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Hydrophobic Surface Characteristics of Nanocomposite Hydrogels

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Summary: The surface of nanocomposite hydrogels (NC gels), consisting of poly(*N*-isopropylacylamide) (PNIPA), exfoliated clay (hectorite) and a large amount of water, showed an extraordinarily high contact angle for water (θ_w) at ambient temperature, despite the fact that all of its constituents are hydrophilic under this condition. The θ_w value varied within the range $100^\circ \sim 150^\circ$, depending on composition, i.e. the water content and the clay concentration. High θ_w values were stable in short-term measurements ($\leq$ 10 s), but during long-term measurements ($\sim$ 20 min), they underwent unique changes which strongly depended on the clay concentration (i.e. the network density). The unusually high hydrophobicity was only observed in PNIPA-based NC gels and was attributed to the alignment of the *N*-isopropyl groups at the gel-air interface. Also, the hydrophobic surface of the NC gel changed to hydrophilic when the gel came into contact with water and rapidly reverted to hydrophobic on subsequent drying. Furthermore, it was found that the high θ_w values of the PNIPA-NC gel were hardly affected by modifications of the network through copolymerization with or interpenetration of a hydrophilic polymer. The adsorption of a hydrophilic (cationic) dye also hardly affected the high θ_w value.

Keywords: clay; contact angle; hydrogel; hydrophobicity; nanocomposite

Introduction

It is well-known that polymeric hydrogels are transparent, soft and wet materials, exhibiting many outstanding characteristics which are distinct from those of solid materials. However, conventional polymeric hydrogels prepared using an organic cross-linker (abbreviation: "OR gels") have shown serious disadvantages in terms of their mechanical, structural and absorption properties, due to their chemically cross-linked structure. Recently, by creating a new type of polymeric hydrogel (nanocomposite gel, or NC gel) based on a unique organic (polymer)/inorganic (clay) combination, all of the mechanical and functional disadvantages of OR gels have been overcome simultaneously.[1–3] Furthermore, NC gels have been shown to have many new functions, such as the generation of reversible force,[4] the formation of unique porous morphologies,[5] characteristic sliding frictional behavior,[6] control over the coil-to-globule transition,[7] cell culture and subsequent detachment of the cells,[8] and abnormally high contact angles for water (θ_w).[9,10]

The last property, the high θ_w value, was observed on the surface of a specific NC gel consisting of poly(*N*-isopropylacrylamide) (PNIPA) and clay. This was somewhat astonishing, since all the constituents of the PNIPA-based NC gel (water, PNIPA below its transition temperature, and clay) individually show hydrophilicity under the same conditions. In the present paper, the extraordinarily high hydrophobicity and its changes observed at the surface of PNIPA-based gel are summarized. Also, the effects

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of network modification and the adsorption of hydrophilic molecules on θ_w are reported.

Experimental Part

Synthesis of NC Gels

The NC gels used in this study were prepared in a manner similar to that reported previously,[3,11] i.e. by the *in-situ*, free-radical polymerization of a monomer, e.g. *N*-isopropylacrylamide (NIPA) or *N,N*-dimethylacrylamide (DMAA) in the presence of exfoliated clay (synthetic hectorite "Laponite XLG") uniformly dispersed in an aqueous medium. NC gel films with a thickness of 2 mm and a cuboid shape (10 mm × 10 mm × 40 mm) were prepared at 20 °C in a laboratory-made molding apparatus. Conventional chemically cross-linked hydrogels (OR gels) and viscous aqueous solutions of linear polymer (LR) were also prepared using the same procedure, with and without an organic cross-linker, methylene bisacrylamide (BIS), instead of clay. The sample codes for the P-NC*n* and P-OR*n'* gels and P-LR were established according to the monomer (P = N for NIPA, P = D for DMAA) and the concentration of each cross-linker, i.e. $n \times 10^{-2}$ mol of clay / 1 L of H_2O ($= C_{clay}$) and $n' \times 10^{-2}$ mol of BIS relative to NIPA ($= C_{BIS}$), respectively. The monomer content was fixed at 1 M for all samples. The water content ($R_{H2O} = W_{water} / W_{dry} \times 100$ (wt %)) was varied over a wide range (0 to 1,500 wt %) by swelling, de-swelling or drying, followed by subsequent storage in tightly-closed glass vessels for more than 4 days in order to achieve a uniform distribution of water throughout the sample.

The copolymerized N-NC6 gels (N-NC6-Co gels) were synthesized using two monomers, NIPA and *N,N*-dimethylaminopropylacrylamide (DMAPAA) with a different side chain. DMAPAA at a concentration of 5 or 10 mol % against NIPA was used and the total monomer concentration of the initial solution was fixed at 1 M.

An N-NC3 gel with a semi-interpenetrating (s-IP) organic/inorganic network (s-IP-N-NC3-G50 gel) was prepared in a similar manner as the N-NC3 gel, except that gelatin was used as the co-existing polymer in the initial reaction solution. Gelatin at a concentration of 50 wt % was used against 1 M NIPA. N-NC3 gel with an interpenetrating (IP) organic/inorganic network (IP-N-NC3-G50 gel) was prepared by subsequent cross-linking of the gelatin in the s-IP-N-NC3-G50 gel with glutaraldehyde.

The adsorption of a hydrophilic cationic dye, methylene blue (MB), on the surface of the N-NC gel was carried out by immersing the N-NC6 gel into aqueous solutions of MB with concentrations of 0.05 mM and 5 mM for 10 seconds, followed by washing of the gel surface with pure water for 10 seconds.

Measurements

The θ_w values were measured by depositing a droplet of water (8 μL) under atmospheric conditions (23 °C, 50% RH). A laser-scanning confocal microscope (LSCM) (1LM15, LaserTec Corp., Japan) was used to observe the surface microstructure and calculate the surface roughness, average roughness (R_a) and mean roughness depth (R_z).

Results and Discussion

High Hydrophobicity of the N-NC Gel Surface

As reported in the previous papers,[9,10] polymeric hydrogels and hydrogel-like materials containing a large amount of water generally exhibit low θ_w values (e.g. $0° \sim 40°$), as can be anticipated from their compositions. Low θ_w values were also observed on newly created cross-sectional surfaces, which should reflect their internal structures. Concerning NC gels, low θ_w values ($\sim 40°$) have likewise been observed for PDMAA-based NC gels (D-NC gel). However, it was found that PNIPA-based NC gels (N-NC gel) had an extraordinarily high hydrophobicity, i.e. abnormally high θ_w values within the range of $100^\circ \sim 150^\circ$, under the same conditions.[9]

Figure 1 shows an N-NC6 gel film ($R_{H2O} = 210$ wt %) and sessile-drop contact angles (θ_w) measured at the surface of N-NC6 gels with different water contents. It was found that the N-NC6 gel with $R_{H2O} = 630$ wt% (as-prepared state) had a θ_w of 128° (Figure 1b), which indicates a distinctly hydrophobic surface despite the hydrophilic nature of all of its constituents. Also, when altering R_{H2O} from 100 to 1,500 wt %, it was observed that the surface of the N-NC6 gel remained hydrophobic, with a θ_w value greater than 100°, and that θ_w exhibited a maximum of 151° (Figure 1c) at 210 wt% of R_{H2O}. Thus, N-NC gels exhibited high θ_w values at a temperature where PNIPA is normally hydrophilic, i.e. below the coil-to-globule transition temperature. The unusually high hydrophobicity observed at the surface of N-NC gels is a characteristic totally distinct from that of the conventional polymeric hydrogels described above ($\theta_w = 0^\circ \sim 40^\circ$), and is comparable to or higher than that of typical hydrophobic solid polymers such as polytetrafluoroethylene ($\theta_w = 110^\circ$) and polypropylene ($\theta_w = 85^\circ$).

The high θ_w of N-NC gels was studied in detail for newly created cross-sectional surfaces produced by cutting immediately prior to the measurement.[10] The following significant facts were established.

Effect of Drying of the NC Gel Surface

The effect of gradually drying an NC gel on θ_w was checked by measuring θ_w at different positions on the same sample (kept on the apparatus stage under atmospheric conditions) at 5-min intervals over a period of 30 min. It was found that the NC gels exhibited quite stable and characteristically

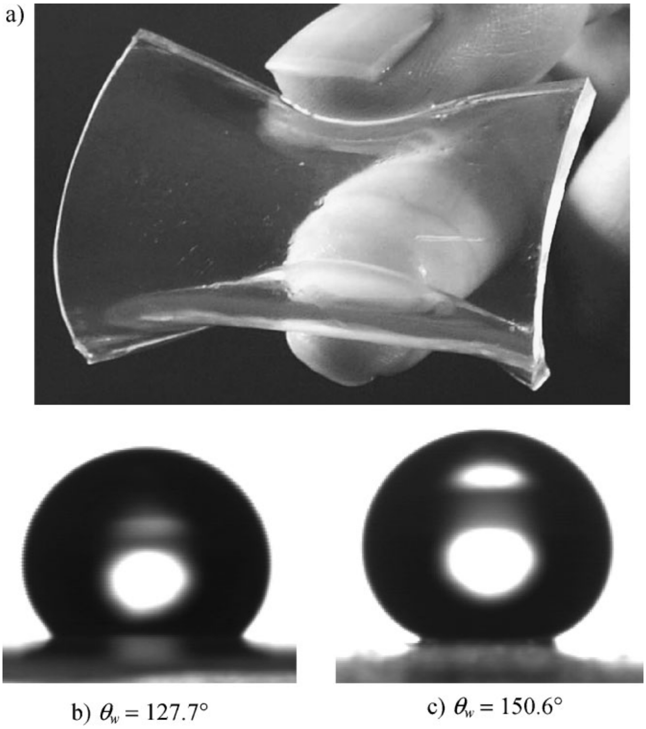


Figure 1.
(a) N-NC6 gel with $R_{H2O} = 210$ wt %. (b) θ_w values for sessile drops on the surface of N-NC6 gels with an R_{H2O} of (b)630 wt % and (c) 210 wt %.

high or low values of θ_w, depending on the kind of NC gel, i.e. high θ_w ($112^\circ \sim 120^\circ$) for N-NC5 gel and low θ_w ($44^\circ \sim 48^\circ$) for the D-NC5 gel. This indicates that the surface structure of the NC gels hardly changed while drying slowly, probably due to the continuous movement of water from the interior of the gel to the outer surface.

Effect of the Clay Content

The clay concentration (C_{clay}) of the NC gels was varied from NC0.5 to NC20, which greatly changed their mechanical and swelling properties. N-NC gels with different C_{clay} values fell into two groups (I and II) according to their θ_w, as shown in Figure 2. N-NC gels with $C_{clay} \geq 3 \times 10^{-2}$ mol / L-H_2O exhibited high θ_w, $110^\circ \sim 116^\circ$ (group II), which varied little with C_{clay} in the range NC3 ~ NC20. In contrast, for N-NC gels with a lower C_{clay} value (group I), θ_w decreased sharply with decreasing C_{clay}, and approached 70° when C_{clay} was close to zero. This is consistent with the result (=71.6°) for the original surface of a viscous gel-like linear PNIPA solution (N-LR) with the same polymer concentration. In contrast, D-NC gels exhibited much lower θ_w values ($36^\circ \sim 50^\circ$) over the whole range of C_{clay} (Figure 2). The clay gel, consisting of a ''house-of-cards'' structure, exhibited very low θ_w values ($8^\circ \sim 15^\circ$) over the whole range of C_{clay}.

Effect of the Water Content

The θ_w value for N-NC gels was strongly dependent on the water content (R_{H2O}), as shown in Figure 3, and N-NC gels with different R_{H2O} values also fell into two groups (I' and II') according to their θ_w. From $R_{H2O} = 0$ wt % (dried gel) to about 200 wt %, θ_w increased steeply with increasing R_{H2O}, and, after reaching a maximum, it gradually decreased with further increasing R_{H2O}. Since the tendency for θ_w to decrease was small, θ_w still exhibited a value of 100° even for a swollen N-NC5 gel with 1,500 wt % R_{H2O}, in which 94 vol % of the total gel was water. On the other hand, D-NC5 gels exhibited a quite different dependence of θ_w on R_{H2O}, as also shown in Figure 3. Unlike N-NC5 gels, most D-NC5 gels exhibited low θ_w values (~40°) regardless of R_{H2O}, except at very low R_{H2O} values. Thus, the variations in θ_w with R_{H2O} for the two kinds of NC gels (N-NC5 and D-NC5 gel), which consisted of different polymers (PNIPA and PDMAA) and the same inorganic clay, were entirely different.

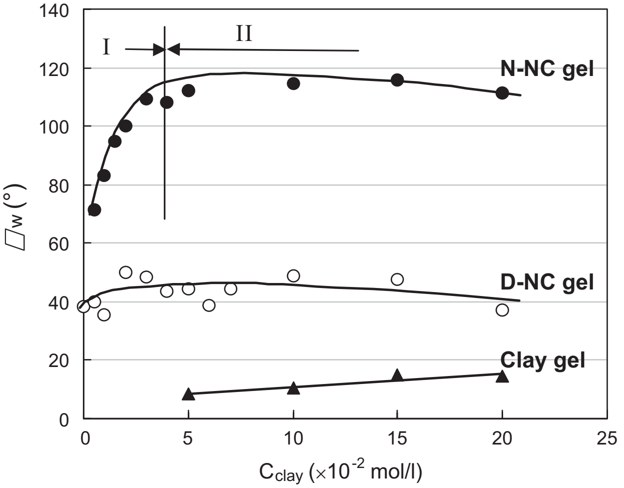


Figure 2.

Effects of C_{clay} on θ_w for various hydrogels (cross section). N-NC gels (●), D-NC gels (○) and clay gels (▲). The θ_w values for N-NC gels fall into two regions, I and II, according to their dependence on C_{clay}.

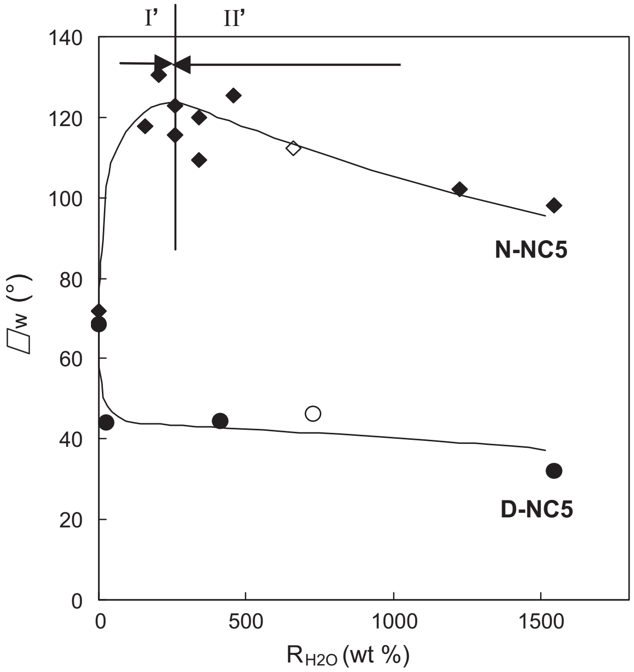


Figure 3.
Effects of R_{H2O} on θ_w for N-NC5 (◆) and D-NC5 (●) gels. ◇ and ○ correspond to as-prepared gels (cross section). The θ_w values for N-NC5 gels fall into two regions, I' and II', according to their dependence on R_{H2O}.

Stability of the Contact Angle

The stability of θ_w at the cross-sectional surface of N-NC gels was examined by the continuous measurement of the θ_w value of a single droplet of water (Figure 4).[10] In short-term measurements ($\leq$ 10 seconds), the NC gels exhibited stable values of θ_w. However, during long-term measurements ($\sim$ 20 min), two different tendencies were observed. One was the gradual decrease of

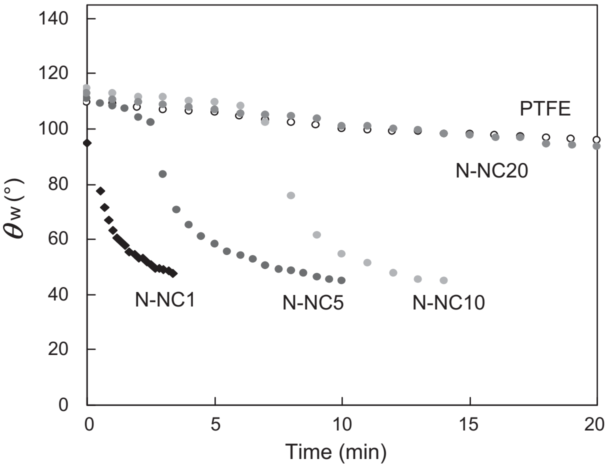


Figure 4.
Time dependence of θ_w for various N-NC gels (cross section) with different C_{clay} values, from NC1 to NC20, and a hydrophobic PTFE substrate.

θ_w, and the other was an abrupt drop after a certain elapsed time. The gradual decrease of θ_w, commonly observed for all samples, could be attributed to the evaporation of water from the droplet, because the same change (decrease) of θ_w was also observed at the surface of PTFE (open circles in Figure 4). On the other hand, the abrupt drop in θ_w was related to some kind of change in the initial structure at the gel-air interface, probably due to the localized swelling of the hydrogel, i.e. the absorption of water from the droplet into the hydrogel. These changes varied strongly depending on C_{clay}. For the N-NC1 gel, θ_w decreased sharply almost from the start, whereas for the N-NC20 gel, only a gradual decrease was observed throughout the measurement. For the N-NC gels with an intermediate C_{clay} value, e.g. the N-NC10 gel, both a gradual decrease and a subsequent abrupt drop in θ_w were clearly observed. From the analysis of the volume and the contact length of the droplet, it was concluded that a little water was absorbed from the droplet into the N-NC gels depending on the C_{clay}, and that, after a certain time, the droplet abruptly spread over the N-NC gel surface. This behavior was most clearly observed for the N-NC gels with intermediate C_{clay} values.

On the other hand, the changes in θ_w on alternating the environment between wet and in-air were also examined on a freshly exposed N-NC5 gel surface.[10] When the gel was wet, θ_w was zero, probably because a very thin layer of free water covered the NC gel surface. Then, as the surface gradually dried (i.e. the surplus water on the surface evaporated) under atmospheric conditions, it was observed that θ_w increased sharply from zero to more than 100°, which indicates that the gel surface rapidly became hydrophobic. Again, on subsequent wetting, θ_w suddenly dropped to zero. The change in θ_w between zero and more than 100° was highly reproducible.

Mechanism of High Hydrophobicity

In an attempt to understand the mechanism that produces high θ_w values for the N-NC gel, we considered the following four factors:[9] (i) the characteristic amphiphilic nature of PNIPA chains, (ii) the unique organic (PNIPA) / inorganic (clay) network structure, (iii) the water content, and (iv) the surface geometry. Their importance was evaluated by comparing the θ_w values measured on newly created cross-sectional surfaces of N-NC, D-NC, N-OR, D-OR and N-LR gels.[10]

Among these five hydrogels, the N-NC gel specifically exhibited high θ_w values. Since all constituents of the N-NC gels (PNIPA, clay and water) individually showed low θ_w values in aqueous media (70°, 10° and 0°, respectively), the high θ_w values of the N-NC gels could not be derived by simply adding together the contribution from each constituent. By comparing the θ_w values of the N-OR gels, it was estimated that organic (PNIPA) / inorganic (clay) networks play an important role in realizing values of θ_w greater than 100°. Consequently, we assumed that the high θ_w values were the result of the formation of a thin hydrophobic layer consisting of aligned *N*-isopropyl groups at the gel-air interface of the PNIPA/clay network. Furthermore, to enhance the effective alignment of the *N*-isopropyl groups, the N-NC gel should have an adequate water content, as shown in Figure 3.

In general, the surface geometry has been considered to be one of the most effective factors of ultra-high or ultra-low θ_w values, as described by the Cassie-Baxter Equation or the Wenzel equation,[12] and has, in fact, been utilized to produce a number of super-hydrophobic or super-hydrophilic surfaces in various systems.[13–17] However, in the present study, all hydrogels had quite flat surfaces on the micrometer scale, but showed surface roughness on the nanometer scale, e.g. ~ 20 nm (R_a) and ~183 nm (R_z), irrespective of θ_w. In three hydrogels (D-NC, N-NC and N-OR), no clear correlation between surface roughness and surface hydrophobicity was found. It was, therefore, concluded that surface roughness does not play a decisive role in producing the high θ_w of the N-NC gels.

Effect of Network Modification on θ_w

Here, the effects of two types of network modification on θ_w are presented: (1) the copolymerization with a hydrophilic monomer (DMAPAA) with a long side chain and (2) the interpenetration of a hydrophilic polymer (gelatin) into an organic/inorganic network.

Copolymerization

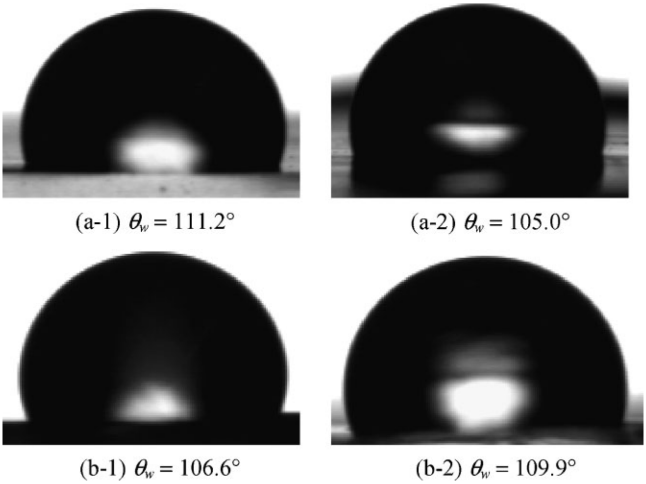
N-NC6-Co5 and N-NC6-Co10 gels were prepared using 5 and 10 mol % of DMAPAA with respect to NIPA, respectively. It was found that the values of θ_w on the surface of the N-NC6-Co gels were high ($111^\circ \sim 105^\circ$), similar to that of standard N-NC6 gel (114°), as shown in Figure 5(a), although they decreased slightly with increasing DMAPAA content. This indicates an unusually high hydrophobicity at the surface of the N-NC gel which slightly and gradually decreases with copolymerization with the hydrophilic monomer with a different side chain.

Interpenetrating Network

We recently reported that intelligent N-NC gels could be obtained by applying interpenetration (IP) or semi-interpenetration (s-IP) techniques. For example, outstanding dual (pH- and temperature-) sensitivity as well as good mechanical properties were realized in the s-IP-N-NC-PAA gel, in which poly(acrylic acid) was used as an interpenetrating polymer.[18] In the present study, we used gelatin (G) as a hydrophilic interpenetrating polymer and formed s-IP and IP organic/inorganic networks. The results are shown in Figure 5(b). It was found that the s-IP-N-NC3-G50 and the IP-N-NC3-G50 gels had high θ_w values (107° and 110°, respectively) almost similar to that of the standard N-NC3 gel (110°). This indicates that the high hydrophobicity of the N-NC gel was not affected by the formation of the s-IP and IP organic/inorganic networks using gelatin. This is probably because the gelatin interacted with the clay strongly and, therefore, was not present at the outermost surface of the resulting gel.

Effect of the Adsorption of Hydrophilic Molecules on θ_w

The high θ_w value at the surface of the N-NC gel was attributed to the formation of a thin hydrophobic layer consisting of *N*-isopropyl groups at the gel-air interface. Here, the effect of the adsorption of



(a-1) $\theta_w = 111.2^\circ$ (a-2) $\theta_w = 105.0^\circ$

(b-1) $\theta_w = 106.6^\circ$ (b-2) $\theta_w = 109.9^\circ$

Figure 5.
Water contact angles for sessile drops on various surfaces. (a-1) N-NC6-Co gel (5 mol% of DMAPAA), (a-2) N-NC6-Co gel (10 mol % of DMAPAA), (b-1) s-IP-N-NC3-G50 gel, (b-2) IP-N-NC3-G50 gel.

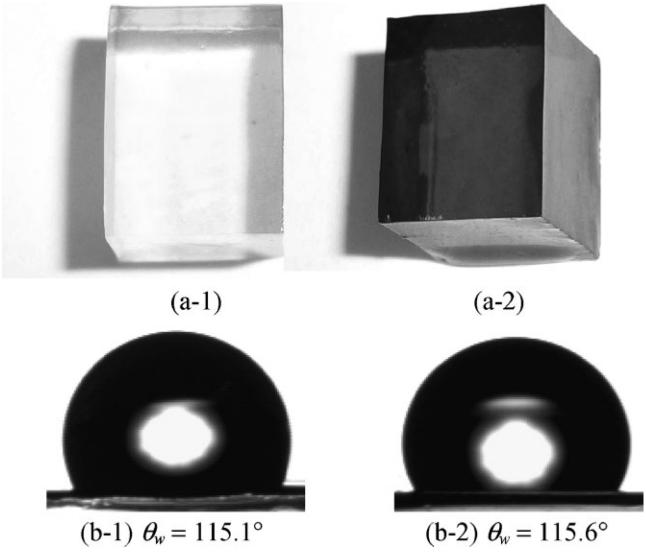


Figure 6.
(a) N-NC6 gels impregnated with methylene blue upon immersion in (a-1) 0.05 mM and (a-2) 5 mM aqueous solutions. (b) Water contact angles for sessile drops on MB-impregnated N-NC6 gels: (b-1) 0.05 mM, (b-2) 5 mM.

hydrophilic molecules (methylene blue, MB, a cationic dye) in the N-NC6 gel was investigated.

Two MB-impregnated N-NC6 gels (N-NC6-MB-0.05mM and N-NC6-MB-5mM) are shown in Figure 6(a). The θ_w values measured on these gels are given in Figure 6(b). It was observed that both MB-impregnated N-NC6 gels showed the same θ_w values as that of the as-prepared gel. This indicates that the adsorption of a cationic dye into the N-NC gel hardly affected its surface hydrophobicity, probably because the MB molecules adsorbed onto the clay surface through ionic interaction, and hardly affected the formation of a thin hydrophobic layer at the outermost surface of the gel.

Conclusion

Unusually high θ_w values ($100° \sim 150°$) were observed on a specific nanocomposite gel (N-NC gel) consisting of a PNIPA/clay network. The high θ_w values changed depending on the composition, such as the clay content and the water content. The θ_w value was stable in short-term measurements but varied both gradually and abruptly in long-term measurements, strongly depending on the clay content. Furthermore, the hydrophobic surface was reversibly transformed into a hydrophilic one by altering the environment of the gel between in-air and wet. The high θ_w value was hardly changed by network modification through the interpenetration of a hydrophilic polymer (gelatin) or the adsorption of hydrophilic molecules (a cationic dye), while it slightly decreased through copolymerization with an increasing amount of a hydrophilic monomer with a different side chain.

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