

AN EFFECTIVE METHOD TO IMPROVE THE WET STRENGTH OF POLY(DIALLYLDIMETHYL-AMMONIUM CHLORIDE) HYDROGELS

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Abstract New IPN hydrogels composed of diallyldimethylammonium chloride (DADMAC) and natural macromolecule, kappa-carrageenan (KC) were prepared by gamma irradiation and their properties were studied. The results show that both the gel strength and the swelling capacity of the IPN hydrogels were enhanced significantly as compared with those of the pure hydrogels of PDADMAC.

Keywords Diallyldimethylammonium chloride, Kappa-carrageenan, IPN hydrogel, Radiation synthesis, Gel strength

INTRODUCTION

In recent decades, polyelectrolyte gels with charged groups on the polymer chain backbone or on the side chains have been the objects of intensive studies due to their various applications in chemical engineering, biomedical, food and agriculture fields^[1, 2].

It is well known that compatible mechanical properties of the hydrogels in the swollen state are extremely important for a given application. When most of the hydrogels are immersed in water, a remarkable decrease of mechanical strength occurs. This is the major disadvantage of hydrogels that can be overcome either by crosslinking or by crystallization^[3]. However, either method may induce the decrease of swelling ratio.

Among many of the attempts to improve the wet strength of hydrogels, interpenetrating polymer network (IPN) structures have been noted by many researchers. IPN hydrogels such as IPN composed of natural macromolecules and synthetic polymers^[4, 5] or two kinds of synthesized polymers^[6] have distinct morphology and exhibit properties different from those of the original polymers^[7]. Unlike many other methods for improving the gel strength of a hydrogel, IPN structures can also retain its good swelling capability.

In our previous work, IPN hydrogels consisting of a widely used monomer, diallyldimethylammonium chloride (DADMAC)^[8], and natural macromolecule, kappa-carrageenan (KC)^[9], were prepared by gamma irradiation. The swelling behavior and gel fraction properties of the IPN gels were studied^[10].

This paper deals with the mechanical strength of the PDADMAC/KC IPN gels.

The crosslinked PDADMAC is a polyelectrolyte gel which is able to absorb a large amount of water, but it has a fatal defect of poor wet strength due to the high charge density along the polymer chains and the rigid five-membered pyrrolidinium rings on the main chains.

As the results of the present work, the mechanical strength of PDADMAC/KC was improved notably by the IPN structure compared with that of the pure hydrogel of PDADMAC or KC.

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EXPERIMENTAL

Materials

The monomer, diallyldimethylammonium chloride (DADMAC, 60 wt% in water), was purchased from Tokyo Kasei Kogyo Co. Ltd. The crosslinking agent, *N,N'*-methylenebisacrylamide (Bis), was available from Beijing Chemical Plant, and kappa-carrageenan (KC WG-115) was obtained from Copenhagen Pectin A/S, Denmark. All the reagents were used without further purification. Redistilled water was used in polymerization and other reagents were analytically pure.

Preparation of PDADMAC/KC IPN

The aqueous KC solutions (1 wt%–3 wt%) were kept at 80–90°C for 2 h and then mixed with the monomer (50% weight in water) and crosslinking agent (0.5% mole of monomer). The hot mixtures were poured into cylindrical tubes. When the mixed samples were cooled to room temperature, some of the KC main chains were crosslinked physically; in the mean time, the monomer, DADMAC, was dispersed homogeneously in the physical network structure of KC. The samples were then irradiated by γ -rays from a Co-60 source (Peking University) at room temperature and the special IPN was formed. Dose rates were set from 28.33 Gy min⁻¹ to 165.5 Gy min⁻¹ and doses up to 80 kGy were used. The prepared gels were cut into thin disks and dried at 50°C under vacuum to constant weight.

Measurements

Gel strength

After irradiation, the gel was removed from the cylindrical tubes and cut into rods of 15 mm height and 11 mm of diameter. Gel strength (yield strength, N stands for Newton) at room temperature was measured by compressing the samples to 50% of their original height between two parallel plates on a Stograph-R1 Material Tester (Toyoseiki Co. Ltd, Japan) at a crosshead speed of 20 mm/min.

Swelling behavior

The dried gel was immersed in distilled water at room temperature. After the excess surface water had been removed with filter paper, the weight of swollen gel was measured at various time intervals. This procedure was repeated until the weight of swollen gel became constant. The swelling ratio was determined according to the following equation:

$$\text{Swelling ratio} = W_t/W_d$$

where W_d is the weight of the dried gel before swelling and W_t is the weight of the gel at time t . The equilibrium degree of swelling (EDS) was also calculated by changing W_t to W_e in this equation which was the equilibrium weight of swollen gel.

To study the EDS of gels in solutions at various pHs, the gels were immersed in either 0.2 mol/L citric acid buffer or 0.2 mol/L phosphate buffer at room temperature. The total ionic strength (μ) of each buffer solution was adjusted to a desired level with a calculated amount of KCl.

RESULTS AND DISCUSSION

Effects of Total Radiation Dose and Dose Rate on Gel Strength

The effect of radiation dose on the strength of pure KC gels, PDADMAC gels and their IPN gels

The effect of radiation on the mechanical strength of KC gels is shown in Fig. 1 (curve a). The gel strength decreases quickly with increase of the dose. When irradiated by 20 kGy, the KC gel became very soft and fragile and its strength was difficult to measure. The decrease in gel strength indicates that the main chain of the KC molecule was broken down by irradiation as was shown in its FT-IR spectra or UV-spectra^[11].

The effect of radiation on the mechanical strength of PDADMAC gels is also shown in Fig. 1 (curve b). It is easy to understand that with the increase of dose, more DADMAC molecules will be polymerized and the

strength of the PDADMAC increases simultaneously (also see Fig. 3). Once the dose has become higher than 10 kGy, additional increments of dose will not affect the strength of the gel any further. This was consistent with the dose effect on the PDADMAC gels fraction^[8].

From Fig. 1, it can be seen that the strengths of the pure KC gels and pure PDADMAC gels were not higher than 10 N and 5 N, respectively. But when KC and DADMAC were mixed to form the IPN hydrogels, the gel strength went up to almost 16 N with increasing dose (curve d). This was due to the crosslinking of DADMAC monomer and the formation of the IPN structure. After that, as the dose was increased, the degradation of KC gel became predominant and the strength of the IPN gel decreased only slightly because there was only a small amount of KC outside the network that can be degraded. When the degradation of this part of the KC molecules finished, the decrease of strength was stopped. As the KC molecules inside the network were protected by the IPN structure, the strength of the IPN gel leveled with the increasing dose, similar to that of the pure DADMAC gel.

From the above discussion, it can be concluded that IPN structure exerts a synergetic effect on the mechanical strength of IPN hydrogels of PDADMAC/KC.

The effect of KC content on the strength of IPN gels

The content of KC did not noticeably affect the IPN gels fraction, as shown in our previous work^[10]. However, when the concentration of KC (W/W%) in the feed went up, the strength of the gels after irradiating was improved significantly (Fig. 2). This indicated that the addition of KC to the polymerization system can provide the framework for DADMAC to form IPN and subsequently enhanced the strength of the gels.

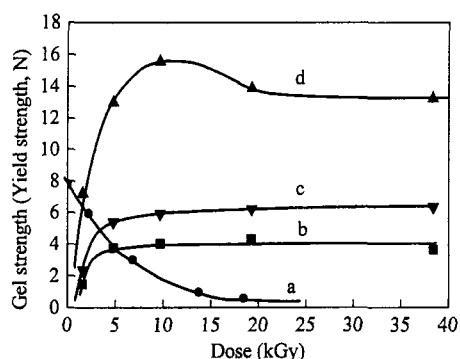


Fig. 1 Gel strength of pure DADMAC gel, KC and their IPN gels

● KC gel (5% KC, 76.5 Gy/min); ■ PDADMAC gel (50% DADMAC, 0.5 Bis, 53.3 Gy/min); ▼ PDADMAC/KC IPN gel (50% DADMAC, 1% KC, 0.5 Bis, 53.3 Gy/min); ▲ PDADMAC/KC IPN gel (50% DADMAC, 1.5% KC, 0.5% Bis, 53.3 Gy/min)

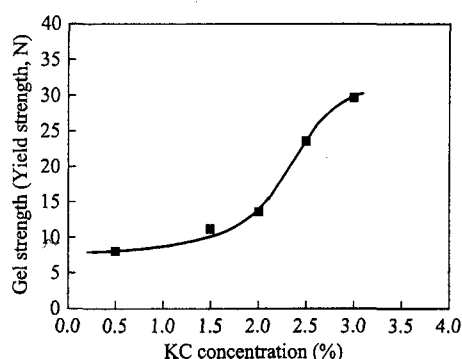


Fig. 2 Gel strength of PDADMAC/KC gels with different KC content

50% DAD, 0.5% Bis, 53.3 Gy/min, 19.2 kGy

Generally, the strength of PDADMAC/KC IPN gels increased with radiation dose less than 10 kGy and remained almost unchanged with increasing dose as shown in Fig. 1 (curve c and d). It was interesting to note that there was a difference in strength between the two kinds of IPN gels with various KC content. When the gel had a small amount of KC in the feed, e.g. 1% of the total weight (curve c), the dose effects on gel strength, i.e. the trend of the curve and the value of the strength were quite similar to those of pure PDADMAC gel as shown in Fig. 1 (curve b). It can be explained that such an amount of KC in the feed was too small to have any effect on IPN strength. When the content of KC was higher, e.g. 1.5% in the feed (curve d), the strength of IPN gel was increased notably and curve d became quite different from curve c due to the different response of KC molecules outside and inside of the network towards radiation.

The effect of DADMAC content on the strength of IPN gels

It is shown in Fig. 3 that the concentration of DADMAC monomer significantly influences the strength of IPN gels, especially when the concentration of monomer exceeds 55%. Because the mechanical strength of a hydrogel is mostly derived from the crosslink density of the system^[12], the higher the concentration of monomer in the system, the more the crosslinkage formed and the higher the strength of the gel. However, the gels obtained at high DADMAC concentration were quite brittle and collapsed very easily in their swollen states. Therefore, the 50% monomer concentration was chosen.

The effect of radiation dose rate on the strength of IPN gels

Figure 4 shows the effect of dose rate on the IPN gel strength. It can also be seen that the effect of dose rate on the strength of IPN gel containing more KC was more prominent than that of IPN gel containing less KC.

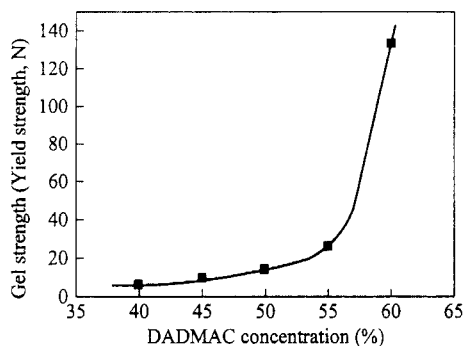


Fig. 3 Gel strength of PDADMAC/KC gels with different DADMAC content
1.5% KC, 0.5% Bis, 53.3 Gy/min, 19.2 kGy

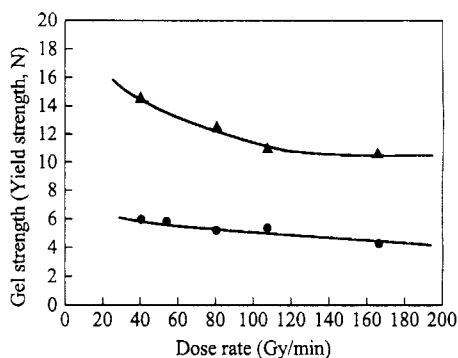


Fig. 4 Effect of dose rate on gel strength of PDADMAC/KC
50% DADMAC, 0.5% Bis, 9.6 kGy
▲ 2% KC; ● 1% KC

Swelling Behavior of IPN gels

Swelling behavior in water and in salt solution

Because the IPN of PDADMAC/KC is a polyelectrolyte complex, swelling of the gels showed a typical polyelectrolyte behavior under different ionic strengths of solution (Fig. 5). Increasing the ionic strength of the solution led to an increase of the osmotic pressure of the solution ions and resulted in shrinking of the gel.

The swelling kinetics of PDADMAC/KC gels in water and in salt solution is illustrated in Fig. 6. Although the three samples of IPN gels with various KC content had almost equal gel fractions, their swelling kinetics in water and in salt solution were quite different. This phenomenon indicates that KC content has no difference effect on the gel fraction of IPN gels but it affects the swelling capacity of gels. When KC was dissolved in hot water and then the solution was cooled down, a physically crosslinked network was formed in KC gel, which provides the frame network for DADMAC to interpenetrate. The swelling of the IPN gels was restricted by the density of the frame network due to the higher concentration of KC.

The effect of pH on the swelling behavior of IPN gels

Figure 7 shows the swelling behaviors of IPN gels in the buffer solutions at pH ranging from 2 to 11. As a whole, the IPN gels of PDADMAC/KC are not responsive to pH except at the two extremities of pH values.

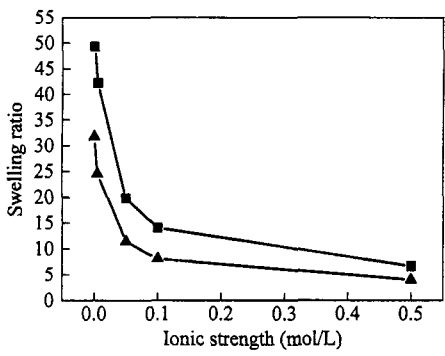


Fig. 5 Swelling behavior of PDADMAC/KC gels in salt solution with different ionic strength
■ 1% KC; ▲ 3% KC
50% DADMAC, 0.5% Bis, 53.3 Gy/min, 9.6 kGy

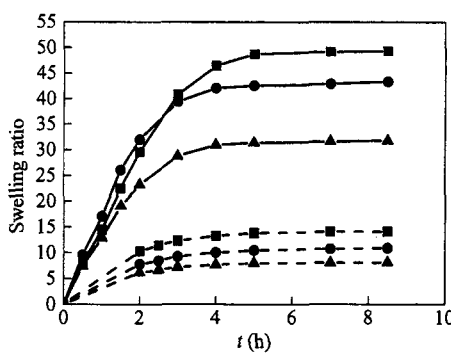


Fig. 6 Swelling kinetics of PDADMAC/KC gels in water (—) and in salt solution (----) ($\mu = 0.1$ M)
■ 1% KC; ● 2% KC; ▲ 3% KC
50% DADMAC, 0.5% Bis, 53.3 Gy/min, 9.6 kGy

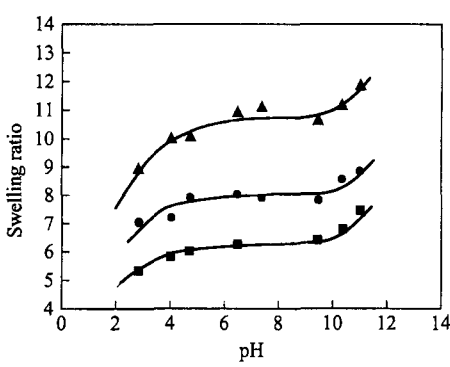


Fig. 7 Swelling behavior of PDADMAC/KC gel in buffer solution ($\mu = 0.1$ M)
50% DADMAC, 0.5% Bis, 53.3 Gy/min, 9.6 kGy
▲ 1% KC; ● 2% KC; ■ 3% KC

CONCLUSION

The mechanical strength of PDADMAC hydrogels was enhanced notably by the formation of IPN structure with KC and increased with increasing KC content. However, the hydrogel containing more than 3% KC was difficult to obtain due to the limited solubility and relatively high viscosity of KC.

In addition, KC content had little effect on the gel fraction of IPN gels but slightly reduced the swelling ratio of gels. Nevertheless, IPN formation is still an effective way to improve the mechanical properties and swelling capability of the gel.

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