Deformation Studies on Polymer-Clay Nanocomposite Gels

Mitsuhiro Shibayama,[*1] *Sho Miyazaki,*[1] *Hitoshi Endo,*[1] *Takeshi Karino,*[1] *Kazutoshi Haraguchi*[2]

Summary: The polymer-clay nanocomposite gels (NC gels), developed by Haraguchi et al. (Adv. Mater., 2001), exhibit extraordinarily high mechanical properties, such as high elongations and high ultimate strengths. In order to understand the origin of these properties, contrast-matched small-angle neutron scattering (SANS) studies were carried out for stretched NC gels. It was found that (1) the scattering function for NC gels is simply given by a Lorentz function, a function for semidilute polymer solutions, without a characteristic cross-link inhomogeneity term for polymer gels, and (2) the unique mechanical properties are ascribed to its network structure, i.e., long polymer chains connected by ''plane'' cross-links.

Keywords: clay; nanocomposite gels; poly(N-isopropylacrylamide); small-angle neutron scattering

Introduction

Polymer-clay nanocomposites have been gathering much attention due to their advanced physical properties than those of the corresponding polymeric systems, such as mechanical properties, heat resistance, improved transmittance, etc.[1] Recently, Haraguchi et al. developed novel polymer-clay nanocomposite gels (hereafter we call NC gels).[2] The gels consist of poly(*N*-isopropylacrylamide) (PNIPA) and synthetic clay, laponite, and water. The NC gels exhibit significant physical properties, such as high elongations, high ultimate strengths, high transparency, large swelling/deswelling ratios, and high deswelling speed, etc.[3,4] Fig. 1 shows an example of the performance of NC gels. The polymer concentration is about 5 wt%, but it can be stretched more than ten times and even one can make a knot as shown in the figure.

In the previous paper, we discussed the structure of NC gels with small-angle neutron scattering (SANS) and dynamic light scattering.[5] Here, we report SANS results on deformed NC gels and discuss the unique deformation mechanism of NC gels by employing contrast-matched SANS in addition to the ordinary SANS.

Experimental Part

Purified *N*-isopropylacrylamide (NIPA) monomer was dissolved in deionized water (or heavy water; D_2O) containing dispersion of the inorganic clay, synthetic hectorite ''Laponite XLG'' (Rockwood Ltd.: $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$). The NIPA monomer concentration was 690 mM (7.8 wt%). Potassium peroxodisulfate (KPS) and *N,N,N′,N′*-tetramethylethyl-enediamine (TEMED) were used as an initiator and catalyst, respectively. The molar ratio of the monomer, initiator, and catalyst was 100:0.426:0.735. NC gels were polymerized in water containing clay, by castig the mixture in a sealed teflon mold of 2 cm-wide, 4 cm-long, and 4 mm-thick. The polymerization was conducted at 20 °C for 20 h. The

[1] Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan
E-mail: shibayama@issp.u-tokyo.ac.jp
[2] Kawamura Institute of Chemical Research, 631 Sakada, Sakura-shi, Chiba 285-0078, Japan

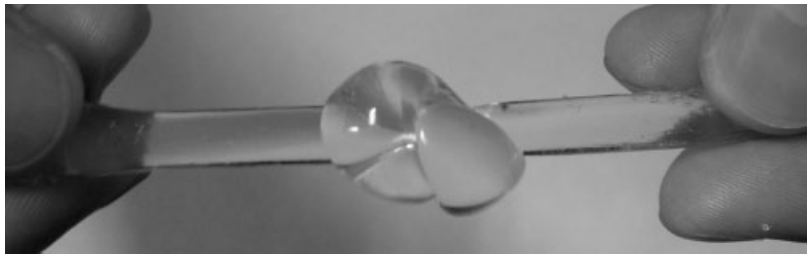

Figure 1.
Photograph of a knot made with a rodlike NC gel.

sample codes were defined by the ratio of the clay and D_2O, i.e., NC2, NC4, and NC6. This indicates 0.02, 0.04, and 0.06 mole of clay (=15.24, 30.48, and 45.72 g) in 1L of D_2O. Thus prepared slab gels were set to a custom-made stretching device as shown in Fig. 2, and SANS experiments were carried out.

In the case of the contrast-matched experiment, the scattering length density was adjusted to that of clay (the volume fraction was H_2O: $D_2O = 0.34{:}0.66$). For comparison, a conventional PNIPA gel cross-linked with *N,N′*-methylenebisacrylamide (BIS) was also prepared. The BIS concentration was 3.00 mol% with respect to NIPA monomer and the NIPA concentration was 1M. Hence, we call this gel an organic gel (OR3). SANS experiments were performed at the two-dimensional SANS instrument (SANS-U), the University of Tokyo.[6] The wavelength of the incident neutrons was $\lambda_N = 7.0$ Å. The temperature of the samples was regulated to be 20 °C. The observable range of the scattering vector, q, was $0.005 \leq q \leq 0.1$ Å^{-1}, where q is defined by $q = (4\pi/\lambda_N)\sin\theta$ and 2θ is the scattering angle. The sample was stretched stepwise with the step of $\Delta\lambda = 0.2$ (up to $\lambda = 2.0$), $\lambda = 2.5$, and then $\Delta\lambda = 1.0$ (from $\lambda = 3.0$ up to $\lambda = 6.0$). Here, λ ($\equiv l/l_0$) is the stretching ratio, and l_0 and l are the sample lengths before and after stretching, respectively. The SANS measuring time was 10 min for the case of the sample-to- detector distance SDD = 2 m and 2 h for SDD = 8 m.

Results and Discussion

Fig. 3 shows the stress, σ, vs. the stretching ratio, λ, plots of OR3, NC2, NC4, and NC6,

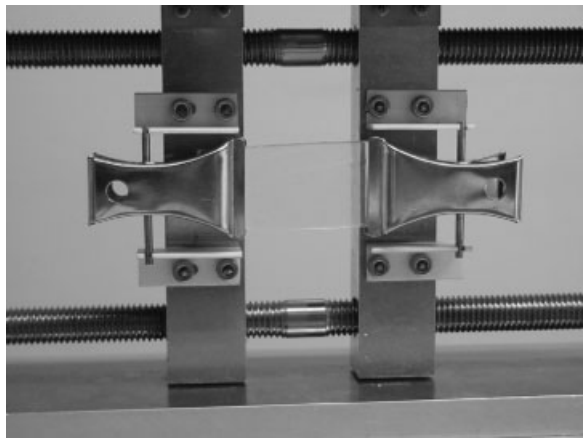

Figure 2.
The stretching device for SANS measurements.

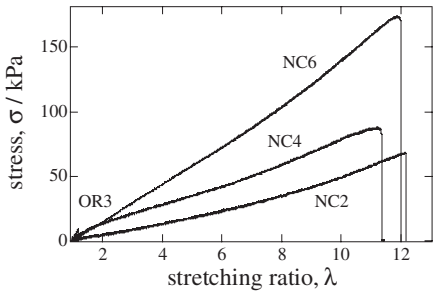

Figure 3.
The stress vs stretching ratio plots for OR3, NC2, NC4, and NC6.

obtained under the following conditions; sample length between jaws 35 mm; crosshead speed 100 mm/min; test temperature 25 °C. The initial cross section (23.75 mm^2) was used to calculate the tensile strengths and the tensile moduli. As shown in the figure, NC gels can be stretched much larger than OR3. The stretching ratio is over 10 times, which is more than 50 times larger than that of OR3. The stress at break of NC4 is more than 10 times as large as that of OR3.

In order to educidate the structural origin of the advanced mechanical properties described above, we carried out SANS measurements for deformed NC gels. Fig. 4 shows a series of two-dimensional scattering patterns obtained for uniaxially deformed NC6 in D_2O (upper) and in the contrast-matched solvent with 66:34 (D_2O:H_2O) (lower). In the case of the former, the two-dimensional (2D) scattering patterns became prolate to the direction perpendicular to the stretching direction (as shown with the white ellipse). In addition to the prolate patterns, there exist a pair of lobe patterns along the strething direction at a lower q region (as shown in a white circle). These lobe patterns are commonly observed in chemically cross-linked gels (chemical gels, OR gels) and are called ''abnormal-butterfly pattern''.[7] These patterns are ascribed to an increase of inhomogeneities due to non- random cross-linking in gels that become explicit by deformation.

However, the lobe patterns observed in NC gels must have a different origin since NC gels contain another component, i.e., clay platelets. These clay platelets are expected to cause a strong scattering as well. In order to remove the contribution of clay scattering, we carried out SANS experiments with a contrast-matched solvent, of

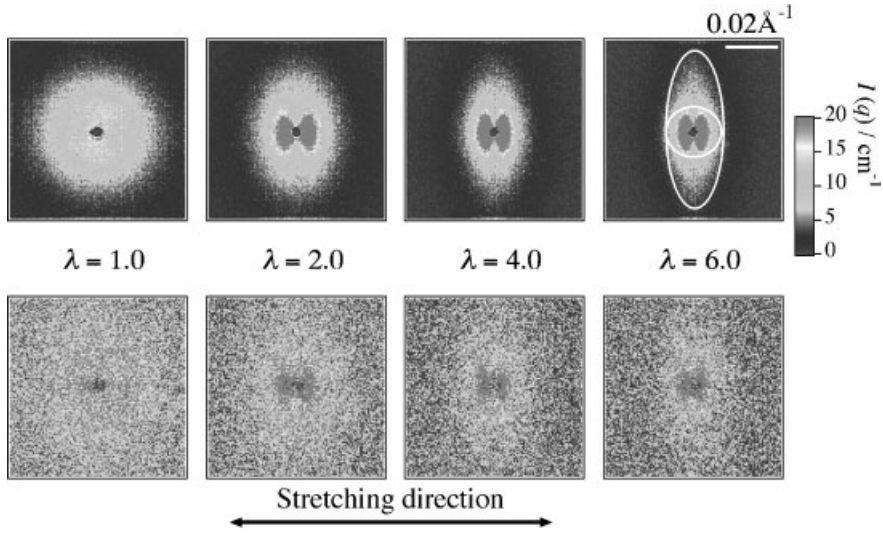

Figure 4.
The stretching ratio λ dependence of two-dimensional (2D) SANS patterns of NC6 in D2O (upper) and in the contrast-matched solvent (lower).

which results are shown in the lower column of Fig. 4. As expected, the scattering intensity is significantly reduced compared to the case in the non-contrast matched solvent, i.e., D_2O. If the scattering length density of the solvent is perfectly matched to that of clay, scattering originated from clay platelets should disapper. However, the lobe patterns still reamined in the stretching direction even in the case of the constrast-matched solvent. This is deduced to be an interference of alligned clay platelets along the stretching direction. Here, it should be noted that the contrast-matching of the clay was attained not to the matrix, i.e., the polymer solution, but to the mixed solvent. Hence, the clay was still visible by neutron scattering. In addtion, it was found that the NC gels had more sophisticated structures than a two-phase system.[8]

In order to assign these lobe patterns, we carried out a more quantitative analysis. First of all, we analyzed the scattering intensity of NC gels at undeformed state, i.e., by taking circular average of the contrast-matched 2D SANS pattern (the left figure in the lower column of Fig. 4). Fig. 5 shows the Ornstein-Zernike (OZ) plot, i.e., $I(q)$ vs q^2 plot, for NC6, and the line shows the fit with the OZ function,

$$I(q) = \frac{I(0)}{1 + \xi^2 q^2} \tag{1}$$

where ξ is the correlation length. Here, two remarks should be given. Firstly, $I(q)$ is fitted only with an OZ function. In general, the scattering intensity functions of polymer gels are described with a sum of OZ and squared-Lorentzian functions. The former represents the dynamic concentration fluctuations, and the latter does the frozen inhomogeneities.[9–11] However, as shown in the figure, $I(q)$ does not contain the squared-Lorentz component. This means that the NC gels do not have considerable frozen inhomogeneities characteristic of polymer gels. Secondly, the evaluated correlation length is much larger (64 and 50 Å for NC2 and NC4, respectively) than those obtained for conventional chemical gels (≈20 Å). Both of these findings indicate that the structure of NC gels is very different from chemical gels. Since frozen inhomogeneities are amplified by deformation,[7] such as stretching and swelling, it is advantageous to investigate NC gels in a deformed state.

The scattering intensities along the stretching and perpendicular directions were obtained by taking sector averages for 2D scattering intensity patterns at $\lambda = 1.0$ to 2.0 with a sector window of $\pm 5^\circ$ along the horizontal and vertical directions. Fig. 6 shows the λ dependence of ξ for NC6. The solid lines are the theoretical predictions by assuming affine deformation, i.e., $\xi_{\text{parallel}} = \lambda\ \xi_0$ and $\xi_{\text{perpendicular}} = \lambda^{-1/2}\ \xi_0$. Although there are systematic deviations from the theoretical curves, the variations of ξ_{parallel} and $\xi_{\text{perpendicular}}$ indicates an affine-like deformation, i.e., a stretching deformation of blobs along the macroscopic stretching direction.

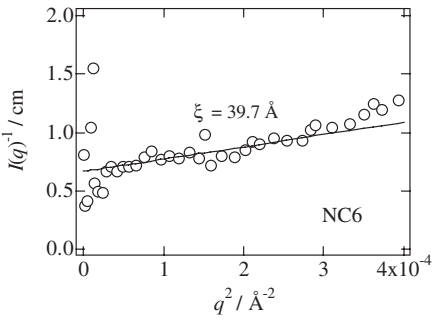

Figure 5.
OZ plot of undeformed NC6.

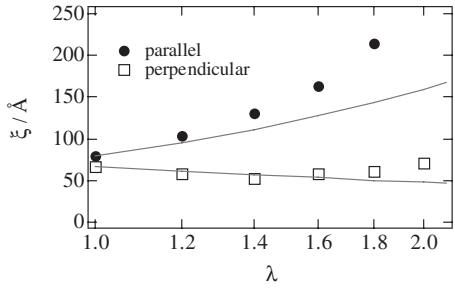

Figure 6.
The stretching ratio, λ, dependence of the correlation length, ξ for NC6.

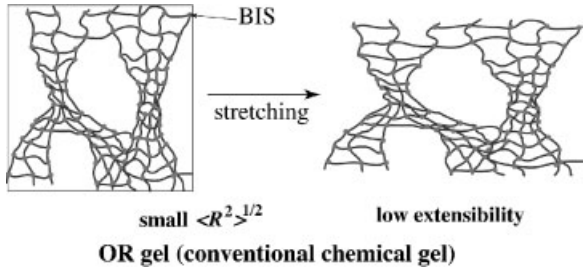

Figure 7.
Schematic representation of the deformation model of OR gels.

Based on the SANS results, we propose a deformation mechanism of NC gels. In the case of conventional chemical gels, polymer chains are highly divided to short sub-chains during polymerization process by incorporation of cross-links. Therefore, the polymer chian size, $\langle R^2 \rangle^{1/2}$ in Fig. 7 is on the order of a few tens Å (for the case of 700 mM PNIPA gels with 5% cross-links), where $\langle R^2 \rangle^{1/2}$ is the mean-square end-to-end distance of the polymer chains between neighbouring cross-links. As a result, a network consisting of short sub-chains does not have high extensibility. In addition, the network contains a large portion of cross-link inhomogeneities as a result of radical polymerization. Hence, it has a lot of defects as shown in the figure, resulting in poor mechanical properties.

Fig. 8 shows the case of NC gels. The cartoons in the figure were drawn based on the stoichiometry and the results of SANS experiments for NC6. The inter-clay platelet distances were estimated to be 35 nm and 70 nm ($\lambda = 2.0$), respectively in the undeformed and stretched state. The deformation of the blobs (indicated by the yellow ellipses) was evaluated from the SANS result (Fig. 4). According to the chemistry of NC gel preparation, NIPA monomer has a tendency to be adsorped on the surface of clay platelets.[3] Hence, once polymeriza-

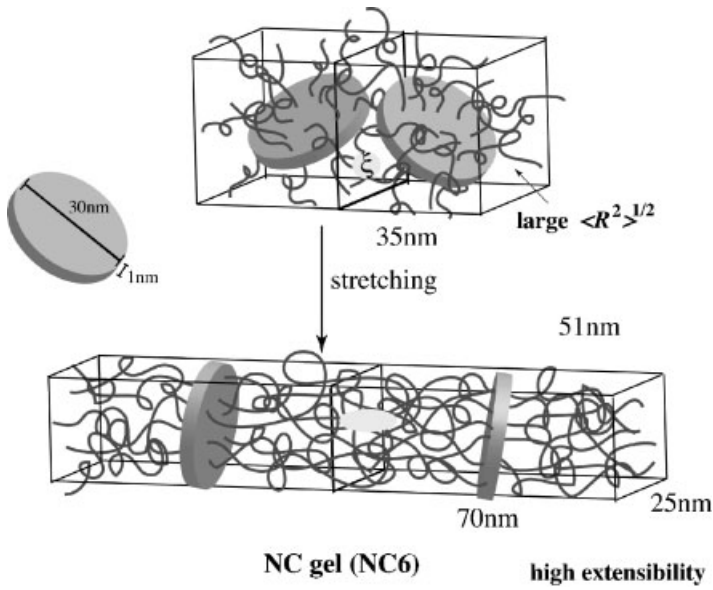

Figure 8.
Schematic representation of the deformation model of NC gels.

tion is initiated, NIPA chains propagates from one platelet to another, resulting in bridging two platelets. Here, the important issue is that the NC gels do not have any ''chemical'' cross-links between neighboring platelets. The molecular weight of PNIPA chain can be estimated from the data of radical polymerization of PNIPA. The molecular weight is a function of the monomer concentration, the polymerization temperature, etc. In our previous report,[12] we evaluated the molecular weight, M, by viscometry, for PNIPA prepared at 20 °C using the following relation reported by Kubota et al.[13]

$$[\eta] = 0.11 \times M^{0.51} \quad \mathrm{cm^3/g\ (at\ 20^\circ C)} \qquad (2)$$

and by[12]

$$M \approx 1.97 \times 10^3 (C/m\mathrm{M})^{1.37} \qquad (3)$$

This allows us a rough estimation of the molecular weight of PNIPA chains between platelets. The estimated value is about 2.0×10^6 g/mol for $C = 690$ mM NIPA, and $\langle R^2 \rangle^{1/2} \approx 400$ Å. Hence, the polymer chian size, $\langle R^2 \rangle^{1/2}$, for NC gels is much larger than that of OR gels. In addition, since there is no ''cross-links'' between platelets, the PNIPA chains behave just as polymer chains in a semi-dilute polymer solution. This means that there are no inhomogeneities originated from ''cross-links''. The mechanical properties, such as high extensivility and high strengh, are ascribed to this unique structure and clay platelets play as ''plane'' cross-linker.[8] Further investigations, such as (1) detailed analyses of the structure of NC gels as a function of clay concentration[14] and (2) studies on gelation mechanism by time-resolved dynamic light scattering,[15] are also carried out and reported elsewhere.

Conclusion

The structure and deformation mechanism of novel NC gels were investigated by using SANS as a function of the stretching ratio. The high-strength and high-extensibility are found to be originated from the unique structure of NC gels. The ''spatial'' inter-cross-link distance of a NC gel, i.e., the inter- platelet distance is much longer (of the order of 400 Å) than the inter-cross-link distance of OR gels (of the order of 10 to 20 Å).[16] Secondly, the ''topological'' chain lengths $\langle R^2 \rangle^{1/2}$, are also very different. Most of PNIPA chains in NC gels are anchored to clay platelets and play a role as active chains, while PNIPA chains in OR gels are divided to short chains by cross-linkers and form clusters with a high density of cross-links. These facts directly result in high elongation ratio and high strength at break of NC gels.

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