Radiation synthesis of polymer/clay nanocomposite hydrogels with high mechanical strength postprint

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Abstract

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Full Text

Preamble

Radiation Synthesis of Polymer/Clay Nanocomposite Hydrogels with High Mechanical Strength

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Abstract: Poor mechanical properties of PNIPAAm hydrogels have limited their applications. Nanocomposite hydrogels (NC gels) that incorporate inorganic clay possess high mechanical strength and other desirable properties. In this paper, we report a facile approach to synthesize NC gels using radiation technique. With exfoliated clay sheets acting as crosslinkers, N-isopropylacrylamide monomers are polymerized and crosslinked to form NC gels under γ-irradiation at room temperature. Apart from regular swelling behavior and interesting performance in thermo sensitivity, the radiation-synthesized NC gel (RNC gel) exhibits good optical transparency, high strength, and flexibility. Through Micro-FTIR, XPS, and TG analyses, a particular chemically crosslinked organic/inorganic network was identified in the RNC gel.

Keywords: Clay, Mechanical properties, Irradiation, Stimuli-sensitive polymers, Composites
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Introduction

Poly(N-isopropylacrylamide) (PNIPAAm) hydrogels are typical thermosensitive materials. They undergo abrupt and significant volume changes in response to temperature variations from external environments, exhibiting a lower critical solution temperature (LCST) at approximately 33 °C [1]. Multi-responsive hydrogels based on PNIPAAm have been developed using various methods. For instance, double-sensitive hydrogels responding to both pH and temperature can be obtained by combining comonomers containing particular functional groups with NIPAAm [2]. Photothermally sensitive hydrogels [3] and electrosensitive hydrogels [4] based on PNIPAAm have also been developed recently. Due to their unique properties, PNIPAAm hydrogels have found applications in chemical devices [5], tissue engineering [6], microfluidic actuators [7], separation processes [8], biomedical fields [9], and other areas.

However, the application of PNIPAAm hydrogels is limited by their poor mechanical properties. Several strategies have been employed to improve the mechanical strength of PNIPAAm hydrogels, such as developing gels with topological structure [10], introducing a double-network structure into PNIPAAm hydrogels [11], and synthesizing nanocomposite gels (NC gels) [12]. Among these, NC gels have attracted considerable research interest due to their desirable properties [13, 14].

Laponite is a synthetic hectorite consisting of layered magnesium silicate platelets measuring Φ20–30 nm × 1 nm [15]. Reactive Si—OH groups and

Mg−OH (or Li−OH) groups are present on the surface of laponite clay sheets [16]. Laponite clay has been introduced into polymer matrices generated from amide monomers to form novel NC gels with outstanding mechanical strength and optical properties. Proper catalysts and initiators with strong physical interactions with the clay sheet surface were necessary for preparing these NC gels [12, 15]. A novel three-dimensional network formed in the NC gel, with clay sheets acting as multifunctional crosslinkers. This physically crosslinked network exhibited excellent self-healing function due to the reversibility of physical interactions [17].

Radiation-induced in-situ polymerization and crosslinking, which can be carried out at room temperature without initiators and catalysts, represent a safe, clean, and effective method for hydrogel synthesis [18–20]. However, to the authors' knowledge, radiation synthesis of organic/inorganic hybrid NC gels has not been reported previously.

We have developed a facile method for preparing NC gels using radiation technique. Neither initiator nor catalyst was used, and the NC gels contained only PNIPAAm, clay, and water, making them suitable for biomedical applications. The effects of synthesis conditions on gel fraction, gel structure, mechanical strength, swelling behavior, and thermo sensitivity of radiation-synthesized NC gels (RNC gels) were investigated. The formation mechanism of RNC gels was studied using microscopic Fourier transform infrared spectroscopy (Micro-FTIR), X-ray photoelectron spectroscopy (XPS), and thermogravimetric (TG) analyses.

Experimental

Materials

NIPAAm (97%, Aldrich Chemical Inc.) and synthetic hectorite "Laponite XLG" ($[Mg_{5\cdot34}Li_{0\cdot66}Si_8O_{20}(OH)_4]Na_{0\cdot66}$, layer size Φ20–30 nm × 1 nm, Rockwood Ltd.) were used as received. Deionized water was used throughout all experiments.

Synthesis of RNC Gels

The RNC gels were prepared by irradiating aqueous solutions containing monomers (NIPAAm) and clay. Laponite clay (0.61–5.47 g) and NIPAAm monomers (9.05 g) were separately dissolved in 40 mL of deionized water. Subsequently, they were mixed at 0 °C under stirring to form a uniform solution. The resulting solution was irradiated in air to 10 kGy, typically, with γ-rays from a ^{60}Co source (Peking University) to obtain RNC gels. The absorbed dose was measured using a Fricke dosimetry system. Due to the stabilizing effect of NIPAAm monomer on the dispersion of laponite clay in aqueous medium [12], the solution remained very stable during the γ-irradiation process.

To investigate cross-linking between laponite particles, aqueous solutions of

laponite clay (0.05 M and 0.09 M) were also irradiated to 10 kGy.

RNC gels with different clay contents were denoted as RNCn gels, where "n" was defined as n = 100c /c , with c and c being the molar concentrations of laponite clay and NIPAAm monomer in the solution, respectively. Clay contents of RNCn (n = 0, 1, 3, 5, 7, 9) gels are 0.00, 0.01, 0.03, 0.05, 0.07, and 0.09 M, respectively. For SEM, Micro-FTIR, XPS, and TGA analyses, RNC gels were used after removal of the sol fraction. For mechanical strength measurements, as-prepared RNC gels were used directly to retain the original water/polymer ratio.

Mechanical Strength of RNC Gels

Compression measurements on samples measuring Φ15 mm × 20 mm were performed at 25 °C at a strain rate of 15% min^{-1} using an Instron-3365 material testing system. The initial cross-section was used to calculate compression strength.

Gel Fraction

The as-prepared RNC gels were cut into small pieces and vacuum-dried at 40 °C to constant weight. The dried RNC gels were immersed in deionized water at room temperature for 7 days to extract the sol fraction, with the deionized water changed several times. RNC gels after sol fraction removal were vacuum-dried at 40 °C to constant weight. Gel fraction (Gf) was calculated using Eq. (2):

$$G_f = (W_g/W_0) \times 100\%$$

where W_0 and W_g are the weights of dried RNC gels before and after removal of the sol fraction, respectively.

Swelling Behavior

Dried RNC gels were immersed in a large excess of deionized water at room temperature and removed at desired times for weighing. Excess water on the gel surface was removed with filter paper before weighing. Eq. (3) was used to calculate the swelling ratio (SR):

$$SR = (W_t - W_0)/W_0$$

where W_t is the weight of the swollen gel at time t and W_0 is the weight of the initial dried RNC gel.

Thermo sensitivity of the RNC gels was determined by observing their temperature-dependent equilibrium degree of swelling (EDS). Purified RNC gels were immersed in deionized water at specific temperatures for 84 h to

reach swelling equilibrium. EDS of RNC gels was studied at 25–40 °C. EDS was calculated by Eq. (4):

$$EDS = (W_e - W_0)/W_0$$

where W_e is the weight of the RNC gel in the equilibrium swelling state and W_0 is the weight of the initial dried RNC gel.

Morphology of RNC Gels

The morphology of RNC gels was observed using SEM. To preserve the network structure, RNC gels in the equilibrium swollen state were immersed in liquid nitrogen and then lyophilized at −20 °C. The lyophilized RNC gels were coated with gold using an ion coater prior to photographing cross-sectional morphology. SEM images of the RNC gels were obtained using a Hitachi S-4800 instrument (Hitachi, Japan) in high vacuum mode at 8.0 kV.

FTIR Analysis

Micro-FTIR spectra of the samples were recorded using a Nicolet (NICOLETIN 10MX) spectrometer in absorbance mode in the range of 4000–600 cm^{-1}.

XPS Analysis

XPS data of the RNC gels after sol fraction removal were obtained with an AXIS Ultra instrument from Kratos Analytical using low-energy electron flooding for charge compensation. Monochromatic Al Kα radiation was used. The data were converted into VAMAS file format, and the Casa XPS software package was used for data manipulation and curve-fitting.

TG Analysis

TG analysis was carried out using a Q600 SDT instrument (TA Instruments, USA) from 25–700 °C at a heating rate of 10 °C/min under air atmosphere.

Results and Discussion

Characterization of RNC Gels

1. Mechanical Strength RNC gels containing a certain amount of clay exhibit good optical transparency, high strength, and flexibility (Fig. 1Figure 1: see original paper). The as-prepared RNC3 gel can endure large deformations, while the RNC0 gel is fragile and easily ruptures with slight stretching. Data in Table 1 indicate that the compression stress of an RNC gel at a given strain increases with clay content. Specifically, the RNC0 gel cannot endure compression deformation beyond 90% and is crushed during the compression test, whereas the RNC3 gel shows no obvious rupture even under a compression

strain of 95% and simply returns to its initial shape when the compression test ends (Figs. 1(b)-1(d)). Apparently, the mobility of macromolecular chains in the network gives the RNC3 gel high elasticity [12], while strong interactions between the clay sheets and polymer matrix endow it with high mechanical strength. RNC5, RNC7, and RNC9 gels can also fully return to their initial shapes after compression to 95% strain, similar to the behavior displayed by the RNC3 gel.

Figure 2[Figure 2: see original paper] shows that compression stresses of the RNC gels increase slowly before 65% strain but rapidly under strains of 65-95%. The compression stresses of the RNC3 gel are 0, 0.072, and 5.15 MPa at strains of 0%, 65%, and 95%, respectively. The elastic modulus of an RNC gel is very low before 65% strain due to long, flexible chains between crosslinking points. With increasing strain, polymer chains gradually approach their full extension, causing higher elastic modulus and leading to a rapid increase in compression stress [21]. The compression stresses of RNC gels are comparable with those of NC gels prepared using other methods [14].

2. Gel Fraction Absorbed dose affects gel formation of RNC gels in an analogous manner, and the relationship between gel fraction and absorbed dose for the RNC3 gel is illustrated in Fig. 3[Figure 3: see original paper]. The Gf increases sharply with dose initially and levels off at 5 kGy. Apart from the RNC3 gel, gel fractions of other RNC gels are all above 90% at 10 kGy (Table 1). Consequently, 10 kGy is suitable for preparing high-performance RNC gels. Additionally, the solution containing only laponite clay did not form a gel after γ-irradiation, indicating that irradiation cannot cause cross-linking between laponite particles.

3. Swelling Behavior As shown in Fig. 4[Figure 4: see original paper], the SR of RNC gels grows rapidly in the first 40 h, followed by slow increases leveling off after 72 h. Table 1 shows that the EDS of RNC gels at room temperature decreases with increasing clay content, indicating that crosslinking density increases when RNC gels incorporate more clay sheets into the polymer matrix. Shorter polymer chains between crosslinking points induce smaller pore sizes in the RNC gel network, resulting in decreased water absorption [22].

Scott proposed the following kinetics model to describe the swelling procedure of hydrogels:

$$dS/dt = k_S(S_\infty - S)^2$$

With the initial condition of t = 0 and S = 0, this can be deduced as Eq. (6):

$$t/S = A + Bt$$

where k_S is the rate constant of swelling, S_∞ is the theoretical maximum swelling degree, $A = 1/k\_S\ S\_\infty^2 = 1/(dS/dt)_0$, which is the reciprocal of the initial swelling rate (r_0), and B is the reciprocal of S_∞. S_∞ and k_S can be calculated from the curve of t/S versus t. The results are given in Table 2. The S_∞ values calculated by Eq. (6) (S_∞,c) are close to those obtained from experiments (S_∞,e), showing that the model fits the swelling behaviors of RNC gels, as confirmed by the correlation coefficients. Generally, RNC gels with higher clay content possess lower EDS and smaller rate constants, indicating that swelling behavior can be easily controlled by adjusting clay content.

The EDS of RNC gels (Fig. 5[Figure 5: see original paper] and Table 1) decreases with increasing temperature because at higher temperatures, hydrogen bonds between polymer chains and water molecules become weaker and the RNC gels become increasingly hydrophobic internally. This is disadvantageous for polymer chains to bind water molecules and exhibit higher water absorption. There is an abrupt decrease in EDS at 34 °C for RNC0 and RNC1 gels and at 35 °C for RNC3 and RNC5 gels, while RNC7 and RNC9 gels do not show any sharp decrease in EDS. Additionally, the EDS decreases gradually with increasing clay content in RNC gels. This occurs because high clay content results in shorter polymer chains between crosslinking points, making it difficult for polymer chains to aggregate together and exhibit abrupt phase transition behavior at the macro level [15]. Consequently, RNC gels lose their thermo sensitivity as clay content increases, instead showing gradually decreased EDS with increasing temperature. The EDS of RNCn gels at 40 °C is given in Table 1. RNC gels with higher clay content show higher EDS at 40 °C due to their lower deswelling ratio.

4. SEM Images SEM images of lyophilized RNC gels are shown in Fig. 6[Figure 6: see original paper]. Homogeneous three-dimensional networks are formed in RNC gels. All RNC gels exhibit cellular structures typical of hydrogels. The pore diameter decreases from dozens of micrometers to several micrometers with increasing clay content in swollen RNC gels. For example, pore diameters are 15 μm in RNC0 and 7 μm in RNC9 gel. This occurs because RNC gels containing more clay sheets have higher crosslinking density, resulting in smaller pore sizes.

Formation Mechanism of RNC Gels

When the solution containing NIPAAm and clay is subjected to ionizing radiation, ·OH and ·H radicals are formed. These radicals can initiate polymerization and crosslinking of NIPAAm monomer. They can also react with Si−OH groups on the surface of clay sheets to form Si−O·radicals, which can react with alkyl radicals of NIPAAm monomer or the PNIPAAm polymer matrix, leading to formation of chemical bonds between clay sheets and polymer matrix. In the prepared RNC gels, clay sheets act as crosslinkers to some extent.

1. FTIR Analysis Micro-FTIR studies provide information about the components of RNC gels. The FTIR spectrum of dried RNC3 gel (Fig. 8[Figure 8: see original paper]) shows characteristic absorptions of both PNIPAAm and clay. The absorption at 2968 cm^{-1} is characteristic of C−H bonds on saturated carbon atoms of PNIPAAm chains, while the absorption at 3280 cm^{-1} corresponds to stretching vibrations of N−H bonds. The absorptions at 1665 and 1554 cm^{-1} are attributed to C=O bonds and C−N bonds, respectively. The absorptions at 1010 and 650 cm^{-1} are characteristic of clay and are attributed to Si−O bonds and Si−O−Si bonds, respectively [24]. Appearance of these absorptions indicates incorporation of clay in the RNC3 gel.

The peaks at 1616 cm^{-1}, attributed to C=C bonds in NIPAAm monomers, disappear in spectra of both RNC0 and RNC3 gels. This indicates that polymerization and crosslinking of NIPAAm monomers have occurred. Additionally, no change in the FTIR spectrum of RNC3 gel was observed even after immersion in deionized water for up to three months (with the deionized water renewed regularly). This implies that there is hardly any loss of clay from the RNC3 gel during three months of soaking. Theoretically, if clay sheets were combined with polymer chains only through physical interactions, the three-month soaking might remove some clay sheets from the network structure of RNC3 gel. This suggests the presence of stronger interactions between clay sheets and polymer matrix, such as chemical interactions.

2. XPS Analysis XPS spectra (Fig. 9[Figure 9: see original paper]) provide further evidence of chemical interactions between polymer chains and clay sheets. An obvious Mg peak appears in the spectrum of RNC3 gel due to clay incorporation. The C 1s XPS spectrum of RNC0 gel shown in Fig. 9(b) exhibits three peaks centered at 284.8, 285.4, and 287.8 eV, which are assigned to C−C bonds, C−N bonds, and C=O bonds, respectively [25].

In the C 1s XPS spectrum of RNC3 gel (Fig. 9(c)), a new peak centered at 286.2 eV is attributed to C−O bonds, which should result from chemical bonds between polymer chains and clay sheets. Considering possible reactions under irradiation, the C−O single bond can be formed from carbon atoms of alkyl radicals and oxygen atoms of Si−O · radicals.

3. TG Analysis TG and DTG curves of RNC gels are shown in Figs. 10[Figure 10: see original paper] and 11[Figure 11: see original paper]. The PNIPAAm portion in RNC gels almost completely decomposes at 700 °C under air atmosphere, and the final weight represents clay content in RNC gels. TG analysis results are listed in Table 3. The experimental residual weight of RNC gels containing clay is slightly less than the theoretical residual. This may result from weight loss of the clay portion in RNC gels. In Fig. 11(a), a pure clay sample shows a weight loss of 14.7% when heated to 700 °C. Weight loss of clay might be caused by loss of bound water in clay or conversion of alkali to metallic oxide.

TG and DTG curves in Fig. 10[Figure 10: see original paper] show that RNC gels undergo three degradation steps. According to Ref. [26], the first degradation starting at about 50 °C corresponds to loss of residual water in the structures of RNC gels. The second degradation is attributed to decomposition of acylamino groups in RNC gels, as data in Table 3 imply that weight ratios of acylamino groups in RNC gels are quite close to the weight loss ratios of the second degradation step. The third degradation is attributed to breakage of −C−C− backbones in RNC gels, and data in Table 3 support this deduction.

From DTG curves in Fig. 10(b) and Table 3, the onset temperature of decomposition for both the second and third degradation steps increases with clay sheet content, following the order: RNC0 ≤ RNC1 < RNC5 < RNC7 < RNC9. These results indicate formation of chemical bonds between polymer chains (including acylamino groups and −C−C− backbones) and clay sheets. It is also found that only one peak appears during the second degradation of RNC0 and RNC1 gels, while two peaks appear for RNC3, RNC5, RNC7, and RNC9 gels. The emerging peak during the second degradation further indicates chemical interactions between acylamino groups and clay sheets. However, the effect of chemical interactions between acylamino groups and clay sheets in RNC0 and RNC1 gels is not strong enough to cause this change due to low clay contents.

Additionally, TG curves of a physical mixture of RNC0 gel and irradiated clay, RNC0 gel, irradiated clay, and RNC3 gel are shown together in Fig. 11[Figure 11: see original paper]. The TG and DTG curves of RNC0 gel and the physical mixture sample are quite similar, while they differ significantly from those of RNC3 gel. The third degradation of RNC3 gel starts at a higher temperature than those of RNC0 gel and the physical mixture sample. As hydrogen bonds or other physical forces are not effective at such high temperatures [27], stronger interactions must exist between polymer chains and clay sheets in the network of RNC gels. It can be concluded from XPS, TG, and DTG analyses that chemical bonds (like C−O bonds) between the polymer matrix and clay sheets are formed during the radiation process.

Conclusion

NC gels based on the PNIPAAm/clay system were successfully synthesized by radiation method for the first time. The novel RNC gel exhibits good optical transparency, high strength, regular swelling behavior, and thermo sensitivity. Micro-FTIR, XPS, and TG analyses proved that chemical bonds between the polymer matrix and clay sheets were formed during γ-irradiation. This work presents a new method for preparing high-performance hydrogels, and these RNC gels are more suitable for biomedical applications due to the absence of residual initiators and catalysts.

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Note: Figure translations are in progress. See original paper for figures.