Study on preparation and properties of pH, temperature and ionic sensitive polyurethanes hydrogel

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Abstract. Polyurethane hydrogel(PUHG), which exhibits pH, temperature and ionic intensity sensitive, was synthesized by using the toluene diisocyanate(TDI), polyethylene glycol(PEG-6000), dimet hylol propionic acid(DMPA) and triethylene tetramine(TEFA).The effect of pH, temperature, ionic intensity and crosslinking agent on welling ratio of the PUHG was studied in detail . The result showed that the swelling ratio of PUHG decreased with the temperature increasing between 20 and 45˚C but didn't change after 45˚C; in alkaline medium (pH=9), the swelling ratio of the PUHG was more than that of In acid medium (pH=4), which indicated it had a good sensitivity; the swelling ratio of PUHG decreased with ionic intensity increasing at a temperature and pH. The results of swelling dynamic indicated that PUHG can change reversibly well at different pH and temperature. So the PUHG is suitable for use in biomedical controlled delivery of medicines.

Introduction

Sensitive hydrogel is a kind of polymer crosslinking network which can swell significantly but not dissolve in water, which can perceive the environment factors such as temperature[1-2], PH[3-4], chemical substances[5], ionic strength[6], light field[7] and electric field[8], show the corresponding shrinkage or swelling characteristics. The unique stimulus response behavior of the sensitive hydrogel has shown a good application prospect in the field of drug release system [9-10], material separation, memory element switch, chemical machinery, active enzyme, artificial muscle and so on.

Polyurethane (PU) has good biological compatibility, excellent physical, mechanical properties, and which can maintain the stability of long-term implantation in the human body[11]. However, the physical and chemical properties of the polyurethane can be changed by changing the composition of the molecular chain of soft and hard segments [12]. The characteristics of the PU are suitable for use in biomedical controlled delivery of medicines and related research is less. Therefore, the paper researched on the factors that influence on the swelling ratio of the PUHG such as pH, temperature, ionic intensity and crosslinking agent in detail and synthesized the PUHG [13-14].

Experiment Part

Materials. Toluene diisocyanate(TDI), polyethylene glycol(PEG-6000), dimet hylol propionic(DMPA), triethylene tetramine(TEFA), sodium tetraborate buffer solution(pH=9.18,I=0.1), mixed phosphate buffer solution(pH=6.86 , I=0.1) and acid-biphthalate buffer solution(pH=4, I=0.1).

Synthesis of polyurethanes hydrogel. First, synthesis process of polyurethanes hydrogel with –NCO functional groups was as follows: A certain amount of PEG-6000 and DMPA were added to the three mouth flask with a magnetic stirrer, a thermometer, and a reflux condenser, A certain amount of butanone and TDI were added when the temperature reached 40˚C, which was kept 2.5 hours when temperature rose to 80˚C. Second, The different amount of TEFA crosslinking agent was added to polyurethanes hydrogel with –NCO functional groups , remained stationary 20 minutes after stirring, the weight of the crosslinking agent accounted for 1%, 2% and 3% of the polyurethane hydrogen was obtained; polyurethane hydrogel with water as crosslinking agent was made by the same method.

Third, polyurethane hydrogel obtained were soaked in water for two weeks and changed the water every 24 hours In order to remove the residual monomer and solvent.

Results and Discussion

Analysis of IR spectra of the polyurethane hydrogel.IR spectra were recorded using KBr pellets on AVATAR-360FTIR. The IR spectra of the polyurethane hydrogel was shown in Fig.1. The curve showed the peak around 1727cm^{-1} was attributed to the characteristic absorption of –NH-COO- on the arm chains, the peaks of the benzene skeleton vibration were around 1602cm^{-1}, 1451 cm^{-1}and 1536 cm^{-1}, the vibration peaks of the benzene(1,2,4)were around 863cm^{-1}, 769 cm^{-1}and 725 cm^{-1}, the peak of the characteristic absorption of -COO- was around 1412cm^{-1}, the peak of the characteristic absorption of -COO- was around 1412cm^{-1} and the stretching vibration absorption peaks of C-O were around 1226cm^{-1}, 1102 cm^{-1}and 1058 cm^{-1}. In addition, there was no peak between 2280 and 2265 assigned to –NCO, which indicated that –NCO was completely consumed in the reaction.

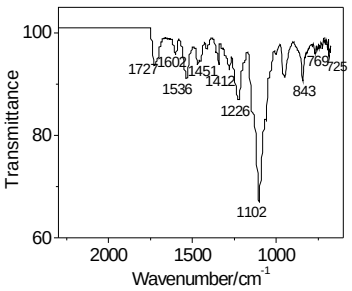

Fig.1 IR spectra of the polyurethane hydrogel

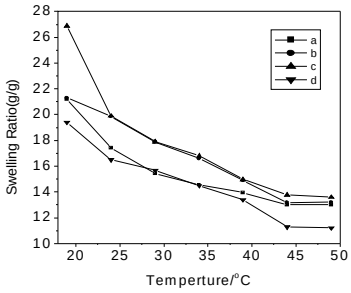

Fig.2 The effect of temperature on swelling ratio of the PU hydrogel

Determination of temperature sensitivity of PU hydrogel under constant pH. The PU hydrogel was placed in pH=7 and I=0.1 buffer solutions that temperature could be ranged from 20˚C to 50˚C, weight of the PU hydrogel was weighted and equilibrium swelling ratios(SR) was calculated by SR formula when the temperature maintain 24 hours after rising 5˚C per time, SR formula was shown in formula (1).

$$SR=(W_0- W_d)/W_d \quad (1)$$

Where W_d is dry PU hydrogel weight after equilibrium swelling, W_0 is PU hydrogel weight after equilibrium swelling.

The concentration of TEFA was 0.1, 0.2, 0.3 and 0 wt% and the effect of temperature on the equilibrium swelling ratios for PU hydrogel in pH=7 and I=0.1 buffer solutions was shown in Fig.2. as curves a, b, c, and d respectively. It was found that the swelling ratio of the 4 kinds of PU hydrogels decreased with the temperature increasing in the range of 20~45˚C, SR decreased rapidly when the temperature was less than 25˚C, SR decreased slowly when the temperature ranged from 20˚C to 45˚C less than 25˚C, SR kept steady when the temperature was lower than 45˚C, which indicated PU hydrogel had significant temperature sensitivity, in particular, change trend of 2wt% PU hydrogel was more obvious. This was probably due to the heat movement of water molecules became violent with the increase of temperature, which caused the osmotic pressure was decreased between PU hydrogel solution and around other solution and the bonding interactions was weakened between the hydrophilic group of the PU hydrogel and water molecules. Moreover, the crosslinking density of the hydrogel network could be affected with the change of the crosslinking dose, the phenomenon that SR of 2wt% PU hydrogel changed greatly with temperature indicated that 2wt% PU hydrogel was more susceptible to temperature change and more appropriate density.

The pH sensitiveness of PU hydrogel. To determine the effect of pH on the PU hydrogel, buffers with the same ionic strength (I=0.1) and various pH (pH =4,7,9) was used in this work. The 0, 0.1, 0.2 and 0.3 wt% TEFA solution in different pH buffer were to be tested, as was shown in Fig.3 such as curves a, b, c, and d. Fig.3 showed that SR of the PU hydrogel was all the highest while pH was 9, SR

of the PU hydrogel was all the lowest while pH was 4 and SR was between the highest and the lowest while pH was 7. This was due to form many H-bonds between–COOH of PU hydro gel and the chain segment in polymer in the acid solution, which leaded to hydrophilicity and SR of PU hydrogel lower; interaction of H-bond between molecules chains was decreased because all–COOH of PU hydrogel were ionized in the alkalescent solution, which caused hydrophilicity of PU hydrogel enhancement and SR of PU hydrogel increasing.

In addition, the SR was also influenced by the weight of TEFA in the PU hydrogel, as was also shown in Fig.3. The PU hydrogel of 2wt% TEFA had higher SR in a wide range of pH, the PU hydrogel of 3wt% TEFA had lower SR, the PU hydrogel of 0wt% or 1wt% TEFA had higher SR in the alkalescent solution but lower SR in the neutral or weak acid solution. These results showed that the SR of PU hydrogel was determined by the molecular interaction force of its network structure and the density of the crosslinking agent, the increase of the concentration of the crosslinking agent increased the density of the molecular chains, and the water molecules were difficult to penetrate into the network molecular of PU hydrogel; But when the concentration of crosslinking agent was smaller, the molecular chain of the PU hydrogel network was larger and the swelling property of the water was weakened, which caused the SR was decreased.

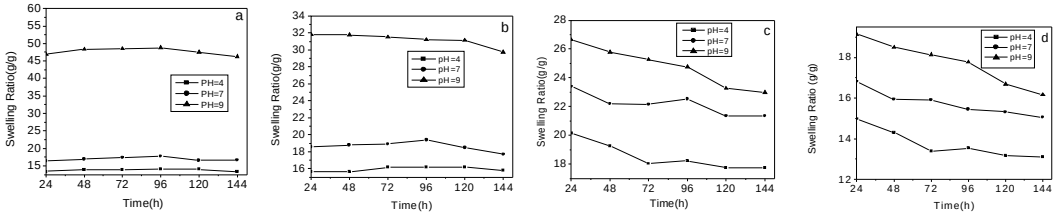

Fig. 3 The change curve of the swelling ratio of PU hydrogel under different pH values

Effect of ionic strength on SR of PU hydrogel. Fig.4 showed swelling ration in various aqueous NaCl concentrations for the PU hydrogel that the concentration of TEFA was 0.1, 0.2, 0.3 and 0 wt% as curves a, b, c, and d respectively at ordinary temperature. Fig. 4 indicated that the ionic strength had a great effect on the swelling ratio of the PU hydrogel, SR of the PU hydrogel decreased rapidly with the increase of ionic strength while the concentration of NaCl changed from 0.01 to 1mol/L; SR of the PU hydrogel decreased slowly with the increase of ionic strength while the concentration of NaCl changed from 0.0001 to 0.01 mol/L. This was due to hydrophobic interaction between polymer chains would be enhanced and the interaction between PU hydrogel molecules and water was weakened as while the concentration of NaCl increased, which caused the total water content of the PU hydrogel decrease. Moreover, as the concentration of NaCl increased, the exterior osmotic pressure increased, and interior osmotic pressure of PU hydrogel remained the same. The exterior osmotic pressure was larger than that in the PU hydrogel, therefore SR of the PU hydrogel decreased with the increase of concentration of NaCl .

Swelling and deswelling kinetics of PU hydrogel. To determine the swelling and deswelling kinetics of the PU hydrogel, the PU hydrogel with the 0, 0.1, 0.2 and 0.3 wt% TEFA as curves a, b, c, and d was alternately put into buffers solution (pH =4 and7) or constant temperature water (T=20˚C and 40˚C), exchange period was 24 hours and weighted it each exchange. Water retention(WR) was countered according to formula (2).

$$WR=(W_t- W_d)/ (W_0- W_d)\times100\% \quad (2)$$

Where W_d is dry PU hydrogel weight after equilibrium swelling, W_0 is PU hydrogel weight after equilibrium swelling, W_t is PU hydrogel weight after equilibrium swelling at time t.

Change curves of the WR were shown in Fig.5 and Fig.6. Fig.5 showed that WR of the PU hydrogel had properties of period change and better swelling and deswelling equilibrium when it was alternately put into buffers solution (pH =4 and7), WR of the PU hydrogel had similar characteristics when it was alternately put into constant temperature water (T=20˚C and 40˚C). The research results showed the

PU hydrogel presents fairly reproducible, reversibility and stability under a certain pH and temperature, which made the PU hydrogel was suitable for using in biomedical controlled delivery of medicines.

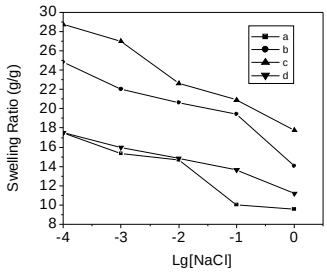

Fig. 4 The effect of ionic strength on SR of PU hydrogel

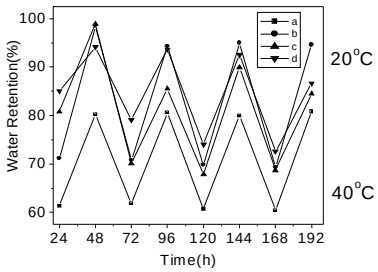

Fig.5 Change curves of the WR of PU hydrogel with time under different temperature

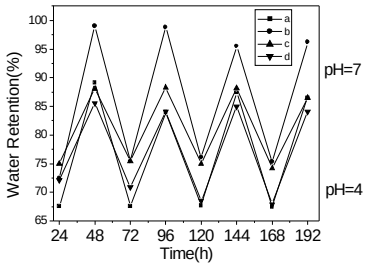

Fig.6 Change curves of the WR of PU hydrogel with time under different Ph

Conclusions

A novel Polyurethane hydrogel(PUHG) was prepared by using the toluene diisocyanate(TDI), polyethylene glycol(PEG-6000), dimet hylol propionic acid(DMPA) and triethylene tetramine(TEFA). We found that the PUHG had temperature sensitivity, pH sensitivity and ionic strength sensitivity; moreover, the results of swelling dynamic indicated that PUHG could change reversibly well at different pH and temperature. So we could use the PUHG to control delivery of medicines.

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