macromolecules* **41,** 3739–3749 (2008).
11. Mredha, M. T. I., Lee, Y., Rama Varma, A. V., Gupta, T., Manimel Wadu, R. R. & Jeon, I. Tardigrade-inspired extremotolerant glycerogels. *NPG Asia Mater* **15,** 1–14 (2023).
12. Nonoyama, T., Wada, S., Kiyama, R., Kitamura, N., Mredha, M. T. I., Zhang, X.,

Kurokawa, T., Nakajima, T., Takagi, Y., Yasuda, K. & Gong, J. P. Double-Network Hydrogels Strongly Bondable to Bones by Spontaneous Osteogenesis Penetration. *Advanced materials (Deerfield Beach, Fla.)* **28,** 6740–6745 (2016).

13. Ma, Q., Lin, D., Liu, Y., Liu, X., Zhao, H., Zhou, G., Liu, S. & Sun, K. Recent research progress of hydrogel on cartilage. *European Polymer Journal* **213,** 113115 (2024).
14. Awaja, F., Gilbert, M., Kelly, G., Fox, B. & Pigram, P. J. Adhesion of polymers. *Progress in Polymer Science* **34,** 948–968 (2009).
15. Kurokawa, T., Furukawa, H., Wang, W., Tanaka, Y. & Gong, J. P. Formation of a strong hydrogel-porous solid interface via the double-network principle. *Acta Biomaterialia* **6,** 1353–1359 (2010).
16. Takashima, Y., Sahara, T., Sekine, T., Kakuta, T., Nakahata, M., Otsubo, M., Kobayashi, Y. & Harada, A. Supramolecular Adhesives to Hard Surfaces: Adhesion Between Host Hydrogels and Guest Glass Substrates Through Molecular Recognition. *Macromolecular Rapid Communications* **35,** 1646–1652 (2014).
17. Yuk, H., Zhang, T., Parada, G. A., Liu, X. & Zhao, X. Skin-inspired hydrogel–elastomer hybrids with robust interfaces and functional microstructures. *Nat Commun* **7,** 12028 (2016).
18. Takahashi, R., Shimano, K., Okazaki, H., Kurokawa, T., Nakajima, T., Nonoyama, T.,

King, D. R. & Gong, J. P. Tough Particle-Based Double Network Hydrogels for Functional Solid Surface Coatings. *Advanced Materials Interfaces* **5,** 1–10 (2018).

19. Bromberg, L., Temchenko, M., Alakhov, V. & Hatton, T. A. Bioadhesive properties and rheology of polyether-modified poly(acrylic acid) hydrogels. *International Journal of Pharmaceutics* **282,** 45–60 (2004).
20. Bovone, G., Dudaryeva, O. Y., Marco-Dufort, B. & Tibbitt, M. W. Engineering Hydrogel Adhesion for Biomedical Applications via Chemical Design of the Junction. *ACS Biomater. Sci. Eng.* **7,** 4048–4076 (2021).
21. Gong, J. P., Katsuyama, Y., Kurokawa, T. & Osada, Y. Double-network hydrogels with extremely high mechanical strength. *Advanced Materials* **15,** 1155–1158 (2003).
22. Tanaka, Y., Kuwabara, R., Na, Y. H., Kurokawa, T., Gong, J. P. & Osada, Y. Determination of fracture energy of high strength double network hydrogels. *Journal of Physical Chemistry B* **109,** 11559–11562 (2005).
23. Nakajima, T., Kurokawa, T., Furukawa, H. & Gong, J. P. J. P. Effect of the constituent networks of double-network gels on their mechanical properties and energy dissipation process. *Soft Matter* **16,** 8618–8627 (2020).
24. Murosaki, T., Noguchi, T., Kakugo, a, Putra, a, Kurokawa, T., Furukawa, H., Osada, Y., Gong, J. P., Nogata, Y., Matsumura, K., Yoshimura, E. & Fusetani, N.

Antifouling activity of synthetic polymer gels against cyprids of the barnacle (Balanus amphitrite) in vitro. *Biofouling* **25,** 313–20 (2009).

25. Zhu, T., Jiang, C., Wang, M., Zhu, C., Zhao, N. & Xu, J. Skin-Inspired Double-Hydrophobic-Coating Encapsulated Hydrogels with Enhanced Water Retention Capacity. *Advanced Functional Materials* **31,** 2102433 (2021).
26. Gao, W., Chang, J., Li, X., Li, S., Zhou, Y., Hou, X., Long, L., Zhao, J. & Yuan, X. A Quenched Double-Hydrophilic Coating for the Enhancement of Water Retention of Hydrogels. *Advanced Functional Materials* **33,** 2303306 (2023).

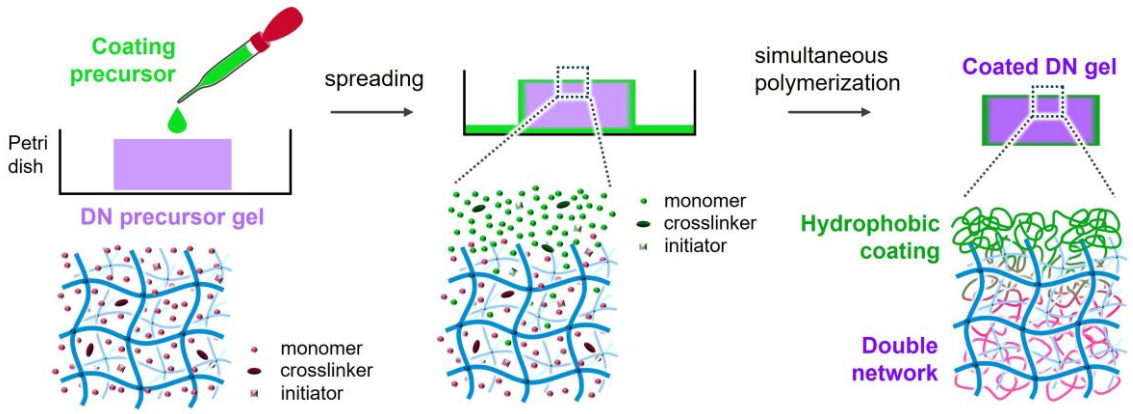

Figure 1. Schematic of the coated DN gel synthesis process. The coating precursor, which consists mainly of hydrophobic monomers, is dropped onto the DN precursor gel, which is the first network gel containing the second network precursor solution. The coated DN gel is obtained upon the simultaneous polymerization of the coating precursor and the second network precursor.

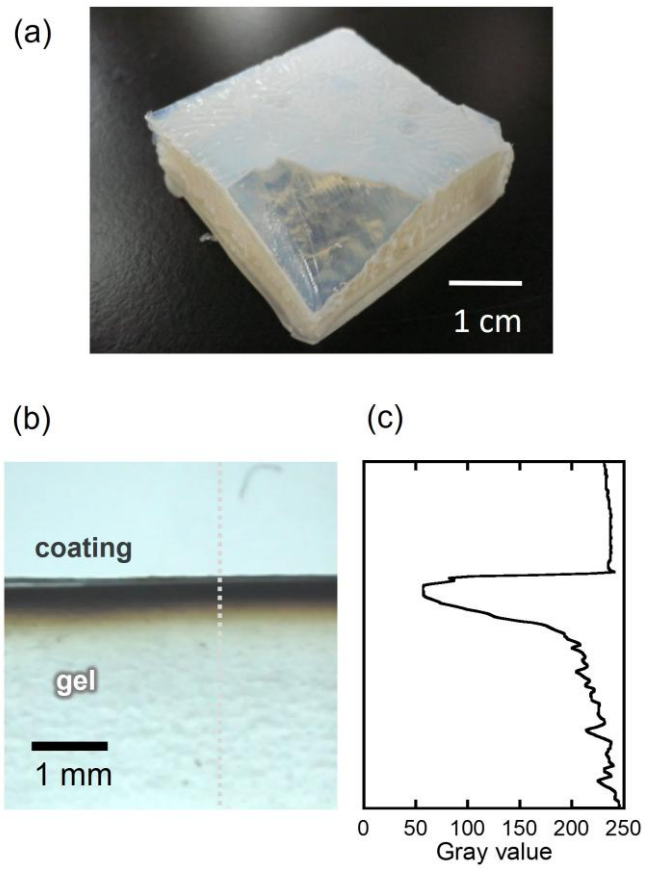

Figure 2. (a) Photograph of the PMMA-coated DN gel. The front edge was removed to visualize the appearance of the coating layer. (b) Optical microscopy image of a cross-section of the coated DN gel. The upper side is the coating layer, and the bottom side is the bulk gel. (c) Line profile of the gray value of the coated DN gel. The profile was obtained along the dotted line of Figure 2(b) using the corresponding grayscale image.

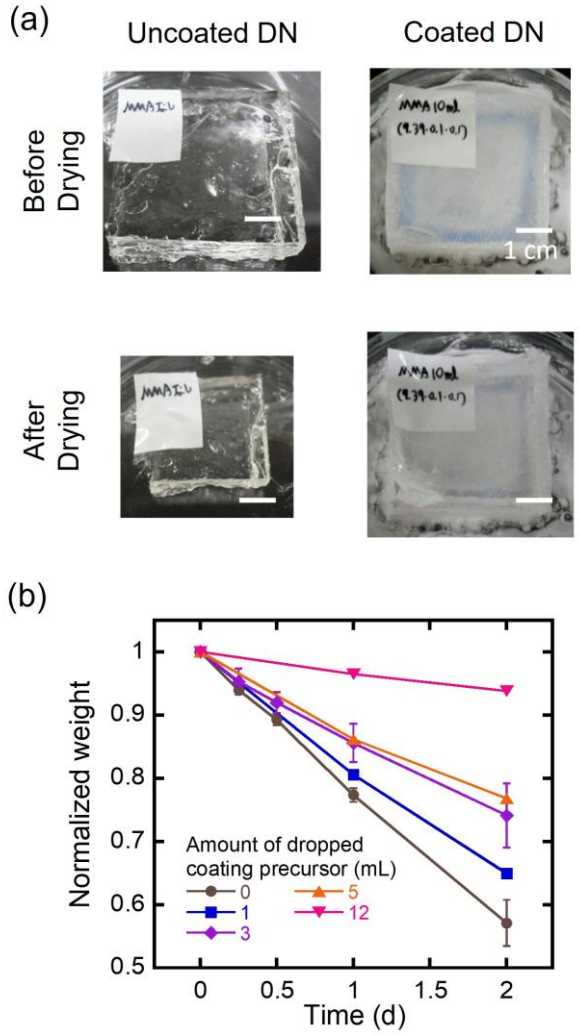

Figure 3. (a) Photographs of the uncoated and coated DN gels before and after drying in a draft chamber for 1 week. Scale bars: 1 cm. (b) Normalized weights of the coated DN gels left in the environment-controlled chamber. The amount of the coating mixture used varied from 0 mL (uncoated DN gel) to 12 mL. Typically, the initial sample thickness was 5–6 mm.

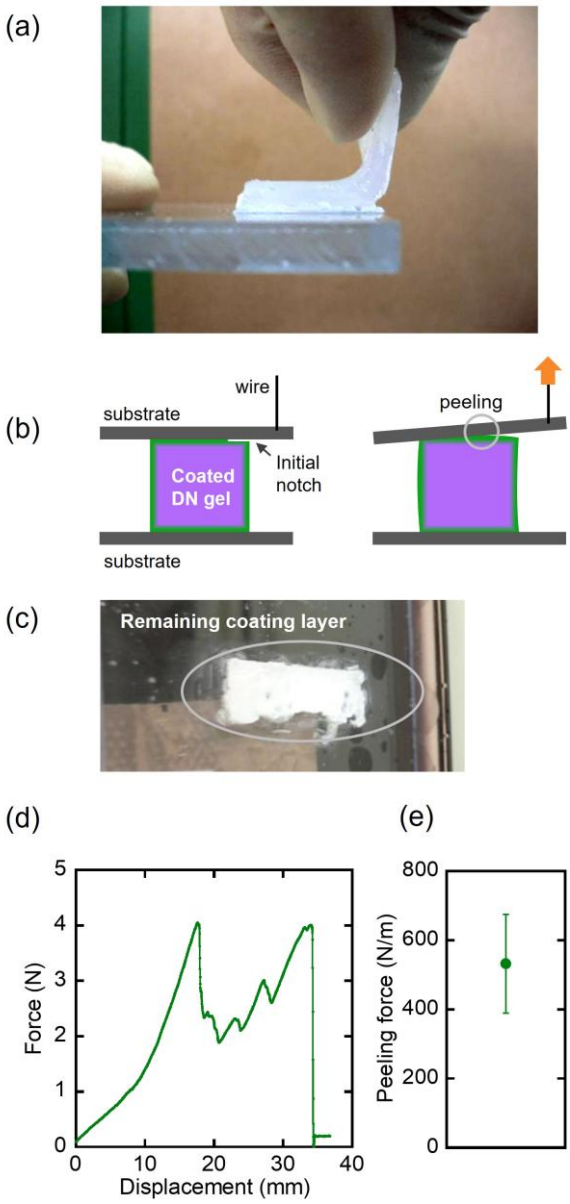

Figure 4. (a) Photograph of the coated DN gel bonded to a solid PMMA board using commercial cyanoacrylate glue. The gel could not be removed by hand. (b) Schematic of the peeling test. (c) Photograph of the upper PMMA substrate with the coating layer that remained after the peeling test. (d) Force–displacement curve from the peeling test and (e) the calculated peeling force of the coated DN gel.