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ARTICLE

Modification of Nancomposite Gels by Irreversible Rearrangement of Polymer/Clay Network Structure through Drying

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ABSTRACT: Nanocomposite gels (NC gels) have a unique organic (polymer)/inorganic (clay) network structure which causes them to exhibit excellent mechanical and swelling properties. It was found that dried and reswollen NC gels showed higher tensile moduli and strengths and low elongations at break as well as lower swelling when compared to those of NC gels as-prepared. The modification in properties brought about by drying was observed in all NC gels, regardless of the type of polymer used and the clay concentration. These changes were attributed to the irreversible rearrangement of the polymer/clay network structure in which additional cross-links are formed due to additional contacts between polymer chains and clay and the strengthening of preformed loose contacts in the concentrated state. The rearranged network structure remained almost unchanged on repeated drying and heating in the dried state. In contrast, conventional chemically cross-linked hydrogels showed no changes in properties in response to drying treatment.

Introduction

Nanocomposite gels (NC gels) consisting of organic (polymer)/inorganic (clay) networks have received a great deal of attention as a new type of polymer hydrogel[1−3] because they simultaneously overcome the disadvantages associated with conventional chemically cross-linked polymer hydrogels (OR gels) such as mechanical fragility, structural heterogeneity, and low thermosensitivity.[4−6] In particular, NC gels composed of poly(*N*-isopropylacrylamide) (PNIPA) or poly(*N*,*N*-dimethylacrylamide) (PDMAA) and inorganic clay (hectorite) showed excellent optical (e.g., transparency), mechanical (e.g., high mechanical toughness), and swelling/deswelling (e.g., large swelling and rapid deswelling) properties.[7,8] In addition, all these properties could be controlled over a wide range by altering the network composition, such as the concentrations of clay (C_{clay}), polymers (C_{p}), and water.[9,10] Moreover, NC gels have a number of novel functions related to the properties of their gel−air and gel−water interfaces, coil-to-globule transition, molecular orientation, interactions with cells, and control of morphology.[11]

The excellent properties and new functions of NC gels can be attributed to the unique polymer/clay network structure (Figure 1), which has been proposed on the basis of analytical data.[4,5,7−9,12−14] The structural aspects of the polymer/clay network are summarized as follows. (1) Exfoliated clay platelets act as multifuncitional cross-linkers; therefore, at least tens of flexible polymer chains link neighboring clay sheets together.[8] In other words, polymer chains in NC gels are cross-linked by a planar series of cross-links. (2) The inter-cross-link (i.e., interclay) distance in NC gels is much larger than that of OR gels, since a small number of exfoliated clay platelets are used as cross-linker in NC gels, in contrast to a very large number of cross-linking units (e.g., *N*,*N*′-methylenebis(acrylamide) (BIS)) used in OR gels. For example, 10 and 5400 in 100 nm cube in NC3 and OR 1 gels, respectively. (3) The interaction between polymers and clay nanoparticles is ascribed to noncovalent bonds, probably hydrogen bonds between the amide side groups (−CONH(R)) on the polymer and the surface of the clay (SiOH, Si−O−Si units).[12,13] (4) On the surface of clay, polymer chains are aggregated in layers about 1 nm thick because a number of polymer chains interact with a single clay platelet and each polymer chain may interact with the clay surface at multiple points.[14] (5) Further, on the basis of the mechanism leading to formation of a polymer/clay network during *in situ* polymerization,[8,12] it has been estimated that various types of polymer chains such as grafts with a free chain end (g_1), looped chains (g_2), and topologically cross-linked chains may be included in the polymer/clay network in addition to cross-linked chains (χ) (Figure 1).

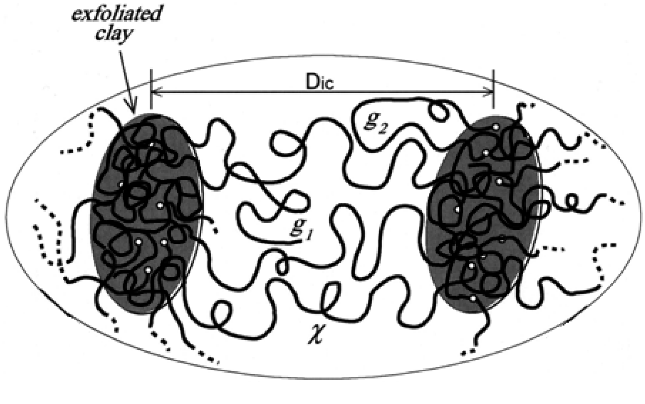

Figure 1. Schematic representation of the structural model of an organic/inorganic network of an NC gel. D_{ic} is the interparticle distance of exfoliated clay sheets, while χ, g_1, and g_2 represent polymeric cross-links, grafts, and loops. The surface of each clay platelet is surrounded by a concentrated polymer layer with a thickness of ca. 1 nm. In the model, only a small number of polymer chains are depicted for simplicity.

Thus, the network structure of NC gels is completely distinct from that of OR gels, which consist of a random arrangement of a

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large number of chemical cross-links. Recently, in addition to NC gels, several new classes of interesting polymer gels which exhibit high mechanical toughness have been developed based on different cross-linking systems.[15−20] Among them, from the multifunctional cross-link point of view, macromolecular microsphere composite (MMC) hydrogels, fabricated by growing hydrophilic polymer chains from the surfaces of hydrophobic polymer microspheres[19] and physically associating ABA-type triblock copolymer gels in a solvent (e.g., alcohol) selective for the midblock,[20] are classified within the same category as NC gels. There, it is important to clarify the role of multifunctional cross-linkers in the network and the capability of network modification by treatment at a fixed composition. In the present article, we report on the modification of the properties of NC gels brought about by a "first-drying" treatment accompanied by an irreversible rearrangement of the polymer/clay network structure.

Experimental Part

Materials. The monomers *N*-isopropylacrylamide (NIPA) and *N,N*-dimethylacrylamide (DMAA), obtained from Kohjin Co. (Japan), were purified by similar procedures as reported previously.[7,8] Potassium persulfate, *N,N,N′,N′*-tetramethylethylenediamine, and *N,N′*-methylenebis(acrylamide) (BIS) were used as the initiator, catalyst, and organic cross-linker, respectively. The synthetic hectorite, Laponite XLG (Rockwood Ltd.: $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$), was used as the inorganic clay after washing and freeze-drying. Ultrapure water supplied by a PURIC-MX system (Organo Co., Japan) was used for all experiments. Oxygen in the pure water was removed by bubbling nitrogen gas for more than 3 h prior to use.

Sample Nomenclature. The sample code for NC gels is defined by the monomers (N- and D- for NIPA and DMAA, respectively) and the concentrations of clay (C_{clay}). For example, N-NC*n* gel indicates an NC gel prepared using (C_{clay} =) $n \times 10^{-2}$ mol of clay and 1 mol of NIPA in 1 L of water. The clay concentration, *n*, was varied between 3 and 10, while the monomer concentration was always fixed at 1 M. OR*n′* gels were prepared using *n′* mol % of BIS relative to the monomer. The concentration of water in the hydrogel was expressed as $R_{H2O} = \{W_{H2O}/W_{dry}\} \times 100$, where $W_{H2O} + W_{dry} = W_{gel}$; W_{H2O}, W_{dry}, and W_{gel} are the weights of water, dried gel, and hydrogel, respectively.

Syntheses of Hydrogels (NC and OR Gels). The synthetic procedure described herein is the same as that reported previously.[9] To prepare an N-NC3 gel, a transparent aqueous solution consisting of water (28.5 mL), inorganic clay (0.686 g), and NIPA (3.39 g) was prepared. Next, the catalyst (24 μL) and an aqueous solution of initiator [30 mg in H_2O (1.5 mL)] were added to the reaction mixture at 0 °C while stirring. The solution was then transferred to a tubular glass vessel with an interior diameter of 5.5 mm and a length of 200 mm. Free-radical polymerization was then allowed to proceed with the sample in a water bath at 20 °C for 20 h. Oxygen was excluded from the solutions and the system throughout the syntheses. The same procedures were used for the OR gel syntheses except that an organic cross-linker was used instead of clay.

Drying Treatment. "Once-dried" NC and OR gels were prepared by drying and subsequent reswelling, which are explained as follows. Here, we use the term "once-dried" NC gels, OR gels, to describe gels in their "as-prepared state" which have been slowly dried to some specified water content and then reswollen with water to their initial water content. Both procedures were performed under the conditions described below. First, NC and OR gels as-prepared were slowly dried under atmospheric conditions in a clean, air-conditioned room maintained at 25 °C and 50% relative humidity. The minimum R_{H2O} attained during drying was termed R_{H2O}^{min}. Generally, 1 day (24 h) was required attain $R_{H2O}^{min} < 100$ wt %. To attain $R_{H2O}^{min} < 10$ wt %, gels were further dried in vacuum at 25 °C. For partial drying (R_{H2O}^{min} = 80−450 wt %), the gel was dried for 5−24 h under atmospheric conditions. Next, the dried gels were immersed in water at 20 °C until they reswelled to their original weight. Finally, the reswollen gels were maintained in tightly closed vessels for more than 3 days prior to use to achieve a uniform distribution of water throughout the sample. To induce annealing, dried NC gels ($R_{H2O}^{min} < 10$ wt %) were subsequently heated at temperatures between 80 and 180 °C for 2 h in the dried state.

Measurements. *Mechanical Properties.* Tensile tests were conducted on as-prepared and once-dried NC and OR gels using a Shimadzu Autograph AGS-H. The tensile properties were obtained under the following conditions: 25 °C; gel size, 5.5 mm diameter × 70 mm long; gauge length, 30 mm; crosshead speed, 100 mm min^{-1}. The initial cross section was used to calculate the tensile strength (TS) and modulus (*E*). Tensile moduli were calculated from the increase in load detected between elongations of 100 and 200%. For any of the conditions tested, 2−5 samples were used to confirm the reproducibility. No significant differences were observed in the stress−strain curves between nominally identical once-dried NC gels.

Swelling Ratio. Swelling experiments were conducted by immersing NC and OR gels (initial size of 5.5 mm $\phi \times 30$ mm length) in a large excess of water at 20 °C for ∼200 h, while changing the water several times. Swelling ratios are represented by the ratio of the weight of the swollen hydrogel (W_{gel}) to the corresponding dried gel weight (W_{dry}).

Results and Discussion

The NC and OR gels used in this study (N-NC*n* gels ($n = 3, 10$), D-NC*n* gels ($3 \le n \le 10$), and N-OR*m* gel ($m = 0.17, 1$)) were all prepared in an aqueous system at 20 °C. It was observed that the optical, mechanical, and swelling properties of all NC and OR gels as-prepared remain unchanged for long periods of time (of the order of several years), regardless of the C_{clay}, C_{BIS}, and type of polymer used, when maintained in a closed vessel at 20 °C. This observation indicates that the polymer/clay networks are very stable in the "as-prepared" condition; this behavior is similar to that of chemically cross-linked networks. Structural changes in the networks can be evaluated by changes in tensile mechanical and swelling behaviors. The tensile stress−strain curve for an N-NC3 gel in its as-prepared state is shown in Figure 3-1a. We first confirmed that the stress−strain curve for an "as-prepared" N-NC3 gel was almost unchanged after mild swelling and/or mild deswelling procedures. For example, a "once-swollen N-NC3 gel", obtained by swelling in water (20 °C) until the weight increased up to 250% of the initial weight, followed by deswelling in water (50 °C) until the original gel weight was reached, produced the same stress−strain curve as that of the as-prepared gel. The same stress−strain curves were also observed for as-prepared and "once-swollen" (swollen to 200−300% of the initial weight and then partially dried to the original weight) D-NC3 and D-NC5 gels, as shown in Figures 2a,b and 2c,d, respectively. These findings indicate that the polymer/clay networks in NC gels can change size reversibly (expand and contract) in response to modest swelling and deswelling without modification.

However, excessive deswelling (e.g., drying) of the NC gels was found to cause irreversible changes to their properties. As shown in Figure 3-1b, the once-dried N-NC3 gel showed remarkable changes in tensile mechanical properties, such as a high *E* (247%), a slightly higher TS (114%), and lower elongation at break (ε_b = 54%) relative to those of the as-prepared N-NC3 gel. The increase in *E* was most likely caused by the formation of additional cross-links in the network. Here, the additional cross-links may arise by the two mechanisms: the formation of entirely new cross-links and the strengthening of the preformed, loose interactions. The former may have resulted from new interactions between the long polymer chains and the clay surface created during the drying treatment. Here, the polymer chains and clay

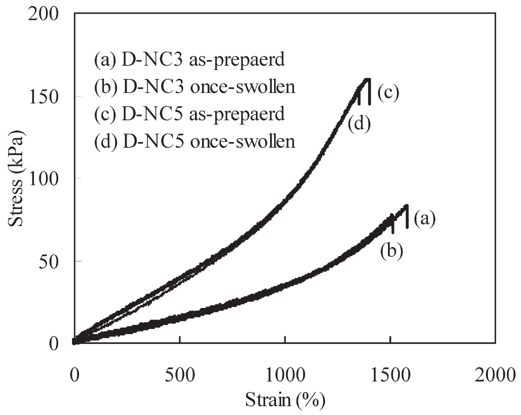

Figure 2. Stress−strain curves for D-NC3 and D-NC5 gels with different histories: (a) D-NC3 gel as-prepared; (b) D-NC3 gel once swollen to 200% of the initial weight; (c) D-NC5 gel as-prepared; (d) D-NC5 gel once swollen to 300% of the initial weight.

come into closer contact during deswelling, and additional, cross-linking points are formed in the concentrated (dried) state. The latter may have resulted from the local rearrangement of polymer chains, which were loosely associated with clay particles, so as to act as more effective cross-links, for example, by strengthening the interactions with clay at multiple points.

The relationship between E and elongation at break (ε_b) in the modified NC gels differed from that in the as-prepared NC gels with different C_{clay}. In the case of as-prepared NC gels, E increased with increasing C_{clay} without large decreases in ε_b and was accompanied by a substantial increase in TS that was almost proportional to the increase in E.[7−9] This is because an optimal network framework was formed in each NC gel during synthesis, depending on the value of C_{clay}. However, in the present study, a preformed polymer/clay network was modified through drying by forming additional cross-links. The formation of additional cross-links, by increasing the points of attachment between existing polymer chains and clay particles, inevitably decreases the average chain lengths between clay particles and, therefore, a decreased ε_b and slightly increased TS along with the increase in E.

The effect of repeating the drying treatment on the tensile properties of NC gels was examined. The results (data not shown) revealed that the tensile stress−strain curves of once-dried N-NC3 gels were almost unchanged in response to repeated cycles of drying and reswelling. These findings indicated that the polymer/clay network structure in the NC gels could be rearranged to increase the cross-link density while simultaneously decreasing the inter-cross-link chain length when the gels were initially dried after preparation. The resulting rearranged structures were stable against subsequent swelling, stretching, and repeated drying treatments.

The change in the polymer/clay network structure was further investigated for its response to heat treatment in the dried state. As shown in Figure 3-1c, stress−strain curves for once-dried N-NC3 gels that were subsequently heated at 180 °C for 2 h in the dried state were virtually unchanged except for a slight increase of TS. Here, it should be noted that the heat treatment in the dried state was carried out at temperatures above the glass transition temperature ($T_g \approx 142$ °C)[7] of the constituent polymer (PNIPA). These findings indicate that the formation of additional cross-links was largely completed during initial drying at room temperature and that the cross-links remained almost unchanged on further heat treatment in the dried state, regardless of the temperature.

The effect of drying on the tensile mechanical properties was also examined for N-NC*n* gels with different C_{clay}. Figure 3-2a shows the tensile stress−strain curves for as-prepared N-NC10 gels, which had much higher E and TS values than N-NC3 gels. It was revealed that that the N-NC10 gels were also modified by drying in a manner similar to that of N-NC3 gels, despite their higher initial tensile properties, as shown in Figure 3-2b. Here, E and TS increased to 170% and 129%, respectively, while ε_b decreased to 88% of the values for the as-prepared N-NC10 gels. Evaluation of the effect of heat treatment in the dried state revealed that E and TS of once-dried N-NC10 gels increased further in response to heating at 180 °C for 2 h (Figure 3-2c), although by heating at 100 °C ($< T_g$), the stress−strain curve was hardly changed. This differs somewhat from the results obtained for N-NC3 gels and indicates that the formation of new cross-links through drying at room temperature was incomplete in N-NC10 gels, probably because the polymer/clay interactions newly formed in the dried state are more complicated than in N-NC3 gel due to the larger number of clay particles and may need more energy (i.e., higher temperature) to reach equilibrium. It should be noted that C_{clay} in NC10 gel is the critical C_{clay} for the change of tensile mechanical properties and the appearance of optical anisotropy.[9,21] Then, on subsequent annealing at temperatures above T_g, values of E and TS were further increased. Also, Figure 3-2b,c indicates that additional cross-links mainly formed by the strengthening of preformed weak interactions, since TS and E increased without a large decrease in ε_b.

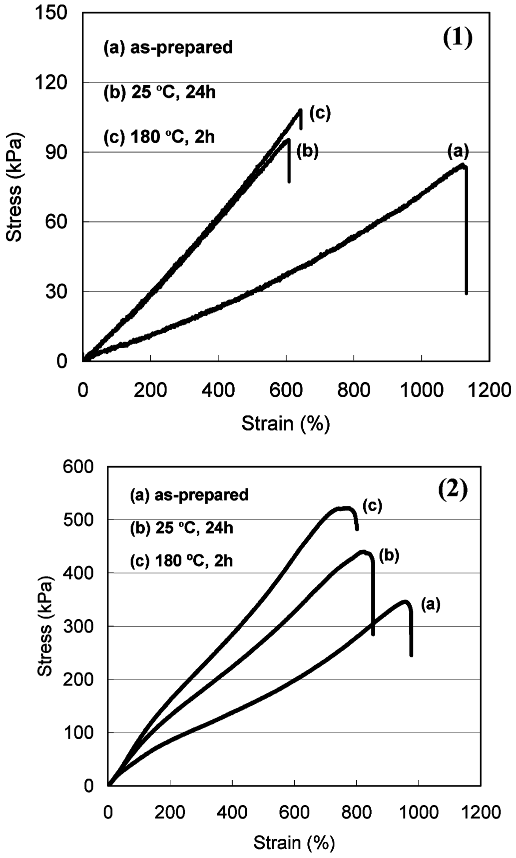

Figure 3. Stress−strain curves for (3-1) N-NC3 gels and (3-1) N-NC10 gels with different histories. (3-1): (a) as-prepared gel; (b) once-dried gel at 25 °C for 24 h; (c) once-dried gel heated at 180 °C for 2 h in the dried state. (3-2): (a) as-prepared gel; (b) once-dried gel at 25 °C for 24 h; (c) once-dried gel heated at 180 °C for 2 h in the dried state.

Rearrangement of the polymer/clay network structure caused by drying NC gels was also detected in their swelling behavior. Figures 4a and 4b show the time dependences of the swelling behaviors in water at 20 °C for the as-prepared and once-dried N-NC3 gels, respectively. The swelling of the once-dried N-NC3 gel was markedly depressed when compared with that in its

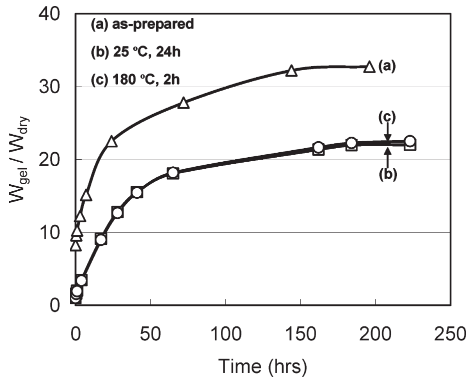

Figure 4. Time dependence of the swelling ratio (W_{gel}/W_{dry}) for N-NC3 gels with different histories, measured in water at 20 °C: (a) as-prepared gel; (b) once-dried gel at 25 °C for 24 h; (c) once-dried gel heated at 180 °C for 2 h in the dried state.

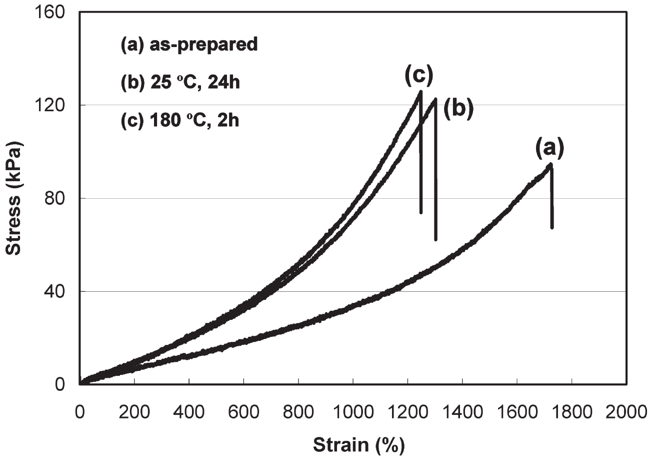

Figure 5. Stress−strain curves for D-NC3 gels with different histories: (a) as-prepared gel; (b) once-dried gel at 25 °C for 24 h; (c) once-dried gel heated at 180 °C for 2 h in the dried state.

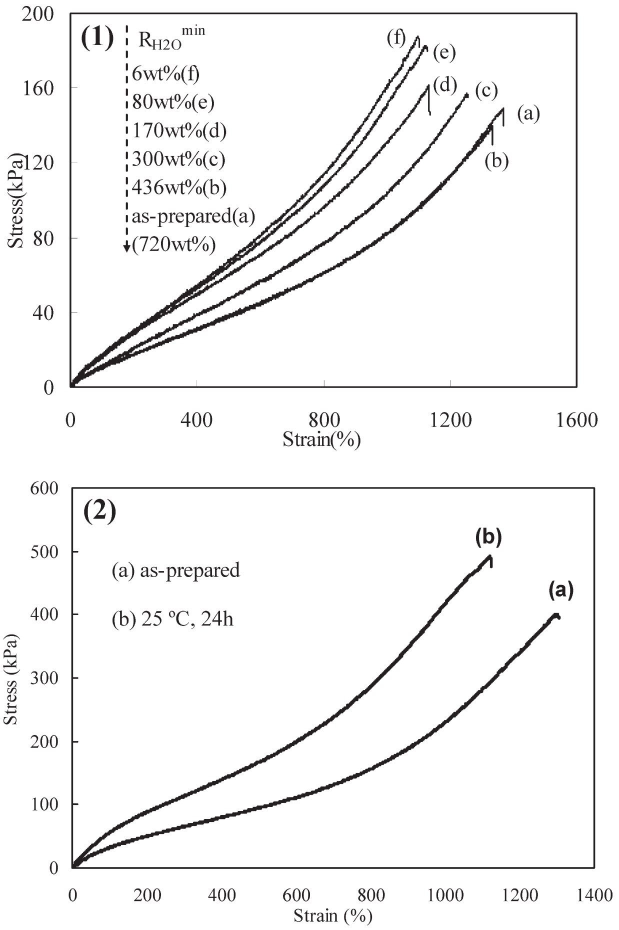

Figure 6. Stress−strain curves for (6-1) D-NC5 gels and (6-2) D-NC10 gels with different histories. (6-1): (a) as-prepared gel (R_{H2O} = 720 wt %); (b) once-dried gel (R_{H2O}^{min} = 436 wt %); (c) once-dried gel (R_{H2O}^{min} = 300 wt %); (d) once-dried gel (R_{H2O}^{min} = 170 wt %); (e) once-dried gel (R_{H2O}^{min} = 80 wt %); (f) once-dried gel (R_{H2O}^{min} = 6 wt %). (6-2): (a) as-prepared gel; (b) once-dried gel at 25 °C for 24 h.

as-prepared form. The equilibrium degree of swelling (EDS) of once-dried N-NC3 gels, defined as W_{gel}/W_{dry} at 200 h, was reduced to 67% of the value attained for the as-prepared gels. The decreased EDS can be attributed to the increase in the effective cross-link density, ν_e. According to the Flory−Rehner theory,[21,24,25] ν_e for once-dried N-NC3 gels ($\nu_e = 0.0131$ mol/L) was 1.51 times greater than that of equivalent as-prepared gels ($\nu_e = 0.0087$ mol/L). Taken together, these findings indicate that the additional cross-links created by the drying treatment amount to ∼50% of the original cross-links. Additionally, as shown in Figure 4c, the swelling of once-dried N-NC3 gels did not change in response to further heat treatment (180 °C, 2 h) in the dried state, which is consistent with the results of the tensile tests described above.

The modification of NC gels by drying was also investigated for different kinds of NC gel, e.g., D-NC*n* gels consisting of PDMAA and clay. Figures 5a and 5b show the tensile stress−strain curves for as-prepared and once-dried D-NC3 gels. The D-NC3 gels showed large changes in property in response to the drying treatment. Specifically, *E* and TS increased to 140% and 131%, respectively, relative to the as-prepared D-NC3 gels, while ε_b decreased to 75%. Moreover, heat treatment in the dried state only had a small effect on the once-dried D-NC3 gels (Figure 5c); this is also consistent with the results observed for the N-NC3 gels. Modification by drying was also observed for D-NC*n* gel with different C_{clay} (e.g., n = 5 and 10: Figures 6-1 and 6-2). Combined, these results indicate that the modification of the NC gels by drying generally occurs in NC*n* gels regardless of the types of polymer or C_{clay}. Actually, NC gels consisting of the other kind of polymer such as poly(*N*,*N*-diethylacrylamide) and poly(acryloylmorpholine) also showed the same effects of drying on mechanical and swelling properties. Furthermore, we presume this may be true for any monomer units that, in the polymer, can adhere to clay particles though hydrogen bonding. It should be noted that drying produces additional cross-links in the polymer/clay network and results in high *E* and TS, low ε_b, and a low degree of swelling. Conversely, OR gels consisting of chemically cross-linked networks did not show any change in properties in response to the drying treatment. For example, as-prepared and once-dried N-OR0.17 gels showed the same tensile stress−strain curves (Figure 7), although the values of *E*, ε_b, and swelling of the gels were quite low. Thus, the rearrangement of the network structure through the drying treatment only occurred in the NC gels. Here, it is also worth describing a feature observed in the stress−strain curves of once-dried NC gels. The large tensile strain behavior of once-dried NC gels is also accompanied by the earlier strain stiffening (a shift in the onset of strain hardening to lower strain) or almost linear response, as shown in Figure 5 (D-NC3 gel) and Figure 3-1 (N-NC3 gel), respectively. These effects should result from the more extended cross-links in the modified polymer/clay network which simultaneously exhibit high *E* and TS. This behavior is similar to the highly elastic nature of self-assembled triblock copolymer gels[22] which were analyzed

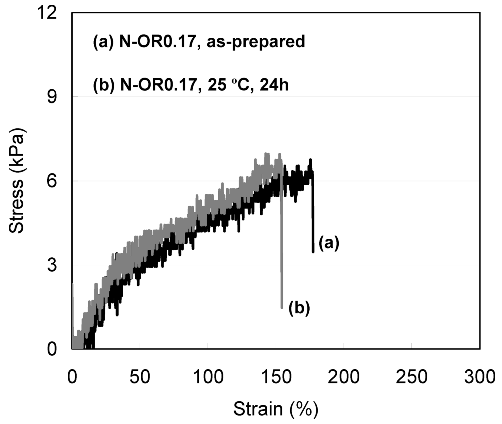

Figure 7. Stress−strain curves for (a) as-prepared and (b) once-dried OR0.17 gels at 25 °C for 24 h.

by a modified Gent model[23] for unentangled polymer networks.

The proposed mechanism for the modification of the NC gels by drying is as follows. Initially, the polymer/clay network structure fabricated during synthesis of the NC gels was thermodynamically stable in the as-prepared condition; therefore, the NC gels remained unchanged when maintained in a closed vessel at their temperature. However, since the junctions of the resulting network were not covalent bonds, but consisted of flexible, mobile physical cross-links formed by interactions between polymer chains and clay (some strong and some loose), the soft network structure of the NC gels could be rearranged in response to changes in R_{H2O} or temperature. During the course of drying, NC gels gradually contracted in response to the loss of water from the interstitial spaces of the swollen network. This contraction probably introduced new contacts between clay and polymer chains due to the loss of hydration as well as a strengthening of preformed loose interactions; therefore, additional cross-links were most probably formed in the concentrated state. Here, some features related to the formation of additional cross-links in dried state may be identified, such as an increase in the number of effective chains between an initial pair of particles or additional loops formed by multiple attachments of the same chain to the same clay particle or even new cross-links formed by new attachments between clay particles which were not previously linked directly. In all cases, the average chain length between cross-linking points will be reduced. Then, when the network is reswollen to its original size and water content, re-establishing the average distance between clay particles, the shorter cross-links will be relatively more extended and will have a decreased entropy per unit length than the original cross-links. This is probably another reason for the higher tensile modulus and lower extension to break.

The number of additional cross-links formed during drying may increase with decreasing R_{H2O}, and the largest number of new cross-links should be formed in the completely dry state. As shown in Figure 6-1b−f, the stress−strain curve for once-dried D-NC5 gels prepared via partial drying (R_{H2O}^{min} = 6−436 wt %) gradually shifted toward a higher E with deceasing R_{H2O}^{min}, even though the stress−strain curve for once-dried D-NC5 gels with R_{H2O}^{min} = 436 wt % did not show any change. The effect of R_{H2O}^{min} on E is summarized in Figure 8, which shows that the critical R_{H2O}^{min}, below which the rearrangement of the network begins, was about 400 wt % for D-NC5 gel and that the rearrangement is almost completed when $R_{H2O}^{min} < 100$ wt %.

Conclusion

The tensile and swelling properties of NC gels consisting of an organic polymer (e.g., PNIPA, PDMAA) and inorganic clay (hectorite) were found to be modified by drying. Once-dried (dried and reswollen) NC gels generally exhibited higher E and TS, and lower ε_b values, as well as lower degrees of swelling, compared with those of the "as-prepared" NC gels. The modifications of the NC gels were attributed to the irreversible rearrangement of the polymer/clay network structure. Specifically, additional cross-links were formed due to the new contacts (interactions) between polymer chains and clay and the strengthening of preformed loose interactions as the NC gels contracted in response to the removal of water and reduced hydration of the polymer chains. The new cross-links formed were stable against subsequent swelling and stretching, and the gels did not change greatly in response to repeated drying or heating in the dried state. The modifications induced by drying were observed in all NC gels, regardless of the types of polymer used or the C_{clay} value. In contrast, OR gels formed from chemically cross-linked networks did not show any change in mechanical and swelling properties in response to drying. The concept that polymer/clay network structures can be irreversibly rearranged according to changes in their hydrated state may also be applicable to other soft, physically cross-linked network systems and provides important information to aid the understanding and control of structure−property relationships in the fields of hydrogels and soft matter.

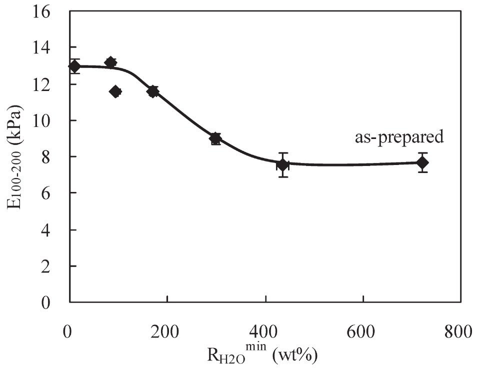

Figure 8. Effects of drying condition (R_{H2O}^{min}) on the E of once-dried D-NC5 gels.

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