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Molecularweight effects on tensile properties of blend hydrogels composed of clay and polymers

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ABSTRACT

Hydrogels with mechanical toughness have attracted the attention of many researchers but still the mechanism remains poorly understood. In this study, we investigated molecularweight effects on the tensile properties for two kinds of blend hydrogels such as clay/sodium polyacrylate and clay/polyacrylamide, which were prepared by simple mixing, in order to clarify key factors of the mechanical toughness. The elastic modulus of the former hydrogel was much higher than that of the latter, while the latter extensibility was much higher than that of the former. It has been found that use of polymers with molecularweights higher than a few millions is necessary to obtain high extensibility for the blend hydrogels. It has been clarified from this study that all of the following three factors, (i) use of high molecularweight polymers, (ii) dispersion of clay particles and (iii) favorable interactions of clay and polymers are necessary to be fulfilled for fabrication of the blend hydrogels with mechanical toughness.

1. Introduction

In recent years, hydrogels with mechanically tough properties have attracted many researchers from both scientific and industrial points of view. Clay/polymer nanocomposite hydrogels prepared by in-situ free-radical polymerization of alkylacrylamide in the presence of clay particles, which have been pioneered by Haraguchi et al., are well-known as one of hydrogels with excellent material properties, e.g., they have remarkable mechanical properties such as high extensibility more than 1500%, extraordinary mechanical toughness and self-healing [1–4]. Clay particles act as a multiple cross-linker in the nanocomposite hydrogels, e.g. the number of polymer chains attached to one clay particle is in the range from about 20 to 130, depending on the clay concentration [1,5]. Moreover, it has been shown that the nanocomposite hydrogels have high transparency due to clay particles homogeneously dispersed in water [3]. The multiplicity of cross-link points and the homogeneously dispersed clay particles may be origins of the amazing mechanical toughness, but the underlying mechanism that brings it is less well understood at the present stage. It has been believed that tough clay/polymer composite hydrogels cannot be produced by simple blending [2]. For understanding of the mechanism, it is important to find out key factors for mechanical toughness.

Recently we found that hydrogels prepared by simply blending a polyelectrolyte, sodium polyacrylate (PAAS) with clay particles including a dispersant, tetrasodium pyrophosphate (TSPP) are mechanically tough, e.g., the blend hydrogels prepared at optimum compositions were not fractured by 90% compression, and almost recovered their initial shape after the compression test [6]. Simple blending has an advantage in an approach to the mechanism of the mechanical toughness in the following reason. The advantage is that composition and characteristics of the constituents in the gel are well-defined, and as a consequence it enables us to definitely control the composition and easily vary molecularweights and kinds of constituent polymers. In a previous study we showed that there exists an optimum concentration of the dispersant and high molecular weight PAAS more than ~10^6 is necessary to fabricate blend hydrogels tough for uniaxial compression [7].

In this work, we investigated the tensile and structural properties of the blend hydrogels composed of polymers and clay, and the molecularweight effects on them using two kinds of polymers, an anionic polymer (PAAS) and nonionic polymer (polyacrylamide) with molecular weights ranging from ~10^5 to ~10^7. Our particular intention in doing this is to clarify effects of the molecularweight and the kinds of constituent polymers on the mechanical toughness of the blend hydrogels.

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2. Experimental

2.1. Sample and sample preparation

In this study, we used Laponite RD ($Na_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]$) as a clay sample, which was kindly supplied by Rock-Wood Ltd, Japan. We used PAASs with different molecularweights ranging from 2.25×10^5 to 2.11×10^7 and PAMs with molecularweights of 4×10^5 to 1.8×10^7. The molecularweights of polymers used in this study are summarized in Table 1. We used tetrasodium pyrophosphate (TSPP) decahydrate as a dispersant, which was obtained from Kanto Chemicals Co., in order to prevent aggregates of clay particles. It was used without purification. The blend hydrogels were prepared in the following method. A TSPP aqueous solution with a given concentration was prepared, and afterward a given amount of Laponite RD was added in the solution. The Laponite RD/TSPP solution prepared thus was stirred more than for 20 min in order to disperse clay particles in the solution. Afterward the mixture was added little by little in a 2 wt % PAAS solution or a 2 wt% PAM solution, and then it was sufficiently stirred. In the case of PAAS, water was used as a solvent, while in the case of PAM a mixed solvent of water and ethylene glycol (EG) was used. The mixture prepared thus was centrifuged for 15–25 min at 7500 rpm in order to be degassed.

2.2. Mechanical measurements

We carried out tensile tests using ORIENTEC TENSILE TESTER STM-20 for the blend hydrogels at a stretching speed of 10 mm/min. The samples with 10 mm long and 15 mm wide were used for the measurements. Stress was calculated with area of an undeformed sample. We obtained the elastic modulus (Young's modulus) E of the hydrogels from a slope of the stress–strain curve in a range of small strain, the fracture stress σ_f and the fracture strain ε_f. These average values were obtained from at least four measurements for each Laponite RD/PAAS/TSPP blend hydrogel and from four measurements for each Laponite RD/PAM/TSPP blend hydrogel. Moreover, we conducted four straight compressive measurements for a 5 wt% Laponite RD/1 wt% PAAS13800K/0.5 wt% TSPP blend hydrogel.

2.3. Synchrotron small-angle X-ray scattering

We performed synchrotron small-angle X-ray scattering (SAXS) experiments under stretching at the beam line 10C (BL10C) of the Photon Factory at the High Energy Acceleration Research Organization in Tsukuba, Japan. The X-ray with a wavelength of 0.9864 Å was used, and the scattered X-ray was detected with a PILATUS3-2M consisting of an array of 8×3 modules. The two-dimensional images were analyzed with a software (Nika) [8] for SAXS data analysis in order to obtain the scattering profiles as a function of the magnitude of wave vector q defined by $4\pi \sin(\theta/2)/\lambda_X$, where θ and λ_X are the scattering angle and wavelength of the X-ray, respectively. Scattering intensity in the direction parallel to stretching was obtained by sector-averaging over azimuthal angles of $0° \pm 10°$ and $180° \pm 10°$, while the scattering intensity in the perpendicular direction was done by sector-averaging over azimuthal angles of $90° \pm 10°$ and $270° \pm 10°$.

Table 1
Molecularweight of samples used in this study.

Sample code	M_w ($\times 10^5$)
PAAS225K[a]	2.25
PAAS564K[b]	5.64
PAAS1550K[c]	1.55×10
PAAS3500K[b]	3.50×10
PAAS13800K[d]	1.38×10^2
PAAS21100K[d]	2.11×10^2
PAM400K[e]	~4
PAM5000K[f]	$5–6 \times 10$
PAM18000K[a]	1.8×10^2

[a] Polysciences.
[b] Wako Pure Chemical Industries.
[c] American Polymer Standards.
[d] Toagosei.
[e] Sigma–Aldrich.
[f] Scientific Polymer Products.

3. Results and discussion

3.1. Mechanical properties of clay/PAAS/TSPP hydrogels

We show pictures of 5 wt% Laponite RD/1 wt% PAAS21100K/0.5 wt% TSPP blend hydrogels in Fig. 1. These pictures show that the gel is mechanically tough and transparent. The latter's result suggests that clay particles are homogeneously dispersed in the gel. Fig. 2 depicts stress–strain curves for Laponite RD/1 wt% PAAS21100K/0.5 wt% TSPP hydrogels (a) and for Laponite RD/1 wt% PAAS564K/0.5 wt% TSPP hydrogels (b) at different clay concentrations. The blend hydrogels with lower molecular weight PAAS564K at both 10 wt % and 5 wt % clay concentrations were fractured after a very short elongation. We could not carry out tensile measurements at 3 wt% and 1 wt% clay concentrations, because their gels were too brittle. On the other hand, blend hydrogels with higher molecular weight PAAS21100K at 5 wt% clay elongated up to ~700%. We obtained the elastic modulus E, fracture stress σ_f and fracture strain ε_f for blend hydrogels with various molecularweights of PAAS and various clay concentrations. Fig. 3 shows plots of E, σ_f and ε_f vs M_w at different clay concentrations, where M_w denotes the weight-averaged molecular weight of polymers. We could not conduct tensile measurements at all clay concentrations for blend hydrogels with PAAS225K and at 1 wt% clay concentrations for those with PAAS of the molecularweight smaller than 1.55×10^6, because of too brittle gels. E gradually decreased with decrease of M_w, while σ_f and ε_f drastically decreased at the molecularweights smaller than 1.55×10^6. The latter's behavior is remarkable especially at low clay concentrations. Thus, it has been shown that use of polymers with molecular weights higher than 3.5×10^6 is necessary in order to obtain high extensibility. Here in order to make sure whether the blend hydrogels with high molecular weight PAAS have continuous toughness or not, we performed four straight compressive tests for a 5 wt% Laponite RD/1 wt% PAAS13800K/0.5 wt% TSPP hydrogel. Fig. 4 depicts their stress–strain curves (a) and the elastic modulus at each test (b). The gel was not fractured after four straight compressive measurements up to ~80%. The elastic modulus obtained from each stress–strain curve was almost constant except for a slight decrease after the first test. This result is similar to that of 5 wt% Laponite RD/1 wt% PAAS21100K/0.5 wt% TSPP hydrogel reported in a previous study [7]. Thus, it has been confirmed that blend hydrogels with high molecularweight PAAS are mechanically tough.

3.2. Mechanical properties of clay/PAM/TSPP hydrogels

Next let us show the tensile properties of blend hydrogels composed of polyacrylamide and clay. Fig. 5 depicts stress–strain curves (a) and the elastic moduli (b) for Laponite RD/1 wt% PAM5000K/0.5 wt% TSPP hydrogels at different clay concentrations. The hydrogels were not fractured until limitation of our tensile testing machine (extensibility of ~1400%) as shown in Fig. S1. Similar to clay/PAAS hydrogels, the elastic modulus increased with