A high mechanical strength hydrogel from polyacrylamide/polyacrylamide with interpenetrating network structure by two-steps synthesis method

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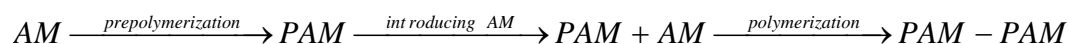
Abstract: A simple two-steps polymerization method was used to prepare a polyacrylamide hydrogel with a full interpenetrating network structure based on the sorption and porous properties of polyacrylamide superabsorbent. In conditions of 10 g acrylamide monomer, 0.04 g crosslinker for the first polymerization and the second polymerization, respectively, and the swelling ratio of 9, the hydrogel possessed a tensile strength of 1.22 MPa and elongation at break of 900 %.

Introduction

Superabsorbent polymer has stronger hydrophilic groups and lightly crosslinked network structure. Not only it is able to absorb a large amount of water, but also the absorbed water is hardly removed under some pressure [1]. The superabsorbent polymer can form a stable hydrogel with three-dimensional (3-D) polymer networks that swell, but do not dissolve in water. Owing to the hydrogel's unique properties such as stimulus-responsive property, osmotic property, elasticity, sorption, it has been used in separation membranes, biosensors, artificial muscles, chemical valves [2, 3], superabsorbents [4], drug delivery devices [5, 6] etc. However, the applications of the hydrogels are always restricted due to their poor mechanical properties. In the past decades, to improve the properties of hydrogels, many efforts such as introduction of dangly comb-chains [7, 8], addition of polymer particles in gel network [9], cold treatment [10] or freeze-drying [11] swollen hydrogel, incorporating clay with polymer [12-15], formation of interpenetrating network structure [16-19] have been made. The formation of a full interpenetrating network structure is believed to be an effective method for enhancing the mechanical strength of hydrogel [16, 17], but the method is moderately complicated.

In this paper, to prepare a polyacrylamide hydrogel with high mechanical strength, based on the sorption and porous properties of polyacrylamide superabsorbent, a full interpenetrating network structure was introduced in the hydrogel and a simple two-steps synthesis method [20] was used. The synthesis course is shown below.

$$AM \xrightarrow{\;prepolymerization\;} PAM \xrightarrow{\;introducing\;AM\;} PAM + AM \xrightarrow{\;polymerization\;} PAM - PAM$$

Polyacrylamide with 3-D network was formed in the prepolymerization reaction (step I), then, acrylamide monomers were introduced in the polyacrylamide network by immersing polyacrylamide in acrylamide monomer solution, an accessional polyacrylamide network was produced in the polymerization reaction (step II). Once

the second network was formed, the whole system became a full interpenetrating structure [17, 19].

Results and discussion

Fig. 1 shows the scanning electron microscope photograph of PAM/PAM hydrogel . Obviously, the hydrogel has full three-dimensional interpenetrating network structure.
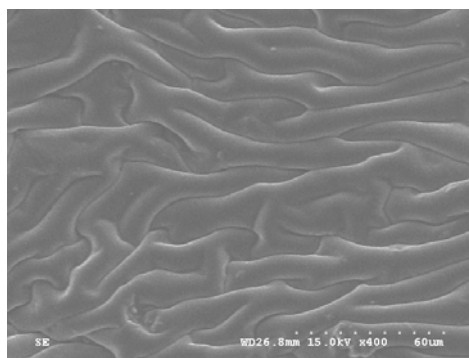

Fig. 1. The SEM of PAM/PAM hydrogel with IPN structure.

The stress-strain curves of the hydrogels with different acrylamide monomer ratios in step I to step II is shown in Fig. 2. From the Figure, it can be seen that when the acrylamide monomer mole ratio in step I to step II ($AM_{I/II}$) is 10 : 10, the hydrogel shows the best mechanical strength; more or less mole ratio results in lower mechanical strength for the hydrogel. This is due to the collaborative effects of the first and the second networks in prepolymerization reaction and polymerization reaction. It is notable that no acrylamide was added in the second polymerization, the resulted hydrogels presented relatively weak mechanical strength to meaure in our experiment. Similar results were also reported in reference [18] by Omida.
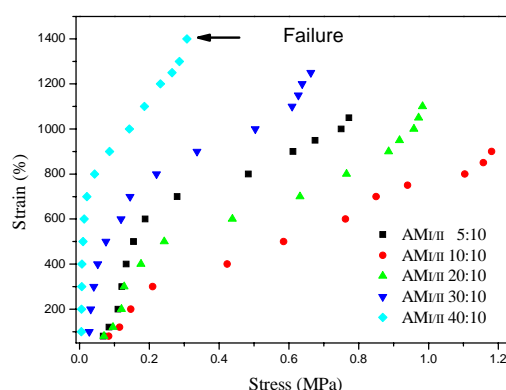

Fig. 2. Stress-strain curves of the hydrogels with different AM monomer mole ratio in step I to step II ($AM_{I/II}$) under the mass ratio for crosslinker to AM_{II} at 0.04 wt % and swelling ratio at 8 g/g.

Fig. 3 shows the influence of the swelling ratio of PAM/PAM hydrogel on the mechanical strength. As well known that the tensile strength and the elongation at

break of a hydrogel is derived from the breakages of hydrogel networks, hydrogen bonds, interlaced, Van der Waals forces and chemical crosslinking. At a lower swelling ratio, the chains of polymer are close, the network density is tight, the interaction between chains of polymers in hydrogel is reinforced, and the mechanical strength of the hydrogel is good. On the contrary, at a higher swelling ratio, the hydrogel network is diluted, interlaced and Van der Waals forces are weakened. Thus the tensile strength of hydrogel declined, and the elongation at break extended.
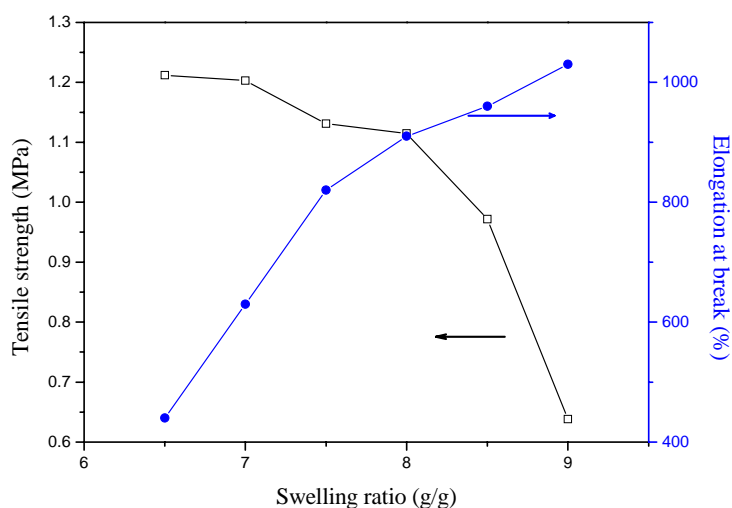

Fig. 3. Influences of swelling ratio on the mechanical properties of hydrogel under $AM_{I/II}$ 10:10, mass ratio for crosslinker to AM_{II} 0.04 wt %.
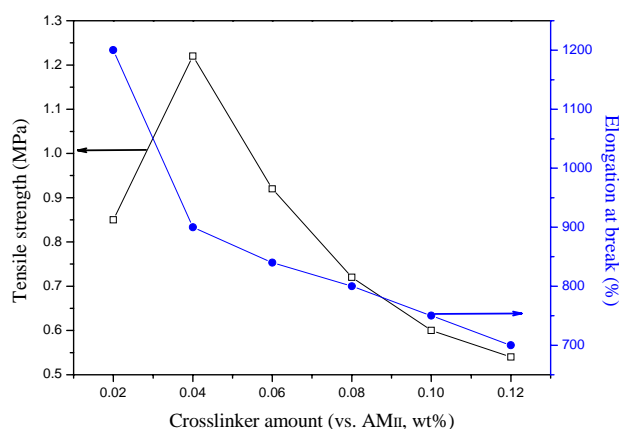

Fig. 4. Influences of crosslinker on mechanical strength of hydrogel under $AM_{I/II}$ 10:10 and saturated swelling.

Crosslinker plays an important role in the formation of 3-D network of hydrogel. The influence of crosslinker amount on the mechanical properties of the hydorgel is shown in Fig. 4. Clearly, a higher concentration of crosslinker produces a large number of growing polymer chains and generate an additional network [12, 13, 21], by which the

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network space gets diminished (Tab. 1), and less water enters the hydrogel. Thereby, swelling ratio decreases with an increase in the crosslinker dosage. Higher crosslinker dosages also means more chemical crooslinking in the second polymerization reaction, which results in the mismatch between the first network and the second network, the interpenetrating network cannot form effectively, and results in the decrease of the tensile strength and elongation at break of hydrogel. On the other hand, at a lower dosage of crosslinker, such as lower than 0.02 wt%, the second polymerization reaction does not occur effectively, the interpenetrating network cannot form effectively, which is the reason for higher elongation and lower tensile strength (Fig. 4). Specially, when no initiator was added in the second step of the polymerization, the resulted hydrogels presented relatively weak mechanical strength to meaure in our experiments. According to the Fig. 4, when the crosslinker dosage was 0.04 wt% (in step II, relative to AM_{II}) the cooperative effects of networks is better, and the hydrogel shows the best tensile strength of 1.22 MPa.

Tab. 1. Crosslinker dosage (step II) vs. saturated swelling ratio at $AM_{I/II}$ 10 : 10.

Crosslinker (wt %)	0.02	0.04	0.06	0.08	0.10	0.12	0.14
Swelling ratio (g/g)	6.24	9.05	7.95	6.74	5.70	4.64	4.30

Conclusions

In conclusion, by using a two-step polymerization method, a PAM/PAM hydrogel with full interpenetrating network structure was prepared. In conditions of 10 g acrylamide monomer, 0.04 g crosslinker for the first polymerization and second polymerization and a swelling ratio of 9, the hydrogel possessed a tensile strength of 1.22 MPa and elongation at break of 900 %.

Experimental part

Preparation of polyacrylamide/polyacrylamide (PAM/PAM)IPN hydrogel

The PAM/PAM IPN hydrogel was prepared by modifying the method descibed in references [12, 20, 21]: A mixed solution of acrylamide monomer and crosslinker was made by agitating 10 g acrylamide and 0.004 g crosslinker (N,N'-methylene bisacrylamide) in 10 ml distilled water at ambient temperature. Under a nitrogen atmosphere, the mixture solution was stirred and heated at 80 ºC in a water bath for 10 min, and then the initiator (potassium persulfate to acrylamide 0.3 wt. %, 0.03 g) was added, the prepolymerization reaction was carried out until the system become a viscous solution, which indicated the formation of polyacrylamide. Another mixed solution of acrylamide monomer, potassium hydroxide and crosslinker in distilled water was poured into the above polyacrylamide solution, after stirring for 1 h to allow the acrylamide monomer and crosslinker to enter the inside of network polyacrylamide evenly and completely; the initiator (mass ratio of potassium persulfate to acrylic acid was 0.3 wt. %) was added. Under a nitrogen atmosphere, the mixture solution was stirred until the polymerization finished. The intermediate product was dried under vacuum at 80 ºC for more than 5 h to constant weight to remove any oligomers and impurities. After that, a polyacrylamide-polyacrylamide (PAM/PAM) composite with full interpenetrating network structure was obtained.

Measurements of mechanical properties

The mechanical properties of hydrogel were measured by using a self-prepared equipment and referring to the reference [22] with a Dejie DXLL-20000. The conditions were as follows: temperature 25 °C; a sample size of 5 mm in diameter and 80 mm length; gauge length of 30 mm; crosshead speed of 100 mm/min. Compressive measurements were performed on hydrogels of the size (8.5×8.5×11 mm (thickness)) and the polymer/water weight ratio (1/8). The cubic sample were compressed by the upper plate, which was connected to a load cell, at a strain rate of 5 %/min. The strain under stress (or compression) is defined as the change in length (or thickness) relative to the initial length (or thickness) of the specimen. The strength and modulus were calculated on the basis of the initial cross section.

Measurement of swelling ratio

The swelling ratio of hydrogel is defined as the mass ratio of swollen hydrogel mass to dry PAM-PAM sample mass, which was measured according to the method in the reference [21]. As-prepared dried hydrogel rods were cut in the same size (5 mm diameter × 30 mm length), and were immersed in a large excess of water to attain swelling equilibrium at 25 °C for 24 h prior to measurement, changing the water several times. Swelling ratios are represented by the ratio of weights of the swollen hydrogel (W_s) to the corresponding dried hydrogel (W_d).

Acknowledgements

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