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Mechanical and Swelling Characteristics of Kappa-carrageenin/Poly-N-isopropylacrylamide Blend Hydrogels

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Abstract

Two- or multi-component hydrogels consisting of the three-dimensional network of polymer chains play more and more significant role in the field of biomaterials such as contact lens, burn dressing drug delivery systems etc or in some technical fields such as gel actuators, sensors, absorbents etc. In the work, a novel blend hydrogel composed of kappa-carrageenin (KC) and polyisopropylacrylamide (PNIPAAm) was prepared via gamma-radiation technology at room temperature. The main component of the hydrogels is a typical temperature sensitive polymer PNIPAAm. As the second component, KC is a kind of natural macromolecules. The properties of the gels, such as gel strength, and swelling behavior were investigated. The incorporation of relatively small content (up to 5 wt.%) of KC could obviously improve the mechanical properties and swelling capacity. 3% KC content in the blend hydrogel is preferable for better strength and swelling properties. On the other hand, as a kind of polysaccharide, KC would be degraded by γ-rays; so suitable dose must be controlled carefully. Here the total dose used was controlled below 3 kGy. KC is soluble in water. If the hydrogels synthesized in the work were as usually extracted in water or other polar solvent such as methanol, the KC in hydrogels would be also washed out completely together with unreacted monomer and linear polymer, and the action of KC in the blend hydrogels would be disappeared. Otherwise, the results published before showed that the unreacted monomer and linear polymer in the hydrogels were very small, no more than 3-5%, which would not affect the properties of the hydrogels.

Introduction

Nowadays the synthesis and characterization study of environmentally sensitive hydrogels attract more and more attention [1,2] because of rapid development of intelligent drug delivery systems (DDS). The typical stimuli responsive hydrogels are prepared from N-substituted acrylamides, especially N-isopropylacrylamide (NIPAAm) which has the aliphatic tertiary amino group [3,4], but the poor mechanical properties of PNIPAAm in swollen state greatly limited its applications. The modification of PNIPAAm via various ways to enhance its strength is of considerable importance. Owing to some unique properties such as nontoxicity, degradation and good biological compatibility, natural polymers have been used for modification of hydrogels to improve their characteristics [5-7]. In this study, KC/PNIPAAm blend gels were synthesized by γ-irradiation technology and their properties were evaluated.

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Experimental

Materials

KC samples (WG-115) were purchased from Copenhagen Pectin A/S (Denmark). NIPAAm was obtained from Kishita Corp.Ltd (Japan). N, N-methylene bisacrylamide (Bis) and other reagents were purchased from Beijing Chemical Works.

Preparation of KC gel and the blend gel

A suitable quantity of KC, KCl and water were poured into a bottle, sealed and then heated at 80°C for two hours to obtain a homogeneous solution. Then it was poured in a tube and cooled at room temperature to form KC gel, a kind of physical KC gel.

For the blend gel, the NIPAAm, Bis, and KCl were added into KC aqueous solution at 80°C and mixed until the homogeneity was achieved. After being cooled, the samples were irradiated to form the blended hydrogels. The potassium chloride (KCl) content in

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all batching samples is 0.05 mol/L in order to enhance the gel strength of the product [8].

Irradiation of samples

The batching samples were irradiated in Co-60 gamma source of Peking University. The dose rate was calibrated by Fricke method. The dose rate used here was 40 Gy/min. The absorbed doses of samples were varied from 0 to 15 kGy according to experimental request.

Purification of blend hydrogels

Before measurements of gel strength and swelling degree, the blend hydrogels synthesized in this work were not extracted by water in soxhlet as usually in order to avoid loss of KC in blend gels together with unreacted monomer and linear homopolymer of NIPAAm since KC is soluble in hot water (near to 100°C). If the blend gels will be used as biomaterials, the residual NIPAAm, which is toxic monomer, must be eliminated out of the gels completely. Therefore, the hydrogel synthesized here should be immersed in distilled water under agitation at room temperature for a week. In that case, KC could be still maintained in the hydrogel and kept its unique role in the blend gels and residual monomer and linear polymer would be washed out completely.

Measurement of the gel strength

The polymerized blend gels were cut into cylinders with 11 mm diameter and 15 mm height. Gel strength was measured by compressing the samples between parallel plates at Strograph-R1 Material Tester (Toyoseiki Co., LTD, Japan) with a crosshead speed of 50 mm/min. The gel strength was characterized by the strength required to compress the gels to a certain percent height.

Swelling dynamic process and EDS

The gels were dried to a constant weight at 52°C vacuum oven without being extracted. The dried gels were immersed in distilled water at 25°C and the weight of gel (M) was measured every certain time. The swelling dynamic process is illustrated by swelling ratio plotted against swelling time. The swelling ratio and equilibrium degree of swelling (EDS) was calculated as:

$$\text{Swelling ratio}=(M-M_0)/M_0 \quad \text{EDS}=(M_e-M_0)/M_e$$

where M_0 and M_e are the gel weight measured in dried state and in swelling equilibrium, respectively.

Results and discussion

Effect of absorbed dose on the strength of KC and PNIPAAm hydrogels

The effect of irradiation on mechanical properties of KC and PNIPAAm hydrogels is shown in Fig. 1. KC is a kind of linear and sulfated polysaccharide. When KC solution is at room temperature, the ionic and physical bonds are formed between KC molecular chains through K^+ to maintain its gel structure. It can be seen from Fig.1 that the strength of KC gel without irradiation was highest. With the dose increasing, the gel strength came down rapidly approaching zero. This is mainly due to KC degradation under irradiation. The chemical bonds between C_1-C_4 in KC gel are very weak to be broken by irradiation. Therefore, the long chain of KC macromolecules was degraded into small molecules with rising dose. When irradiation dose was up to 15 kGy, almost all KC long chain macromolecules were broken and then the gel strength became very weak. While in case of NIPAAm, it was polymerized under irradiation. When dose was above 10 kGy, almost all of the NIPAAm molecules were polymerized and crosslinked into network structure and then the gel strength was unchangeable. The results indicated that the hydrogel of PNIPAAm is quite soft; it needs to be improved in someway.

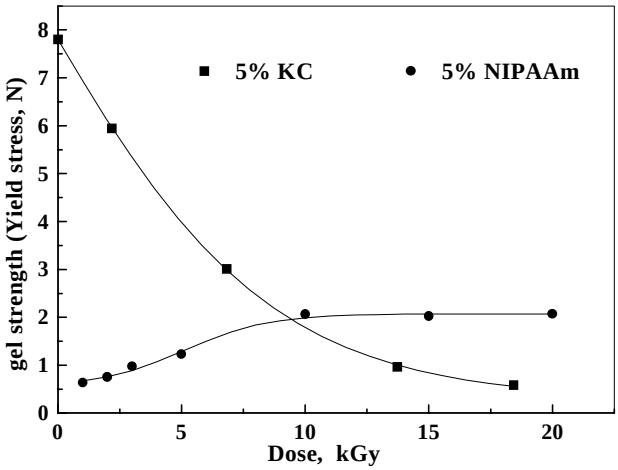

Fig. 1. Gel strength of 5% KC and 5% NIPAAm hydrogels as a function of absorbed dose.

Effect of absorbed dose on mechanical properties of KC/NIPAAm blend gels

The changes of mechanical properties of the blend gels with an increase of absorbed dose are illustrated in Fig. 2. Two conclusions can be made from the analysis of the curves. Firstly, the incorporation of KC greatly enhanced the gel strength of PNIPAAm. The highest gel strength of pure PNIPAAm was 2.06 N, while that of KC/NIPAAm gel was up to 40 N for 5% KC content if a suitable dose was chosen. Secondly, the change of gel strength with dose could be divided into three stages during irradiation. The first stage is the gel strength rising process when the absorbed dose is below 5 kGy. It is well known that NIPAAm is very sensitive to irradiation. For this reason, the absorbed dose was firstly used by NIPAAm to polymerize and crosslink and the gel strength was enhanced. The second stage is the gel strength decline process due to the degradation of KC under irradiation. When dose was up to 5 kGy, the radicals produced by irradiation began to react with KC because the polymerization of NIPAAm is fulfilled. The gel strength came down and eventually became unchangeable and then the third stage is started. At this stage, the structure of interpenetrating polymer network (IPN) composed of KC and PNIPAAm is formed. So the gel strength was obviously higher than that of pure PNIPAAm and quite stable with dose increasing up to 30 kGy. The process can be partially confirmed by element analysis. The weight content of sulfur was 2.83% in the blend gels with 5 kGy irradiation and then tended towards lower and stable. They were 0.47% and 0.53% separately at 15 kGy and 20 kGy. From the curves of blend gels with different KC content in Fig. 2, it also can be concluded that the more KC content, the higher the gel strength.

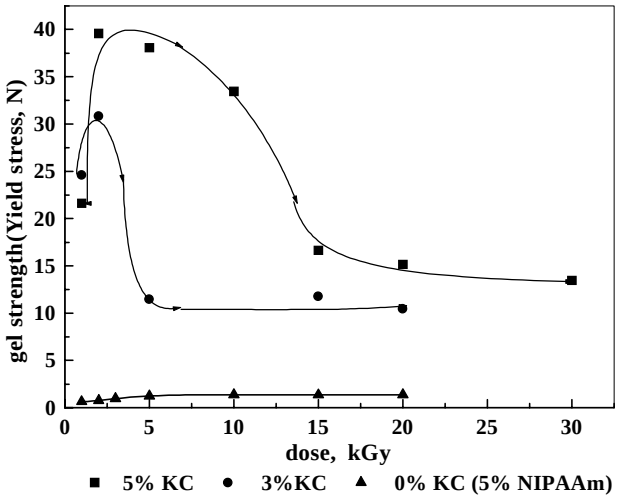

Fig. 2. Strength of different KC content NIPAAm gels as a function of absorbed dose.

Swelling behavior of KC, PNIPAAm and KC/NIPAAm hydrogels

Swelling behavior of KC, NIPAAm and KC/NIPAAm hydrogels at room temperature was illustrated in Fig. 3. Compared to KC and PNIPAAm hydrogels, KC/NIPAAm blend gels have a higher EDS. This is mainly attributed to the sulfated groups in KC, which makes water molecules easier to get into the network structure because of the electrostatic attraction between sulfated groups and hydroxonium ions. It can be also concluded that the incorporation of KC is greatly improved PNIPAAm swelling properties. The weight of KC gel is increased firstly, and then it is decreased after swelling in water for 5 hrs and finally it is disappeared after 24 hrs. The molecules of KC, especially the fragments of degraded molecules by irradiation were dissolved in water easily.

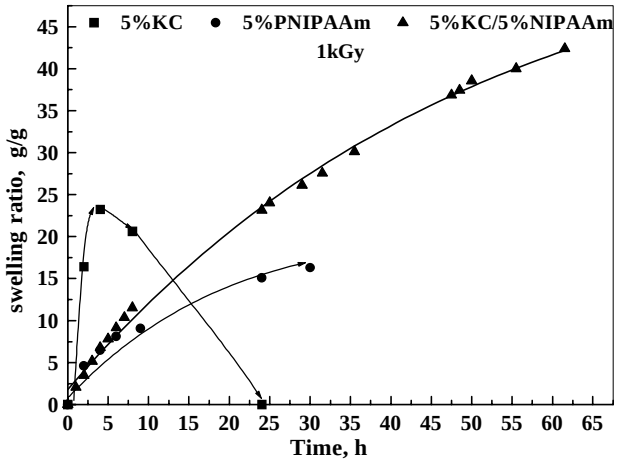

Fig. 3. Swelling behavior of KC, NIPAAm and KC/NIPAAm gel.

Effect of absorbed dose and KC content in blend gel on swelling properties of the blend gel

Figures 4 and 5 separately show the swelling kinetics of blend gels with 1% and 5% KC content. The EDS values of the gels are also shown in Fig. 6. For the blend gel with 1% KC, the curves of swelling kinetics under different dose were distinct from each other under different doses. The gels with lower absorbed dose undergo a much quicker swelling speed

and a larger equilibrium degree of swelling. While for blend gels with 5% KC, the swelling process under different dose was quite close to each other and their equilibrium degrees of swelling were rather low and almost the same. In the blend gels, the KC formed a physical network structure as framework by K^+ ion bridge and NIPAAm is dispersed in it. After irradiation, the NIPAAm was polymerized and the IPN structure was formed. In the case of 1% KC, the interspace in the network is relatively large due to the low concentration of KC, which made water molecules easy to penetrate. On the other hand, as the dose increasing, the crosslinking degree is increased and the crosslinked holes of polyNIPAAm chains became smaller. Therefore, a higher dose leads to obtaining of hydrogels with lower equilibrium swelling degree. In the case of 5% KC content, the interspace in KC network is relatively small due to the high concentration of KC. Despite of NIPAAm polymerization after irradiation, the interspace is almost unchangeable because of its original small size. Thus, the absorbed dose has no effect on the equilibrium swelling degree (Fig. 6). The swelling kinetics of blend gels with 1%, 3% and 5% KC content were shown in Fig. 7. The blend gels with 1% and 3% KC content have quite similar swelling dynamics. Their EDS are relatively high (near to 40 g/g). While for 5% KC content, the blend gel has a much lower EDS (below 13 g/g). Figure 7 indicates that a suitable concentration of KC (say, lower than 3%) can be chosen to obtain a novel blend hydrogels with good swelling and mechanical properties.

Conclusion

The incorporation of KC into PNIPAAm system

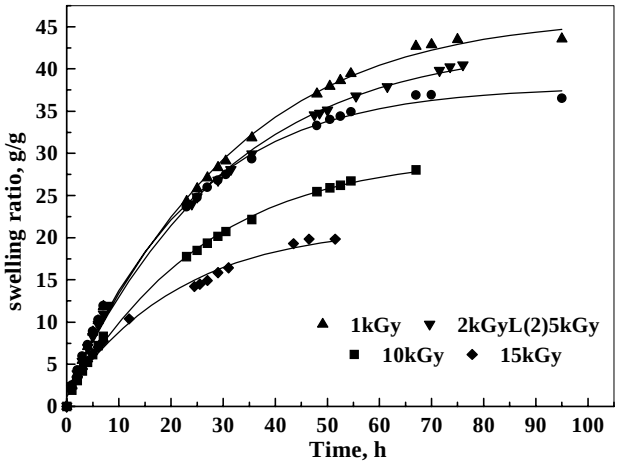

Fig. 4. Dose effect on the gel swelling ratio. [KC]=1%, [NIPAAm]=5%, [Bis]=0.02%.

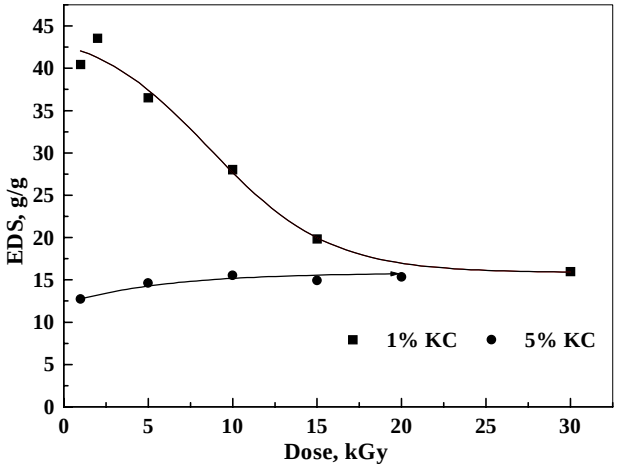

Fig. 6. Dose effect on EDS of gels with different KC content. [NIPAAm]=5%, [Bis]=0.02%.

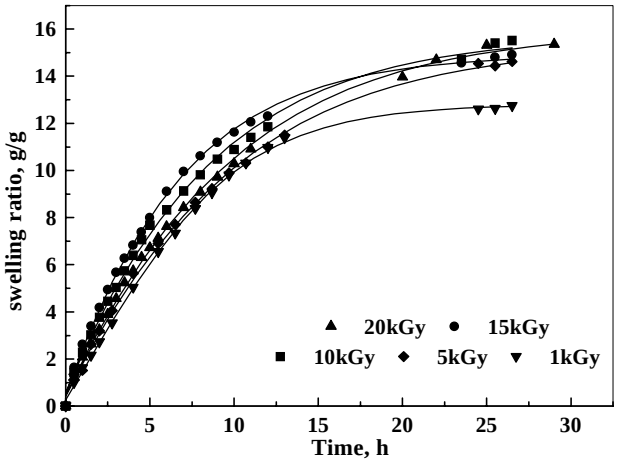

Fig. 5. Dose effect on blend gel swelling behavior. [KC]=5%, [NIPAAm]=5%, [Bis]=0.02%.

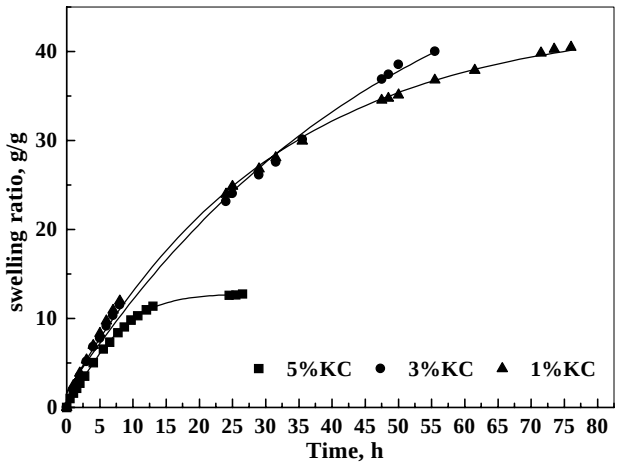

Fig. 7. Different KC content effect on gel swelling ratio. [NIPAAm]=5%, [Bis]=0.02%.

greatly enhanced its mechanical and swelling properties. The content of KC in blend gels also has contribution to strength and swelling properties of blend gels. 3% KC content is preferable for a better strength and swelling properties.

The absorbed dose has a great effect on the mechanical strength and swelling behavior of KC/NIPAAm blend gels. In order to obtain the better gel with higher strength and swelling properties, a small dose, such as 3 kGy, is preferred.

The formation mechanism and structure of the blend gels were discussed. The preparation of blend gels of polymer with suitable content of KC by radiation technology may be one of suitable ways to improve both their mechanical properties and swelling capacity.

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