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Hydrogels with Hydrophobic Surfaces: Abnormally High Contact Angles for Water on PNIPA Nanocomposite Hydrogels

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Surface wettability is one of the most important properties of all materials, since it reflects the real structure and chemical composition at the outermost surface, and is a decisive factor in many properties such as biocompatibility, adhesion, lubricity, selective absorption and controlled release of molecules, etc. In the past decade, control of surface wettability of solid materials has been extensively studied, including superhydrophobicity showing high contact angle for water, by adopting various surface modifications[1−4] such as coatings of fluorinated compounds, deposition of metals, aligned carbon nanotubes, and fabricating topologically rough surfaces. As readily expected from their compositions, soft hydrogels, which consist largely of water and a hydrophilic polymer network, are naturally hydrophilic, and their surfaces generally show very low contact angles for water (θ_w). For example, hydrogels, made of synthetic or natural polymers, such as poly(vinyl alcohol), carboxymethyl cellulose, or agarose, all exhibit low values of θ_w (0−40°) in their swollen states. Also, widely used practical hydrogels, such as soft contact lenses, superabsorbent polymer hydrogels, and edible gelatin show similarly low values of θ_w.

In the present paper, we report extraordinarily high hydrophobicity, i.e., abnormally high values of θ_w, 100°−150°, observed at the surfaces of polymeric hydrogels consisting of hydrophilic constituents: poly(*N*-isopropylacrylamide) (PNIPA), hydrophilic clay, and large amounts of water. High values of θ_w are observed for hydrogels over broad ranges of water and clay contents. The origin of these high values of θ_w and their stability are discussed on the basis of gel composition and the surface structure at the gel−air interface.

To date, PNIPA hydrogels have been widely studied because of their well-defined stimuli sensitivities of gel volume, optical transmittance, drug release, etc., that arise from the coil-to-globule transition of PNIPA at its lower critical solution temperature (LCST) in aqueous media.[5] PNIPA hydrogels used in previous studies were all chemically cross-linked and prepared using an organic cross-linker (e.g., *N,N*′-methylenebis(acrylamide): BIS) or γ-radiation. It was known that these chemically cross-linked PNIPA hydrogels (abbreviated to N-OR gels) have limited applicability because of their poor mechanical properties (e.g., weak and fragile), structural heterogeneity (e.g., lack of transparency), and functional restrictions (e.g., slow and limited swelling and deswelling) due to the random and large numbers of cross-links. We recently succeeded in creating a novel nanocomposite-type hydrogel (abbreviated to NC gel) with a unique organic (polymer)/inorganic (clay) network structure.[6] It was found that NC gels exhibit excellent mechanical, optical, and swelling/deswelling properties, which could solve the most of the problems associated with OR gels by providing, for example, ultrahigh extensibility (in excess of 1000%), widely controlled moduli, strengths and high fracture energies (more than 3000 times that of OR gels), constant high transparency, and large swelling and rapid deswelling rates.[7] Furthermore, new phenomena, such as the first observation of the generation of a contractile force by changing the temperature across the LCST, unique sliding frictional behavior on gel surfaces, formation of a layered porous structure by freeze-drying, and total control of the coil-to-globule transition of PNIPA chain, cell cultivation on the surfaces of NC gels with specific compositions, and the subsequent detachment of cultivated cell sheets without treating with tripsin, were all realized using PNIPA-NC gels.[8]

PNIPA-NC gels (abbreviated to N-NC gels) used here were prepared in a similar manner to that reported previously,[7] i.e., by in-situ, free-radical polymerization of NIPA monomer in the presence of exfoliated clay (synthetic hectorite “Laponite XLG”) uniformly dispersed in aqueous media. N-NC gel films of 2 mm thickness were prepared at 20 °C in a laboratory-made molding apparatus made from poly(methyl methacrylate) substrates. Conventional PNIPA-OR gels (N-OR gels) and viscous solutions of linear PNIPA (N-LR) were also prepared using the same procedure, with and without organic cross-linker (BIS), instead of clay. The sample codes for NC*n* and OR*n*′ gels are defined by the concentration of each cross-linker, i.e., $n \times 10^{-2}$ mol of clay/1 L of H_2O and $n' \times 10^{-2}$ mol of BIS relative to NIPA, respectively. The cross-linker contents (C_{clay} or C_{BIS}) were varied widely, NC2 to NC10 for C_{clay} and OR1 to OR5 for C_{BIS}. Water contents ($C_{H_2O} = W_{water}/W_{dry} \times 100$ (wt %)) were also varied over a wide range, 100−1000 wt %, by subsequent swelling, deswelling, or drying. Values of θ_w were measured by depositing a drop of water (8 μL) under atmospheric conditions (23 °C, 50% RH). Also, the surface contact angle for air (θ_a) in water was also measured. The protocol for θ_w and θ_a measurements were carefully controlled, as described in the Supporting Information. A laser scanning conforcal microscope (LSCM) (1LM15, LaserTec Corp., Japan) was used to observe the surface microstructure and to calculate the surface roughness. Confocal illumination was provided by a red HeNe laser (632.8 nm excitation). The gel surface roughness was observed for as-prepared N-NC6 gel with water content 630 wt %.

Sessile-drop contact angles (θ_w) measured at the surfaces of N-NC6 gels are shown in Figure 1. It was found that N-NC6 gel containing $C_{H_2O} = 630$ wt % (as-prepared) shows a θ_w of 128° (Figure 1b), which indicates a distinctly hydrophobic surface for the N-NC6 gel despite the hydrophilic nature of all of its constituents (water, PNIPA below its LCST, and clay). Also, by altering C_{H_2O} from 100 to 1000 wt %, it was observed that the surface of N-NC6 gel remains hydrophobic, showing θ_w greater than 100°, and that θ_w exhibits a maximum of 151° (Figure 1c), at 210 wt % of C_{H_2O}. Thus, N-NC gels exhibit abnormally high θ_w at a temperature where PNIPA is normally hydrophilic. The remarkable hydrophobicity observed at the

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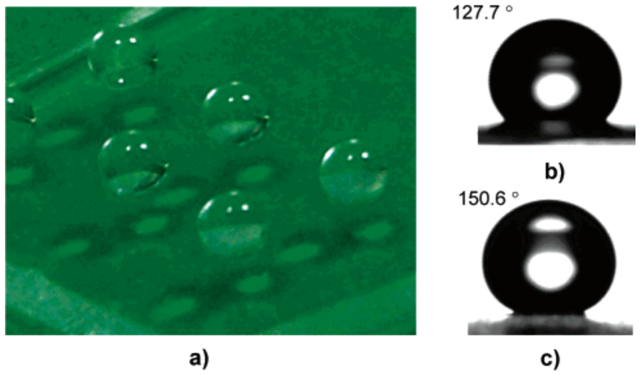

Figure 1. (a) Water droplets on N-NC6 gel film. (b, c) Values of the water contact angles for sessile drops on the surfaces of N-NC6 gels with water contents of (b) 630 wt % and (c) 210 wt %.

surfaces of N-NC6 gels is totally distinct from that of conventional polymeric hydrogels described above (0 ~ 40°) and is comparable to or higher than that of typical hydrophobic solid polymers such as polytetrafluoroethylene (PTFE: $\theta_w = 110°$) and polypropylene (PP: $\theta_w = 85°$).

As previously reported,[6,7] NC gels, as a whole, can swell extensively in water. So, it was initially expected that water from the droplet used for measuring contact angles might be absorbed into NC gels over time, regardless of the initial θ_w, which is a totally different situation from that of solid substrates. However, in the present study, the local penetration of water into NC gel for swelling through the tiny surface area underneath the droplet was very limited. Also, such local swelling, i.e., expansion of a defined small volume of network, requires energy to deform the surrounding network (compression) or to swell the network itself (expand upward). The fact that, in an NC gel, a unified polymer network should deform locally to allow local absorption is totally different from a spongelike material which contains enough vacant space to allow water absorption. Thus, absorption of water from the droplet into an NC gel can only occur to a limited extent and at very slow rate, although the rate depends on the diffusion coefficient, defined as the ratio of the osmotic bulk modulus of the network, and the frictional coefficient between the network and water.[9] Consequently, it is expected that the form of a droplet (determined by θ_w) deposited on the surface of an NC gel can reflect its wettability and is quite stable with elapsed time.

The stability of θ_w at the surfaces of N-NC gels was examined by continuous measurement of θ_w of a single drop for 600 s. The results (the time dependencies of θ_w) are summarized in Figure 2. Although θ_w changed slightly with the elapsed time, depending on the C_{H_2O}, the overall tendency to show high hydrophobicity ($\theta_w > 100°$) was upheld throughout the period of measurement, regardless of C_{H_2O}. In detail, the gradual decrease of θ_w, commonly observed for all samples, could be attributed to the evaporation of water from the droplet because a similar change (decrease) of θ_w was also observed at the surface of PTFE (open circles in Figure 2). Also, the change of θ_w is almost consistent with the result calculated by assuming the simple evaporation of a droplet of water (which means no penetration into NC gel in the present study) under the conditions of a constant solid−liquid contact area.[10] The fairly large decrease in θ_w, observed in the early stages for N-NC6 gel, may be due to some local change of surface structure or local swelling caused by deposition of a water droplet. We also examined the effect of clay content (NC2 to NC10) on θ_w. Then, it was found that all N-NC gels showed high θ_w (>100°) with a slight dependence on C_{clay}.

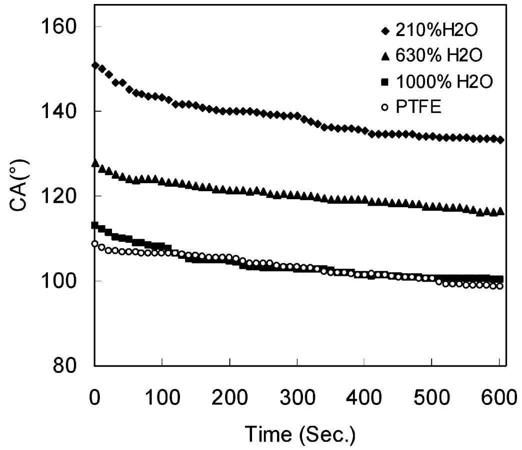

Figure 2. Time dependencies of the surface contact angle of water (θ_w) on N-NC6 gels with different water contents, $C_{H_2O} = 210$, 630, and 1000 wt %. Open circles indicate changes in θ_w for PTFE.

To explain the origin of high values of θ_w observed for N-NC gels, we consider that the following four factors could play important roles. One is "the amphiphilic nature of PNIPA chains". It is well-known that PNIPA shows a well-defined, coil-to-globule transition in water at the LCST (≈32 °C),[5] and so PNIPA hydrogel (N-OR gel) exhibits a temperature-modulated amphiphilicity, i.e., hydrophilic (swollen) below the LCST and hydrophobic (collapsed) above the LCST. Actually, in regard to the contact angles for water of N-OR gels, there are many reports of changes of surface from hydrophilic (below the LCST) to hydrophobic (above the LCST), mostly by using dynamic contact angle measurements.[11] However, the results for N-NC gels in the present study indicate that PNIPA is not perfectly hydrophilic but exhibits amphiphilicity at temperatures even below the LCST, probably because of the *N*-isopropyl groups in the side chains. The isopropyl groups may align at the gel−air interface, similar to the alignment of amphiphilic polymers or surfactants with alkyl groups at water−air interfaces, thereby causing the remarkable hydrophobicity at the surfaces of N-NC gels. The necessity for specific side groups to cause high values of θ_w for NC gels is confirmed by the observation that another type of NC gel (D-NC gels), consisting of poly(*N*,*N*-dimethylacrylamide) with two methyl groups, showed low θ_w (58°). The low θ_w of D-NC gels was almost independent of both clay and water contents.

The second factor is "network structure". It was observed that θ_w of N-OR gels is, on the whole, lower than that of N-NC gels, although N-OR gels also exhibit quite high θ_w (80°−90°), as shown in Figure 3a-1 (for N-OR1 gel), compared with the other types of OR gels such as D-OR gels ($\theta_w = 20°−40°$). Thus, formation of an organic (PNIPA)/inorganic (clay) network structure is considered to increase θ_w. Here, it should be noted that, in terms of composition, N-NC and N-OR gels only differ in the kind of cross-linker used (clay or BIS, respectively). However, the clay itself is hydrophilic and can be swollen in water at a molecular level. In fact, as shown in Figure 3a-3, clay gels, consisting of exfoliated clay and water, show very low θ_w (10°−15°) over the whole range of C_{clay} used for N-NC gels. So, it is deduced that simple incorporation of exfoliated clay into polymeric network should not increase θ_w, but, instead, may actually decrease it. Therefore, the high θ_w of N-NC gels cannot be attributed to the mere existence of clay in the network but is attributed to the characteristic network structure of PNIPA cross-links between clay platelets, i.e., lightly cross-linked PNIPA chains with flexible conformations which enable *N*-isopropyl groups to rotate and enrich on the top surface layer

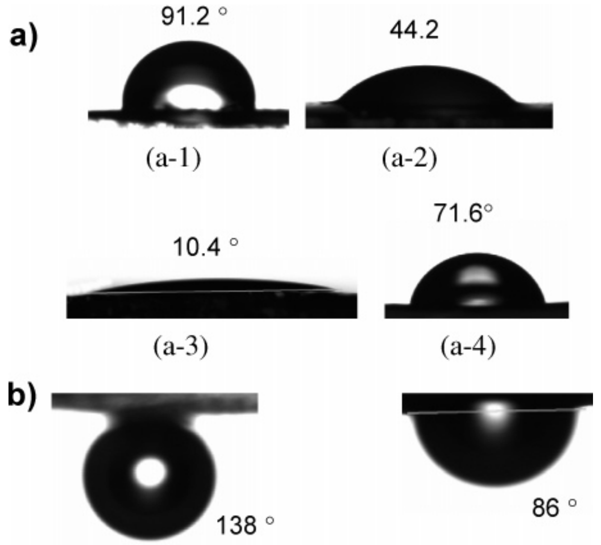

Figure 3. (a) Values of the water contact angles for sessile drops on various surfaces: (a-1) N-OR1 gel at 3 s; (a-2) N-OR1 gel at 600 s; (a-3) clay gels with $C_{\text{clay}} = 6 \times 10^{-2}$ mol/L H_2O; and (a-4) N-LR. (b) Surface contact angle to air for samples immersed in water: (b-1) N-NC6 gel, (b-2) PTFE.

of the gel under air. On the other hand, linear PNIPA solution (N-LR), at the same polymer concentration, which is actually a viscous gel-like material due to the presence of quasi-cross-links created by physical entanglements, also shows low θ_w (72°: Figure 3a-4) compared with that of N-NC gel. This indicates that free, flexible PNIPA chains with only entanglements cannot achieve high θ_w. Thus, it was concluded, by comparing values of θ_w for N-NC gels, N-OR gels, and N-LR, that organic (PNIPA)/inorganic (clay) networks only can realize values of θ_w greater than 100°, probably by enabling the effective alignment of *N*-isopropyl groups at the gel−air interface. Further, in the case of N-OR gels, it was observed that θ_w decreased quite rapidly during the measurement and decreased to 20°−50° (Figure 3a-2) for all N-OR gels, with different C_{BIS}, over several minutes. This may be the reason why quite low and different values of θ_w were previously reported for N-OR gels.

The third factor is "water content ($C_{H_2O} = W_{H_2O}/W_{\text{dry}}$)". It was observed that N-NC gels exhibit quite a strong dependence of θ_w on C_{H_2O}. In the case of N-NC6 gels, by altering the C_{H_2O} from 100 to 1000 wt %, θ_w was maximum (151°; Figure 1b) at 210 wt %. This abnormally high value of θ_w has never previously been observed for hydrogels. With increasing or decreasing C_{H_2O}, θ_w of N-NC6 gel decreased. However, it is interesting that θ_w gradually decreased with increasing C_{H_2O} and that a high θ_w of 113° was observed even for a swollen N-NC6 gel with 1000 wt % C_{H_2O}.

The fourth factor is surface geometry. A rough surface is known to be effective in producing ultrahigh values of θ_w,[1−4] as described by the Cassie−Baxter model.[12] In the present study, however, it was observed by optical microscopy (magnification ×1000) that as-prepared N-NC gels have flat surfaces (Figure 4a) equal to that of the molding apparatus. This is consistent with the fact that NC gels can generally duplicate any template roughness on a micrometer scale. On the other hand, as shown in the LSCM images of the surface microstructure (Figure 4b), N-NC6 gel shows surface roughness on a nanometer scale. From the 2D surface profile (Figure 4c), the root-mean-square roughness (R_q) and mean roughness depth (R_z) was found to be 16 nm and 114 nm, respectively. Therefore, it is concluded that the abnormally high contact angles on the surface of N-NC gels are derived from the combined effects of the four factors, i.e., the amphiphilicity of PNIPA, the unique network structure, an adequate water content, and the surface roughness. Since it has been reported that, on a flat solid surface, there is an upper limit of 119° for dynamic θ_w,[13] we will clarify the precise contribution of each factor on high θ_w of N-NC gels in more detail, by using the other techniques such as atomic force microscopy, environmental scanning electronic microsopy, and sum-frequency spectroscopy in addition to LSCM.

Thus, abnormally high values of θ_w were observed on the surfaces of N-NC gels which, as a whole, are hydrophilic materials. Then, the hydrophobicity of N-NC gels may naturally exhibit different behaviors from those of normal hydrophobic surfaces. Figure 3b shows the surface contact angle toward air (θ_a), measured by depositing an air bubble under the substrate (N-NC6 gel and PTFE) placed in water. Although both samples showed distinct hydrophobicity ($\theta_w = 128°, 110°$) in air, N-NC6

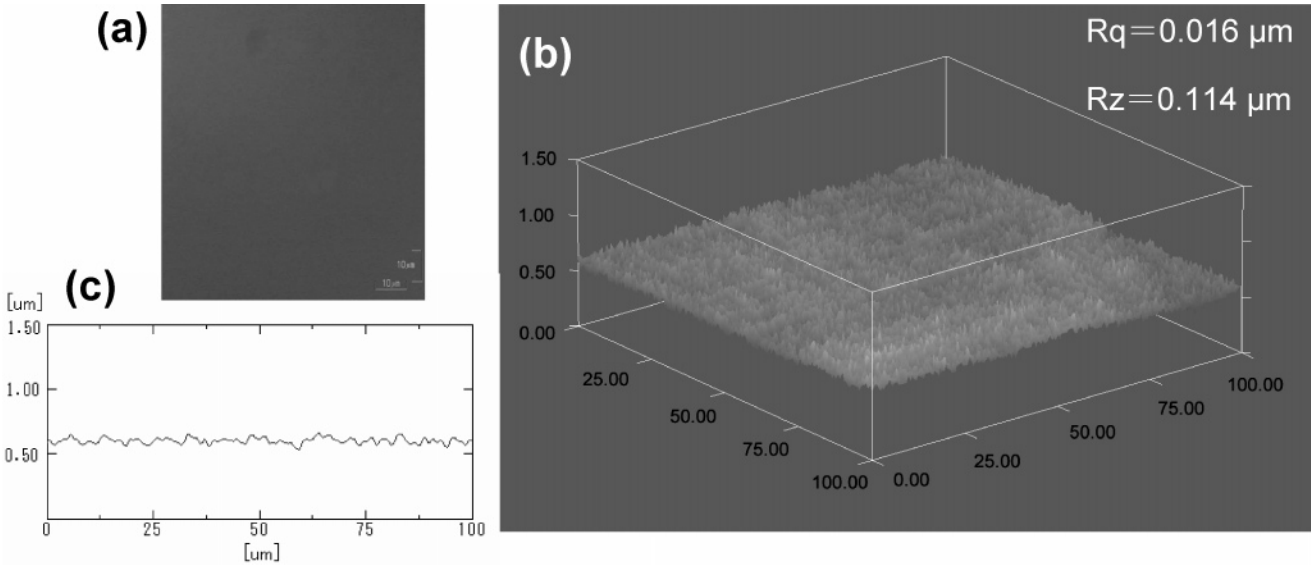

Figure 4. Surface of N-NC6 gel with water content 630 wt %. (a) Optical micrographs (×1000). Scale bar is 10 μm. (b) LSCM topographical image. The scales for the *x*, *y*, and *z* coordinates are 0−100, 0−100, and 0−1.5 μm, respectively. (c) Surface profiles from LSCM. R_q and R_z are the root-mean-square roughness and mean roughness depth.

gel and PTFE exhibited different values of θ_a in water, 138° (Figure 3b-1) and 86° (Figure 3b-2), respectively, which indicates that, in water, a completely hydrophilic surface for N-NC6 gel and unchanged hydrophobic one for PTFE are observed. This is also supported by the high total (266°) of the values of θ_w and θ_a for an N-NC6 gel which is very far from that of ideal value (180°) if the nature of the surface was the same for both measurements, as is the case for PTFE. This indicates the disruption of the alignment of isopropyl groups on changing from a gel−air to a gel−water interface. Also, it was found that the hydrophobicity of N-NC6 gel can be recovered by returning the sample to an atmospheric environment.

In conclusion, extraordinarily high hydrophobicity was observed on the surfaces of PNIPA nanocomposite hydrogels (N-NC gels). Values of θ_w observed were generally greater than 100° over broad ranges of clay and water contents of N-NC gels and showed a maximum 151° for N-NC6 gel with $C_{H_2O} = 210$ wt %. The high hydrophobicity of N-NC gels may be caused by the effective alignment of *N*-isopropyl groups of PNIPA chain at the gel−air interface and is enhanced by the other factors, such as network structure, water content, and topological roughness. The surface of N-NC gels exhibit hydrophobic-to-hydrophilic changes by changing the circumstance from dry (in air) to wet (in water), and vice versa. We believe that these findings are very useful in clarifying the real surface structure of stimulus-sensitive PNIPA hydrogels and in designing the surface properties of hydrogels in their many potential applications.

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Supporting Information Available: Details of sample preparation and contact angle measurements in air and water. This material is available free of charge via the Internet at http://pubs.acs.org.

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