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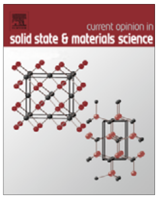

# Nanocomposite hydrogels

Kazutoshi Haraguchi *

*Material Chemistry Laboratory, Kamamura Institute of Chemical Research, 631 Sakado, Sakura, Chiba 285-0078, Japan*

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ABSTRACT

Hydrogels, which consist of three-dimensional polymer networks and large amounts of water, have long been believed to be interesting but mechanically fragile materials limited to specific uses. Recently, important breakthroughs have been made as a result of the creation of nanocomposite hydrogels (NC gels), and most of the traditional limitations of hydrogels have been overcome. NC gels are prepared by in situ free-radical polymerization at high yield under mild conditions (near ambient temperature, without stirring), and various shapes and surface forms are readily obtained. Because of their unique organic (polymer)/inorganic (clay) network structure, high toughness and excellent optical properties and stimulus-sensitivity are simultaneously realized in NC gels. Furthermore, NC gels exhibit a number of interesting new characteristics. In this paper, the fundamental and recent developments related to NC gels are reviewed.

## 1. Introduction

Organic/inorganic nanocomposites (NCs) are functional materials consisting of immiscible organic and inorganic components, and complex nanometer-scale structures can be fabricated therefrom. As a typical example, polymer/clay NCs have been extensively studied and successfully developed for many applications [1]. In 2002, Haraguchi reported the creation of a novel "nanocomposite hydrogel" with a unique organic–inorganic network structure by extending the concept of NC to the field of soft hydrogel materials [2]. The nanocomposite hydrogel (abbreviation: NC gel) exhibited extraordinary mechanical, optical, swelling/deswelling properties which could simultaneously overcome the limitations of conventional chemically crosslinked hydrogels (abbreviation: OR gels). The construction of NC gels was achieved, not by the mere incorporation of clay nano-particles into a chemically crosslinked network, but by allowing the clay platelets to act as multifunctional crosslinkers in the formation of polymer/clay networks. Due to their superior properties, NC gels have attracted much attention and are believed to be a revolutionary type of hydrogel [1]. This article reviews the fundamental and recent developments in the field of NC gels.

## 2. Synthesis and network structure

### 2.1. Synthesis procedure and composition

The synthetic procedure for NC gel formation consists of the in situ free-radical polymerization of a monomer (e.g., *N*-substituted acrylamides) in the presence of inorganic clay platelets uniformly dispersed in an aqueous medium [2]. Here, the use of exfoliated clay platelets instead of an organic crosslinker such as *N*,*N*-methylenebisacrylamide (BIS) is important. The use of both clay and BIS (i.e., the use of clay as a reinforcing agent) results in hydrogels with poor mechanical properties, similar to those of conventional OR gels [3–5]. In order to achieve the superior characteristics of NC gels, it is necessary for inorganic nano-particles (clay platelets) to act as multifunctional crosslinkers [1,6,7]. Attempts to prepare NC gels by other procedures, such as mixing clay and polymer solutions, have been unsuccessful [8].

As the inorganic component, the clays in the smectite group (e.g., hectorite, montmorillonite), their modifications (e.g., by fluorination or addition of pyloric acid), synthetic mica, and so on, can be used, providing that they can be swollen and exfoliated in water. Several kinds of clay and their effects on the tensile mechanical properties of NC gel are shown in Table 1 and Fig. 1 [9]. The non-water-swellable clay minerals (e.g., sepiolite) cannot produce NC gels, although modified hectorite or montmorillonite can be used to produce NC gels [9–13]. Concerning the size of the clay particles, a diameter of about 30 nm (for synthetic hectorite) is enough for the construction of NC gels and clay particles of larger sizes (e.g., >300 nm for natural montmorillonite) are not necessary; sometimes large clay particles are not even effective (Fig. 1), probably due to the insufficient exfoliation and moderate aggregation in the aqueous solution. As for the other minerals, polyhedral oligomeric silsesquioxane [14,15], rigid polysiloxane [16,17], fibrillar attapulgite [18] and hydrotalcite [19] have been used with selected polymers. Silica and titania nano-particles have been found ineffective as multifunctional crosslinkers [8].

For the polymer, water-soluble monomers containing amide groups, such as *N*-isopropylacryamide (NIPA), *N*,*N*-dimethylacryla-

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* Tel.: +81 43 498 2111; fax: +81 43 498 2182.
*E-mail address:* hara@kicr.or.jp

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**Table 1**
Compositions of various inorganic clays

| Clay | Type | Composition (wt%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | MgO | $Li_2O$ | $Na_2O$ | F | $P_2O_5$ |
| *Water swelling* | | | | | | | |
| XLG[a] | Synthetic hectorite | 59.5 | 27.5 | 0.8 | 2.8 | – | – |
| SWN[b] | Synthetic hectorite | 54.3 | 27.9 | 1.6 | 2.7 | – | – |
| XLS[a] | XLG + dispersing agent 54.5 | 26.0 | 0.8 | 5.6 | – | 4.1 | |
| SWF[b] | Fluorinated hectorite | 54.5 | 27.2 | 1.6 | 5.8 | 2.9 | – |
| B[a] | fluorinated hectorite | 55.0 | 27.0 | 1.4 | 3.8 | 5.6 | – |
| S[a] | B + dispersing agent | 51.0 | 25.0 | 1.3 | 6.0 | 5.0 | 3.3 |
| *Partially swelling in water* | | | | | | | |
| F[c] | Natural montmorillonite | 61.3 | 3.43 | – | 4.1 | $Al_2O_3$ = 22,<br>$Fe_2O_3$ = 1.9 | |
| *Non-swelling in water* | | | | | | | |
| IGS[d] | Sepiolite | Magnesium silicate | | | | | |

From Ref. [9].

[a] Rockwood Additive Ltd.

[b] Coop Chemical Ltd.

[c] Kunimine Ind. Co.

[d] Tomoe Ind. Co.

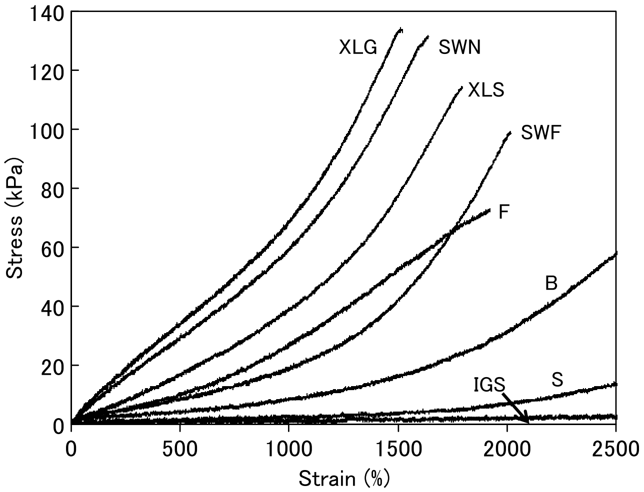

**Fig. 1.** Tensile stress–strain curves for (PDMAA-)NC gels prepared using various kinds of clay shown in Table 1. $C_{clay} = 3.9 \times 10^{-2}$ mol/L $H_2O$. From Ref. [9].

mide (DMAA) and acrylamide (AAm), are the most effective, probably due to their adequate interaction with the clay surface. Other monomers (e.g., those containing carboxyl, sulfonyl or hydroxyl groups) can also be used alone [20] or as co-monomers [21,22]. By using a similar procedure and a specific acrylate monomer (2-methoxyethylacrylate), Haraguchi et al. succeeded in preparing an interesting novel, flexible and transparent NC (M-NC: solid) [23]. In M-NCs and NC gels, it should be noted that the content of clay ($C_{clay}$) can be varied to a large extent because they are prepared from aqueous solutions, which is in stark contrast to the procedure for fabricating conventional polymer/clay NCs.

### 2.2. Various shapes and surface patterns

Since the synthetic procedure is quite simple and versatile, NC gels can be prepared in many shapes, such as huge blocks, sheets, thin films, rods, hollow tubes, spheres, bellows and uneven sheets, by means of different molds (Fig. 2) [24]. This is due to the easy injection of the reaction solution and the very high toughness of the resulting gel. Also, microgels with dimensions of several hundred nm [25] and porous NC gels with a density of 0.2 g/cm$^3$ [24] have been prepared. Furthermore, micrometer-scale, surface-patterned NC gel films have been successfully prepared by direct replica molding [26].

### 2.3. Network structure and the gel formation mechanism

The extraordinary properties and new functions of NC gels are attributed to their unique network structure. The organic (polymer)/inorganic (clay) network structure (Fig. 3) was first proposed on the basis of analytical data from TEM, XRD, TGA, DSC and FTIR measurements [2], and it has been confirmed to be consistent with the observed mechanical, optical and swelling properties [6,7,27]. Based on classic rubber-elasticity theory, the number of crosslinking points per clay platelet for NC gels has been calculated [6,7], and it is several tens to more than 100, indicating that each clay particle acts as a multifunctional crosslinker. This conclusion has also been confirmed by rheological measurements [28]. Also, the effective crosslink density ($\nu_e$) has been calculated using the degree of equilibrium swelling according to the Flory–Rehner theory (Table 2) [24,29]. In general, the $\nu_e$ value of NC gels is much smaller than that of OR gels, which is consistent with the observed mechanical properties.

The process of forming the unique organic/inorganic network structure of NC gels has been studied based on the changes in viscosity, optical transparency (Fig. 4a), XRD data and mechanical properties, and the formation mechanisms of the solution structure and the clay-brush particle have been proposed (Fig. 4b) [8]. The network structure and gelation mechanism have also been investigated by dynamic light scattering (DLS) and small-angle neutron scattering (SANS) measurements. It has been confirmed that clay platelets disperse homogeneously in the polymer matrix [30] and act as multiple crosslinkers [31,32]. Also, the thermal fluctuations of the clay platelets are largely suppressed upon network formation [33]. The gelation of NC gels is classified as an ergode–nonergode transition, as in OR gels, except that huge clusters of NC microgels (corresponding to clay-brush particles) are formed before the gelation threshold [34]. Further, by contrast-variation SANS, it has been found that there is a polymer layer surrounding the clay platelets with a thickness of about 1 nm, irrespective of $C_{clay}$ [34].

## 3. Mechanical properties

For a long time, the mechanical properties were not the main theme in the study of hydrogels such as PNIPA hydrogels, which are typical smart gels. However, after the creation of NC gels by Haraguchi et al. [2], it became possible to conduct all the conventional mechanical tests, and hydrogels can now be treated as rubbery materials. In fact, NC gels can withstand high levels of deformation, not only in the form of elongation and compression, but also bending, tearing, twisting and even knotting (Fig. 5) [6].

### 3.1. Tensile properties

In general, an NC gel can be elongated to more than 1000% of its original length, and the extensibility depends on the kind of clay and polymer used. In a specific clay/polymer system, the elongation at break ($\varepsilon_b$) is almost constant regardless of $C_{clay}$ and the polymer content ($C_p$), e.g., 1000% for PNIPA-NC gel [6,27] and 1600% for PDMAA-NC gel [7]. Thus, fragile OR gels are dramatically changed to stretchable NC gels by simply changing the crosslinker from BIS to clay. When the network is not effectively established, $\varepsilon_b$ becomes much larger (>2000%), as shown in Fig. 1 [9]. Also, NC gels exhibit high time-dependent recovery from large strains [27], and this ability changes according to the clay/polymer system [11] and composition [27].

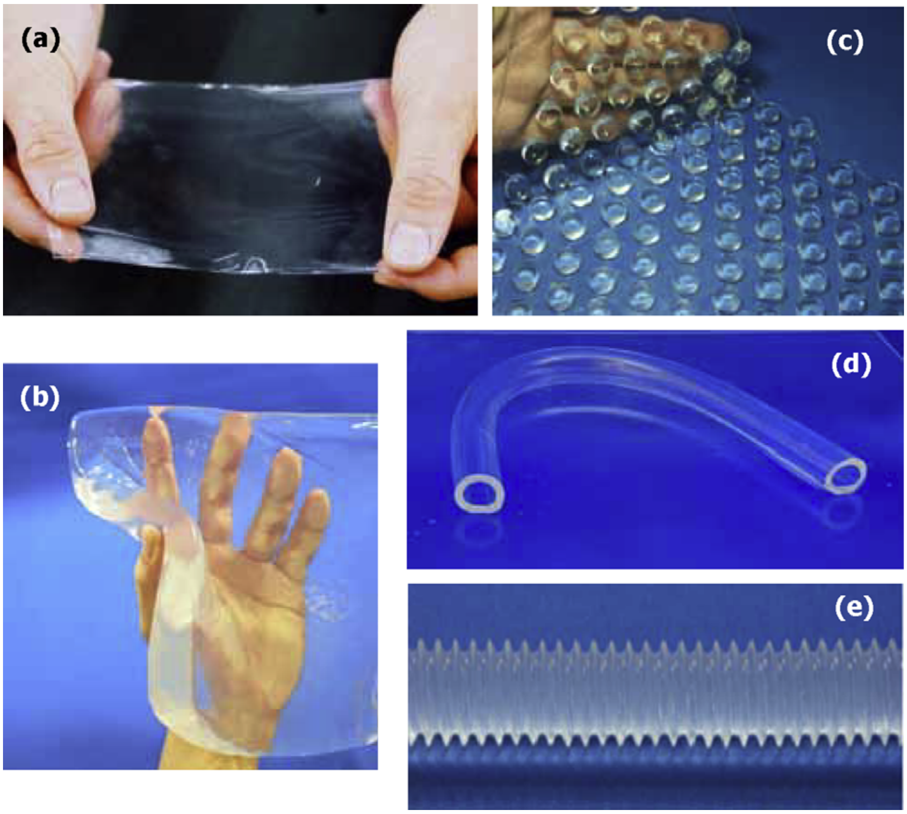

**Fig. 2.** NC gels with various shapes: (a) thin film, (b) sheet, (c) uneven sheet, (d) hollow tube and (e) bellows.

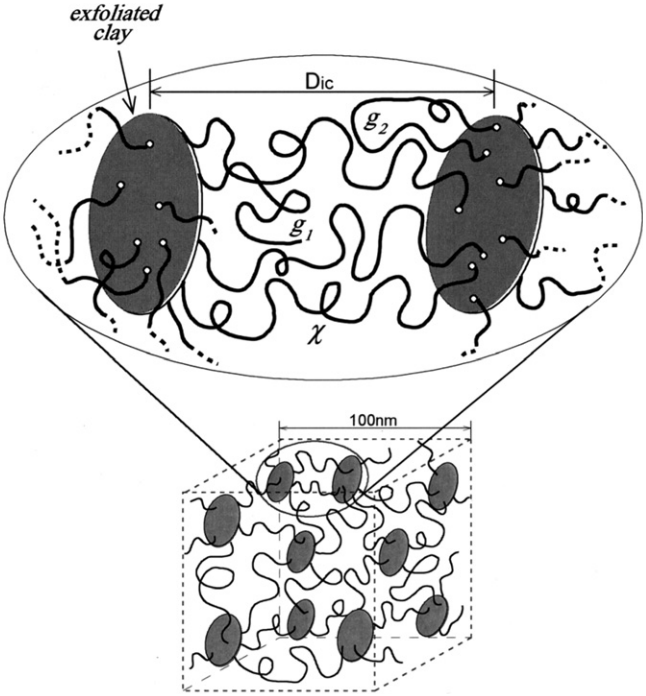

**Fig. 3.** Schematic representation of the organic (polymer)/inorganic (clay) network structure of NC gel. $D_{ic}$ is the inter-particle distance of the exfoliated clay platelets. $\chi$, $g_1$ and $g_2$ represent the crosslinked chains, grafted chains and looped chains, respectively. In the model, only a small number of polymer chains are depicted for simplicity. From Ref. [7].

The modulus and strength can be improved greatly by increasing values of $C_{clay}$ and $C_p$ [6,7]. Here, it should be noted that the modulus is increased (e.g., 500 fold) without sacrificing $\varepsilon_b$, which is totally different behavior from that of conventional polymeric materials. Consequently, the fracture energy increases to 3300 times that of OR gels [27,35]. Also, in NC gels, properties such as time-dependent recovery, the tensile properties on the second cycle and the disappearance of the glass transition change at a critical $C_{clay}$ ($C^*_{clay} \approx 10 \times 10^{-2}$ mol/L $H_2O$) [27]. The structural change during uniaxial stretching of NC gels has also been investigated by SANS [31,36] and optical anisotropy [37].

### 3.2. Compression and other properties

NC gels generally withstand ~90% compression, in contrast to OR gels, which are readily broken into pieces under small strains. The compression modulus and strength increase almost proportionally to $C_{clay}$ [27]. Also, it has been found that, due to the formation of co-crosslinked network (NC–OR gel), the compression strength improves considerably at low BIS contents ($C_{BIS}$) [5]. This is attributed to the formation of a microcomplex structure consisting of clay platelets with enhanced densities of chemical crosslinks.

In viscoelastic measurements, very stable $G'$ (storage modulus) and $G''$ (loss modulus) ($G' > G''$) values in the frequency range of $10^{-1} \sim 10^2$ rad$^{-1}$ and relatively high tan$\delta$ (loss factor) (~0.1) values have been observed for PDMAA-NC [24] and PAAm-NC gels [28], respectively, which indicates that the NC gels are much more viscous than conventional OR gels.

## 4. Swelling and stimulus-sensitivity

### 4.1. Swelling

NC gels generally exhibit a high degree of equilibrium swelling (DES) in water compared with OR gels [2,29]. This is due to the

**Table 2**
Degree of equilibrium swelling (DES) and effective network density ($\nu_e$) for NC and OR gels, calculated according to the Flory–Rehner theory

| Hydrogel | NC1 | NC5 | NC10 | NC15 | NC20 | OR1 | OR5 |
|---|---|---|---|---|---|---|---|
| DES($W_s/W_{dry}$) | 50.94 | 28.94 | 22.57 | 17.61 | 12.94 | 16.93 | 8.55 |
| $\nu_e$ (mol/L) | 0.0048 | 0.0099 | 0.0127 | 0.0170 | 0.0256 | 0.0431 | 0.1582 |

From Ref. [29].

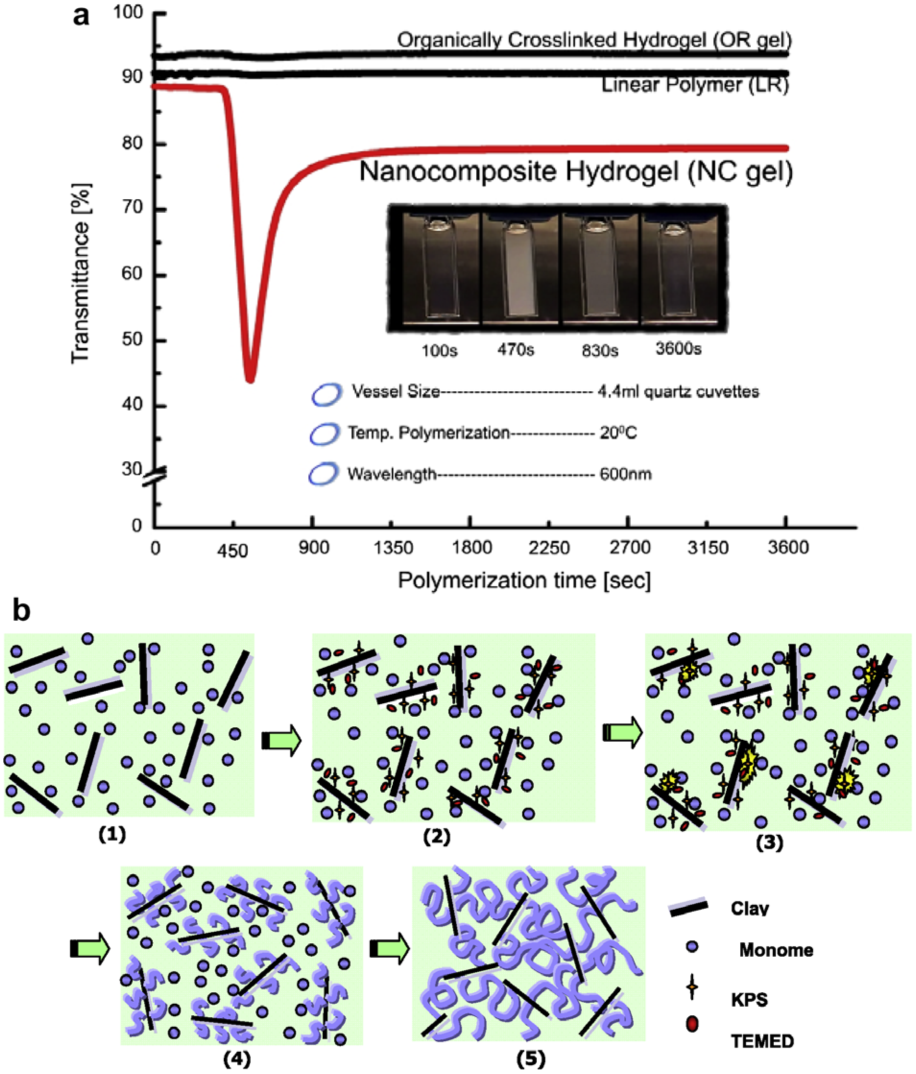

**Fig. 4.** (a) Changes in optical transparency during the polymerization of NC gel and OR gel. (b) Model structures of (1–3) the reaction solutions, (4) the clay-brush particles and (5) NC gel. From Ref. [8].

relatively low value of $\nu_e$ for the polymer/clay network. The value of DES changes depending on the kind of clay and polymer as well as $\nu_e$. In a fixed clay/polymer system, the DES decreases with increasing $C_{clay}$ and $C_p$ [7,29]. For the purpose of constructing a superabsorbent (high-swelling) hydrogel, a more hydrophilic polymer (e.g., PAAm and PAAc) [11,38] or co-polymerization with an ionic monomer [21,39] has been applied.

In the swelling of NC gels, unusual behaviors, such as the appearance of a maximum in the swelling curve [40] and a remarkable increase in DES due to post-treatment in a specific NC gel with the retention of high mechanical properties [41], have been observed. Both phenomena are explained by the rearrangement of the entangled polymer chains and clay particles during the course of swelling or post-treatment.

### 4.2. Stimulus-sensitivity

Thermo-sensitivity and its control in hydrogels have attracted much attention because of their many potential applications [42]. However, for example, conventional PNIPA-OR gels have several important limitations, such as low volume change (VC) and slow deswelling rate (DSR), as well as low mechanical properties. It has been revealed that these limitations are simultaneously solved in (PNIPA-)NC gels, which exhibit large VC and high DSR as well as excellent mechanical properties [2]. Interestingly, the effect of $\nu_e$ on the DSR is opposite in NC and OR gels [6]. The thermo-sensitivity of NC gels can be varied widely in a controlled manner by altering the gel composition [35], and even non-thermo-sensitive NC gels can be obtained by increasing $C_{clay}$ and thereby restricting

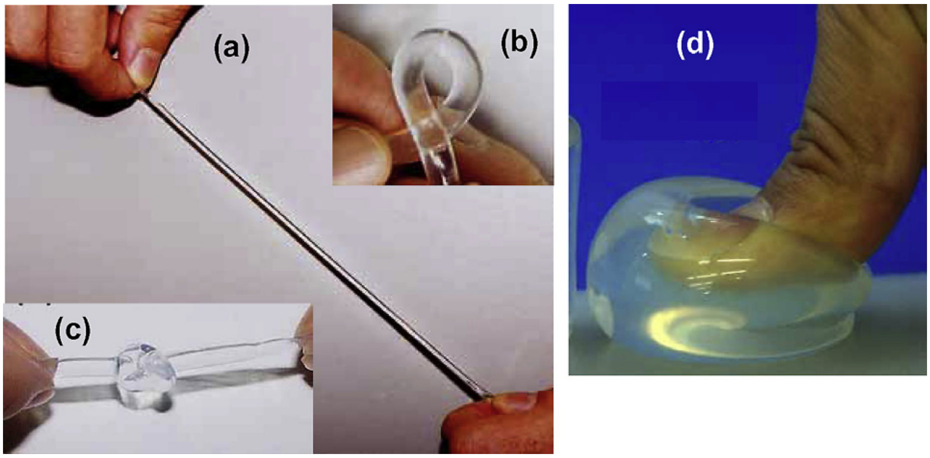

**Fig. 5.** NC gels exhibit extraordinary mechanical toughness: (a) stretching, (b) bending, (c) knotting and (d) compression.

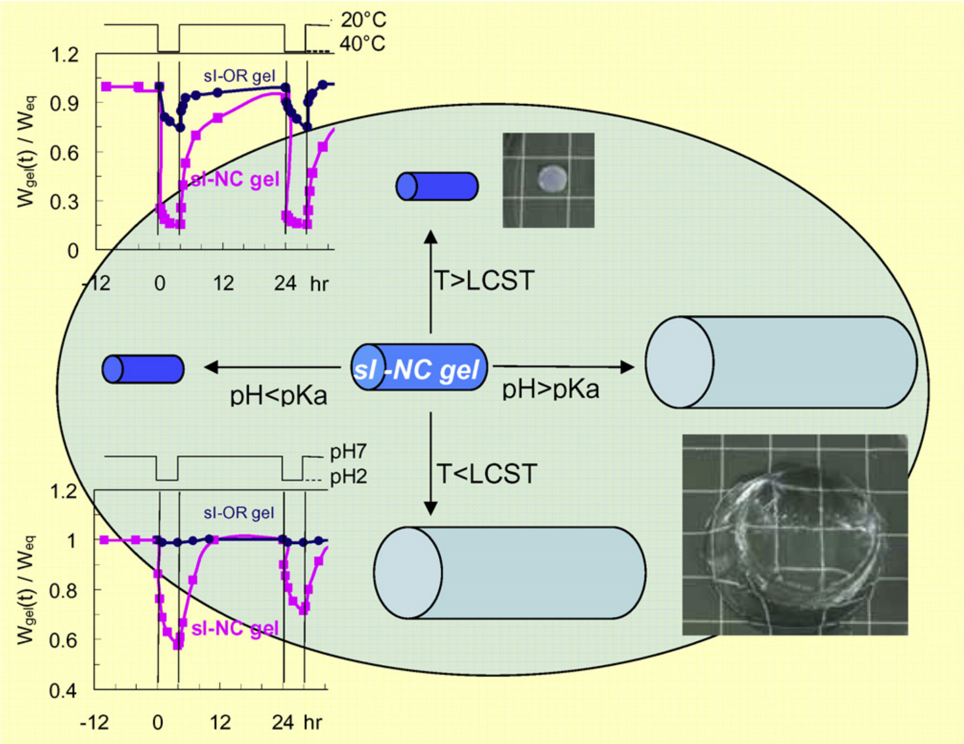

**Fig. 6.** Semi-interpenetrated NC gel (sI-NCgel), consisting of a PNIPA/clay network including linear poly(acrylic acid) chains, exhibited outstanding temperature- and pH-sensitive swelling/deswelling behaviors as well as superior tensile mechanical properties. From Ref. [14].

the thermal molecular motions of the PNIPA chains attached to the hydrophilic clay surfaces or in their proximity [29]. The transition temperature (lower critical solution temperature: LCST) of NC gels is hardly changed by altering $C_{clay}$ [6,29], but shifts toward a lower or higher temperature on adding an inorganic salt or cationic surfactant to the surrounding aqueous solution, respectively [43].

NC gels with a semi-interpenetrating (semi-IPN) organic/inorganic network structure have been prepared using linear poly (acrylic acid) [44] or linear carboxymethylchitosan [45]. The resulting semi-IPN NC gels manifest outstanding swelling/deswelling behavior in response to both temperature and pH (Fig. 6) while retaining their remarkable tensile mechanical properties. The response to electrostimulation has been studied in chitosan/clay gel [46]. Haraguchi et al. have reported the first observation of the reversible generation of retractive tensile forces in NC gels as a result of the coil-to-globule transition of PNIPA chains, in response to the alternation of the temperature across the LCST [47].

## 5. New functions in NC gels

### 5.1. Transparency and its changes

Transparent OR gels generally turn opaque with increasing $C_{BIS}$ ($\propto v_e$) due to the inhomogeneous distribution of crosslinking points, and the critical value of $C_{BIS}$ at which the loss of transmittance changes depending on the polymer [6,7]. In contrast, NC gels are generally transparent, almost regardless of the crosslink density ($\propto C_{clay}$ and $C_p$) and the kind of polymer, except for a slight decrease at low $C_{clay}$ (ca. $2 \times 10^{-2}$ mol/L $H_2O$) [7] and very high $C_{clay}$ ($\sim 25 \times 10^{-2}$ mol/L $H_2O$) [27]. These findings indicate that the organic/inorganic network structure forms uniformly throughout the NC gel regardless of $C_{\mathrm{clay}}$ and $C_{\mathrm{p}}$. The homogeneity of the network structure has been investigated in detail by SANS and DLS [30,34].

### 5.2. Optical anisotropy and its changes

Since hydrogels consist of polymer networks swollen with large amounts of water, hydrogels are normally amorphous (optically isotropic). It has been found that an NC gel exhibits optical anisotropy when its $C_{\mathrm{clay}}$ exceeds a critical value ($C^*_{\mathrm{clay}} \approx 10 \times 10^{-2}$ mol/L $H_2O$) [27]. This $C^*_{\mathrm{clay}}$ is consistent with the critical value calculated for spontaneous clay aggregation (layer stacking) in NC gels [29]. Furthermore, the optical anisotropy of an NC gel changes uniquely on uniaxial deformation, regardless of the optical characteristics in the original (as-prepared) state [37]. That is, upon uniaxial stretching, all NC gels exhibit remarkable optical anisotropy, and the birefringence shows distinct maxima and sign inversions (Fig. 7). The contributions of clay and PNIPA to the birefringence of stretched NC gels have been evaluated.

### 5.3. Sliding frictional behaviors

Sliding frictional measurements have been conducted on the surfaces of NC gels under different environmental conditions and loads [48]. In air, NC gels exhibit a characteristic force profile with a maximum static force and a subsequent constant dynamic frictional force, both of which vary markedly depending on the gel composition and the load on the sliding plate. In contrast, under wet conditions, NC gels generally exhibit very low frictional forces and the dynamic frictional coefficient decreases with increasing load. The distinct change in frictional force with the surroundings is particularly observed in NC gels with low $C_{\mathrm{clay}}$.

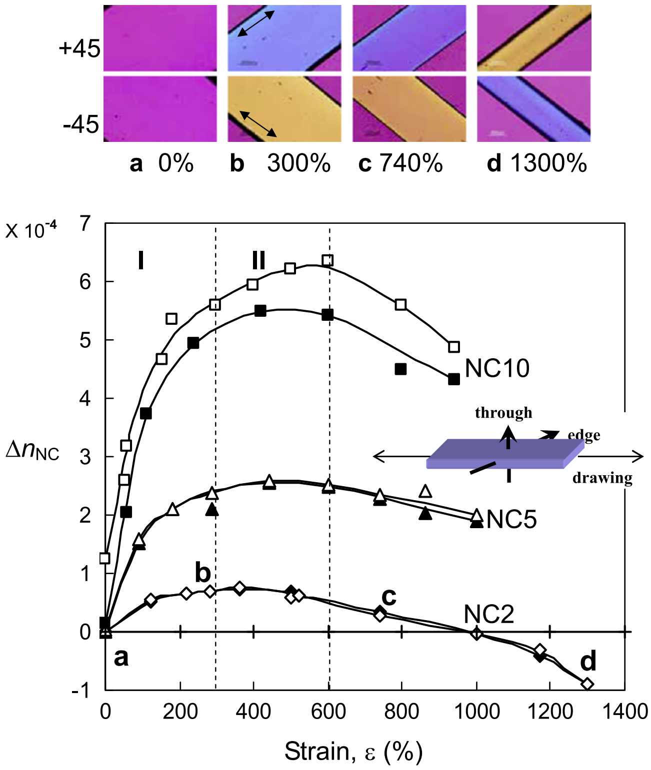

**Fig. 7.** Birefringence, $\Delta_{\mathrm{NC}}$, of (PNIPA-)NC gels with different $C_{\mathrm{clay}}$ (NC2–NC10) values as a function of strain. The closed and open symbols represent measurements in the through- and edge-directions, respectively. The inserted photo images (a–d) show polarized-light micrographs of stretched NC2 gels under crossed polarizers in conjunction with a 530 nm retardation plate. From Ref. [37].

### 5.4. High water contact angles

Hydrogels, which consist of a hydrophilic polymer with water filling the interstitial space of the network, are naturally hydrophilic, and their surfaces generally show very low contact angles for water ($\theta_{\mathrm{w}}$). Haraguchi et al. [49] have found that the surface of an NC gel consisting of a PNIPA/clay network can exhibit extraordinarily high hydrophobicity, although all the constituents of the NC gel were hydrophilic under the testing conditions (Fig. 8). $\theta_{\mathrm{w}}$ was generally greater than 100° over broad ranges of $C_{\mathrm{clay}}$ and $C_{\mathrm{water}}$ and showed a maximum contact angle of 151° at a specific composition. The high hydrophobicity of NC gels is primarily attributed to the amphiphilicity of PNIPA and, more specifically, to the spontaneous alignment of *N*-isopropyl groups at the gel–air interface, and is enhanced by other factors, such as the network structure and gel composition. Also, the surfaces of NC gels exhibit reversible hydrophobic-to-hydrophilic changes on changing the surroundings from dry (in air) to wet (in water) conditions, and vice versa.

### 5.5. Cell cultivation and biocompatibility

It has been found that cells such as human dermal fibroblasts and human umbilical vein endothelial cells (HUVEC) can be cultured to confluence on the surface of an NC gel consisting of a PNIPA/clay network (Fig. 9a and b); in contrast, cell cultures hardly develop on OR gels. Also, the cultured cells can be detached as cell sheets without trypsin treatment, simply by decreasing the temperature to 20 °C (below the LCST of PNIPA) (Fig. 9(1–3)) [50].

The effectiveness of NC gels in biomedical applications is being investigated in terms of extraction tests for contact lenses, absorption of saline, sterilization by autoclaving, blood compatibility and intramuscular implantation [51].

### 5.6. Porous NCs with layered morphology

Porous solid NCs with characteristic layered morphologies, such as a three-layer morphology with controlled porosity, have been

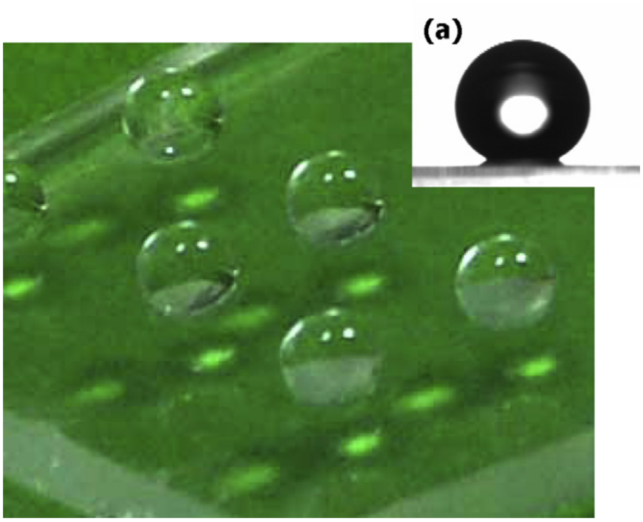

**Fig. 8.** Water droplets on PNIPA-NC gel film. (a) Value of the water contact angle for a sessile drop on the surface of PNIPA-NC gel with a water content of 210 wt% ($= W_{\mathrm{H_2O}}/W_{\text{dry-gel}} \times 100$). From Ref. [49].

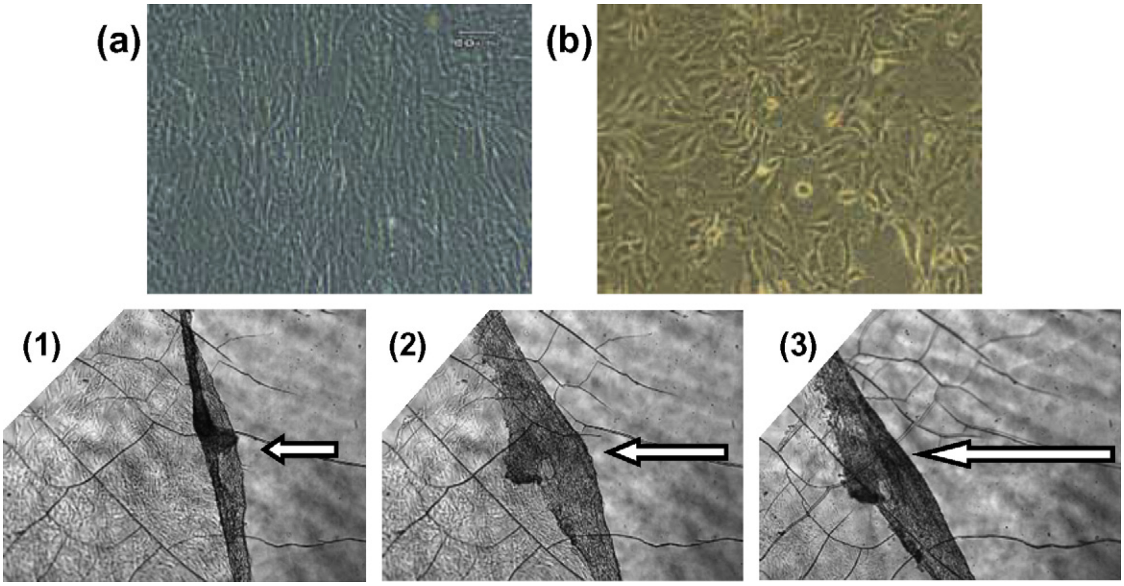

**Fig. 9.** Phase-contrast photomicrographs of (a) fibroblast and (b) HUVEC proliferated on (PNIPA-)NC gel. (1–3): Cell sheet detachment of fibroblast by decreasing the temperature to 10–20 °C. From Ref. [50].

obtained by freeze-drying NC gels without the use of an added porogen [52].

## 6. Conclusion

Hydrogels are transparent, soft materials made mainly of water, and can possess characteristics of both a solid and a liquid. By creating NC gels, the limitations in properties and applications, which had previously been thought impossible to overcome, have been eliminated. Furthermore, a number of "super-functions" (the internal consistency of pairs of mutually conflicting properties), such as softness and toughness, extensibility and rigidity, swelling and deswelling, elongation and recovery, optical isotropy and anisotropy, cell cultivation and detachment, inorganic inclusion and transparency, etc., can now be induced. Since the primary component is water, NC gels can be utilized as environmentally friendly rubbery materials in the management of resources and waste, and may open new doors in various areas of advanced research and technology.

## Acknowledgement

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