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Hydrophilic Double-Network Polymers that Sustain High Mechanical Modulus under 80% Humidity

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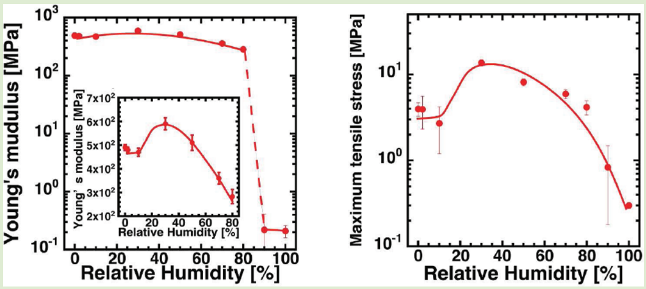
S *Supporting Information*



ABSTRACT: The effects of water on the mechanical properties of synthetic hydrophilic polymers with double-network (DN) structures were studied under different relative humidities (RH). It was found that they could sustain nearly the same high Young's modulus as dry DN polymers in the RH range 10−80% (water content 3−17 wt %), that is, more than 10^2 MPa. However, when the RH exceeds 80%, DN polymers abruptly absorb large amounts of water (water content 90 wt %) and transform to a highly water-swollen "gel state" with a decrease in the Young's modulus of 3 orders of magnitude. Spectroscopic analyses revealed that water molecules below RH 80% are strongly bound to hydrophilic moieties with highly restricted mobility; water under such states improves rather than reduces mechanical properties by behaving as a plasticizer. DN polymers capable of sustaining high mechanical properties, even under RH 80%, have potential uses as hydrophilic materials.

When hydrophilic materials, either natural or synthetic, are placed in a humid atmosphere, they absorb water and swell, and the interstitial spaces of the materials are filled with water. When they absorb substantial amounts of water, they form water-swollen polymer networks called hydrogels.

Most hydrophilic materials under such condition have significantly reduced Young's moduli and mechanical toughness. For example, the stiffness of natural silks is reduced by up to an order of magnitude by treating with moisture.[1] Even synthetic hydrophobic polymers such as poly(methyl methacrylate), nylon, Nafion, and epoxy resins undergo monotonic decreases in both Young's modulus and fracture stress with increasing humidity.[2−5] Thus, water absorption by the materials decreases their mechanical stiffness and strength and restricts their use.

In contrast, certain biological materials such as hair, nail, skin, and bone exhibit excellent mechanical toughness, appropriate softness and extensibility, and increased mechanical modulus in the presence of water. For example, bone contains 20 wt % water and has an elastic modulus higher than 1 GPa, with an extensibility of up to 3% of strain. When bone loses water, it becomes weak and brittle.

However, the structure, properties, and behavior of water in synthetic materials and biomaterials have not been investigated in detail. What is the process of water incorporation? How does water behave in these materials and what is the effect of water on the mechanical properties? It is therefore important to clarify the behavior and nature of water incorporation into hydrophilic materials.

Osada and Gong et al. reported a novel method for synthesizing hydrogels with extremely high mechanical stiffness and strength.[6,7] The gel has a double-network structure composed of ionic and nonionic polymer networks (DN gels). These gels, containing 90% water in the swollen state, exhibit several tens of megapascals of fracture strength and more than 17 MPa of compressive strength; these values are almost equivalent to those of articular cartilage in the human body.

Because the major part of a DN gel consists of water, it is interesting to determine how the mechanical properties of DN gels are related to the amounts of water incorporated. Recently, Itagaki et al. observed a ductile-brittle transion of a DN gel containing above 30% water.[8] In this study, we prepared totally dry DN gels, placed them under different humidity atmospheres at room temperature, and studied the effects of water on the mechanical stiffness and strength. It was found that DN polymers equilibrated even under a relative humidity (RH) of 80% could sustain nearly the same Young's modulus as dry DN polymers, that is, more than 10^2 MPa. They showed a maximum Young's modulus and tensile stress at 30% RH.

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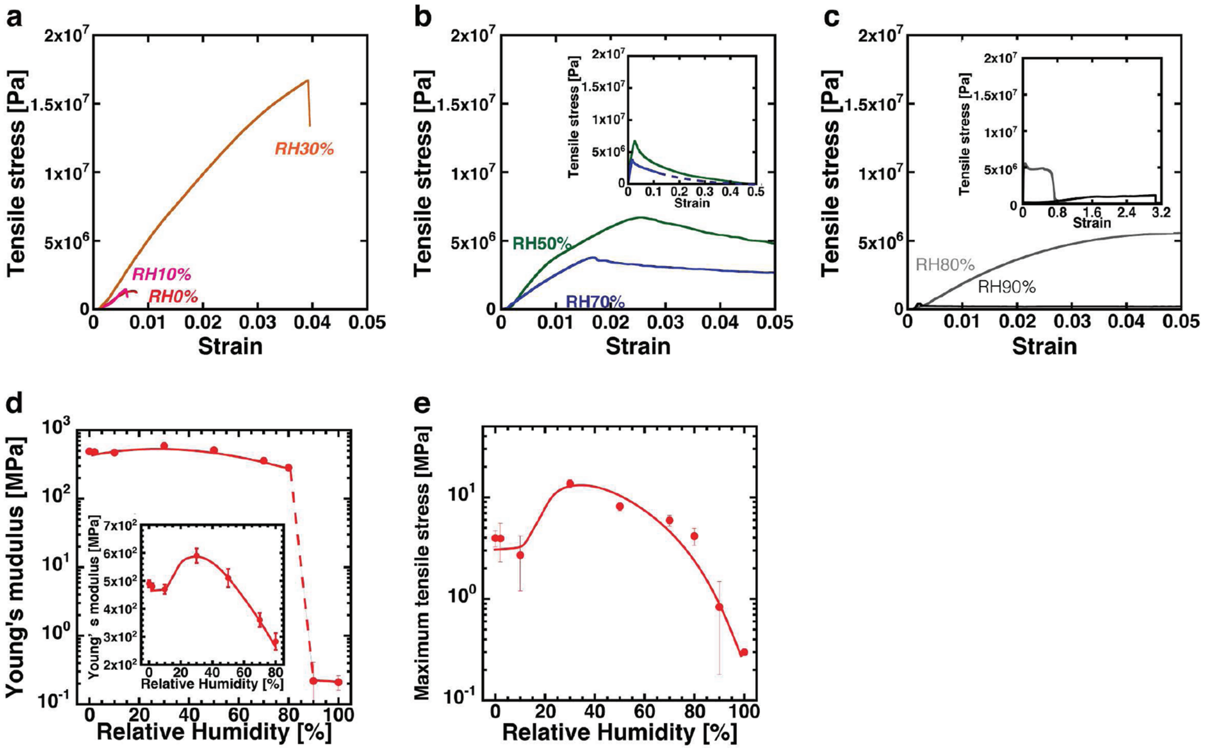

Figure 1. Stress−strain curves for freeze-dried double-network polymers under different relative humidities (RH); RH: (a) 0, 10, and 30%; (b) 50 and 70%; and (c) 80 and 90%; Young's modulus (d); and maximum tensile stress (e) as a function of RH. The tension tests were performed in a constant humidity flow chamber at room temperature. The elongation velocity is 10 mm min^{-1} as a function of the frequency.

Prior to studying the effects of moisture, we removed water from the DN gel by freeze-drying in vacuo, followed by prolonged extraction using dry acetone (see Supporting Information). This dry DN gel, hereafter called a DN polymer, is highly porous, with a density of 0.48 g cm^{-3} at RH 40%, and hazy white under 0−80% RH, but almost transparent at 90% RH or higher. It is important to note that a DN polymer remains stable under 80% of RH for at least 6 months. In contrast, individual dried polymer gels were instable against RH conditions used in this study.

Stress−strain curves of DN polymers stretched under various RHs are shown in Figure 1a−c. From the shape of the stress−strain curves, the stretching profiles are roughly classified into four types. Below 10% RH, the DN polymer is brittle and easily fractured under a strain of 0.01. Under 30% RH, substantial increases in both fracture stress and extensibility are obtained; fracture does not occur up to a strain of 0.04. From 50 to 80% RH, the DN polymer shows concave stress−strain curves with compliant fracture curves up to strains of 0.02−0.6. Under 90% RH, the DN polymer shows very low tensile stress with very high extensibility up to a strain of 3.0.

The dependence of Young's modulus, *E*, is shown in Figure 1d as a function of RH. *E* is maximum at 30% RH and decreases gradually with increasing humidity up to 80% RH (Figure 1d, inset). DN polymers equilibrated under 2, 10, 30, 50, 70, and 80% RH have almost the same high *E* values as that of the dry DN polymer, maintaining a value of more than 10^2 MPa, but *E* of a DN polymer under 90 and 100% RH is very low: only 0.2 MPa. When RH changes from 80 to 90%, Young's modulus of the DN polymer abruptly decreases by more than 3 orders of magnitude. The maximum tensile stress, which denotes the fracture stress *F*, is shown in Figure 1e as a function of RH. In this figure, one can see that *F* also has a maximum value at 30% RH and gradually decreases with increasing humidity.

It is striking that DN polymers can sustain almost the same high Young's modulus as that of a dry polymer, even under 80% RH. This is in strong contrast with the case for common hydrophilic materials. For example, the Young's modulus of peptidoglycan decreases from 2 to 0.05 GPa when the RH increases from 47 to 80.7%.[9] The Young's modulus of spider thread also decreases, from 13.7 to 1.4 GPa, when the RH increases from 25 to 80%.[10] This result might be interesting with regard to moisture-adjustable, antidew, and antielectrostatic functions, which could provide more human-friendly and comfortable materials.

Next, we obtained water sorption isotherms by measuring the weight increase of DN polymers equilibrated under different RHs and investigated the incorporation process and the role of water incorporated into DN polymers. As shown in Figure 2a, the water content increased gradually with increasing

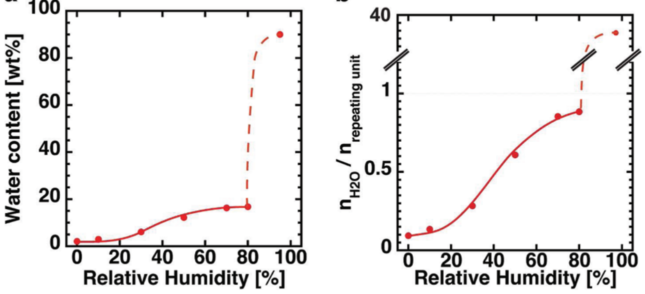

Figure 2. Water content (wt%; a) and $n_{H_2O}/n_{\text{repeating unit}}$ (b) as a function of RH.

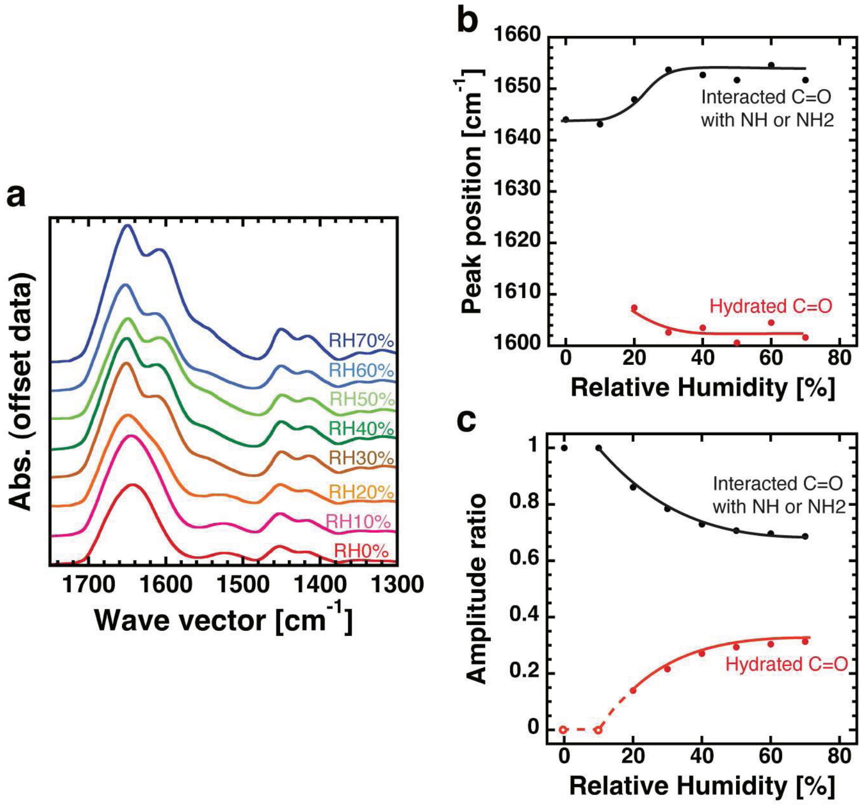

Figure 3. ATR-FTIR spectra of freeze-dried DN polymer at different RHs.

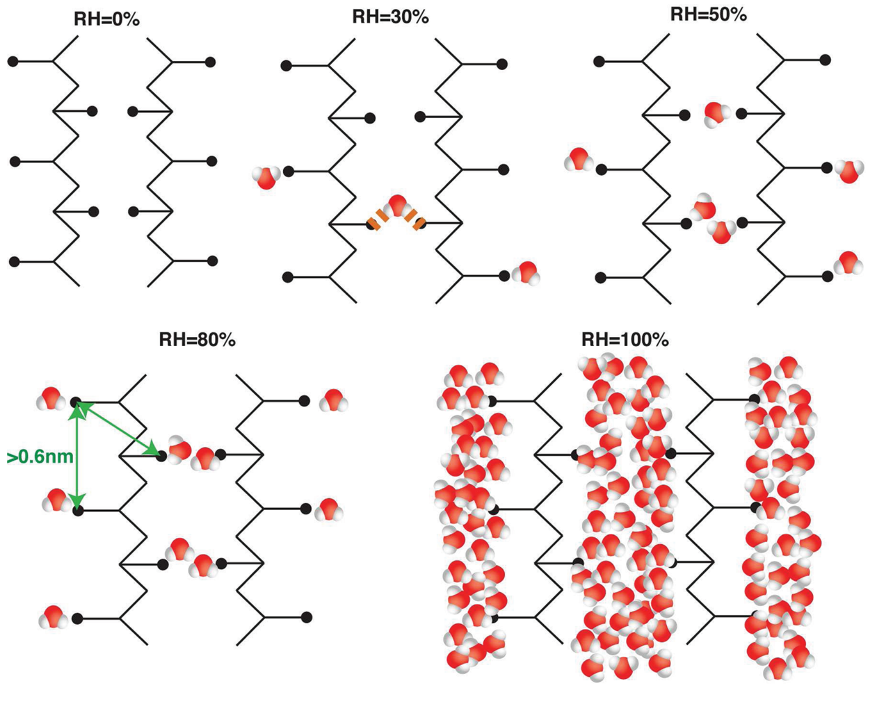

Figure 4. Schematic model of water incorporation.

RH and attained 17 at 80% RH. It is interesting that when RH exceeds 80%, the water content abruptly jumps from 17 to 90% and the DN polymer becomes a transparent hydrogel.

Based on this isotherm curves, $n_{H_2O}/n_{repeating\ unit}$, which is the molar ratio of water molecules incorporated in the network (n_{H_2O}) to the repeating units of the polymer network ($n_{repeating\ unit}$), was calculated and plotted against RH (Figure 2b). It is seen that $n_{H_2O}/n_{repeating\ unit}$ increases from 0.1 to 0.9 when RH increases from 0 to 80% with a sigmoidal shape. When the humidity increases from 80 to 90% RH, $n_{H_2O}/n_{repeating\ unit}$ abruptly increases from 0.9 to 39 and the Young's modulus abruptly drops by 3 orders of magnitude, as previously

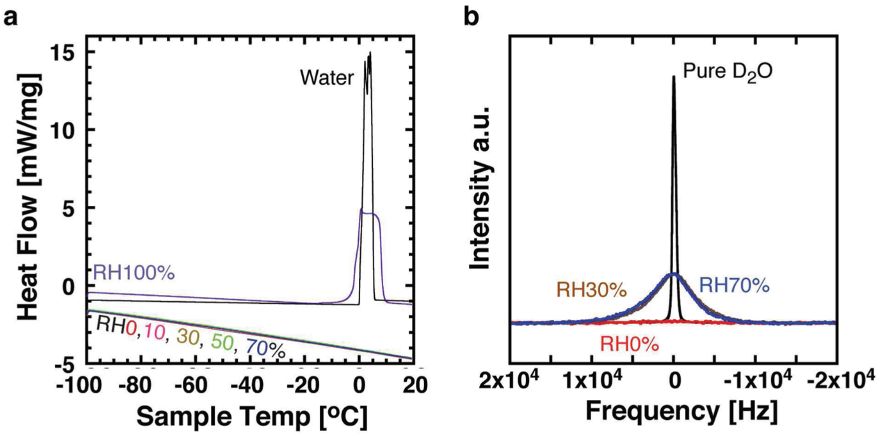

Figure 5. DSC curves of DN polymers equilibrated under various RHs (a) and deuterium solid-echo wide-line NMR spectra of freeze-dried DN polymers at RH 0% (red), 30% (orange), and 70% (blue) (b). Spectrum of water is also shown for reference.

described, transformation into a highly water-swollen "hydrogel" occurs. Because the transition from elastic to viscoelastic matter occurs at n_{H_2O}/n_{unit} = 0.9, this phenomenon could be associated with the stoichiometric incorporation of water molecules. This suggests that water absorption occurs via a one-by-one process with moderate acceleration. The sigmoidal curve in Figure 2 suggests that a self-accelerating process and the acceleration parameter (the Hill coefficient) was calculated as 3.8 from the slope.

The roles and behaviors of water incorporated under RH < 80% and RH > 80% are therefore quite different; in the range RH < 80%, water does not essentially decrease the mechanical performance of DN polymers and even improves them at RH = 30%. In the case of RH > 80%, water brings about an abrupt and substantial reduction in mechanical stiffness and strength.

Based on these experimental results, the process of water incorporation into DN polymers was elucidated. Below 30% RH, where the water content is less than 5 wt % or $n_{H_2O}/n_{unit} < 0.3$, water would be preferentially adsorbed to sulfonic and amide groups of the network because of their hydrophilic nature. At 30% RH, water may form bridges with hydrophilic groups through hydrogen bonds, which behave as cross-linkers. This may give a DN polymer increased extensibility and increased *E* and *F* values. The pronounced hydration of amide groups could be observed at 30% RH by attenuated total reflectance−Fourier transform infrared (ATR-FTIR) spectroscopy. It is known that the peak in an ATR-FTIR spectrum at around 1600−1650 cm^{-1} is assigned to stretching of amide carbonyls, and when carbonyls are water-hydrated, the peak is split to give a new peak at lower frequency.[11−13] As shown in Figure 3a−c, a new peak from hydrated carbonyls appears at around 1600 cm^{-1} for the DN polymer equilibrated under RH 30%, and the intensity increases with increasing humidity. At the same time, the absorption at around 1640 cm^{-1}, which is assigned to absorption between amides, shifts toward a higher frequency and its relative intensity decreases.

When the RH is further increased from 50 to 80%, where the water content is 10−17 wt % and n_{H_2O}/n_{unit} = 0.6−0.9, water behaves as a plasticizer and enables stretching up to a strain of 0.6−0.8. At RH 90%, water is abruptly incorporated by as much as 90 wt %, or n_{H_2O}/n_{unit} = 39, and the DN polymer is transformed into a fully swollen hydrogel, presumably forming continuous water layers in the network through a cooperative process. Water incorporation could therefore occur as shown schematically in Figure 4. Water molecules would be incorporated by occupying hydrophilic adsorption sites step-by-step until almost every site is occupied, that is, n_{H_2O}/n_{unit} = 0.9 or 80% RH. Because a hydrophilic moiety is located at every two carbon atoms, which are separated by about 0.6 nm (assuming the polymer chain is stretched with zigzag *trans* C−C bonds), the water molecules have enough space to occupy every adsorption site. Once water molecules occupy every adsorption site, the incorporated water would form a water network between the sites through hydrogen bonding to give a continuous water layer, inducing mass water introduction and transformation to the gel state. Because the energy difference between a hydrogen bond of water with itself and that with an amide group is not large,[14] hydration would occur abruptly, accompanied by formation of a hydration network between water molecules, and this drives the abrupt transition to the gel.

However, the absolute value of hydrogen bonding between a water molecule and an amide is large, of the order of 5 kcal mol^{-1}, so one can assume that the adsorption sites would bind water molecules strongly enough to restrict their mobility to give so-called "immobilized water" in some cases. We assume that the formation of water with restricted mobility might be why water molecules incorporated below 80% RH do not reduce the mechanical properties. To experimentally prove the presence of "immobilized water", differential scanning calorimetry (DSC) was performed (Figure 5a). When the temperature decreased, the DN polymer equilibrated at 100% RH exhibited a strong exothermal peak at around 0 °C. However, no peak can be seen at all in the cases of polymers equilibrated at 70% RH and lower. This is a well-established example of "nonfreezing water", which is another form of "immobilized water".[15]

We also attempted to determine the relaxation time of water using NMR. A DN polymer was swelled in D_2O and the relaxation spectra were measured using quadrupole solid-echo NMR. Figure 5b shows the wide-line deuterium NMR spectrum of a DN polymer after 5 h of soaking in D_2O gas. Because the hydration layers contribute to the inertia of the DN polymer, the lifetime of a water molecule near the hydrophilic polymer must be long compared with that of water as a solvent, and should give a wider peak.[15] Figure 5b shows that DN polymers soaked in D_2O give very wide D_2O peaks, indicating the presence of water with a very slow relaxation time, in contrast with the case of D_2O used as a solvent. The profile is different from that of crystalline water (ice),[16] but quite similar to the water strongly adsorbed in starch and protein.[17,18] In the case of protein, a monolayer of water molecules is formed around the protein with a binding enthalpy of about −15 kcal mol^{-1} and remains liquid with restricted rotation mobility even well below freezing temperatures, and subsequent layers bind progressively more weakly.[19]

On the basis of these reports, the DSC and NMR results suggest that a DN network contains water with a very slow relaxation time, with thermal fluctuations, resulting from strong binding large enough to overcome the entropy of ordering that determines the heat of fusion and restrict the mobility of the water. The specific nature of water under such conditions might be different from that of normal "liquid" water and does not reduce the high mechanical properties relative to those of dry polymers.

Polymer scientists have long been trying to make water-containing organic materials without reducing their mechanical stiffness and strength, because the presence of water in the materials makes them more comfortable when used. This might be the first example of an organic material that does not have reduced mechanical stiffness and strength, even when kept under 80% RH or when containing as much as 17 wt % water.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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