Characterization of Hydrogels Based on Chitosan and Copolymer of Poly(dimethylsiloxane) and Poly(vinyl alcohol)

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ABSTRACT: Copolymers composed of poly(vinyl alcohol) (PVA) and poly(dimethylsiloxane) (PDMS) were crosslinked with chitosan to prepare semi-interpenetrating polymer network (IPN) hydrogels by an ultraviolet (UV) irradiation method for application as potential biomedical materials. PVA/PDMS copolymer and chitosan was cast to prepare hydrogel films, followed by a subsequent crosslinking with 2,2-dimethoxy-2-phenylacetophenone as a nontoxic photoinitiator by UV irradiation. Various semi-interpenetrating polymer networks (semi-IPNs) were prepared from different weight ratios of chitosan and the copolymer of PVA/PDMS. Photocrosslinked hydrogels exhibited an equilibrium water content (EWC) in the range of 65–95%. Swelling behaviors of these hydrogels were studied by immersion of the gels in various buffer solutions. Particularly, the PCN13 as the highest chitosan weight ratio in semi-IPN hydrogels showed the highest EWC in time-dependent and pH-dependent swelling. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2591–2596, 2002

Key words: hydrogels; swelling

INTRODUCTION

Hydrogels are water-swollen, crosslinked polymeric structures produced by the simple reaction of one or more monomers, which find an extremely wide range of applications in the fields of medicine, pharmacy, biotechnology, agriculture, and controlled release of drugs. In recent years, hydrogels have been used for the immobilization of enzymes, proteins, antibodies, and antigens, due to their versatile application in biomedicine and biotechnology. Especially, hydrogels have become excellent carriers for release of drugs and bioactive macromolecules either in their swollen equilibrium state or as dynamically swelling state. Their major disadvantage can be overcome either by crosslinking, by formation of interpenetrating networks, or by crystallization that induces crystallite formation and drastic reinforcement of their structure.[1–3]

Semi-Interpenetrating polymer networks (IPNs) are defined as a composition in which one or more polymers are crosslinked, linear, or branched. Many hydrogels are generally formed from water-soluble polymers by crosslinking them either using radiation or chemically or by

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polymerizing hydrophilic monomers in the presence of a crosslinker. Crosslinked polymers seem to be one of the candidates to improve wet strength.

Chitin is derived from the shell of crab or shrimp, and has a similar structure to cellulose. It is also known to be biocompatible, biodegradable, and nontoxic, and therefore, has been used in drug delivery systems and also in biomedical applications. Chitosan is partially deacetylated chitin. As an ideal film, fiber-, and gel-forming material, chitosan has found increasing use in the purification of water, immobilization of enzymes, cells, drugs, and so forth, due to their unique performance, as well as environmental and economical advantages.[4,5] Chitosan possesses excellent biocompatibility and mechanical properties and has been used as biomedical materials.[6,7] In the recent literature, Lee et al. reported IPN hydrogels composed of chitosan and poly(acrylic acid) (PAAc), and studied their swelling behaviors and thermal analysis.[8] Yao reported on the chitosan semi-IPNs hydrogels crosslinked with glutaraldehyde and studied their swelling kinetics.[9,10] Wang et al. blended chitosan and PAAc and used glutaraldehyde to crosslink chitosan.[11]

Also, Gudeman and Peppas reported on the pH-sensitive membranes from PVA and PAAc IPN. In this case, the IPN was crosslinked by using glutaraldehyde.[12,13] Shin et al. reported novel pH- and temperature-responsive IPN hydrogels composed of PVA and PAAc crosslinked by ultraviolet (UV) irradiation.[14] Kim et al reported drug release behavior of electrically responsive PVA/PAAc IPN hydrogels under an electric stimulus.[15,16] In the case of pH as another external signal to stimuli-sensitive hydrogel, Nishi and Kotaka[17] and Yao et al.[18] have studied pH-sensitive hydrogels. Charged polymeric networks have been recognized as useful matrices for drug delivery because their volume changes in responsive to repulsion between charged groups incorporated in the gel matrix. Reports of hydrogels using silicone are few. However, Lopour et al. reported silicone rubber–hydrogel composites as polymeric biomaterials.[19] In their report, they showed the relations between the properties and the influence of the interaction of polymeric phases on the mechanical properties of silicone rubber–hydrogel composite materials.

In this study, we would like to report on the preparation and swelling properties of novel time- and pH-dependent hydrogels. In addition, differential scanning calorimetry (DSC) studies were performed to understand the state of water for the swollen gel and dry in semi-IPN hydrogels. Further work including the electrostatic interactions are under way in our laboratory.

EXPERIMENTAL

Materials

The chitosan was submitted from Jakwang Co., Korea, and used without purification. Silicone, vinyl-terminated polydimethylsiloxane (PDMS) was obtained from Shinetsu Co., Japan. PVA was purchased from Aldrich Chemical Co., and the average molecular weight was 1.5×10^5g/mol. 2,2-Dimethyl-2-phenylacetophenone (DMPAP) as an initiator and all other chemical reagents were used extra pure grade.

Preparation of Semi-IPNs

PVA was added to deionized water and heated at 80°C for 1 h to make a solution containing 10% PVA by weight. Then PDMS was added. This mixture was heated at 80°C for 2 h; 2 wt % chitosan solution (dissolved in 1% acetic acid aqueous solution) and DMPAP in tetrahydrofuran (THF) were added to the PVA mixture and heated at 80°C for 30 min. Then THF was used to dissolve the DMPAP. After 30 min, the mixed solutions were poured into Petri dishes and stored in a box and exposed to a 450 W UV lamp (Ace Glass Co. USA) placed above the mold at a height of 20 cm for 2 h under N_2 atmosphere. The irradiated samples were dried in the oven at 80°C for 12 h. Various semi-IPNs were prepared from different compositions (1 : 1, 1 : 3, 3 : 1 weight ratio) of chitosan and the copolymer of PVA/PDMS. The synthesized gels were removed from the Petri dishes and washed by deionized water to remove any reacted monomers. The swollen gels were dried.

Characterization

Fourier transform infrared (FTIR) spectroscopy (Bruker Model EQUINOX 55) was used to confirm the structure of semi-IPN hydrogels. To measure the equilibrium water content (EWC), preweighed dry samples were immersed in various buffer solutions. After excessive surface water was removed with the filter paper, the weight of swollen samples was measured at various time intervals. The procedure was repeated until there

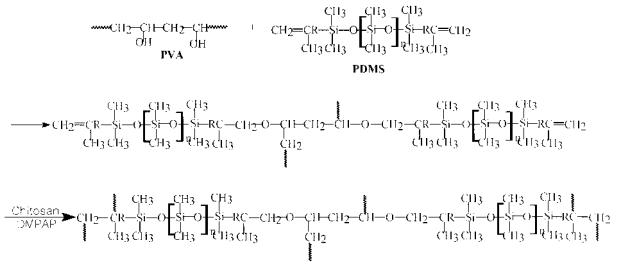

Figure 1 Scheme of the synthesis of semi-IPNs.

was no further weight increase and five times. EWC was determined according to the following equation:

$$\text{EWC}\ (\%) = ((W_s - W_d)/Ws) \times 100$$

where, W_s and W_d represent the weight of swollen and dry-state samples, respectively. To investigate the melting endothermic of IPNs, the measurement of differential scanning calorimetry was conducted by a TA Instrument DSC 2010, in aluminum pans at 5°C/min scanning rate under N_2 flow.

RESULTS AND DISCUSSION

The IPNs composed of chitosan and a copolymer of PVA/PDMS was synthesized by UV irradiation using DMPAP as a photoinitiator. Figure 1 shows the reaction scheme of IPNs.

In FTIR spectra, characteristic peaks of chitosan are located at 3450 cm^{-1} for the hydroxyl group and 1650 cm^{-1} and 1550 cm^{-1} for amide I and II, respectively. The stretching vibrations of the hydroxyl group in PVA appeared at 3450 cm^{-1}, and Si—C group in silicone appeared at 1300 cm^{-1}.

The pH-dependent swelling behavior was observed with changes in pH of buffer solution. Swelling kinetics of IPN hydrogels in pH 7 buffer solution at 35°C are plotted in Figure 2 as the average of five trials. All hydrogels swelled rapidly and reached equilibrium within 2 h. The pH-dependent swelling behavior was observed at 35°C, with changes in pH 2–10 buffer solution as shown in Figure 3. At pH 2–4, chitosan exists as an ammonium ion. Thus, due to the dissociation of intermolecular ammonium salt, the EWC increases at pH 2–4. The PCN13 dissolved at pH 2 for high dissociation of intermolecular ammonium salt. At pH 7–10, however, chitosan is in the

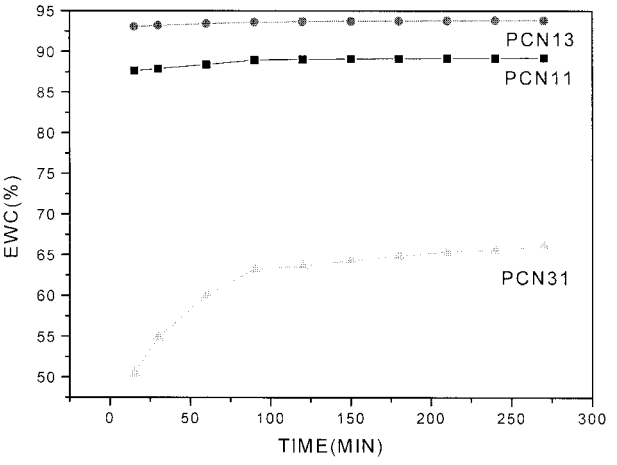

Figure 2 Time-dependent swelling behavior of semi-IPNs in pH 7 at 35°C (PCN11, PCN13, and PCN31 is weight ratio of copolymer of PVA/PDMS and chitosan; 1 : 1, 1 : 3, and 3 : 1, respectively).

form of —NH_2, resulting in even lower EWC than at lower pH. Because the semi-IPN, PCN13 possesses more chitosan in its structure, the swelling degree was highest, with the highest total water content at all conditions of the experiments.

Also, the content of chitosan and copolymer of PVA/PDMS in IPNs, of course, affected EWC. For example, the PCN13 that containing the highest content of chitosan among samples shows the highest EWC value due to the ionization of chitosan at all pHs. Meanwhile, the PCN31 that containing the lowest content of chitosan among samples showed the lowest EWC value at all pHs. In summary, the EWC of semi-IPNs depended on

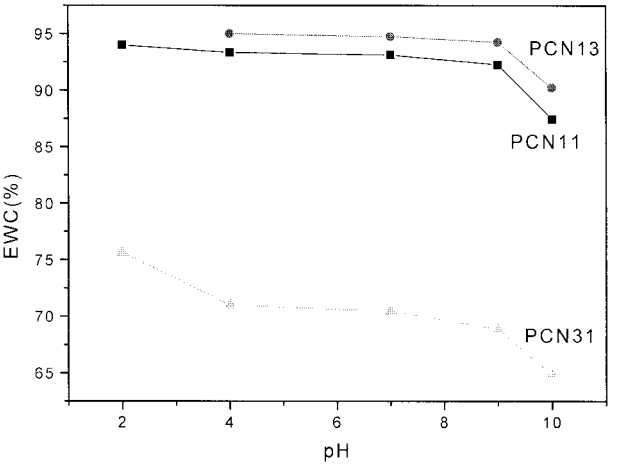

Figure 3 pH-dependent swelling behavior of semi-IPNs at 35°C; PCN11, PCN13, and PCN31.

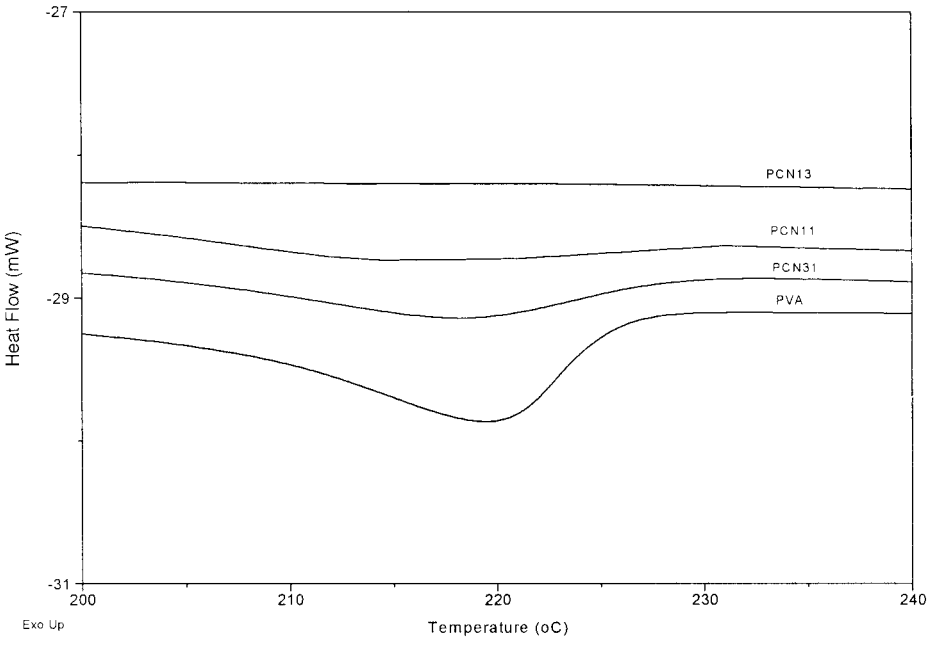

Figure 4 DSC thermogram of semi-IPNs; PCN11, PCN13, PCN31, and PVA.

pH and the amount of complex that is content of chitosan and copolymer of PVA/PDMS within the IPNs.

DSC thermograms exhibit the melting endotherms of chitosan and crosslinked segments in the semi-IPNs. PVA gives a sharp endothermic peak at 219.49°C, and semi-IPNs showed melting peaks close to these, as seen in Figure 4. Chitosan is very rigid, and we cannot detect any noticeable transition temperature in the DSC thermogram; probably the characterics of this natural polymer are similar to cellulose.[4,5] As the weight ratio of chitosan to copolymer of PVA/PDMS decreased from 1 : 3 to 3 : 1, the integration of the peaks of IPNs became more intensive. This result implies that an increase of chitosan content in the semi-IPN hydrogels caused a rapid decrease of crystallinity of the PVA. Figure 5 shows the DSC thermogram of fully swollen IPN hydrogels. The endothermic peak of swollen gels appeared between −4 to 1°C. The fraction of free water is approximately estimated by the ratio of endothermic peak, integrated between these ranges, to the melting endothermic peak of heat of fusion for pure water. Bound water is expressed as the difference between total water and free water. EWC values, free water contents and bound water contents, respectively, are calculated and listed in Table I. Free water contents in the semi-IPN of PCN13, PCN11, and PCN31 were 65.81, 51.84, and 34.7 at pH 7, respectively. PCN31 showed the lowest EWC and free water content. This result confirmed that PCN31 had a more compact structure than PCN11 or PCN13. The fraction of free water in the total water is approximately calculated as the ratio of the endothermic peak area for water-swollen hydrogel to the melting endothermic heat of fusion (79.9 cal/g) for pure water.

$$W_b = W_t - (W_f + W_{fb}) = W_t - Q_{\text{endo}}/Q_f$$

where Q_{endo} is the heat of fusion for ice (equal to 79.7 cal/g) and Q_f is the heat of fusion for the sample.

In the present study, the EWC was calculated in pH 7 buffer solution at 35°C. The free water has good mobility, because it has no interaction with the polymer chains. However, the bound water is involved in the hydrogen bonding with polymer.

CONCLUSIONS

To prepare a polymeric biomedical material, semi-IPN hydrogels composed of chitosan and copolymer of PVA/PDMS by crosslinking were synthesized by UV irradiation and their properties were studied. Hydrophilic PVA/PDMS copolymer

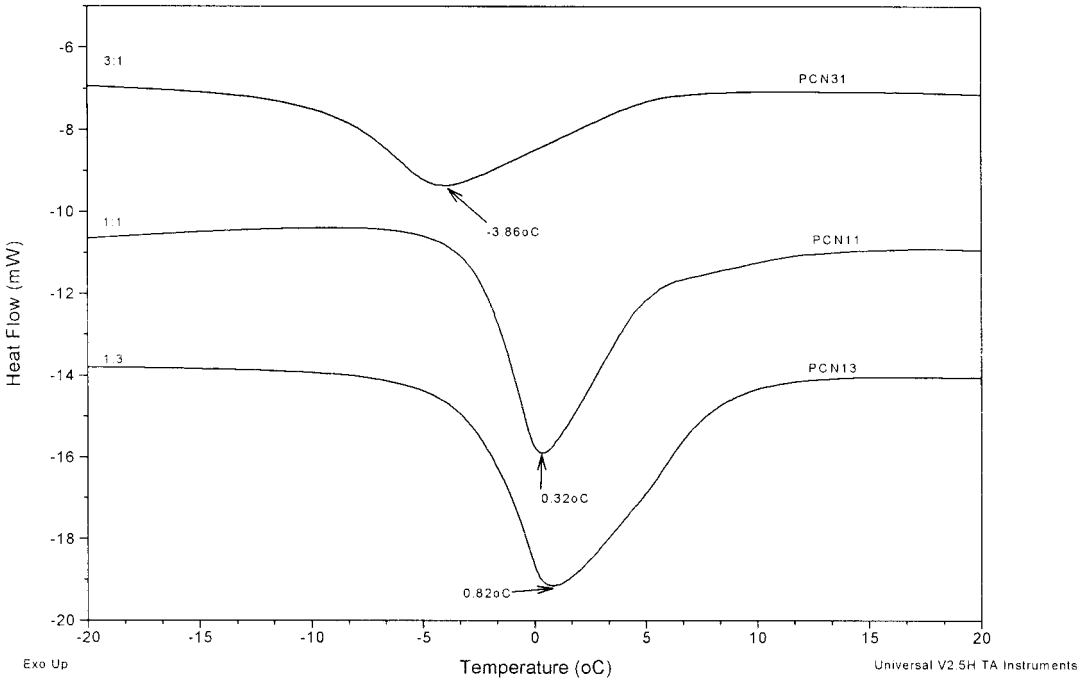

Figure 5 DSC thermogram of hydrogels, which were fully swollen in pH 7.

segments were crosslinked with chitosan. All hydogels exhibited a high EWC in the range 65–95%. Prepared semi-IPNs was characterized and confirmed by FT-IR and DSC.

The pH-sensitive characteristics of IPNs were studied by a swelling test under various pH conditions at 35°C. PCN13 sample appeared highest swelling ratio in pH- and time- dependent swelling behaviors.

PCN31 exhibited the lowest EWC value among three IPNs due to low free water content and relatively high content of bound water, as evidenced by DSC analysis. This means that PCN31 has the most compact complex structure in comparison with PCN11 and PCN13.

Chitosan semi-IPN hydrogels based on PVA/PDMS copolymer prepared in this study might be expected to be useful in the biomedical field, such as wound dressing materials and drug delivery system.

Table I Water State of IPN Hydrogels Calculated by Using DSC

Sample	EWC (%)	Free Water (%)	Bound Water (%)
PCN31	66.05	34.7	31.35
PCN11	89.22	51.84	37.38
PCN13	93.83	65.81	28.02

All samples were swelled in pH 7 at 35°C.

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