Compositional Effects on Mechanical Properties of Nanocomposite Hydrogels Composed of Poly(*N*,*N*-dimethylacrylamide) and Clay

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ABSTRACT: Nanocomposite type hydrogels (DMAA-NC gels) consisting of organic (polymer)/inorganic (clay) networks were prepared by in-situ free-radical polymerization of *N*,*N*-dimethylacrylamide (DMAA) in the presence of inorganic clay in aqueous solution. The composition of the NC gels could be controlled directly by altering the composition of the initial reaction mixture. The resulting DMAA-NC gels were mostly uniform and transparent, irrespective of their clay and polymer contents. From DSC, X-ray, TEM, and tensile mechanical measurements, the network structure was established. Contrary to conventional chemically cross-linked hydrogels (DMAA-OR gels) prepared by chemical cross-linking with a difunctional monomer, DMAA-NC gels exhibit superb mechanical properties with astonishingly large elongations at break, near to or greater than 1500%. The effects of the composition, such as the amounts of clay, polymer, and water content in DMAA-NC gels, on the tensile mechanical properties were investigated in detail. With increasing clay content from $C_{\text{clay}} = 1$ to 7 (C_{clay} is proportional to the weight of clay per unit volume of water, and a value of 1 corresponds to 0.762 g clay per 100 mL of water), the modulus and the ultimate tensile strength increased almost proportionally to the clay content, but the elongation at break decreased slightly. By altering the polymer content over 2 orders of magnitude, it was observed that the nature of the mechanical properties of DMAA-NC gels changed markedly. Above a lower critical polymer content ($C_p \approx 0.13$), the elongation at break increased rapidly from near zero to more than 1000%. Thereafter, the hydrogels became very tough NC gels. With further increases in polymer content, the strength and the elongation at break showed maxima at certain polymer contents, whereas the modulus increased monotonically. The mechanical properties were also changed by altering the water content. The cross-link density was estimated for DMAA-NC gels with different clay contents. The effects of clay and polymer contents on the mechanical properties, as described above, were discussed on the basis of the network structure model for NC gel.

Introduction

Polymer hydrogels can be divided into two main classes, i.e., chemically cross-linked hydrogels, which are composed of polymer networks with covalent bonding, and physically cross-linked hydrogels, which are composed of physical networks with noncovalent interactions. To date, hydrogels of poly(*N*-alkylacrylamides) such as poly(*N*-isopropylacrylamide) (PNIPA) and poly(*N*,*N*-dimethylacrylamide) (PDMAA), which have attracted extensive attention as water-absorbing, soft and stimuli-sensitive materials,[1−15] were all prepared by chemical cross-linking reactions using an organic cross-linker such as methylenebis(acrylamide) (BIS).

However, because of the random nature of the cross-linking reactions produced by a large number of organic cross-linkers, the conventional chemically cross-linked hydrogels (hereinafter, abbreviated as OR gels) have many limitations in morphology and properties, e.g., morphological inhomogeneity, mechanical weakness, limited swelling at equilibrium, and slow response to stimuli. Therefore, for example, NIPA-OR gels consisting of PNIPA chemical networks readily become turbid due to structural inhomogeneities induced by increasing the cross-link density,[16] pressure,[17] and polymerization temperature.[18] Also, swelling ratios or deswelling rates are not always sufficient for certain applications.[5,19,20] These limitations mainly arise from restricted molecular motions of PNIPA chains caused by cross-linking with a large number of organic cross-linkers. Furthermore, the most serious limitations of OR gels are due to their weak and brittle nature.[21,22] Irrespective of the composition or conditions of preparation, NIPA-OR gels always broke at elongations less than 30% or when bent through 180°[23] and so were very difficult to handle in applications requiring significant applied stress or strain. This limitation is due to the low average and broad distribution of chain lengths between cross-linking points in OR gels.

Recently, and in order to overcome the limitations of OR gels, we succeeded in synthesizing a new type of polymer hydrogel: nanocomposite type hydrogels (herein after abbreviated as NC gels, e.g., NIPA-NC gel) consisting of a unique organic (polymer, e.g. PNIPA)/inorganic (clay) network.[23] We found that we could break through all the limitations described above with NC gels which showed remarkable improvements in mechanical, optical, and swelling−deswelling properties. That is, NC gels simultaneously exhibit high transparency (structural homogeneity) irrespective of the preparation conditions, excellent, tough mechanical properties, with astonishingly large elongations, large swelling ratios, and rapid deswelling responses to temperature changes. NIPA-NC gels were prepared by in-situ free-radical polymerization of *N*-isopropylacrylamide, in the presence of inorganic clay exfoliated in an aqueous media. The formation of effective polymer/clay networks could be achieved using inorganic clays which act as multifunctional cross-linking agents through noncovalent interactions instead of using organic cross-

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linkers. The characteristics of NC gels strongly depend on their compositions. In other words, they could be controlled over a wide range by altering their composition and network structure.

In previous papers,[24] we have shown that the clay content had a large effect on the characteristic properties of NIPA-NC gels and that the main result of increasing the clay content was an increase in the cross-link density. The tensile modulus and the ultimate tensile strength increased with increasing clay content, while the large elongation at break showed a tendency to decrease slightly. In addition, both the swelling ratio at equilibrium below the LCST (lower critical solution temperature ∼ 32 °C) and the rate of deswelling above the LCST gradually decreased with increasing clay content. The structural homogeneity, as observed by optical transparency, remained high irrespective of clay content. All these improvements in properties can be explained by the dependence of the cross-link density on clay content.

In the present study, we deal with DMAA-NC gels in which the polymer content can be altered easily because DMAA monomer dissolves in water in all proportions,[25] and the polymer, PDMAA, does not exhibit LCST behavior; i.e., the polymer solutions are stable against temperature changes. We confirmed the formation of NC gels in DMAA/clay systems, and the main features investigated were the effects of composition, such as clay, polymer, and water contents, on their mechanical properties. On the basis of the proposed network structure model, the structural changes of network were thereby discussed.

Experimental Section

Raw Materials. *N*,*N*-Dimethylacrylamide (DMAA) monomer, provided by Kohjin Co., Japan, was purified by filtering through activated alumina. Other reagents were purchased from Wako Pure Chemical Industries, Japan, and used without further purification. Milli-Q ultrapure water was used for all experiments, including swelling experiments. For hydrogel preparation, nitrogen gas was bubbled through the water for more than 3 h prior to use. As an inorganic clay, synthetic hectorite “Laponite XLG” (Rockwood Ltd., UK; $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$: a layer size = 20−30 nm $\phi \times 1$ nm, cation exchange capacity = 104 mequiv/100 g) was used after washing and drying. Here, the term inorganic clay is used in contrast to organophilic clay, which contains substantial amounts of organic surfactant and is ordinarily used in the preparation of polymer−clay nanocomposites.[26]

Sample Nomenclature and Synthesis of PDMAA Hydrogels. NC and OR gels were prepared using initial solutions consisting of monomer (DMAA), cross-linker (clay or *N*,*N*′-methylenebis(acrylamide) (BIS)), solvent (H_2O), initiator (potassium peroxodisulfate (KPS)), and catalyst (tetramethylendiamine (TEMED)). The same amount of water (30 mL), initiator (1.11×10^{-1} mmol), and catalyst (1.60×10^{-1} mmol) were used for all preparations of NC and OR gels. To prepare various DMAA-NC gels with different compositions, the monomer and cross-linker contents in the initial solution were varied over a wide range as, in part, listed in Table 1. Since the monomer was completely consumed in the polymerization and all of the clay was included in the hydrogel, the polymer and clay contents of the gels as prepared were identical to the monomer and clay contents of the initial reaction mixtures.

Sample Nomenclature. The contents of clay, BIS, and polymer in hydrogels, designated C_{clay}, C_{BIS}, and C_{p}, respectively, are expressed using a simplified numerical value n, n', and m, respectively. As there was no syneresis on gel formation, apart from initiator consumed, C_{clay}, C_{BIS}, and C_{p} in the gel as prepared are all identical with the initial reaction mixture. Clay contents (C_{clay}) are expressed in terms of n, which represents {100 × (weight of clay per 1000 mL of water)/(molecular weight of $Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4Na_{0.66}$)}. A value of $n = 1$ corresponds to an initial solution of (0.762 g of clay/100 g of H_2O). The polymer content (C_{p}) is expressed as m, which corresponds to the number of moles of DMAA monomer in 1000 mL of water. Since the monomer was totally converted to polymer on gel formation, the initial monomer content was identical with C_{p}.

Table 1. Compositions of Initial Aqueous Solutions for Typical DMAA-NC and -OR Gels

hydrogel	composition[a] clay (g)	BIS (g)	DMAA (g)	water/hydrogel (wt %)
NC2.5-M1	0.572		2.97	89.4
NC2.5-M8	0.572		23.79	55.2
NC4.0-M1	0.914		2.97	88.5
NC5.5-M2.5	1.257		7.43	77.5
OR1-M1		0.042	2.97	90.9
OR5-M1		0.210	2.97	90.4

[a] All solutions contain 30 g of water and constant initiator and catalyst.

The compositions of NC gels are expressed using n and m as DMAA-NCn-Mm gel to define the content of clay and polymer. In this study, n ($=C_{\text{clay}}$) and m ($=C_{\text{p}}$) for NC gels were varied within the ranges 1−7 and 0.1−8, respectively. When m is 1, the last numeral, e.g. 1 in -M1, is often deleted for simplicity. For OR gels, the BIS cross-linker content (C_{BIS}) is expressed as n', which corresponds to the number of moles of BIS in the DMAA monomer and expressed as a percentage. In this study, the polymer content in OR gel is always fixed at $m = 1$. Then, OR gels are expressed as DMAA-ORn' gel. Since we mostly deal with DMAA in this study, the initial symbol DMAA- is sometimes deleted from NC and OR gels where there is no possibility of confusion. For swollen gels prepared by swelling the original NCn-Mm gel, the composition of the swollen gel is expressed as (xw)NCn-Mm gel using a swelling ratio where x is (weight of swollen hydrogel/weight of dried gel).

Synthesis of DMAA Hydrogels. The synthetic procedure is almost the same as that reported previously.[24] For example, to prepare DMAA-NC2.5-M2 gel, a transparent aqueous solution consisting of water (28.5 mL), inorganic clay (0.572 g), and DMAA (5.94 g) was prepared. Next, the catalyst (TEMED, 24 μL) and finally the aqueous solution of initiator [KPS (0.03 g) in H_2O (1.5 mL)] were added to the former solution with stirring at ice−water temperature. Then, free-radical polymerization was allowed to proceed in a water bath at 20 °C for 20 h. In this study, amounts of clay and DMAA were varied over the ranges 0.229−1.60 g and 0.30−23.8 g, respectively. In the preparation of OR gels, BIS (0.021−0.378 g) was used as a cross-linker. Throughout all experiments, oxygen was excluded from the system. Both NC and OR gels were synthesized in two kinds of tubular glass vessels, one with interior size = 27 mm $\phi \times 50$ mm length and the other with interior size = 5.5 mm $\phi \times 200$ mm length; here, ϕ represents the diameter. For analytical and transparency measurements, NC and OR gels were purified prior to use by immersing them in an excess of water at 20 °C for 48 h, changing the water several times. For measurements of mechanical properties, hydrogels were used as-prepared in order to retain the original water/polymer ratio equal to that in the initial gel samples, unless otherwise noted.

Characterization. Analytical measurements such as TG, TEM, SAXS, and DSC were performed using dried NC and OR gels in order to analyze their compositions and structures. Dried NC and OR gels were prepared by drying purified NC and OR gels under atmospheric conditions for 3 days and then at 80 °C in a vacuum oven for 24 h. Thermogravimetric (TG) analyses were carried out using a TG/DTA 220 (Seiko Denshi Ind. Inc.) instrument, heating samples from 30 to 1000 °C at a heating rate of 10 °C min^{-1} in an air flow. The clay content in the NC dried gel was evaluated from the residual weight at 1000 °C. Transmission electron microscopy (TEM) was undertaken using a JEM-200CX (Nihon Denshi Co.) instrument at 100 kV for NC dried gels. Ultrathin films (ca. 50 nm thick) were prepared for TEM observation by cutting dried gels embedded in epoxy resin, using an ultra-microtome (Reichert Ultracut S). X-ray diffraction profiles were obtained using milled dried samples with Cu Kα X-rays (X-ray diffractometer (Rigaku-Denki RX-7) was used). As internal reference, a small amount of silicon metal was used by incorporating it into the sample. Differential scanning calorimetry (DSC) measurements were performed using a DSC-7 (Perkin-Elmer Inc.) in a nitrogen gas atmosphere with milled NC and OR dried gels, heating from 30 to 250 °C at a heating rate of 1 °C min^{-1}. Glass transition temperatures (T_g) were obtained from the second run after heating to 250 °C in the first run.

Measurements. *Mechanical Properties*. Tensile mechanical measurements were, in general, performed on NC and OR gels of the same size (5.5 mm $\phi \times$ 70 mm length) using a Shimadzu Autograph AGS-H. Tensile properties of NC gels were obtained under the following conditions: sample length between jaws, 35 mm; crosshead speed, 100 mm min^{-1}; test temperature, 25 °C. The initial cross section (23.75 mm^2) was used to calculate the tensile strengths and the tensile moduli. Tensile moduli were calculated from the increase in load detected between elongations of 100% and 200%.[27] For samples of gel subjected to additional swelling, samples with an original size of 5.5 mm $\phi \times$ 35 mm (marked) length were used and clamped in their final swollen state: jaws were located at points of 35 mm. In contrast, tensile mechanical properties of OR gels could not be obtained using the same test method because OR gels were too weak to carry out the measurements. In particular, it was too difficult to clamp OR gels tightly enough for the tensile tests and OR gels always broke before obtaining precise mechanical data. Approximate mechanical data for OR gels were obtained using a simple elongation method with a ruler and weight.

Swelling Ratio. Swelling experiments were performed by immersing as-prepared gels (initial size of 5.5 mm $\phi \times$ 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}).

Transparency. Transparencies were measured using a NDH-300 turbidimeter (Nippon Denshoku Inc.) with a white halogen light for NC and OR gels (gel size = 27 mm $\phi \times$ 30 mm length) synthesized in glass vessels. The original water/polymer ratios were maintained after purification. All hydrogels within the glass vessels were maintained in a 1 °C water bath for 2 h immediately prior to each measurement. The total transmittance (T) was measured within a few seconds of removing the gel from the water bath.

Results

1. DMAA-NC and -OR Gels. DMAA-NC and -OR gels were prepared at 20 °C using the same procedures as used previously for NIPA-NC and NIPA-OR gels. Polymerization yields were almost 100% for both DMAA-NC gels and -OR gels, calculated from the weight of dried gels. This means that because the C_{clay} and C_p in NC gels were the same as those in the corresponding initial solutions, the final composition could be controlled directly by altering the composition of the initial solution. Typical initial solution compositions for DMAA-NC and -OR gels are listed in Table 1. No free PDMAA was observed in the aqueous media used in the purification and swelling processes. This observation indicates that all polymer chains are incorporated into the hydrogel and attached to the clay sheets.

The resulting DMAA-NC gel (e.g., DMAA-NC2.5-M2 gel) is shown in Figure 1. Almost all DMAA-NC gels and some DMAA-OR gels were transparent. The effect of the clay content (C_{clay} = 1−7) in NC gels and of the BIS content (C_{BIS} = 1−9) in OR gels on the transparency is shown in Figure 2. DMAA-NC gels with C_p = 1 exhibited good transparencies (T = 78−95%) throughout the range of C_{clay} used, although they showed a slight dependence on C_{clay} with a minimum at relatively low C_{clay} (= ca. 2). However, all NC gels with higher C_p ($\geq$2.5) exhibited high transparency (T > 95%) as shown in Figure 2. On the other hand, the transparency of DMAA-OR gels changed markedly (T = 3−99%) on changing C_{BIS}. That is, for $C_{BIS} \leq 5$, OR gels were transparent while for $C_{BIS} > 5$, the transmittance decreased rapidly with increasing C_{BIS}. OR gels were totally opaque for $C_{BIS} > 7$. The significant increase of opacity at high C_{BIS} was attributed to the morphological inhomogeneity resulting from irregular cross-linking by a large number of BIS molecules. None of the DMAA-NC or -OR gels exhibited an abrupt change in transparency or volume (deswelling) with an alteration of temperature. In other words, they are all stable against temperature changes. This is simply because in water PDMAA, unlike PNIPA,[5,28] does not exhibit a coil−globular transition in the temperature range 0−80 °C.

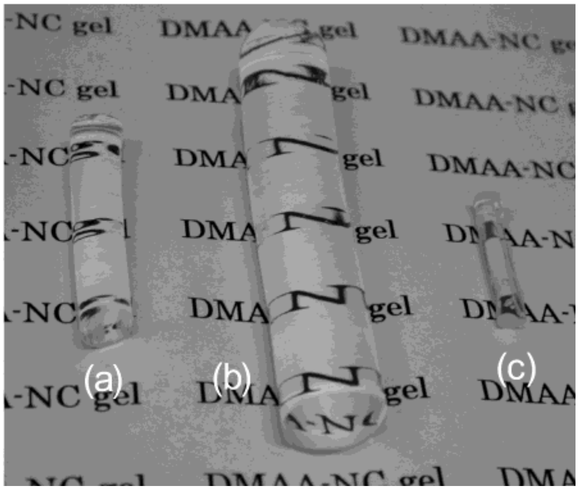

Figure 1. Typical DMAA-NC gel (DMAA-NC2.5-M2 gel) and the derived swollen and dried gels. The water/polymer weight ratio in the gel is shown in parentheses: (a) as-prepared gel (5/1), (b) swollen gel (30/1), (c) dried gel (0/1).

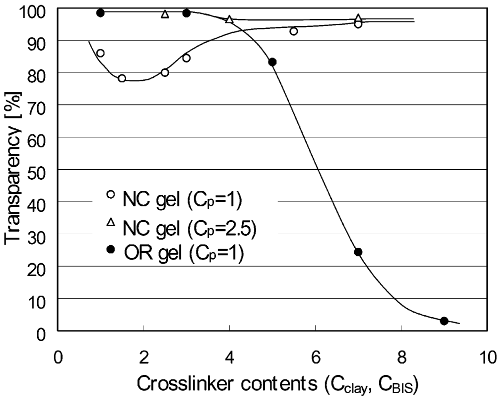

Figure 2. Changes in optical transparencies of DMAA-NC and -OR gels with different clay and polymer contents. Optical transmittance was measured at 1 °C for hydrogels, synthesized and purified at 20 °C, with a gel size (27 mm $\phi \times$ 30 mm length) in a glass vessel.

In their as-prepared state, the DMAA-NC gels are not fully swollen. To enhance their swelling, they can be soaked in a large amount of water. In parts a, b, and c of Figure1, an as-prepared DMAA-NC gel and the derived swollen and dried gels are shown, respectively.

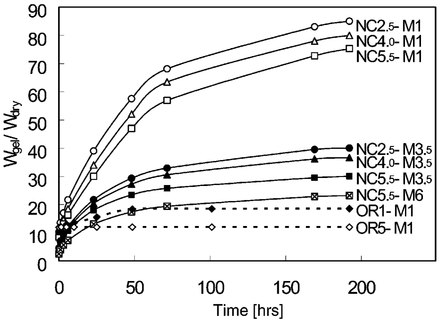

Figure 3. Time dependence of swelling ratio (W_{gel}/W_{dry}) measured for DMAA-NC and -OR gels with different clay and polymer contents. All original gels had the same size (5.5 mm $\phi \times 30$ mm in length), polymerized and swollen at 20 °C.

The time dependence of swelling ratio (= weight of swollen hydrogel/weight of solid), measured at 20 °C, is shown in Figure 3 for NC gels with different C_{clay} and C_p. Here, the swelling ratios at time = 0 correspond to the initial water contents of as-prepared NC and OR gels. It was found that, at all times and at equilibrium, the swelling ratio decreased with increasing C_{clay} and C_p. As described below, the increases in C_{clay} and C_p correspond to increased cross-link densities; hence, the decreased swelling with increasing C_{clay} and C_p is understandable. Several hundred hours was needed for swelling to reach equilibrium. It should be noted that values of n and m, defined earlier, relate to the amounts of clay and monomer used in the syntheses so that although the swelling ratio for DMAA-NC5.5-M6 gel in Figure 3 is the lowest, the total amount of water absorbed by the NC gel was largest because it had the highest dried weight.

2. Network Structure of DMAA-NC Gels. We presume that DMAA-NC gels consist of organic/inorganic networks similar to those of NIPA-NC gels, established previously.[23] The proposed model structure, shown in Figure 4, consists of networks of inorganic clay cross-linked by PDMAA through noncovalent interactions (probably hydrogen bonding, ionic, and/or coordinate interactions) between the PDMAA chains and the clay. Here, it is noted that, in the NC gels, free linear PDMAA chains could not be detected during the purification and swelling processes. This suggests that all polymer chains are attached to the clay and involved in the network. Also, the PDMAA component of the NC gel forms not only cross-linked chains (χ) but also grafted chains with a free chain end (g_1) or looped chains (g_2) in which both ends are attached to one clay sheet. Further, as for cross-linked chains, topologically cross-linked chains consisting of looped chains or trapped interchain entanglements, etc., might be included in NC gels. Although the precise nature of the interactions and the mechanism of network formation are still under examination, the interactions between (P)DMAA, initiator, and clay in the aqueous media and in the dried state were observed by similar means to those used for the PNIPA−clay system: viz, by solution viscometry and by IR spectroscopy. The proposed model for the nature of PDMAA/clay networks seems reasonable on the basis of analyses of their characteristic rubbery mechanical properties and their swelling behavior.

To verify the proposed model, the clay dispersion and the chain flexibility of the polymer in DMAA-NC gels were examined. For the clay, the fact that the resulting NC gel and its dried gel were both optically transparent, almost regardless of C_{clay}, indicates that it is finely and uniformly dispersed in the hydrogels. The nature of the clay dispersion was also elucidated by SAXS measurements. Parts a and b of Figure 5 show X-ray diffractograms for DMAA linear polymer and dried DMAA-NC2.5-M1 gel, respectively. As a reference, the X-ray diffraction profile of clay itself is also shown in Figure 5c. No X-ray diffraction peak at around for 2θ in the range 1°−9° was observed for either DMAA-NC2.5-M1 dried gel or PDMAA linear polymer (NC0), while the clay showed a strong diffraction peak at $2\theta = 6°$. This indicates that clay was sufficiently exfoliated in the dried gel state since the X-ray diffraction peak corresponding to a layer spacing of 1.5 nm for regularly stacked clay sheets was not observed. Therefore, it was considered that exfoliated clay was uniformly dispersed in the NC gel, which was largely expanded with water. The exfoliation and uniform dispersion of clay were also supported by TEM measurements. Figure 6 is a transmission electron micrograph of an ultrathin film of dried NC4-M1 gel. It shows that, even in the dried gel, the

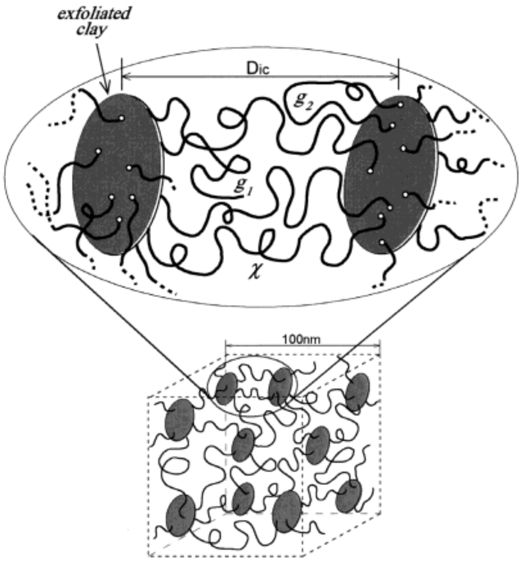

Figure 4. Schematic representation of the structural model with organic/inorganic networks in the NC gel. D_{ic} is interparticle distance of exfoliated clay sheets. χ, g_1, and g_2 represent cross-linked chain, grafted chain, and looped chain. In the model, only a small number of polymer chains are depicted for simplicity. Actual numbers of clay sheets and cross-linked chains estimated for various NC gels are listed in Table 2.

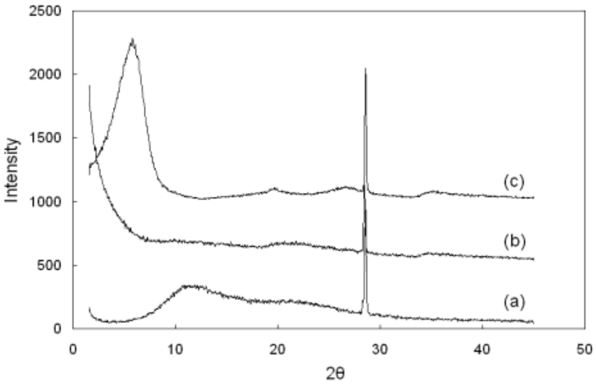

Figure 5. X-ray diffraction profiles with Cu Kα X-rays for milled dried materials of (a) linear PDMAA (NC0), (b) DMAA-NC2.5-M1 gel, and (c) clay. Dried materials of NC gel, linear polymer, and clay were prepared by drying after purification.

Table 2. Mechanical Properties, Structural Parameters, and Glass Transition Temperatures for Various DMAA-NC and -OR Gels

hydrogel	modulus (kPa)	strength (kPa)	elongation (%)	F^a at $\alpha = 2$ (kPa)	N^{*b} (/(100 nm)^3)	n^c (/(100 nm)^3)	N^*/n^d	T_g^e (°C)
NC2.5-M1	1.16	34.5	1654	1.26	175	9	19	128
NC4.0-M1	4.37	99.6	1347	6.11	847	15	56	128
NC5.5-M1	8.49	161.9	1264	12.42	1724	20	86	128
NC7.0-M1	15.55	255.6	1319	24.21	3360	26	129	128
OR3-M1		ca. 7	ca. 50					140
OR7-M1								160

[a] Stress at elongation of 100%. [b] Number of cross-linking polymer chains per unit volume (100 nm cube) of NC gels. [c] Number of clay sheets per unit volume (100 nm cube) calculated are based on complete exfoliation and clay sheet size of 30 nm $\phi \times 1$ nm. [d] Number of cross-linking polymer chains per clay sheet. [e] T_g of dried linear PDMAA was 124 °C.

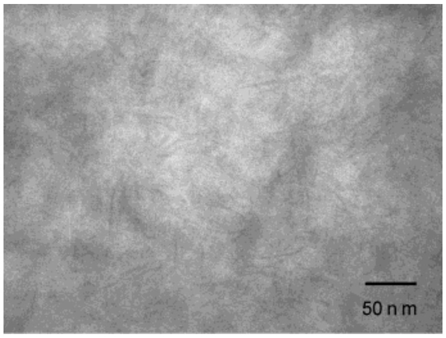

Figure 6. Transmission electron micrograph of dried DMAA-NC4-M1 gel at a magnification of 500 000. In the dried gel, the clay content in the solid was 23.5 wt %.

clay was substantially exfoliated and dispersed uniformly throughout the sample. The diameter and thickness of each clay sheet (as discrete platelike crystals) were mainly observed at about 30 and 1 nm, respectively, which indicate almost complete exfoliation of clay. The diameter and thickness observed here are almost consistent with those reported for Laponite XLG or Laponite RD particles in dilute solution by dynamic light scattering, small-angle X-ray, and small-angle neutron scattering.[29−31] The thicknesses of dispersed Laponite particles in dilute solution were somewhat different in each report, such as 1,[29] 2−4,[30] and 3.5 nm.[31] In the present study (NC gels), Laponite particles were well exfoliated probably due to the effect of interaction with PDMAA. Since the clay in the dry gel state was about 9 times more concentrated than in the hydrogel, it was concluded that a fine, homogeneous dispersion of clay must have been achieved in the hydrogel state.

The chain flexibility of the polymer component was evaluated by measuring T_g of PDMAA in its dried state. Table 2 lists T_gs measured by DSC for various DMAA-NC and -OR dried gels together with that for linear PDMAA. Almost the same T_g (ca. 128 °C) was observed unequivocally in dried DMAA-NC gels, irrespective of the C_{clay}, as that for linear PDMAA (124 °C). This indicates that the PDMAA chains in the NC gel network are sufficiently long and flexible to exhibit micro-Brownian motions above T_g, similar to those in linear PDMAA. On the contrary, since T_g in DMAA-OR gel increases with increasing C_{BIS} (130 °C for OR1 gel to 160 °C for OR7 gel), it can be concluded that the molecular motion of polymer chains in DMAA-OR gels was severely restricted by cross-linking.

The unique network formation made by these two components resulted in almost all of the DMAA-NC gels withstanding high levels of deformations (more than 1000% elongation, 360° torsion, and 90% compression), which was totally distinct from conventional DMAA-OR gels. In the following sections, the tensile mechanical properties of DMAA-NC gels are examined in detail, and the effects of composition, such as clay, polymer, and water contents, on the network structure are evaluated.

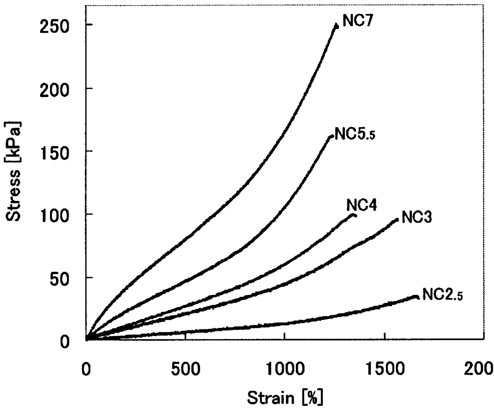

Figure 7. Stress−strain curves of DMAA-NC-M1 gels with different clay content (NC2.5 to NC7). All hydrogels had the same polymer/water ratio (= 1/10 (w/w)).

3. Mechanical Properties of DMAA-NC Gels. a. Effect of Clay Content. It was generally observed that DMAA-NC gels exhibited excellent tensile mechanical properties compared with conventional DMAA-OR gels. Similar to NIPA-OR gels,[23,24] DMAA-OR gels broke at very low extension, ca. 50%, irrespective of cross-linker content ($C_{BIS} = 1−9$), and showed very low ultimate tensile strengths (ca. 7 kPa). On the contrary, DMAA-NC gels generally exhibited very large elongations at break and high strengths. Also, it was observed that the tensile properties of DMAA-NC gels strongly depend on C_{clay}. Figure 7 shows tensile stress−strain curves measured for DMAA-NC gels with different C_{clay}, where both modulus and strength exhibit remarkable increases with increasing C_{clay}. On the other hand, elongations at break decreased slightly with increasing C_{clay}, particularly at relatively low C_{clay} (< NC4). In samples with higher C_{clay} (≥NC4) the elongation at break changed little, staying at an almost constant value of ca. 1300%.

The effects of C_{clay} on the mechanical properties of DMAA-NC gels described above were very similar to those for NIPA-NC gels,[24] although the absolute values of properties and their detailed dependencies on composition were somewhat different. Changes in tensile modulus, tensile strength, and elongation at break by altering C_{clay} for both DMAA-NC-M1 and NIPA-NC-M1 gels are summarized in Figure 8a−c. It was shown that DMAA-NC gels exhibit, as a whole, lower moduli and higher elongations at break than those of NIPA-NC gels, while the ultimate strengths were similar for both gels.

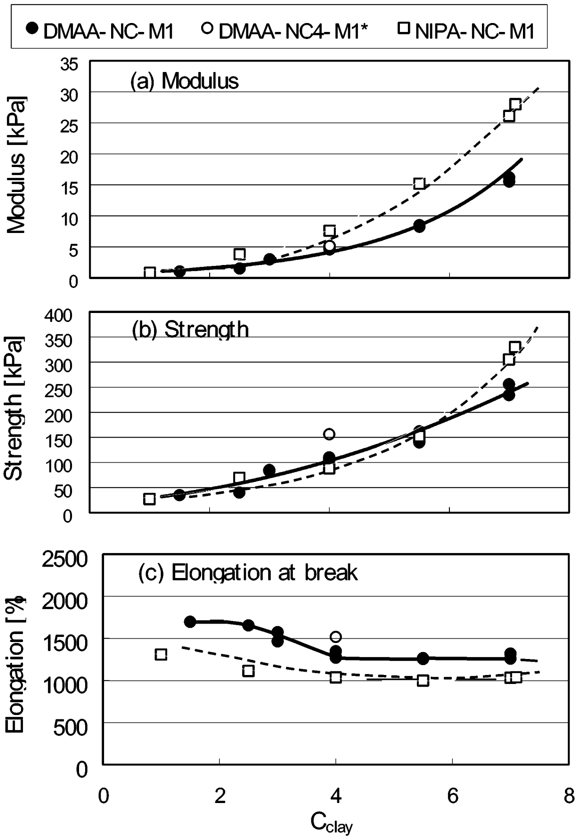

Figure 8. Changes of (a) tensile modulus, (b) tensile strength, and (c) elongation at break by altering clay contents for two series of NC gels: DMAA-NC-M1 gels (closed circle: solid line) and NIPA-NC-M1 gels (open square: dotted line). The properties of DMAA-NC4-M1* gel with the same polymer weight with NIPA-NC4-M1 gels are also plotted.

According to the nomenclature, NC gels prepared using different kinds of monomer contained the same C_p on a molar basis, but not on a weight basis. Thus, DMAA-NC4-MC1 gel contains a smaller weight of polymer (8.8 wt %) than does NIPA-NC4-MC1 gel (9.9 wt %). In Figure 8, the mechanical properties of DMAA-NC4-MC1* gel containing the same amount of polymer by weight as that of NIPA-NC4-MC1 gel are also shown. DMAA-NC4-MC1* gel exhibited both enhanced strength and elongation at break and a slight increase in modulus compared with the normal DMAA-NC4-NC1 gel. Therefore, it was concluded that the overall differences in mechanical properties between DMAA- and NIPA-NC gels shown in Figure 8 were not due to the difference in C_p, but from the characteristics of the constituent polymer or its network. From the mechanical property data, it was estimated that the network in DMAA-NC gels consisted of a smaller number of cross-linking chains, but with longer average chain length. This difference may arise from the different reaction kinetics and the different polymer characteristics such as higher chain flexibility and the greater hydrophilic nature of PDMAA compared with PNIPA, e.g., T_g(PDMAA) = 124 °C, T_g(PNIPA) = 142 °C; DMAA dissolves freely in water, but the solubility of NIPA is limited.

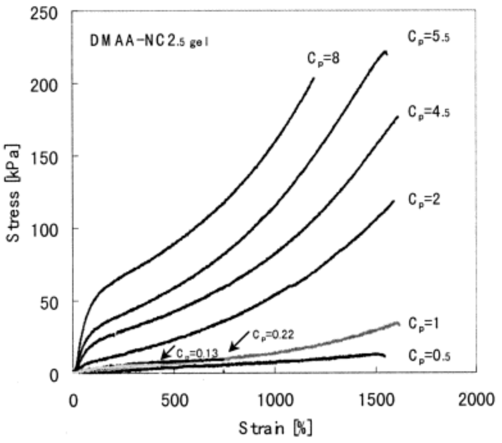

Figure 9. Effect of polymer contents (C_p = 0.13−8) on the stress−strain curves of DMAA-NC2.5 gels. All hydrogels had the same clay/water ratio (= 0.23/10 (w/w)).

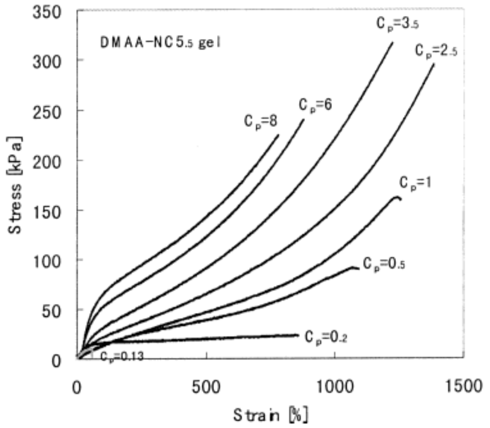

Figure 10. Effect of polymer contents (C_p = 0.13−8) on the stress−strain curves of DMAA-NC5.5 gels. All hydrogels had the same clay/water ratio (= 0.42/10 (w/w)).

b. Effect of Polymer Content. Figure 9 and Figure 10 show the stress−strain curves for a series of DMAA-NC2.5 and -NC5.5 gels with different C_p, respectively. Here, C_p was varied over about 2 orders of magnitude, from C_p = 0.1 to 8. In both figures, it was clearly shown that NC gels prepared using fixed conditions, apart from C_p, showed a large change in their mechanical characteristics, from very brittle to very tough, on increasing C_p. In the very low C_p region, a lower critical polymer content (C_p*), below which NC gels became brittle, was observed at ca. 0.13 for both DMAA-NC2.5 and -NC5.5 gels. Hydrogels with $C_p < C_p$* were too brittle to carry out standard tensile testing. Also, hydrogels prepared with C_p around C_p* were often neither uniform nor transparent. In the relatively low C_p region (C_p* ∼ ca. 0.5), the mechanical properties of NC gels changed dramatically with increasing C_p, as shown in Figures 9 and 10. In particular, elongations at break increased markedly from near zero to 1100−1600%. This indicates that the formation of the fundamental network of NC gels requires this magnitude of C_p. Then, in the following intermediate C_p region, it was estimated that increasing C_p may result in an increase in number of effective cross-links. Actually, it was observed that the modulus and the strength clearly increased significantly with increasing C_p in this region (C_p = 0.5−5.5). On the other hand, the elongation at break was almost constant or changed little on increasing C_p. For example, in a series of NC2.5 gels (Figure 9), the elongations at break were observed to be constant at ca. 1600%, irrespective of C_p. However, in a series of NC5.5 gels, elongations at break gradually changed with C_p in this region, as shown in Figure 10. Also, the absolute maximum

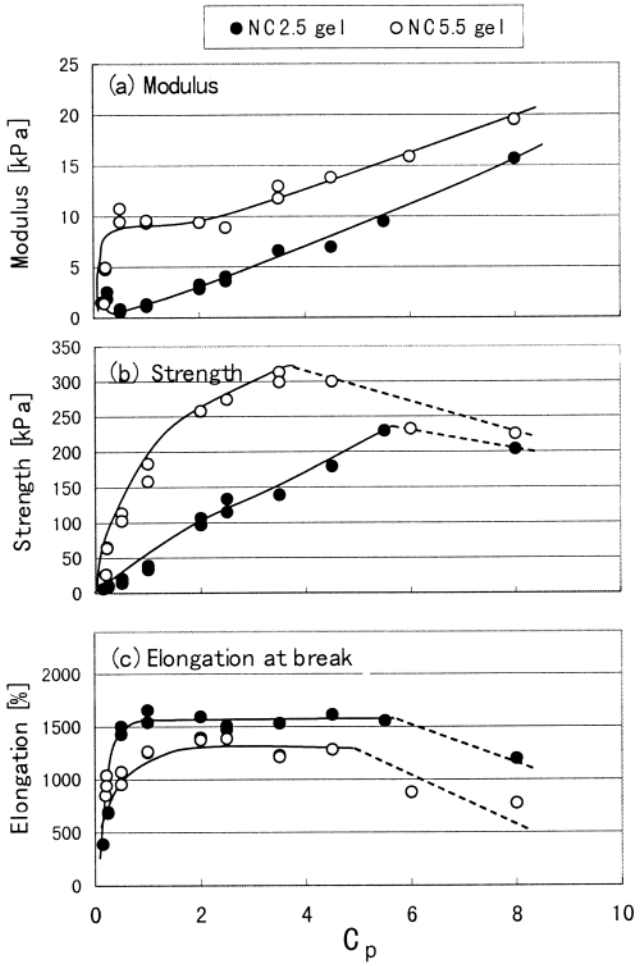

Figure 11. Variations in (a) tensile modulus, (b) tensile strength, and (c) elongation at break with C_p for DMAA-NC2.5 and -NC5.5 gels.

elongations of NC5.5 gels were, on the whole, a little less than those of NC2.5 gels.

The effects of C_p on tensile modulus, tensile strength, and elongation at break are summarized in parts a, b, and c of Figure 11, respectively, for DMAA-NC2.5 and -NC5.5 gels. It was revealed that the modulus increased almost linearly with increasing C_p in all NC gels and did not show any saturation throughout the range of C_p used. At very low C_p ($C_p \leq 0.5$), the behavior is more complex, and the greater C_{clay}, the more rapidly the modulus increases with C_p. On the other hand, although at low C_p the ultimate strengths are approximately proportional to C_p, the strengths showed a maximum at certain C_p followed by a gradual decrease at higher C_p. For example, NC2.5-MC5.5 gel, containing 5.5 times the standard C_p, exhibited a strength almost 6 times that of NC2.5-MC1 gel, while NC2.5-MC8 gel exhibited 5 times that strength. The increase in strength with increasing C_p also depended on C_{clay}. That is, the strength of NC gels increased more rapidly with C_p at high C_{clay}. The reason for the decrease in strength and elongation at break for higher C_p NC gels (e.g., $C_p = 8$) seems to be due to the increase of crack sensitivity, which caused premature fracture adjacent to the clamps.

c. Effect of Water Content. The effects of water content on the tensile mechanical properties were evaluated for a few swollen gels prepared by partial further swelling of the standard preformed NC4-M1 gel ($x = 8.7$) up to 2.1 times. The mechanical properties for partially swollen gels, (xw)NC4-M1 gels ($x = 13.4$ and 18.1), are shown in Figure 12. Since the partially swollen gels had different sizes (length and diameter) depending on the swelling ratio, the load−strain curves instead of stress−strain curves are shown in Figure 12. Also, to compare the results with those for the standard NC4-M1 gel, the elongation at break observed for each swollen gel was revised to correspond to the initial standard length of 35 mm. The revised data are shown in Figure 12 as dotted lines. It was found that the revised load−strain curves coincide with that of the standard NC4-M1 gel. Therefore, the force at $\alpha = 2$, i.e., the total number of cross-links in the specimen, was the same regardless of the degree of swelling. This result indicates that the NC gel network was merely expanded and not destroyed by further swelling. As a matter of course, the modulus (and cross-link density per unit volume) decreased with increasing water content because the cross section increased according to the extent of swelling. On the other hand, the maximum load and the revised elongations at break for partially swollen gels gradually decreased with increasing the degree of swelling. These effects may be due to the effect of the swelling in the lateral direction. NC gels swollen in the lateral as well as the longitudinal direction may break at slightly lower elongations by smaller applied forces.

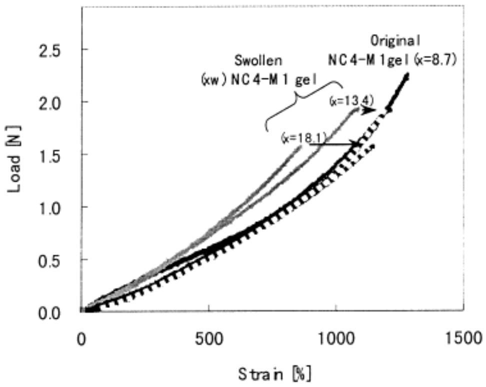

Figure 12. Load−strain curves for partially swollen gels of the original preformed NC4-M1 gel and their revised data based on the same original length.

d. Cross-Link Density in Various DMAA-NC Gels. The number of cross-linked polymer chains per unit volume of hydrogel, N^*, can be estimated according to (1)[32] by using the stress at 100% elongation ($\alpha = 2$).

$$F = \Phi N^* kT\{\alpha - (1/\alpha)^2\} \tag{1}$$

Here, F is the force per unit original (undeformed) cross-sectional area of the swollen network, Φ is a front factor (=1), α is the elongation ratio, and k and T are Boltzmann's constant and the absolute temperature.

From the tensile stress−strain curves shown in Figure 7, N^* for DMAA-NC gels with different C_{clay} were calculated (Table 2). Since N^* is proportional to the stress at $\alpha = 2$, N^* is seen to vary considerably, depending on C_{clay}.

In Table 2, the structural parameters, such as N^*, n (number of clay sheets per unit volume (100 nm cube)), and N^*/n, for typical NC gels are listed as well as their tensile mechanical properties. Here, the calculation of n is based on the assumption of complete exfoliation of the clay and a clay sheet size of 30 nm $\phi \times 1$ nm. For NC gels with high C_p, it is not appropriate to evaluate N^* from the tensile stress−strain curves; the effect of polymer−polymer interactions must be taken into account because the water content for NC gels with high C_p is small.

Discussion

The proposed network structure model for NC gels (Figure 4) is based on the characteristics outlined below. (1) An exfoliated clay sheet acts as an effective multifunctional cross-linking agent for the polymer. In other words, many polymer chains link the neighboring clay sheets together. (2) Exfoliated clay sheets are dispersed quite uniformly throughout the aqueous media. Since the number of cross-linking agents per unit volume is so much smaller in NC than OR gels, e.g., 9 (exfoliated clay sheets) for NC2.5 gel and 5400 (BIS units) for OR1 gel, the inter-cross-linking distance in NC gels, which is equivalent to the distance between neighboring clay sheets, is much larger than the average distance between junction points in conventional OR gels. (3) Cross-linked polymer chains in NC gels are flexible and behave like free linear polymers not subject to any severe restrictions.

The distinctive mechanical properties of NC gels can be explained in terms of the above model. The very large, reversible elongation and the superb flexibility are attributed to the existence of long, flexible polymer chains between cross-linking points. The high strength was due to the large chain extension possible without chain scission. The modulus and the swelling ratio could be controlled over a wide range by changing the cross-link density. The well-defined bonding type at cross-linking point is not yet completely elucidated; the present study clearly shows that the bonding is sufficiently strong to sustain the network structure under large mechanical deformation and external stress. Here, we discuss the effect of clay and polymer contents on the mechanical properties based on the proposed network structure.

Stress−Strain Curves. Since PDMAA has a high T_g (ca. 124 °C), the polymer chains in bulk and at ambient temperatures are frozen in a glassy state. However, in hydrogels containing a sufficient amount of water, the PDMAA chains are solvated and behave as if they are flexible polymer chains in the molten state and above their glass transition temperature. Therefore, a DMAA hydrogel is expected, at ambient temperatures, to be a soft material with rubberlike elasticity and reversible deformation. The conventional DMAA-OR gel formed by random cross-linking through covalent bonds, however, was very brittle and did not show such a rubbery nature. An enormous elongation of 1600% and tough mechanical properties were first realized simultaneously in the present nanocomposite-type DMAA hydrogel (NC gel). In this type of gel, the elongation at break was comparable to or greater than those of conventional natural or synthetic rubbers.[33] The softness and reversible deformability are also similar to those of rubbers. Consequently, NC gels can be called rubbery or elastomeric hydrogels.

In Figure 7, all stress−strain curves, irrespective of C_{clay}, resemble a typical affine−deformation curve in the relatively low strain region below several hundred percent strain. Also, in the higher strain region, over 700 or 1000%, the gels show typical strain-hardening behavior in which elongated polymer chains cause the curves to rise steeply. On the other hand, in Figures 9 and 10 for DMAA-NC gels with different C_p, the stress−strain curves showed more distinct changes in shape. In the higher strain region, over 600 or 1000%, similar steep rises in stress due to strain hardening arising from the effects of orientation on stretching were observed. In addition, in the very low strain region, less than 100%, very steep rises in the curves were clearly observed, which represent high initial modulus arising from large numbers of elastically effective chains per unit volume. The initial slopes and heights reached prior to the onset of strain hardening were almost proportional to C_p. Further detailed studies of mechanical properties, such as reversibility of deformation and stress relaxation for NC gel, will be presented in a subsequent paper.

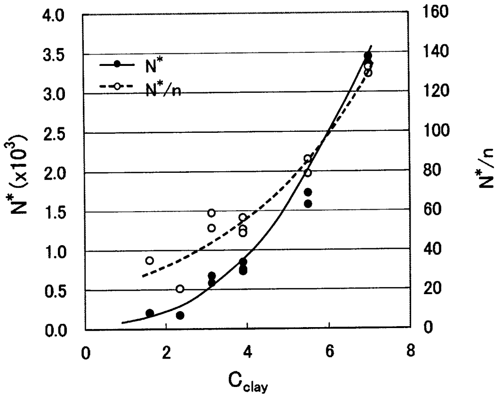

Figure 13. C_{clay} dependencies of the number of cross-linked chain (N^*) and the N^* per clay sheet (N^*/n) for DMAA-NC-M1 gels.

Effect of Clay Content. As shown in Figures 7 and 8, the tensile mechanical properties of DMAA-NC-M1 gels can be controlled over a wide range by altering C_{clay}. Also, from the results of the large elongation and good transparency of NC gels and almost constant T_g of constituent PDMAA chain regardless of C_{clay}, it is clear that the fundamental structural factors in the model (Figure 4), i.e., composed of the long flexible cross-linked chain and uniformly dispersed clay sheets, were accomplished over the range of C_{clay} used in this study. The variation of the estimated number of cross-linked polymer chains (N^*) and N^* per clay sheet (N^*/n) with C_{clay} is shown in Figure 13. N^* increases with C_{clay}, and the increase becomes steeper at higher C_{clay}. The property changes caused by varying C_{clay} can be explained, as a first consideration, by the insertion of additional clay sheets between two existing neighboring clay sheets. Then, at low clay contents (e.g., $C_{clay} \leq 2.5$), the additional clay particle may, in effect, produce additional cross-linking points at locations along the existing cross-linked chains. While at high C_{clay} ($C_{clay} \geq 2.5$), the formation of cross-linked chain is enhanced probably due to the effective conversion of graft or looped chains, which were attached to one clay sheet, into effective cross-linking chains because of the decreased interclay particle distance. Thus, the number of cross-linked polymer chains per clay sheet (N^*/n) also increased with increasing C_{clay} (Figure 13). Here, it is noted that N^* (=3360) estimated for NC7 gel with highest C_{clay} was still smaller than the number of difunctional cross-linker molecule (BIS) in conventional OR gels (e.g., 5400 for OR1 gel). This indicates that OR gels generally exhibit higher moduli than NC gels, although the moduli of OR gels could not be measured accurately in the normal tensile tests.

Effect of Polymer Content. It is readily expected that altering C_p may have a large effect on the mechanical properties through changing the number and/or length of cross-linked chains. In fact, as shown in Figures 9−11, all the values found for modulus, strength, and elongation at break varied depending on C_p as well as on C_{clay}, in different ways, as described in the Results section. The structural changes of the network corresponding to the C_p changes can be interpreted in terms of the proposed model structure.

In the low C_p region (∼0.5), it is expected that the increase of C_p corresponds to the formation of a real network. When the amount of monomer was insufficient, a completed network throughout the sample could not form. Instead, many polymer grafts formed on the clay sheets resulted in a material that was very weak and brittle and/or not uniform (partially phase separated). By increasing C_p in this range, network formation was accomplished throughout the sample, followed by each cross-linking polymer chain becoming longer and longer until adopting fully random conformations in the aqueous media between neighboring clay sheets. Therefore, modulus, strength, and elongation at break, starting from very small values, increased rapidly with increasing C_{clay}. In particular, strength and elongation at break increased steeply with the accomplishment of the network formation.

In the intermediate range of C_p (0.5 to ca. 5), the number of cross-linking polymer chains per unit volume increases with increasing C_p. Therefore, the modulus and strength increased almost proportionally to C_p, while elongation at break remained constant. By further increasing C_p, it was observed that the strength as well as the elongation at break eventually reached a plateau value and began to decrease slightly, although the modulus continued to increase monotonically. This is partly due to technical problems in the measurement procedure. The means of holding the sample became inadequate and often caused damage and/or slippage at very high C_p. An improvement in testing procedures would probably allow be possible higher strengths and elongations to be recorded for NC gels in this C_p range.

The above-mentioned qualitative explanations on the effect of C_{clay} and C_p will be further elucidated by additional studies on the mechanism of network formation and their mechanical creep and relaxation behaviors.

Conclusion

Nanocomposite type hydrogels, DMAA-NC gels, composed of poly(dimethylacrylamide) and inorganic clay (hectorite) were synthesized in aqueous solution by in-situ free-radical polymerization at 20 °C. Since the polymerization yield was nearly 100% and with no syneresis in any case, DMAA-NC gels with various predetermined C_{clay} and C_p were prepared by using initial solutions corresponding to the same compositions. NC gels obtained were mostly uniform and transparent except ones with very low C_p. It was confirmed, by swelling and mechanical tests, that an effective network structure was formed in the DMAA-NC gels without the use of any organic cross-linker. A network structure, consisting of organic (PDMAA)/inorganic (clay), was deduced from analysis of data from DSC, X-ray diffraction, and TEM observations and from swelling behavior. The resulting NC gels exhibited exceptional mechanical properties, distinct from those of conventional DMAA-OR gels. NC gels showed very high elongation at break, close to or greater than 1500%. The strength and modulus could be varied to a large extent depending on C_{clay} and C_p. The effects of C_{clay} and C_p on the tensile mechanical properties were substantiated. With increasing C_{clay}, the modulus and the strength increased almost proportionally, although the elongation at break decreased slightly. As for the effect of C_p, elongations at break for NC gels increased rapidly with C_p just above a certain lower critical C_p (≈0.13) and became very tough at high C_p. With further increase in C_p, the modulus and the strength increased, although the latter showed a maximum. It was observed that the shape of the stress−strain curve also changed with increasing C_p, particularly in the range of very low and very high strains, probably due to the increase of polymer−polymer interactions and the strain-hardening effect. The mechanical properties were also observed to be affected by water content (swelling ratio) in the swollen gel. Cross-link densities for NC gels with different C_{clay} were evaluated by using the tensile stress at 100% elongation. The changes in mechanical properties described above were discussed on the basis of the proposed organic/inorganic network structure.

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