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Nanocomposite Gels: New Advanced Functional Soft Materials

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Summary: Nanocomposite gels (NC gels) consisting of poly(N-alkylacrylamides) and exfoliated inorganic clay were prepared by in-situ, free-radical polymerization at high yield under mild conditions (near ambient temperature, without stirring). Various shapes and different surface forms of NC gels were readily obtained using corresponding vessels and templates, since NC gels were always mechanically tough. The view that polymer/clay networks are formed in NC gels was supported by dynamic viscoelastic and swelling measurements. The entirely different mechanical properties of NC gels, compared with conventional, chemically-crosslinked hydrogels (OR gels), are discussed on the basis of their network structure. In addition to functions previously reported, NC gels exhibit further interesting characteristics, such as inherent incombustibility, good thermal conductivity, large heat capacity, they can be readily colored and fabricated as foams. NC gels can be utilized as environmentally-friendly, soft materials from the viewpoints of resources and waste, as their primary component is water.

Keywords: clay; hydrogel; nanocomposite; networks; organic/inorganic

Introduction

Polymer hydrogels are mechanically-stable materials containing large amounts of water within three-dimensional polymer networks. Many polymer hydrogels are found in our surroundings. For example, as refrigerants (coolers), super-absorbent polymers (SAP) (used in diapers and napkins), thickener, cosmetics, electrophoresis gel, wound dressing, soft contact lens and foods, such as agar, elephant's-foot, tofu and jelly. Furthermore, most of the organs in our bodies are polymer hydrogels consisting of protein and/or polysaccharide. However, from the viewpoint of chemical products, polymer hydrogels have not been developed extensively to date, except for SAPs and soft contact lenses.

Their lack of application is mainly because conventional synthetic polymer hydrogels, most typically chemically-crosslinked polymer hydrogels (OR gels), have serious disadvantages from a materials point of view, particularly, in their mechanical properties (fragility) and (inadequate) functions as smart gels. To overcome these problems, we successfully extended the concept of "organic/inorganic nanocomposite", in which two quite different (organic and inorganic) components are compounded on a nanometer scale, into polymer hydrogels for the first time. As a result, we created a new type of polymer hydrogel (nanocomposite gel: NC gel) with extraordinary optical, mechanical and swelling/de-swelling properties.[1] In more detail, high transparency (regardless of the crosslinker concentration), excellent mechanical properties (such as ultra-high elongation, high strength, controlled modulus and very high fracture energy), high resistance to bending or compression, high swellability, rapid swelling/de-swelling

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rates and well-defined changes in transparency in response to thermal transitions were all achieved simultaneously.[2–5] Furthermore, many new functions were found in NC gels, such as the generation of reversible forces,[6] the formation of unique porous morphologies,[7] characteristic sliding frictional behavior,[8] control over the coil-to-globule transition,[4] cell cultivation with subsequent detachment of cells,[9] and so on.

With regard to the structure of NC gels, we proposed a unique organic/inorganic network structure in which clay platelets act as super multi-functional crosslinking units linking a number of flexible polymer chains together.[1] The proposed network structure, capable of accounting for all the properties and functions described above, was confirmed by analytical data such as transmission electron microscopy, differential scanning calorimetry and X-ray diffraction,[1–3] in addition to dynamic light scattering and small angle neutron scattering (SANS).[10] Also, the results of repeated tensile tests [4] and changes in SANS patterns[11,12] on unidirectional elongation of NC gels were well explained by the proposed network structure. Further, the mechanism of forming organic/inorganic network structures during in-situ, free-radical polymerization was also revealed.[13] In this paper, we present further evidence for the advantages of NC gels as advanced, functional, soft materials in gel syntheses, and their mechanical, swelling and thermal properties.

Experimental Part

Syntheses of NC and OR Gels

The synthetic procedure for NC gels is the same as that reported previously.[3,4] Uniform aqueous solutions containing clay (hectorite, "Laponite XLG") with a wide range of concentration, 0.05×10^{-2}–10×10^{-2} mol/L-H_2O, monomer (N-isopropylacrylamide (NIPA) or N,N-dimethylacrylamide (DMAA)) at a constant concentration of 1 mol/L-H_2O, catalyst (N,N,N′,N′-tetramethylethylenediamine) and initiator (potassium persulfate) were prepared. The molar ratios of monomer, catalyst and initiator were fixed at 100:0.735:0.426. The solutions were poured into vessels of various shapes with different surface templates. Subsequently, in-situ, free-radical polymerization was allowed to proceed in a water bath at 20 °C for 20 h. For OR gels, the same procedures, except for the use of an organic crosslinker (N,N′-methylenebis (acrylamide) (BIS): 0.001–3 mol % relative to monomer) instead of clay, were adopted. The clay content of NC gel, C_{clay}, or the BIS content of OR gel, C_{BIS}, were expressed using a simplified numerical value of 0.05–10 and 0.001–3, respectively, corresponding to the clay and the BIS concentrations described above. Thus, NC and OR gels are identified using monomer type (prefixes D- and N-, refer to DMAA and NIPA, respectively) and their C_{clay} and C_{BIS} as in D-NC0.1 gels and N-OR3 gels, respectively.

Measurements

Tensile measurements were performed on samples of NC and OR gels of the same size (5.5 mm diameter × 70 mm long) using a Shimadzu Autograph AGS-H under the following conditions. 25 °C; gauge length 30 mm; crosshead speed 100 mm min^{-1}. Dynamic viscoelastic properties were measured for D-NC5 gel films (25 mm $\phi \times 2$ mm) using a RFS-II (Rheometrics Inc.) under the following conditions: 22 °C, $\omega = 0.1$–100 (rad/sec), torsional oscillating mode. Thermal conductivities were measured using a laboratory-made apparatus. NC gel sheet was set on the heater (60 °C) and the temperature change of upper side of gel sheet was measured. Swelling experiments were performed by immersing as-prepared gels (initial size: 5.5 mm in diameter × 30 mm length) in a large excess of water at 20 °C for 200 h, changing the water several times. Swelling ratios are represented by the ratio of weights of the swollen hydrogel (W_{gel}) to the corresponding dried gel (W_{dry}).

Results and Discussion

Syntheses of NC Gels

NC gels were prepared by in-situ, free-radical polymerization of acrylamide derivatives in the presence of inorganic clay that was exfoliated and uniformly dispersed in aqueous media. As inorganic clay, a variety of clay minerals with layered crystal structures and water-swelling abilities can be used, for example, inorganic clays classified in the smectite group (e.g. hectorite, saponite and montmorillonite) and mica group (e.g. synthetic fluorine mica). Consequently, uniform, transparent hydrogels (NC gels) were obtained without syneresis or phase separation. Polymerization yields were almost 100% (>99.9%) regardless of composition. Thus, the compositions of NC gels can be controlled precisely over a wide range by altering the composition of the initial reaction solution. For the synthesis of NC gels, it should be noted that organic crosslinkers which form conventional, chemically-crosslinked polymer networks with covalent bonds are not needed and, more precisely, should not be used in conjunction with clay. When two crosslinkers, clay and BIS, were used together, e.g. $C_{clay} = 5$ and $C_{BIS} = 1$, the resulting hydrogel, (NC5 + OR1 gel), was weak and brittle and similar to OR1 gel.

As previously reported,[2,3,5] all NC gels showed remarkable improvements in both tensile and compressive mechanical properties (e.g. in modulus, strength, deformability and fracture energy) when compared with conventional OR gels. Also, since the initial reaction solution is an aqueous liquid of fairly low viscosity, then, NC gels can be readily formed in various shapes, such as film, sheet, rods, cubes, spheres, and hollow tubes, as shown in Figure 1, by pouring the solution into closed vessels of the appropriate shape. Also, NC gels with uneven surfaces, for example, a surface with a regular array of pillars (Figure 2(a)), or rods with different local diameters, e.g. like bellows (Figure 2(b)), can be prepared by using templates with the corresponding cavities or hollows. In the latter case, bellows-like rods can be obtained just by pulling the NC gel from the mold in its as-prepared state without breaking or opening the template, because protuberances on the surface are flexible and can be deformed during extraction. All these variant shapes and forms are very difficult to prepare or handle as OR gels because of their mechanical brittleness.

To meet specific requirements, NC gel films with a wide range of thicknesses, from micrometer scale (Figure 2(c): 200 μm) to centimeter scale (Figure 2(d): 3 cm) can be readily prepared. Thin NC gel films can also be reversibly stretched as a result of their mechanical toughness. Also, because of the simplicity of the preparative procedures for NC gels, i.e. the preparation of reaction solution by just mixing, and subsequent polymerization at ambient temperature under static conditions (no mixing), it is possible to prepare NC gels of huge size, even a meter thick. Thus, a variety of NC gels can be synthesized in order to meet the requirements of various fields of science and industry.

Mechanical Properties of NC and OR Gels

NC gels showed extraordinary mechanical properties, as reported previously, which were entirely unexpected and are distinct from those of OR gels having the same compositions as NC gels, except for the crosslinker. In the following paragraphs, the different mechanical properties observed for NC and OR gels are considered from the standpoint of the network structures formed using different types of crosslinker.

(a) OR Gels

For OR gels, the changes in tensile mechanical properties of N-OR gels produced by altering the concentration of the organic crosslinker (C_{BIS}) over a wide range are shown in Figure 3. Firstly, it was found that an aqueous solution of PNIPA linear polymer (LR) with 1 base mole per liter H_2O, prepared under the same conditions as OR gel except for the absence of a crosslinker, was very viscous

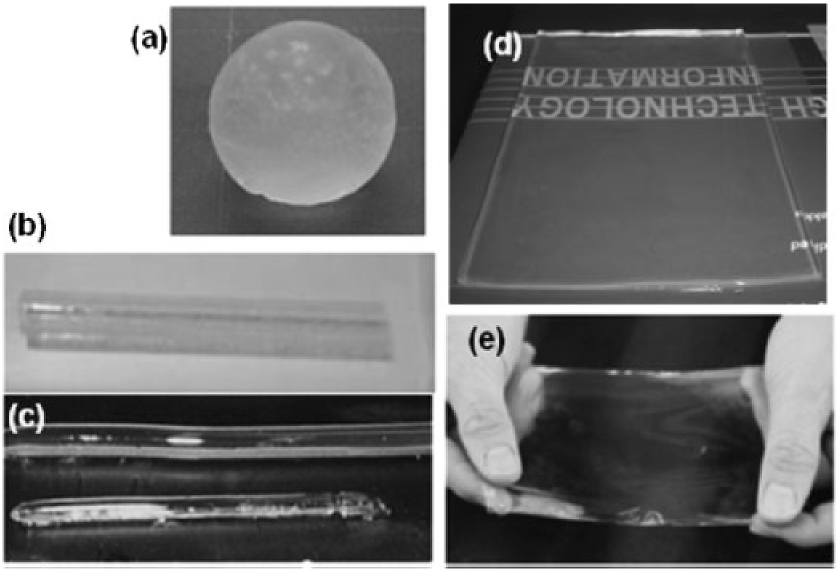

Figure 1.
NC gels with various shapes. (a) cubic. (b) hollow tube. (c) rods. (d) sheet. (e) film.

and formed a sticky gel-like material. The LR can be elongated to a great extent (near to or more than 3000%) at very low stress (<4 kPa) (Figure 3). This is because the linear polymer has a high molecular weight and forms a quasi network by topological entanglements, but that the interactions between polymer chains are very low as the polymer chains are fully hydrated. The molecular weight of LR could not be measured by liquid chromatography because of difficulties in filtering as a result of its high molecular weight. According to the empirical Equation (1) reported by M. Shibayama et al.,[14] the molecular weight of linear polymer prepared at the above concentration (C = 1000 mM) is simply expected to be more than ten million ($>10^7$).

$$\mathrm{M.W.} \approx 1.97 \times 10^3\,(\mathrm{C/mM})^{1.37} \qquad (1)$$

Figure 3 illustrates the effects of introducing chemical crosslinks into LR at different C_{BIS} ($=0.001 \sim 3$). From observations of optical transparency, it was estimated that crosslinking points were introduced uniformly, i.e. randomly distributed, in systems with up to 3 mole % BIS (less than in N-OR3). At higher C_{BIS}, the modulus gradually increased, but simultaneously the elongation at break (ε_b) rapidly decreased. Consequently, the ultimate strength remained low throughout the whole range of C_{BIS}, as shown in Figure 3. Thus, in conventional OR gels, it was concluded that only very low strengths and fracture energies can be realized by altering the crosslink density (ν) ($\propto C_{BIS}$) over a wide range.

These weak and brittle properties of OR gels are explained by using the model network structure as follows. Figure 3(a) shows a schematic representation of a chemically-crosslinked polymer network in OR gels, which consists of a large number of crosslinking points distributed randomly throughout the sample. Thus, there is a broad distribution of polymer chain lengths between crosslinking points and their average length is quite short. On unidirectional extension (Figure 3(b)), the shorter polymer chains present at any instant brake preferentially and successively, since the external stress is localized in the shortest chains. Further, in hydrogels with high water content, as in the present case, the number of polymer chains per unit

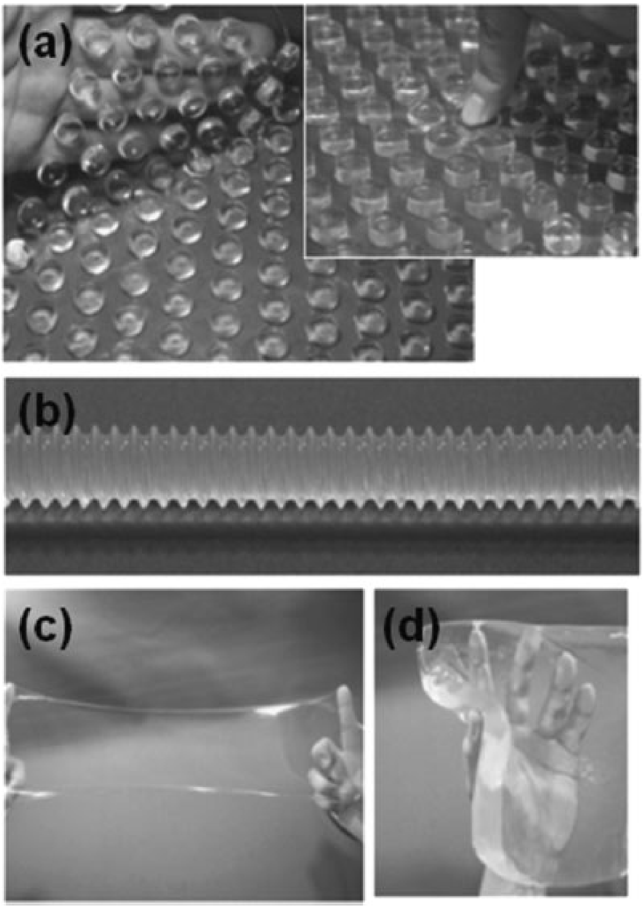

Figure 2.
NC gels with uneven surfaces: (a) regular array of pillars. (b) corrugated. NC gel films: (c) 200 μm thickness. (d) 3 cm thickness.

volume is small (only 10% of the sample is polymer) and also the interactions between neighboring polymer chains are low as the polymer chains are fully hydrated. As a result, OR gels fracture easily at small deformations and low stress. The fact that the ultimate strength is almost independent of C_{BIS}, Figure 3, indicates that the stress-localization mechanism and the number of polymer chains subjected to stress hardly changes by increasing ν. Thus, it is concluded that a broad distribution of inter-crosslinking polymer chain lengths, including short chains, is a principal factor responsible for the fragility of OR gels. Therefore, in order to achieve a dramatic increase in mechanical properties, it is necessary to fabricate networks having fairly large average inter-crosslink distances (D_{ic}) at sufficiently high ν with more homogeneous (narrow) distributions. In other words, ν and D_{ic} should be independently controlled, which is different from the case for OR gels in which D_{ic} is inversely proportional to ν, i.e. $\nu \propto D_{ic}^{-1}$.[15]

(b) NC gels

We created NC gels which simultaneously solve all the problems associated with conventional OR gels, such as weak and brittle mechanical properties, decreased optical transparency (increase in structural

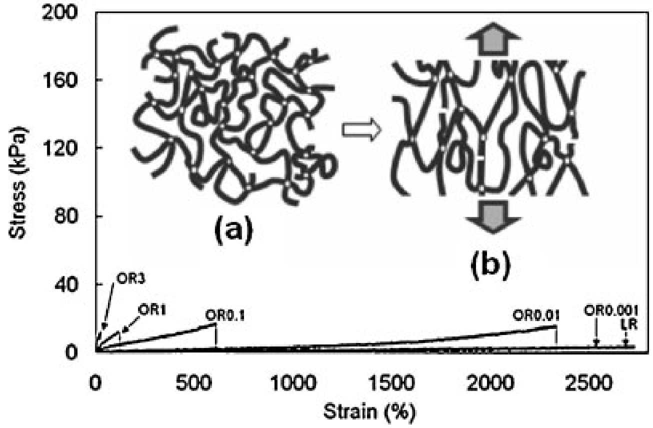

Figure 3.
Tensile stress-strain curves of LR (PNIPA viscous gel-like material) and N-OR gels with different C_{BIS} (0.001–3). (a) Schematic representation of the network of chemically crosslinked hydrogel (OR gel). (b) Rupture of crosslinked chains on unidirectional extension.

heterogeneity), low degree of swelling and slow de-swelling rates.[1] The breakthrough with NC gels was attributed to the formation of unique organic (polymer)/inorganic (clay) networks. Here, we discuss the effect of inorganic crosslinker (clay) on mechanical properties compared to the OR gels described above.

Figure 4 shows the influence of C_{clay} on the tensile stress-strain curves of N-NC gels. Different C_{clay}s ($=0.05 \sim 10$) were introduced into LR in a similar manner to C_{BIS} in OR gels. From the optical transparencies, it was concluded that exfoliated clay platelets were uniformly distributed throughout the aqueous media for all values of C_{clay} used. As seen from Figure 4, the modulus gradually increased with increasing C_{clay}, and ε_b decreased quite sharply to about 1000% (~N-NC1). However, values of ε_b were approximately constant ($\varepsilon_b \approx 1000\%$) at C_{clay} higher than for N-NC1, although the modulus continuously increased. Also, as shown by the dotted line, the increase in ultimate strength was almost proportional to C_{clay}. The maximum strength reached was more than 1000 kPa for N-NC25 gel for which ε_b

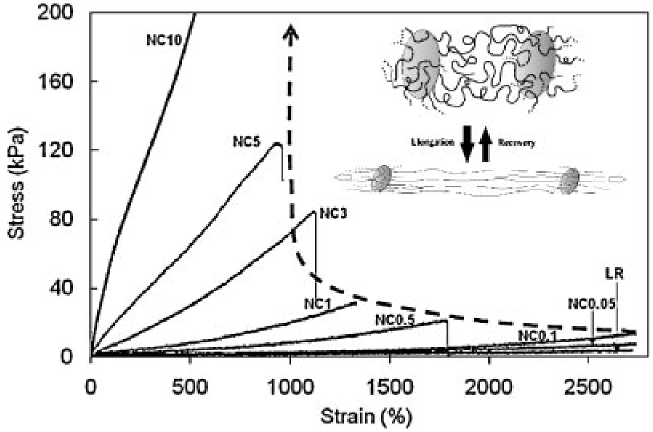

Figure 4.
Tensile stress-strain curves of LR and N-NC gels with different C_{clay} (0.05–10). The inset is a schematic representation of the unit structure of an organic/inorganic network.

was still about 1000%.[5] Thus, the effect of crosslinker on the tensile mechanical properties is clearly different from that of OR gels shown in Figure 3. This is due to the formation of a unique organic/inorganic network structure, in which small numbers of clay platelets act as super-multi-functional crosslinkers. Figure 4 indicates that a well-defined organic/inorganic network may be formed at C_{clay} above N-NC1 for the present system based on 1 M of NIPA. The numbers of crosslinking units in NC and OR gels are quite different, by almost a factor of 5×10^2, e.g. 16 (NC3 gel) and 7500 (OR3 gel) per 100 nm cube. Thus, D_{ic} in NC gels should be very large and more narrow distributed than those of OR gels. The reason for high values of ε_b, regardless of high C_{clay}, is attributed to the large deformability of flexible polymer chains in the unit structure (see the inset to Figure 4) of organic/inorganic networks. In addition to the influence of C_{clay}, ν can be controlled independently by changing the polymer content, since the number of polymer chains linking neighboring clay platelets increases with increasing polymer content. In contrast, ν in OR gels, which was determined by C_{BIS}, is independent of polymer content.

(c) Network formation in NC gels

The formation of polymer networks with inorganic clay in NC gels was proposed and confirmed in previous papers on the basis of mechanical and swelling properties, as well as the analytical data. In this section, the evidence for networks in NC gels is further investigated by dynamic mechanical measurements and the analysis of swelling behavior. Figure 5 shows the dynamic viscoelastic properties (frequency sweep at 22 °C) for D-NC5 gel. It was observed that G′ (storage modulus) is always greater than G″ (loss modulus) in the frequency range $10^{-1} \sim 10^2$ rad s^{-1}, and that G′ and G″ change little with frequency. These observations are consistent with the dynamic viscoelastic properties that characterise hydrogels with three-dimensional network structures. Thus, it was concluded that, in NC gels, the polymer chains form networks by using clay platelets as effective crosslinkers.

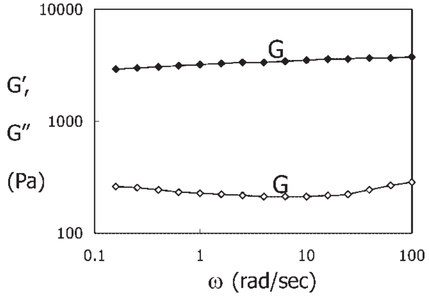

Figure 5.
Dynamic viscoelastic properties (G′ and G″) of D-NC5 gel measured at 22 °C in the range of 0.2–100 (rad/sec).

With regard to the swelling behvior, it was reported that NC gels do not dissolve in water but swell until they reach an equilibrium state. During the swelling test, neither free linear polymer nor free clay particles separated from the network, which indicates that all polymer chains and clay particles are incorporated into the polymer/clay networks. NC gels generally showed higher degrees of swelling than OR gels, although the extent of swelling depended on C_{clay}. Degrees of equilibrium swelling (DES) for N-NC and N-OR gels are listed in Table 1. Here, we used the swelling data at 200 h as DES. The effective crosslink densities (ν_e) of NC and OR gels calculated using DES and the Flory-Rehner Equation (2)[16,17] are also listed in Table 1.

$$\phi + \ln(1-\phi) + \chi\phi^2 = -V_s\nu_e\left[\left(\frac{\phi}{\phi_0}\right)^{1/3} - \frac{2}{f}\left(\frac{\phi}{\phi_0}\right)\right] \qquad (2)$$

Here, ϕ and ϕ_0 are, respectively, the network volume fractions at equilibrium swelling and for the reference state (as-prepared gel). (2/f) (f is the functionality) is 0.5 for BIS in OR gels, and nearly 0 for clay in NC gels because of its high functionality. V_s is the molar volume of water. $\chi = \chi_1 + \phi\chi_2$, where $\chi_1 = (\Delta H - T\Delta S)/k_BT$, $\chi_2 = 0.518$, $\Delta H = -12.462 \times 10^{-21}$ J, and $\Delta S = -4.717 \times 10^{-23}$ J/K.[18] k_B

Table 1.
Equilibrium swelling for N-NC5, 10 gels and N-OR1, 5 gels, and their effective crosslink density calculated by Equation (2).

Hydrogel	N-NC5	N-NC10	N-OR1	N-OR5
Equi.swelling(W_{gel}/W_{dry})	29.9	22.6	16.9	8.55
ν_e(mol/L)	0.010	0.013	0.043	0.158

is Boltzmann's constant. The fact that ν_e of N-NC gels increased with increasing C_{clay}, analogous to the influence of C_{BIS} in N-OR gels, indicates that networks are formed by using clay as crosslinker in NC gels. The result that ν_e of NC gels is much smaller than those of OR gels is consistent with the observed mechanical properties.

Extended Characteristics of NC Gels

It was reported that NC gels exhibit many unique characteristics in addition to excellent optical, mechanical and swelling/de-swelling properties. For example, reversible force generation as a result of the coil-to-globule transition of PNIPA chains in response to cycling the temperature across the lower critical solution temperature (LCST),[6] the formation of unique porous morphologies with a three-layered structure in the freeze-dried state,[7] the characteristic sliding frictional behaviors with remarkable changes in the coefficient of friction at the surfaces of NC gels,[8] biocompatibility including implantation and antithrombogenicity,[19] total control over the coil-to-globule transition of PNIPA chains by inorganic clay nanoparticles,[4] cell cultivation on the surfaces of NC gels with specific compositions and the subsequent detachment of cultivated cell sheets without treating with tripsin,[9] and so on.

Below, we briefly describe other characteristics of NC gels which make them useful as advanced or environmentally-friendly materials.

(a) NC gels are virtually incombustible because the primary component is water (normally about 90 wt %). As shown in Figure 6 (D-NC5 gel), NC gels generally show excellent flame-retardancy. In some cases, NC gels can even extinguish a surrounding fire by releasing water. Also, in a flame, it is difficult to burn film or paper wrapped closely over the surface of an NC gel. Furthermore, it is expected that dried NC gels, after evaporating their water, show fire retardancy (slow heat release rate) by analogy with polyamide/clay nanocomposites reported by J.W. Gilman et al.,[20] because the dried NC gels are actually polymer/clay nanocomposites containing a large amount of exfoliated clay uniformly dispersed in a polymer matrix. The dried D-NC5 and D-NC20 gels are contain 28 and 61 wt % of inorganic clay, respectively.

(b) Thermal conductivity, by which heat is conducted or dissipated, is one of the most important properties required in many industries. As is well known, soft organic materials such as silicones, polyurethane and natural rubber have fairly low thermal conductivities. Large quantities of many kinds of additives, such as carbon black, graphite, milled carbon fibers and fine metal powders, may be compounded with such materials to increase their thermal conductivities, although the additives often harden the materials. As shown in Figure 7, NC gels being soft, rubbery materials show fairly good heat conduction. In the experiment shown, the temperature increase was much higher than for silicone rubbers. This result is because heat can flow through the water contained within an NC gel, although the water is strongly retained within the material from a mechanical property point of view.

(c) Of the materials shown in Table 2 water has the highest specific heat (C_p). Therefore, NC gels, containing large amounts of water should have high heat capacities. NC gels may be

Figure 6.
Flame – retardancy of D-NC5 gel.

useful as components of both coolers and heaters with high heat capacity.

(d) NC gels are normally obtained as transparent materials. On the other hand, coloring is always required to distinguish products. Also intense colors are useful in many applications, including printing and display industries. It was found that NC gels can be colored during the synthesis or by an after-treatment. NC gels with various colors (black, red, blue and transparent) are shown in Figure 8(a). The stability of the color depends on the composition and the conditions of preparation.

(e) In general, polymeric materials have fairly low densities, around $0.9 \sim 1.3$ g/cm^3, compared with those of metals or metal oxides. However, to meet the requirements for more light-weight materials, porous polymeric materials such as foamed polystyrene and polyurethane have been developed. NC gels have a density in the range of $1.05 \sim 1.3$ g/cm^3. Porous NC gels (Figure 8(b)) with a density of 0.2 g/cm^3 were prepared by using a porogen during NC gel synthesis. The porous NC gel was white and very soft (with very low modulus) as well as being very light.

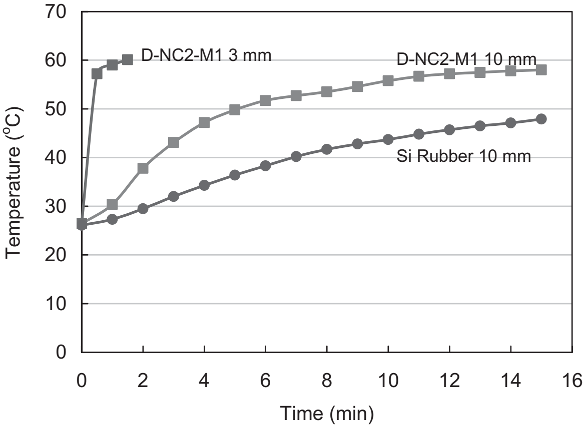

Figure 7.
Temperature changes by thermal conduction through D-NC2 gel and silicon rubber.

Table 2.
Heat capacities of various materials including water.

Materials	Water	Ice water	Polyethylene	Wood	Aluminum	Concrete
Heat Capacity (J/g · K)	4.22	2.13	2.23	1.25	0.88	0.84

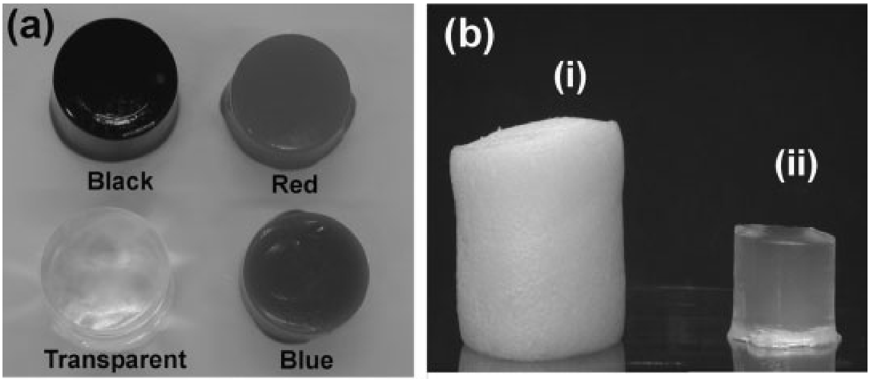

Figure 8.
(a) Colored D-NC5 gels. (a) Foamed D-NC5 gel. (i) Foamed. (ii) As-prepared.

Finally, it should be emphasized that NC gels are one of the most ideal environmentally-friendly materials. Although NC gels have various characteristics similar to conventional soft organic materials, such as extraordinary mechanical toughness and high transparency, in addition to many other functions described above, the primary component of NC gels is water, while 5 ~ 65 wt % of the solid components are inorganic clay which can be returned to the soil without harmful effects. Thus, only 5 ~ 10 wt % of an NC gel is a polymeric component derived from petroleum. From a resources viewpoint, NC gels are made from large amounts of water and a small amount of petroleum-derived materials. NC gels are the first materials in which water is used as a primary raw material. Also, they are environmentally-friendly materials from the view point of energy used in their preparation, because NC gels can be prepared in high yield (near to 100%) without heating (i.e. at ambient temperature) and without stirring. Further, NC gels show an inherent nonflammability without incorporating any harmful halogen or phosphate. The situation is also the same from the viewpoint of waste, as only 5 ~ 10 wt % of NC gels become organic waste.

Conclusion

It was demonstrated that NC gels can be prepared in various shapes including films, rods, spheres, hollow tubes etc, with different thicknesses or diameters, by using vessels with the corresponding space. Also, the surface was arbitrarily changed to various forms by using corresponding uneven templates during the synthesis. These developments were possible because of the simple procedures used for preparation and the high mechanical toughness of the resulting NC gels. NC and OR gels showed entirely different mechanical properties, although both have the same composition except for the crosslinker. The effect of crosslinker (BIS or clay) on the mechanical properties is discussed in terms of network structure. In conventional OR gels, the strength hardly increased with BIS content because ε_b decreased sharply while the modulus increased. In contrast, in NC gels, ε_b remained constant for C_{clay} greater than that at which the organic/inorganic network is formed. At higher C_{clay}, increases in strength and modulus were almost proportional to C_{clay}. Network formation by clay was also confirmed by dynamic viscoelastic measurements. Further, the crosslink density was evaluated, based on the Flory-Rehner equation for swelling. In addition to the functions previously reported, NC gels exhibit the interesting characteristics, such as inherent incombustibility, good thermal conductivity, high heat capacity, and can be readily colored and fabricated as foams. Since the primary component is water, NC gels should be expected to be utilized as environmentally-friendly materials from the viewpoints of resources and waste.

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