Spontaneous Formation of Characteristic Layered Morphologies in Porous Nanocomposites Prepared from Nanocomposite Hydrogels

Kazutoshi Haraguchi* and Kaori Matsuda

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

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In the last two decades, polymer−clay nanocomposites (P/C−NCs) have been extensively investigated as advanced composite materials.[1] Conventional P/C−NCs consist of exfoliated clay sheets and thermoplastic or thermosetting polymers, such as nylon 6, polypropylene, polyurethane, or epoxy resin. It was reported that P/C−NCs show remarkable improvements compared with virgin polymers in mechanical (e.g., modulus), thermo-mechanical (e.g., heat distortion temperature), surface (e.g., gas-barrier), and thermal (e.g., nonflammability) properties by the inclusion of small amounts of clay sheets.[2] These P/C−NCs were generally prepared by using organophilic clay pre-modified by an alkylammonium surfactant. In most cases, P/C−NCs include 1−5 wt %, and less than 10 wt %, of clay. P/C−NCs with higher clay contents were not satisfactory in use because of difficulties in both preparing uniform P/C−NCs and their molding. Also, it was reported that a porous (polypropylene/organophilic clay) P/C−NC could be prepared using supercritical CO_2 as porogen,[3] and that the average pore size was reduced from 153 to 93 μm by incorporating 4 wt % clay.

We recently developed a novel series of nanocomposite hydrogels (NC gels) with unique organic (polymer)/inorganic (clay) network structures.[4] These NC gels were obtained by in situ free-radical polymerization of N-substituted acrylamide derivatives in the presence of exfoliated inorganic clay in aqueous media. In the network, neighboring clay sheets are linked by large numbers of long, flexible polymer chains. Each clay sheet acts as a super-multifunctional cross-linking agent. Here, the most probable interaction between polymer and clay, which is not covalent bonding, is a hydrogen bonding interaction, although an ionic interaction involving initiator (potassium peroxodisulfate) fragments might also contribute. Because of their unique network structure, NC gels simultaneously exhibit extraordinarily tough mechanical properties (high elongation and strength), high transparency (structural homogeneity), high swelling ratio, and excellent thermo-responsive characteristics (gel volume and transparency transitions).[4−6] It was also found that transparent P/C−NCs with high contents of exfoliated clay were readily obtained by drying the NC gels.[5,6] Here, we report the preparation of porous nanocomposite materials composed of poly(*N*-isopropyl acrylamide) (PNIPA) and clay by freeze-drying NC gels. The resulting porous nanocomposites exhibit characteristic layered morphologies with controlled porosities.

NC gels, as monoliths, were synthesized and analyzed by the same procedures as reported previously.[5] Standard uniform aqueous solutions containing clay (synthetic hectorite $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$, 3.31 g), monomer (*N*-isopropyl acrylamide, 10 g), catalyst (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, 80 μL), initiator (potassium peroxodisulfate, 0.1 g), and water (100 g) were first prepared at 1 °C. A standard solution was clay/monomer weight ratio = 0.33, water content = 88.3 wt %. The solution was introduced to a glass vessel under a nitrogen atmosphere and kept at 20 °C for 20 h for free-radical polymerization. The clay/polymer weight ratio can be varied over the range 0.05 to 0.5, or more, by changing the clay concentration under the fixed monomer content in the initial reaction mixture.

All NC gels prepared were uniform and transparent, and exhibited high elongations near to or greater than 1000%. NC gels were cut into disks (5.5-mm diameter, 5-mm thickness), frozen in liquid nitrogen (−200 °C) or in a freezer (−20 °C), and freeze-dried for 24 h using a freeze-dryer in which the pressure was always kept below the triple point pressure (611 Pa), and mostly below 5 Pa. White porous materials with low bulk density (ca. 0.12 g cm^{-3}) were obtained without large volume shrinkages by removing the water in the freeze-drying process. In contrast, when NC gels were dried conventionally, e.g., by heating or evaporation under vacuum, normal dense nanocomposites of PNIPA and clay were always obtained.[5,6] Therefore, the porous materials prepared from NC gels were named porous G-nanocomposites (hereinafter, abbreviated to porous G-NCs), which signifies porous nanocomposites produced from gel. The morphologies of cross sections (and surface) were observed by using scanning electron microscopy (SEM) after coating freeze-dried samples with Pt to a thickness of 5 nm.

For all NC gels prepared here, the porous G-NC disks exhibited characteristic layered morphologies as shells of different porosity regardless of the clay/polymer ratio. The layered morphologies were of three types: (A) a three-layer morphology consisting of fine-porous, dense, and coarse-porous layers; (B) a two-layer morphology consisting of dense and coarse-porous layers; and (C) a uniform morphology consisting of only a fine-porous material. On the other

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* To whom correspondence should be addressed. E-mail: hara@kicr.or.jp. Fax: 81-43-498-2182. Tel: 81-43-498-0062.

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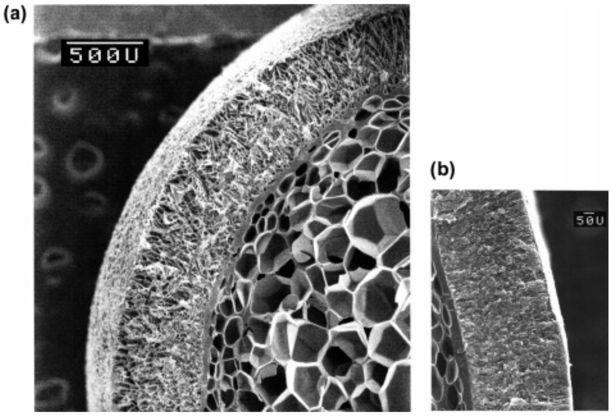

Figure 1. (a) Three-layer morphology observed by SEM for a cross-section of porous G-NC (freeze-dried NC gel in liquid nitrogen, clay/polymer = 0.33 (w/w)). Fine-porous, dense, and coarse-porous layers were observed from the outer surface to the interior. (b) Fine porous layer with smaller thickness and pore size in porous G-NC with clay/polymer = 0.46 (w/w). The bar indicates 500 μm (a) and 50 μm (b).

hand, conventional drying under vacuum or heating gave (D) a nonporous G-NC (dense solids). Also, drying NC gels after de-swelling at 50 °C (i.e., at a temperature greater than the lower critical solution temperature of PNIPA aqueous solution at 32 °C so that water is excluded from the gel) also gave dense solids. Among these morphologies, (A) is the most typical, while (B) and (C) were obtained by specific changes in conditions of preparation.

Figure 1a shows a typical three-layer morphology, observed by SEM, of a cross section of a porous G-NC prepared by freezing a standard NC gel in liquid nitrogen and subsequent freeze-drying. From the surface to the interior, a fine-porous layer, a dense layer, and a coarse-porous layer are formed with thicknesses of about 500, 50, and 4500 μm, respectively, retaining the dimensions of the original gel. Here it should be noted that since the water content, in its fluid or frozen state, in the outermost surface has inevitably been modified slightly during sample handling or in the circumstances before freezing or during freeze-drying, a very thin boundary layer between the porous structure and the external surroundings often forms with a thickness of tens or hundreds of nm, in addition to the main morphologies. Pore sizes in the fine- and coarse-layers, Figure 1a, were in the range of 3−30 μm and 100−500 μm, respectively. The pore size in the coarse layer can be changed slightly by altering the clay/polymer ratio or water content in the original gel. That pore size increases on decreasing the clay/polymer ratio or on increasing the initial water content. On the other hand, the thickness and the pore size of the fine-porous layer strongly depend on the preparation conditions, such as the initial gel composition (i.e., clay/polymer ratio and water content) and the subsequent freeze-drying conditions. It was found that the thickness of this layer increased on decreasing the clay/polymer ratio and/or the freezing rate, and also by increasing the water content, and vice versa. For example, the thickness was increased to 850 μm by doubling the water content by swelling a standard NC gel in water before freezing, and was decreased to 250 μm by increasing the clay/polymer ratio to 0.46 (Figure 1b). As to pore sizes in the fine-porous layer, a few examples of different porosities are shown in Figure 2a and b. Approximate average pore sizes were a 0.8 and 3 μm, respectively. The different porosities in Figure 2 were obtained under the same freeze-drying conditions by altering the NC gel sample size or its composition: (a) a standard NC gel of small size (ca. 0.5-mm diameter and thickness); and (b) an NC gel of normal size with a low clay/polymer ratio (0.066).

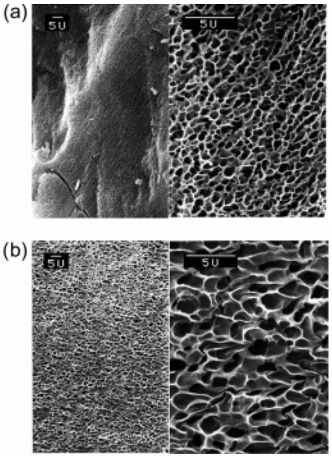

Figure 2. SEM observations for cross-sections of porous G-NCs with different porosities in the fine-porous layer: (a) porous G-NC prepared from a small sample of standard NC gel (ca. 0.5-mm diameter and thickness); (b) porous G-NC prepared from NC gel with clay/polymer = 0.066 (w/w). Approximate average pore sizes are (a) 0.8 μm and (b) 3 μm.

Pore sizes in the fine-porous layer were small and quite uniform.[7] It is considered that the pores in that layer reflect the size and shape of ice crystals formed within the frozen NC gel; the uniform small pore size indicates that a large number of small ice crystals develop uniformly in frozen NC gels on rapid freezing in liquid nitrogen.

A proposed mechanism for the formation of the 3-layered morphology in porous G-NCs is as follows (see Scheme 1). First, the original soft NC gel is frozen (model I). The frozen NC gel is then dried by sublimation under vacuum in a commercial freeze-drier. During freeze-drying, water molecules sublime from crystals to vapor below the triple point of the phase diagram and are removed under vacuum. Sublimation starts at the outer surface and gradually proceeds toward the interior (model II). The first outer layer with fine pores is formed in this initial stage.

Thus, an outer dehydrated region and an inner hydrated (frozen gel) region coexist and sublimation continues at the boundary. As sublimation proceeds, the thickness of the outer layer increases. When the outer layer consists of interconnected pores (i.e., an open-cell structure), sublimation can proceed to completion (i.e., to the center of the sample) without hindrance. However, in the present case, since the pore walls, formed of dense nanocomposite, may persist between the ice crystals, the pores are not always interconnected. Therefore, the vapor pressure in the dried layer near the sublimation boundary can increase as resistance to flow increases with vapor passing through an increasingly tortuous series of closed cells. Thus, the rate of sublimation decreases as the outer layer increases in thickness. Finally, sublimation stops at some critical thickness of the outer layer

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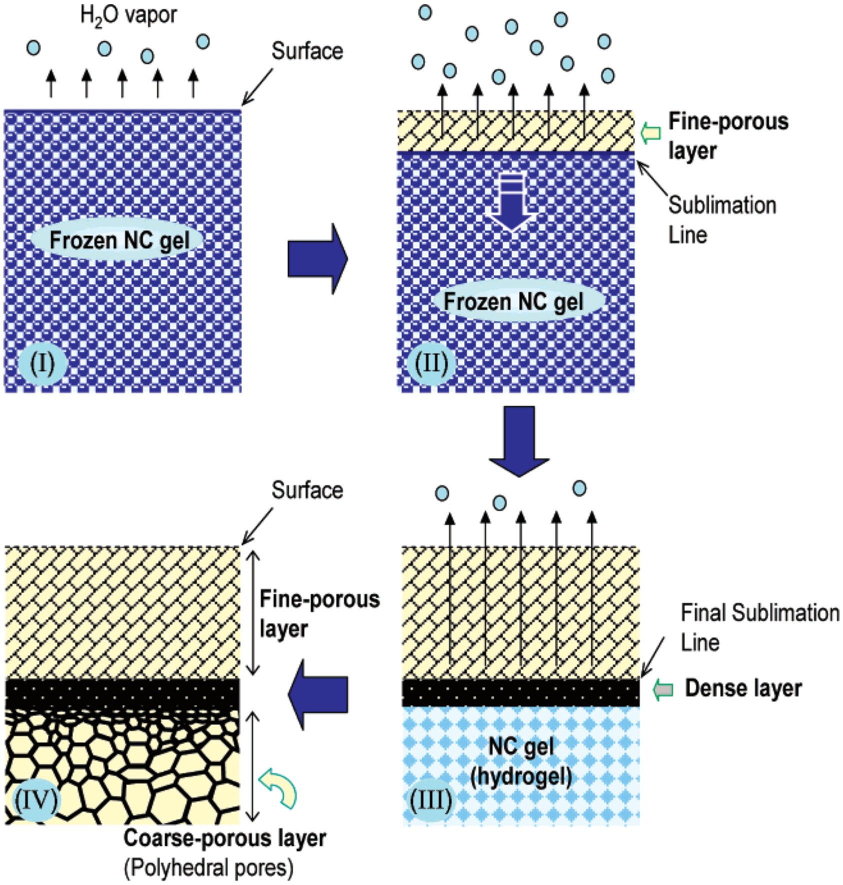
(7) It was observed, as shown in Figure 1b, that the fine pores near the outer surface are often aligned in the radial direction.

Scheme 1. Proposed Mechanisms for the Spontaneous Formation of the Three-Layer Morphology Formed during the Freeze-Drying of NC Gels: (I) Sublimation Starts from Frozen NC Gel; (II) Formation of Fine-Porous Layer; (III) Sublimation Stops and Dense Layer Forms; (IV) Formation of Polyhedral Pores in the Interior Coarse Layer



(model III) and the cooling associated with the latent heat of sublimation also stops. As a result, the temperature near the boundary increases toward ambient (room temperature) and the ice melts. Subsequent drying is similar to the normal vacuum-drying of nonfrozen NC gels. Thus, a dense layer forms adjacent to the porous layer (model III).

Thereafter, once the dense layer has become established, the interior of the hydrogel (in which ice has melted) is subject to slower drying under vacuum at a temperature near ambient. Although the interior of the hydrogel might be expected to decrease in volume by about 90% by subsequent removal of the remaining water, this overall shrinkage cannot occur because its external form is fixed by the now rigid outer layers. Therefore, the inner hydrogel forms its most stable structure as a result of losing water under the restricted external conditions (model IV). The spontaneous formation of the assembly of large polyhedral pores may be qualitatively explained as follows. As water is lost, tiny spherical bubbles form initially and deform the NC gel locally by stretching the polymer chains in the network structure around them. Eventually, when more than ~70% of the water is lost, the bubbles are unable to remain spherical (spherical voids of comparable size cannot fill more than about 70% of volume) but develop polyhedral forms. At this stage the composition of the hydrated polymer matrix is about 33% polymer and clay and 67% water and is semi-fluid. Total surface area (energy) in this situation is minimized by cells (bubbles) always coming together in threes, forming junctions with angles of 120°,[8] as in Figure 3c for four bubbles in contact, where the forces of interfacial tension balance. Cells in undifferentiated tissue such as fat, bubbles in foam, and the polystyrene inclusions in rubber particles of high-impact polystyrene all take on the same characteristic polyhedral form.[8,9] In NC gels, it is presumed that the long flexible polymer chains between junction points can deform sufficiently to allow the morphology to develop; it has previously been demonstrated that elongations of NC gels can reach >1000% before fracture. Consequently, as shown in

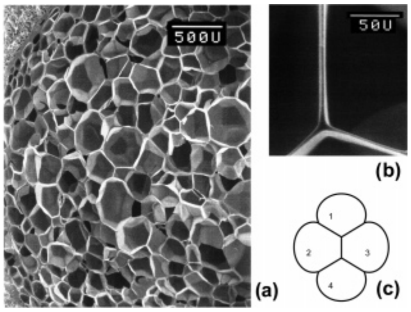


Figure 3. (a) SEM observation of an assembly of polyhedral pores in the coarse-porous layer; (b) a junction between adjacent polyhedral pores, and (c) four bubbles contact model with minimum surface energy comprising three walls junctions at 120°, after ref 8a.

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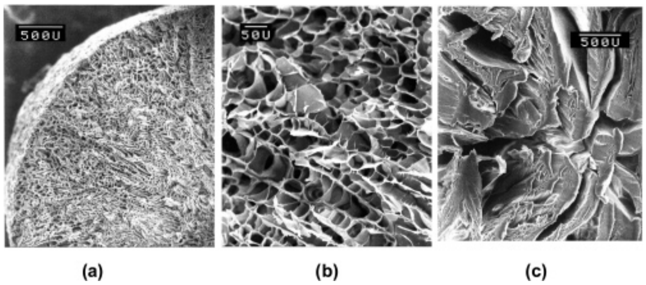

Figure 4. (a) One-layer morphology observed by SEM for a cross section of a porous G-NC prepared by freeze-drying after freezing at −20 °C; (b) magnified observation of pores; and (c) morphology with many large and irregular cracks observed by SEM for freeze-dried samples of the conventional OR gel.

Figure 3a, an assembly of quite regular polyhedral pores of 100−500 μm size and with characteristic cell wall junctions (Figure 3b) form spontaneously. Thus, the third layer, the coarse-porous layer consisting of large polyhedral pores, is formed. It is interesting that in other work, Tanaka et al. observed that during the extensive swelling of ionized acrylamide hydrogel at the volume phase transition, a similar regular pattern with specific angles of 120° was formed on the originally smooth gel surface by mechanical constraint.[10]

The mechanism for formation of the polyhedral pores described above was confirmed by the following experiments. A rigid dense layer was first prepared as the outermost surface of an NC gel by drying it under atmospheric condition for a short time. The sample was subsequently subjected to vacuum-drying. It was found that a similar coarse-porous structure, consisting of a quite regular array of large polyhedral pores, was created throughout the interior. This porous G-NC obtained exhibited a two-layer morphology composed of dense and coarse-porous layers. Here, it should be noted that in the three-layer morphology described above, the dense layer formed spontaneously during the freeze-drying process.

As expected from the above considerations, the formation of a one-layer morphology could be achieved by decreasing the resistance to water vapor passing through the outer porous layer. If the diffusion rate is sufficiently high for sublimation to continue uninterrupted, a uniform fine-porous structure should result throughout without forming the intermediate dense layer and thereby the three-layer morphology. By changing the freezing temperature to −20 °C, a one-layer morphology was obtained using the same NC gel, as shown in Figure 4a. This resulted from the formation of at least partially interconnected large pores with a broad size distribution. It is considered that ice crystals grew to larger sizes because of the lower freezing rate at the higher temperature; the process took more than 100 hrs.

Figure 4b shows the magnified structure of pores in the one-layer morphology. In Figure 4a and b, there is a lot of irregular cell shapes and many pores are not spherical but often elongated and even square in section. Here, among many irregular cell shapes, a number of small walls at 90° to the large long walls form the partitions between two voids, which is distinct from the morphology in Figure 1. Although the mechanism for forming this structure has not been elucidated, examples of this type of morphology are seen in nature, such as radiolaria, wood, and other plant tissues, etc. Also, it is observed that major features often align in the radial direction of the dried gels, particularly near the surface. The formation of quite large pores may be attributed to the deformability of the NC gels, since the networks can readily deform to a large extent without break,[4,5] corresponding to the ice crystal formation. Thus, large ice crystals, often with a long needlelike shape, can grow in the network matrix depending on the freezing conditions, and pore walls are controlled by their shape as they form.

The layered morphologies and widely different porosities described above are characteristic of the porous G-NCs prepared by freeze-drying NC gels. By using conventional organic cross-linked hydrogels or linear polymers in aqueous solution, these morphologies and porosities cannot be obtained. Instead, many large and irregular cracks often form in the resulting porous materials produced from organic cross-linked hydrogels as shown in Figure 4c, probably due to the mechanical weakness (brittleness) of the networks. From linear PNIPA aqueous solutions, a one-layer morphology with uniform interconnected pores of several to several tens of μm in diameter, the size of which depends on the polymer concentration, is always formed.

In summary, novel, porous nanocomposites (porous G-NCs) with characteristic layered morphologies were obtained by freeze-drying NC gels without the use of an added porogen. The most typical morphology was a concentric three-layer morphology consisting of successively a fine-porous layer/a dense layer/a coarse-porous layer from the exterior to the interior. In the coarse layer, a quite regular assembly of polyhedral pores formed spontaneously. We propose a mechanism for the formation of the unique three-layer morphology and other morphologies during the freeze-drying process. The clay/polymer ratio in porous G-NCs can be controlled over a wide range from 5 to 50 wt %. The spontaneous formation of characteristic layered morphologies has been first achieved in the porous G-NCs via NC gels and the porous G-NCs could be useful for applications such as forms with fine pores (exterior) and high strength (interior), filters or absorbents with specific porosities.

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