

RADIATION SYNTHESIS AND CHARACTERIZATION OF POLY(AA-co-NVP)/CLAY HYDROGELS*

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Abstract The pH-sensitive P(AA-co-NVP)/clay hydrogels were prepared with the monomers of acrylic acid (AA) and *N*-vinyl-2-pyrrolidone (NVP) based on γ -ray irradiation technique. The influence of pH values of buffer solutions and contents of clay and NVP on the equilibrium swelling ratio (SR) and compressive properties of the hydrogels was investigated in detail. The results of swelling property tests showed that, with the increase of clay content, the SR of hydrogels increases in the same buffer solution, and the SR of hydrogels with different contents of HTMAB-clay is higher than that of P(AA-co-NVP) hydrogels without clay. When the content of clay is 15%, the SR of P(AA-co-NVP)/clay hydrogel is 201 at pH = 9.8, which is 1.23 times of that of the P(AA-co-NVP) hydrogel (164). In addition, the SR of P(AA-co-NVP)/clay hydrogel is higher than that of PAA/clay hydrogel in the same solution. The compressive properties of the hydrogel were also examined. The results showed that the compressive properties of the P(AA-co-NVP)/clay hydrogels were improved distinctly as compared to those of the conventional hydrogels without clay. When the content of clay is 15%, the compression strength of the P(AA-co-NVP)/clay hydrogel is 23 times of that of the P(AA-co-NVP) hydrogel.

Keywords: pH-sensitive hydrogels; Clay; Radiation; Compressive properties.

INTRODUCTION

Polymeric hydrogels have attracted much attention and have been applied in many fields because of their sensitivity to environmental stimuli such as temperature^[1, 2], pH^[3–8], pressure^[9], ionic strength^[10] and electric fields^[11, 12]. However, the application of the conventional polymeric hydrogels is often limited because of the low gel strength and the poor stability of the hydrogel. Clay was introduced into the hydrogel matrix to improve the mechanical, swelling and thermal properties of the hydrogels^[13–16], which had been studied by several groups. Messersmith and Znidarsich first reported stimuli-responsive hydrogel-clay composites by direct copolymerization of *N*-isopropylacrylamide with methylene bisacrylamide in aqueous suspensions of Na-montmorillonite^[17]. However, the swelling ratio of hydrogels became bad with increasing of the contents of Na-montmorillonite. Haraguchi and Tkehisa obtained hydrogel nanocomposites with exceptional mechanical properties by incorporating the inorganic clay into poly(*N*-iso-propylacrylamide) and poly(*N,N*-dimethylacrylamide) matrix without using chemical crosslinking agents^[18–20]. Liu *et al.*^[21] synthesized a series of high hectorite content hydrogels. It was found that these hydrogels showed surprising mechanical properties (*i.e.* tensile strength: 1 MPa). However the above composite hydrogels were temperature sensitive hydrogels. At the present time the report about pH-sensitive composite hydrogels by adding clay was very lack. Zhang *et al.* synthesized nanocomposite hydrogels with high thermal stability and swelling ratio by grafting acrylic acid on the organophilic montmorillonite^[22], but without researches on the mechanical properties of hydrogels. Besides,

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some of their potential applications are hindered for bad biocompatibility or low purity because of the catalysts or additives in chemosynthesis processes.

For improving mechanical, swelling and thermal properties of the hydrogels, in this work, we report the preparation of a novel P(AA-co-NVP)/clay hydrogel by γ -rays radiation and the influence of *N*-vinyl-2-pyrrolidinone (NVP) and clay on swelling and compressive properties of these hydrogels.

EXPERIMENTAL

Materials

Acrylic acid (AA) monomer was purchased from Zhengzhou Zhongliang Chemical Co. and used without any further purification. *N*-vinyl-2-pyrrolidinone (NVP) was obtained from Boai Xinkaiyuan Pharmacy limited company, China. *N,N'*-methylenebis-acrylamide (Bis; Keou Reagent Company, Tianjin, China) and hexadecyl trimethyl ammonium bromide (HTMAB, Yuanhang chemistry limited company, Tianjin, China) were all of analytical grade and used as received. Sodium montmorillonite (Na-clay) was purchased from Fenghong clay company, Zhejiang, China.

Organic Modification of Clay

A 3 wt% Na-clay solution was stirred for an hour at room temperature and stewed for 7 days. The HTMAB was dissolved in the solution and stirred for 8 h at 60°C. The mixture was centrifugal separated, and the clay was washed by rote and dried in vacuum at 50°C. At last the modified clay was sifted at 360 meshes.

Preparation of P(AA-co-NVP)/Clay and PAA/Clay Hydrogels

Preparation of PAA/clay hydrogels

AA was dissolved in distilled water, and clay was dispersed in the monomer solution at room temperature. Bis was used as crosslinker (2.0 wt% based on AA), the monomers solutions were bubbled with nitrogen for 10 min in order to remove the remaining oxygen and sealed. Then the mixture was under ultrasonic treatment for 8 h, and then polymerization of suspension solution was initiated by irradiation of a ^{60}Co γ -ray source with 14 kGy absorbed dose and 95.7 Gy/min absorbed dose rate at room temperature. Hydrogels obtained were cut into pieces of 2 mm long and were dried in vacuum at 50°C to constant weight. The sample codes ATi-10, A0 correspond to the HTMAB-clay contents of 10 and 0 wt%, respectively.

Preparation of P(AA-co-NVP)/clay hydrogels

Five components were used in the preparation of poly(AA-co-NVP)/clay hydrogels, namely AA, NVP, Bis, clay and distilled water. The poly(AA-co-NVP)/clay hydrogels were prepared by using the same procedure described above. The poly(AA-co-NVP)/clay sample codes AN0, ANTi-1, ANTi-5, ANTi-10 and ANTi-15 correspond to the HTMAB-clay contents of 0, 1, 5, 10 and 15 wt%, respectively.

X-ray Diffraction

X-ray diffraction (XRD) measurements were performed by using a D/BAX-3B X-ray diffractometer at a scanning rate of 0.1°/s ($\lambda = 0.15418$ nm) at room temperature.

Measurements of Swelling Kinetics of Hydrogels

The swelling kinetics of gels was measured gravimetrically at 25°C after blotting the excess surface water with a moistened filter paper. The weight changes of gels were recorded during the course of swelling at regular time intervals. The swelling ratio at a given time interval t is defined as $\text{SR}_t = (W_t - W_d)/W_d$, where W_t is the weight of the swollen gel at time t , and W_d is the dry weight of the hydrogel after drying in vacuum overnight.

Swelling Studies

For measuring the equilibrium swelling ratio (SR) the weighted dry gels were immersed in the swelling medium with different pH. The weight of swollen samples was measured at various time intervals after the excess surface water was removed using filter paper. The procedure was repeated until there was no further weight increase. The SR of the hydrogels can be calculated as $\text{SR} = (W_s - W_d)/W_d$, where W_d is the initial weight of dry gel and W_s is the equilibrium weight of swollen hydrogels.

Measurements of Compressive Properties

Compressive strength measurements were performed on hydrogels of cylindrical shape (12 mm (diameter)/11 mm (thickness)) and the same polymer/water weight ratio. The samples were compressed by the upper plate, which was connected to a load cell, at a compression rate of 2 mm/min. The strain under stress (or compression) is defined as the relative change in thickness of the specimen. The compression strength (CS) was calculated on the basis of the initial cross section. The strains (%) at maximum compression force ($S_{\max}$) were measured out directly.

RESULTS AND DISCUSSION

Structure Characteristics of Clay

Clay is a kind of phyllosilicates with exchangeable cations between clays. X-ray diffraction shows that the distance between Na-clay layers is changed from 1.1 nm to 2.6 nm because Na-clay pieces can be intercalated or exfoliated by HTMAB, and P(AA-co-NVP)/clay pieces shows a distance of 3.6 nm (Fig. 1).

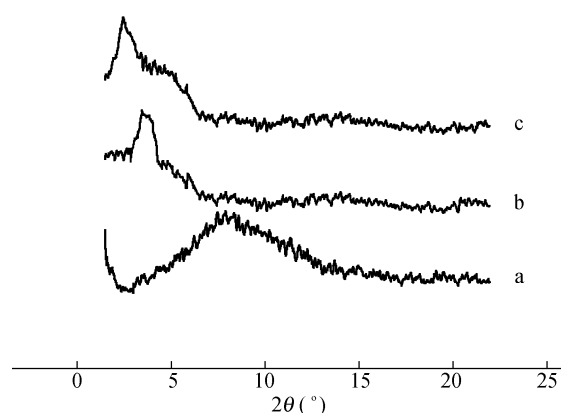


Fig. 1 XRD patterns of (a) Na-clay, (b) HTMAB-clay and (c) P(AA-co-NVP)/clay

Swelling Kinetics of P(AA-co-NVP)/Clay Hydrogels

Figure 2 shows the swelling kinetics curves of P(AA-co-NVP)/clay hydrogels in pH = 1.4 and 9.8 buffer solutions at 25°C. When the pH is 1.4, the SR of P(AA-co-NVP)/clay hydrogel increases rapidly at the beginning, and after 13 h the hydrogels almost reach the equilibrium of swelling, that is to say, the equilibrium swelling time of P(AA-co-NVP)/clay hydrogel in pH = 1.4 buffer solution is about 13 h (Fig. 2a), while the equilibrium swelling time of this hydrogel is about 20 h (Fig. 2b) in pH = 9.8 buffer solution. In this work, 24 h was selected as equilibrium swelling time in order to swell sufficiently.

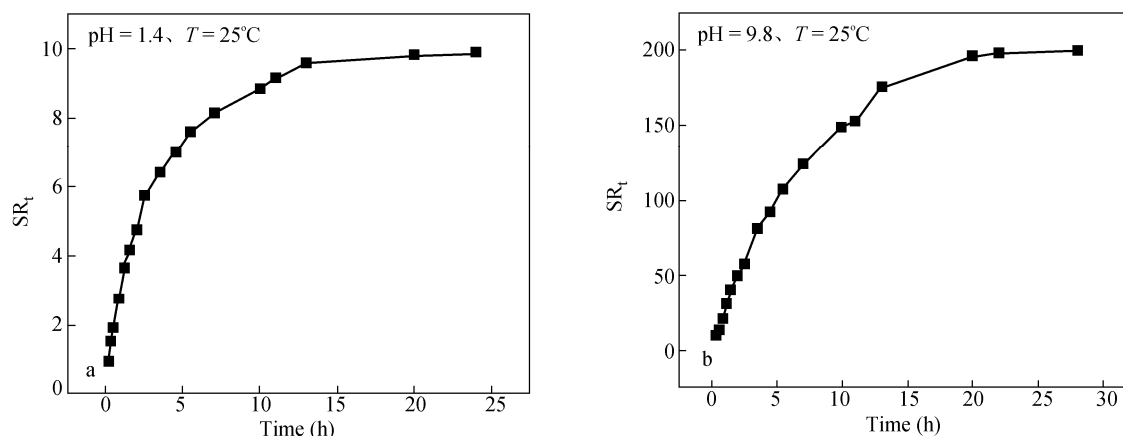


Fig. 2 Swelling kinetics curves of P(AA-co-NVP)/clay hydrogel in buffer solutions with different pH:

(a) pH = 1.4 and (b) pH = 9.8

The content of clay in P(AA-co-NVP)/clay hydrogel is 10 wt%; AA/NVP: 80/20 (W/W)

From this figure, it is known that the swelling behavior of absorbents is significantly affected by the characteristics of the external solution.

Swelling Behavior of P(AA-co-NVP)/Clay Hydrogels

Effect of NVP on SR of hydrogels in buffer solutions with different pH

The SR of PAA/clay and poly(AA-co-NVP) hydrogels were investigated as a function of pH. Figure 3 shows the effect of both pH and NVP on the SR of the hydrogels. It can be found that these hydrogels possess abrupt change in the SR with the increase of pH value. When pH values are lower than the acid exponent of acrylic acid, (pK_a) value of AA, the carboxylic groups are completely collapsed, and the SR is very low. When pH values are higher than the pK_a , the SR increases due to the dissociation of the carboxylic groups and breakage of hydrogen bonds^[23]. In alkaline buffer solutions, the carboxylic groups become progressively more ionized with increasing of pH value. Therefore, the hydrogels swell more rapidly due to a larger swelling force created by the electrostatic repulsion, which results in the expansion of the network structure.

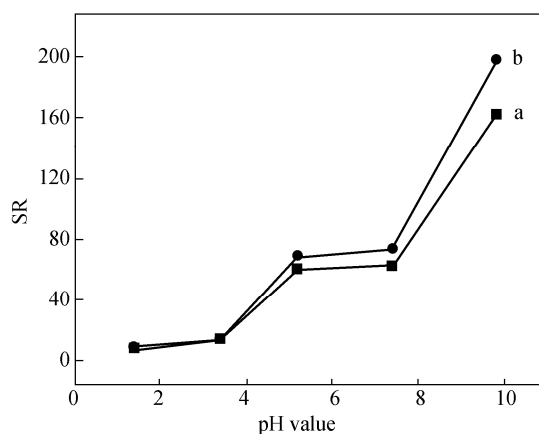


Fig. 3 Swelling behavior of PAA/clay and P(AA-co-NVP)/clay hydrogel in buffer solutions with different pH at 25°C
a) PAA hydrogel with 10% HTMAB-clay; b) P(AA-co-NVP) copolymer hydrogel with 10 wt% HTMAB-clay

In addition, Fig. 3 shows that the effect of NVP on the SR of hydrogels in buffer solutions. In this figure, the SR of hydrogels is corresponding to the NVP in the monomer solution. The SR of P(AA-co-NVP)/clay hydrogel is higher than that of PAA/clay hydrogel. This result can be explained as followed: the pyrrolidone groups in the gel network are introduced because of the existence of NVP, and consequently the free volume available for swelling increases due to the repulsion between the pyrrolidone groups.

Swelling ratio of P(AA-co-NVP) hydrogels with different contents of HTMAB-clay via pH

Figure 4 shows that the swelling behavior of P(AA-co-NVP) hydrogels with different contents of HTMAB-clay. From this figure, it can be found that, with the increase of clay content, the SR of hydrogels increases in the same buffer solution, and the SR of hydrogels with different contents of HTMAB-clay are higher than that of P(AA-co-NVP) hydrogel without clay. When the content of clay is 15%, the SR of P(AA-co-NVP)/clay hydrogel is 201 at pH = 9.8, which is 1.23 times of that of P(AA-co-NVP) hydrogel (164). This result can be explained as follows. On one hand, clay itself is hydrophilic, it can imbibe a lot of water; on the other hand, the sheets of the clay are well-dispersed in the hydrogels, and the pores in the hydrogels should be bigger and are much better dispersed than those in the conventional hydrogel. The hydrogel composites have higher swelling ratio than the conventional hydrogels.

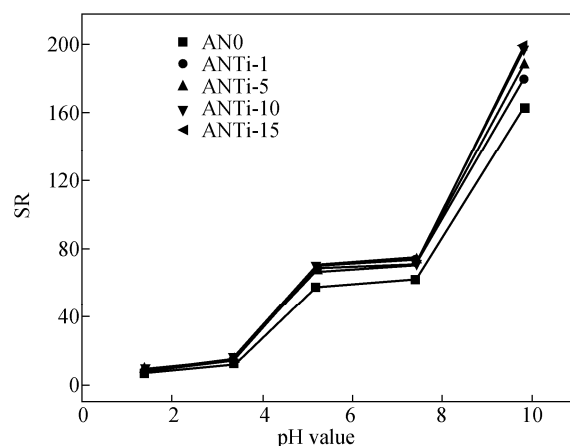


Fig. 4 Swelling ratio of P(AA-co-NVP) hydrogels with different contents of HTMAB-clay *via* pH at 25°C

Compressive Properties of P(AA-co-NVP)/Clay Hydrogels

Figure 5 shows that the compressive properties of P(AA-co-NVP)/clay hydrogels. It can be seen from this figure, the compressive properties of the P(AA-co-NVP)/clay hydrogels are better than those of conventional hydrogels. In addition, with the increase of clay content, compression strength (CS), strain(%) in maximum compression force ($S_{\max}$) of hydrogels increase at the same buffer solution. Moreover, in the whole compressive process, when the content of clay changes from 5% to 15%, the hydrogels are not damaged, and it is found that the hydrogel can recover to about 70% of its original length at room temperature after the compressive process. The result indicates that the hydrogels are hardly damaged by compressive deformation, similar to rubber.

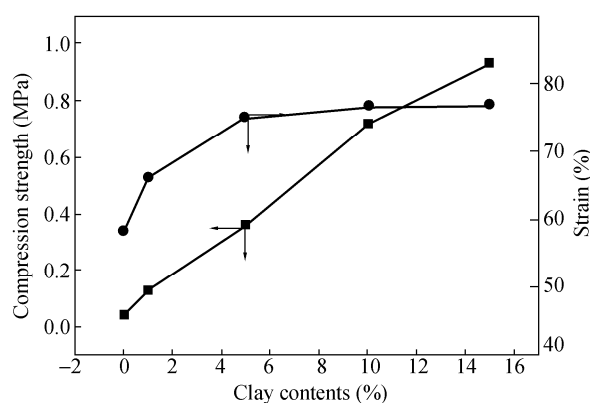


Fig. 5 Effects of different clay content on compressive properties of P(AA-co-NVP)/clay hydrogels

Table 1. Swelling ratio, mechanical properties of hydrogels

Sample	c (%)	SR (pH = 9.8)	CS (MPa)
A0	0	150	0.02
ATi-15	15	167	0.43
AN0	0	164	0.04
ANTi-15	15	200	0.93

A0: PAA hydrogel; ATi-15: PAA hydrogel with 15% HTMAB-clay; AN0: P(AA-co-NVP) hydrogel, (AA/NVP = 80/20, *W/W*); ANTi-15: P(AA-co-NVP) hydrogel with 15% HTMAB-clay; The concentration of monomer in the four hydrogels is the same and with the same polymer/water weight ratio.

The data of Table 1 show the swelling ratio and mechanical properties of four hydrogel samples. The SR and CS of hydrogels with NVP are higher than those of hydrogels without NVP, and the hydrogel with 15% clay shows the excellent balanced properties.

In this report, clay was added in the P(AA-co-NVP) hydrogel matrix, which results in several advantages. First, the SR of composite hydrogels is higher than that of conventional hydrogels. Secondly, the compressive properties of composite hydrogels are improved abruptly.

The phenomenon is probably caused by two reasons. One is that polymer chain segments retain high mobility in solution, so the polymer is in the elastic state. Another reason is Na-clay sheets can be intercalated by HTMAB. The sheets of clay can be effectively used to enhance the hydrogel strength because of strutting of clay to molecular chains. A diagrammatic sketch of the P(AA-co-NVP)/clay hydrogel is shown in Fig. 6.

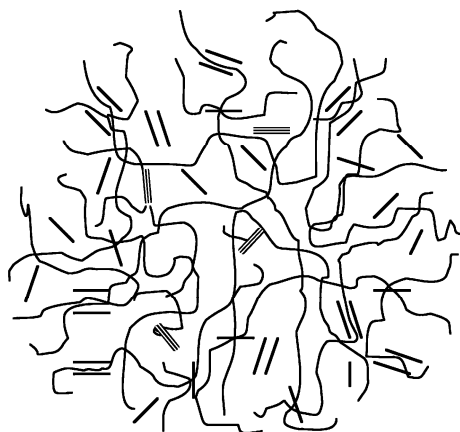


Fig. 6 Diagrammatic sketch of the poly(AA-co-NVP)/clay hydrogel

CONCLUSIONS

In this study, the pH-sensitive P(AA-co-NVP)/clay hydrogels were prepared with the monomers of acrylic acid and *N*-vinyl-2-pyrrolidone based on the γ -ray irradiation technique. The influences of pH value of buffer solution and content of clay and NVP on the swelling ratio (SR) and compressive properties of the hydrogels were investigated in detail. The results of swelling property tests show that with the increase of clay content, the SR of hydrogels increases at the same buffer solution, and the SR of hydrogels with different contents of HTMAB-clay is higher than that of P(AA-co-NVP) hydrogels without clay. When the content of clay is 15%, the SR of P(AA-co-NVP)/clay hydrogel is 201 at pH = 9.8, which is 1.23 times of that of P(AA-co-NVP) hydrogel (164). In addition, the SR of P(AA-co-NVP)/clay hydrogel is higher than that of PAA/clay hydrogel in the same solution. The compressive properties of hydrogel composites were also examined. The results showed that the compressive properties of P(AA-co-NVP)/clay hydrogels were improved obviously as compared to those of the conventional hydrogels without clay. When the content of clay is 15%, the compression strength of the P(AA-co-NVP)/clay hydrogel is 23 times of that of the P(AA-co-NVP) hydrogel.

REFERENCES

- 1 Sershen, S. and West, J., *Adv. Drug. Deliv. Rev.*, 2002, 54: 1225
- 2 Gehrke, S.H., *Adv. Polym. Sci.*, 1993, 110: 81
- 3 Alvarez-Lorenzo, C. and Concheiro, A., *J. Control. Release*, 2002, 80: 247
- 4 Nagasaki, Y., Luo, L.B., Tsuruta, T. and Kataoka, K., *Macromol. Rapid Commun.*, 2001, 22: 1124

- 5 Byung, K.K. and Sang, H.P., *J. Polym. Sci. Part A: Polym. Chem.*, 1999, 37: 2703
- 6 Sahoo, S.K., De, X., Ghosh, P.K. and Maitra, A., *J. Colloid Interf. Sci.*, 1998, 206: 361
- 7 Tang, L.M. and Dai, Y., *Acta Polymerica Sinica (in Chinese)*, 2003, (3): 426
- 8 Huang, J., Huang, Z.M., Bao, Y.Z. and Weng, Z.X., *Chinese J. Polym. Sci.*, 2006, 24(2): 195
- 9 Yan, H., Herber, S., Olthuis, W. and Bergveld, P., *Sens. Mater.*, 2002, 14: 129
- 10 Suzuki, A., *Adv. Polym. Sci.*, 1993, 110: 201
- 11 Kwon, I., Bae, Y.H., Okano, T. and Kim, S.W., *Nature*, 1991, 354: 291
- 12 Liu, G.Q., Zhao, X.P. and Tang, T., *Acta Polymerica Sinica (in Chinese)*, 2003, (3): 398
- 13 Santiago, F., Mucientes, A.E. and Rivera, C., *Eur. Polym. J.*, 2007, 35: 1
- 14 Xia, X.H., Yih, J., D'Souza, N.A. and Hu, Z.B., *Polymer*, 2003, 44: 3389
- 15 Liu, Y., Zhu, M.F., Liu, X.L. and Zhang, W., *Polymer*, 2006, 47: 1
- 16 Zhou, S.H., Yang, J.G. and Wu, C.P., *Acta Polymerica Sinica (in Chinese)*, 2003, (3): 326
- 17 Messersmith, P.B. and Znidarsich, F., *Mater. Res. Soc. Sym. P.*, 1997, 457: 507
- 18 Haraguchi, K., Takehisa, T. and Fan, S., *Macromolecules*, 2002, 35: 10162
- 19 Haraguchi, K. and Takehisa, T., *Adv. Mater.*, 2002, 14: 1120
- 20 Haraguchi, K., Farnworth, R., Ohbayashi, A. and Takehisa, T., *Macromolecules*, 2003, 36: 5732
- 21 Liu, Y., Zhu, M.F., Liu, X.L., Zhang, W., Sun, B., Chen, Y.M. and Adler, H-J.P., *Polymer*, 2006, 47: 1
- 22 Zhang, W.A., Luo, W.B. and Fang, Y.E., *Mater. Lett.*, 2005, 59: 2876
- 23 Zhang, H.L., Guo, Y., Li, S.B. and Wang, Z.L., *Journal of Chemistry & Bioengineering (in Chinese)*, 2004, 10: 28