Preparation and Characteristics of Poly(propylene glycol) and Poly(acrylic acid) Interpenetrating Polymer Network Hydrogels

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ABSTRACT: Interpenetrating polymer network (IPN) hydrogels based on poly(propylene glycol) diacrylate macromer and poly(acrylic acid) (PAAc) were prepared by UV irradiation and characterized by swelling in water. The swelling behavior of these IPNs was analyzed in buffer solution at various temperatures. Swelling ratios of all IPNs were relatively high and showed reasonable sensitivity to temperature. Hydrogels showed both positive and negative swelling behavior depending on PAAc content. PA22 and PA13 showed positive and PA31 showed negative temperature-sensitive swelling behavior. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 1384–1388, 2003

Key words: interpenetrating networks (IPN); hydrogels; swelling; poly(acrylic acid) (PAAc); poly(propylene glycol) diacrylate macromer (PPGM)

INTRODUCTION

Since the pioneering work of Wichterle and Lim in 1960 on crosslinked HEMA hydrogels, and because of their hydrophilic character and potential to be biocompatible, hydrogels continue to be of great interest to biomaterials scientists.[1] Hydrogels are polymeric networks that absorb and retain large amounts of water. In the polymeric network, there are hydrophilic groups or domains that are hydrated in an aqueous environment, thereby creating the hydrogel structure. As the term "network" implies, crosslinks have to be present to avoid dissolution of the hydrophilic polymer chain/segments into the aqueous phase.[2] Synthetic polymer hydrogels have been proposed for many biomedical applications because of their good biocompatibility and water permeation properties, and the possibility of synthesizing materials with a broad spectrum of micromorphologies and specific properties.[3] Hydrogels can change their volume and shape reversibly, depending on several external physicochemical factors such as temperature, solvent composition, pH, ionic concentration, and light.[4] Environ-

mentally sensitive hydrogels are also called "intelligent" or "smart" hydrogels.[5] The reinforcement of a polymer hydrogel is a major problem in the expansion of its applications because a hydrogel has a poor mechanical property in water. Polymers with microphase-separated morphologies, such as copolymers in which hydrophobic and hydrophilic domains alternate, seem to possess improved mechanical properties.[6] This morphology can also be achieved with interpenetrating polymer networks (IPNs).

IPNs are defined as "a combination of two or more polymers in network form that are synthesized in juxtaposition."[7] They can also be described as crosslinked polymer networks held together by permanent entanglements. The networks are held by "topological bonds," essentially without covalent bonds between them. By definition, an IPN's structure is obtained when at least one polymer network is synthesized and/or crosslinked independently in the immediate presence of another. As long as the reacting ingredients are blended thoroughly during synthesis, thermodynamic incompatibility can be overcome as a result of permanent interlocking of network segments. IPNs with limited phase separation are obtained. It has been reported that polymeric materials with improved mechanical properties can be obtained by IPNs' structures.[8]

Poly(acrylic acid) (PAAc) is known to form a complex with polyoxyethylene (POE) in IPN form. PAAc/POE IPNs show that swelling–deswelling and mechanochemical reactions proceed reversibly for full IPNs, but irreversibly for the semi-IPNs upon chang-

ing pH. It was also reported that PAAc/poly(*N*,*N*-dimethyl acrylamide) IPN hydrogels showed an upper critical solution temperature (UCST) behavior mainly because of the presence of PAAc.[9] Poly(propylene glycol) (PPG) has more hydrophobic polyether than poly(ethylene glycol) (PEG) and has been used in various biomedical areas such as lubricious coating on absorbable sutures and as the soft segment of biocompatible polyurethanes.[10]

In this study, we focused our attention on the properties of PPG diacrylate macromer (PPGM)/PAAc IPN hydrogels. We prepared them by UV irradiation and examined the changes in their swelling as affected by temperature.

EXPERIMENTAL

MATERIALS

PPG (M_n = 3500) was purchased from Aldrich Chemical Co. (Milwaukee, WI) and was dried by azeotropic distillation with benzene. Acryloyl chloride and 2,2-dimethoxy-2-phenylacetophene (DMPA), a photoinitiator, were obtained from Aldrich Chemical Co. and used without further purification. Acrylic acid (AAc) monomer was purchased from Junsei Chemical Co. (Japan) and used after purification with an inhibitor-removal column. Methylenebisacrylamide (MMBAAm) was used as a crosslinking agent. All other chemicals were reagent grade and used as purchased without further purification.

Synthesis of PPGM

PPG (12 g, 3.2 m*M*) was dissolved into 150 mL of benzene and heated to 80°C. A total of 0.89 mL (3.2 m*M*) of triethylamine and 0.61 mL (7.5 m*M*) of acryloyl chloride were added and the reaction mixture was stirred for 3 h at 80°C. After filtering triethylamine·HCl, the macromer was purified by pouring the reaction mixture into a large excess of hexane. A solvent from the filtrate was removed by rotary evaporation. The resulting syrup containing viscous macromer was dried under vacuum for 1 day.

Preparation of PAAc/PPGM semi-IPNs

The IPNs were prepared by simultaneous method. PPGM and AAc monomer were dissolved in ethyl alcohol. The crosslinkers *N*-vinylpyrrolidione and MMBAAm and initiator DMPA were mixed with that solution. The solutions were poured into a circular glass mold and irradiated using a 450-W UV lamp (Korea Ultra-Violet Development Co. Ltd., Korea) placed above it at a height of 20 cm for 10–20 min until gelation occurred. The mold was then kept under reduced pressure to evaporate the solvent. After 1

TABLE I
Composition and Designation of Hydrogels

Sample	PPGM : PAAc (wt %)
PA04	4 : 0
PA31	3 : 1
PA22	2 : 2
PA13	1 : 3
PA04	0 : 4

day, a dry film was obtained and was washed to remove unreacted chemicals. The detailed composition and designation of PPGM/PAAc hydrogels are listed in Table I.

Measurements

FTIR spectroscopy (Model Magma IR 550; Nicolet Analytical Instruments, Madison, WI) was used to confirm the hydrogen bondings between PPGM and PAAc in the IPNs. The swelling ratio was measured in deionized water. Preweighed dry IPN films were immersed in deionized water at various temperatures until they swelled to equilibrium. It was confirmed that 8-h equilibration was enough to reach the equilibrium swelling of films. The swelling ratio can be calculated as a function of time:

$$\text{Swelling ratio (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where W_s is the weight in the swollen state at any given time and W_d is the weight in the dry state. Equilibrium water content (EWC) was calculated from the following equation[13]:

$$\text{EWC (\%)} = \frac{W_e - W_d}{W_e} \times 100 \quad (2)$$

where W_e represents the weight in the swollen state at equilibrium.

The state of water in the IPN hydrogels was investigated by DSC (Du Pont Instruments DSC 910, Boston, MA). The IPN films equilibrated in deionized water were cooled to 20°C and then rescanned up to 20°C at a heating rate of 5°C/min under N_2 flow. Amounts of free water and bound water were calculated from the melting enthalpies.

RESULTS AND DISCUSSION

Figure 1 shows FTIR spectra of PPG, PPGM, PAAc, and PAAc/PPGM IPN hydrogel. A new peak appears at 1730 cm^{-1} in PPGM that can be attributed to the formation of a carbonyl bond arising from the reaction between acryloyl chloride and hydroxyl groups in
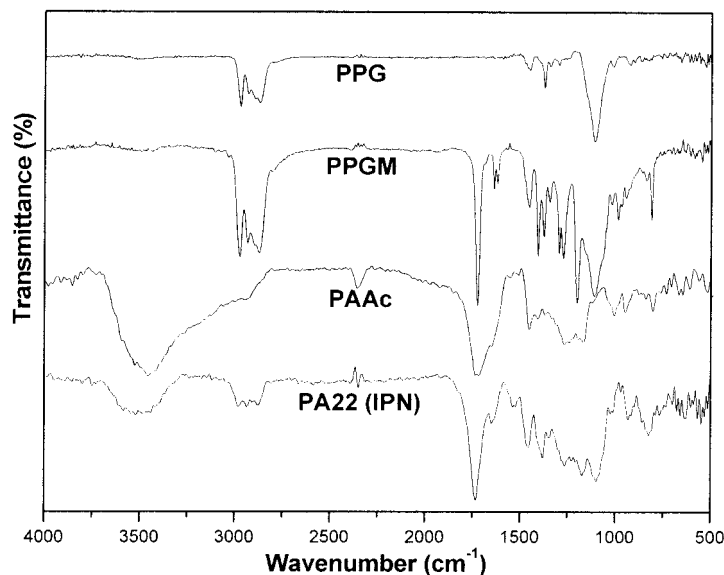
Figure 1 FTIR spectra of PPGM and PPGM/PAAc IPN.

PPG. Another two peaks at 1629 and 1430 cm^{-1} indicate the presence of C=C bond. Meanwhile, the IR spectra of crosslinked PAAc hardly varied from that of PAA without crosslinking.[11,12] The IR spectrum of PAA exhibits the characteristic absorption band at 1720 cm^{-1} attributed to the C=O stretching vibration of the carboxylic groups. In PPGM/PAAc hydrogel, peaks of the carboxylic acid group and aliphatic ethers appear at both 1713–1718 and 2840–2995 cm^{-1}. This result shows that PPGM/PAAc hydrogel was synthesized.[13,14]

The swelling ratio of IPN hydrogels was calculated according to eq. (1) and swelling kinetics of IPN hydrogels in a pH 7 buffer solution at room temperature are plotted in Figure 2. All hydrogels swelled rapidly and reached equilibrium within 4 h. PA13, whose PAAc content is greater than its PPGM content, reached its equilibrium rapidly compared to PA31, which contained more PPGM. Because PAAc is hydrophilic, the more PAAc in the IPNs, the higher the swelling ratio. The swelling ratio of IPN hydrogels increased to 12–65% as the PAAc content increased.

The swelling behavior of IPN hydrogels was investigated as a function of temperature. As shown in Figure 3, all hydrogels had significant changes in swelling ratio over the temperature range between 25
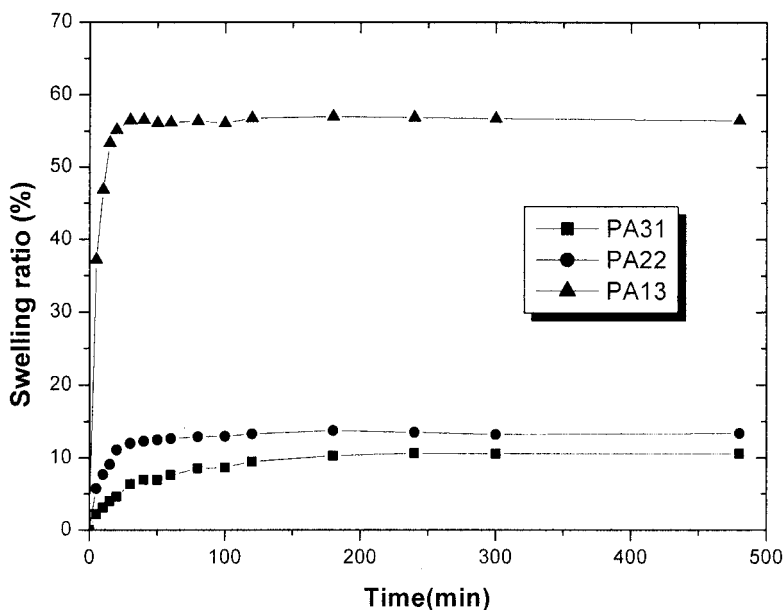

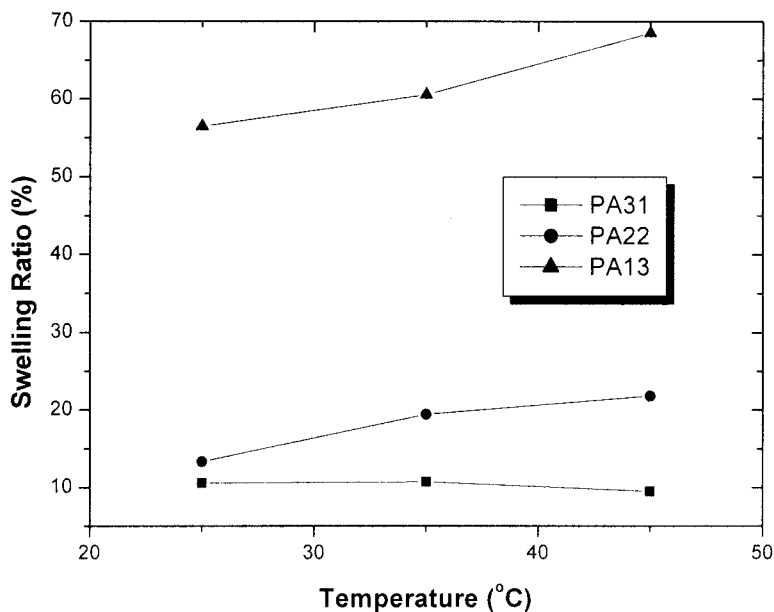**Figure 2** Swelling kinetics of PPGM/PAAc IPNs at 25°C.

Figure 3 Swelling ratio as a function of temperature for PPGM/PAAc IPNs.

and 45°C. As the temperature of the hydrogels in the swelling states increased, the swelling ratio of PA22 and PA13 increased and the PA13 sample appeared to have the highest swelling ratio in temperature-dependent swelling behavior.[14] However, the PA31 sample showed a decrease in swelling ratio. At lower temperatures, hydrogen bonding between hydrophilic segments of the polymer chain and water molecules predominates, leading to enhanced dissolution in water. As the temperature increases, however, hydrophobic interactions among hydrophobic segments become strengthened, while hydrogen bonding becomes weaker. The net result is shrinking of the hydrogels attributed to interpolymer chain association through hydrophobic interactions.[5]

The water state in hydrogels is closely related to swelling behavior and we reported this phenomenon in previous studies.[15] In general, the state of water in the polymer can be divided into nonfreezing bound water, freezing bound water, and free water, explained as follows.

1. *Nonfreezing water or bound water*. This term refers to the water molecules that are bound to polymer molecules through hydrogen and are immobilized. This kind of water shows no endothermic peak in the temperature range −70 to 0°C.
2. *Freezing bound water or intermediate water*. Other water molecules that interact with polymer molecules are referred to as intermediate water. This kind of freezing water has a melting point below 0°C.
3. *Free water*. Water molecules that do not take part in hydrogen bonding with polymer molecules

are called free water because of their greater degree of mobility compared to that of other water molecules. Free water is freezing water showing a melting point of 0°C. It has a transition temperature, enthalpy, and DSC curves similar to those of pure water.

Amounts of free water and bound water were calculated from the melting enthalpies.[16,17] As a rule, DSC is used to determine the amount of free water that is not bound by hydrogen bonding. The following equation assumes that the heat of fusion of free water in the hydrogel was the same as that of the ice.[18]

$$W_b \, (\%) = W_t - (W_f + W_{fb}) = W_t - (Q_{endo}/Q_f) \times 100$$

(3)

where W_t is the equilibrium water content (EWC, %); W_b is the amount of bound water (%); W_f and W_{fb} represent the amount of free water and freezing bound water, respectively; and Q_{endo} and Q_f represent the heat of fusion of free water in IPN hydrogel and that of the ice (79.9 cal/g),[19] respectively.

The endothermic peaks appearing around 0°C, shown in Figure 4, were attributed to the presence of free water in the hydrogels. The fraction of free water in the total water is calculated approximately as the ratio of the endothermic peak area for water-swollen hydrogel to the melting endothermic heat of fusion for pure water.[20] Table II shows the content of water corresponding to free and bound water as well as total water. The amount of free water increased with increasing PAAc content in the IPN hydrogels. This
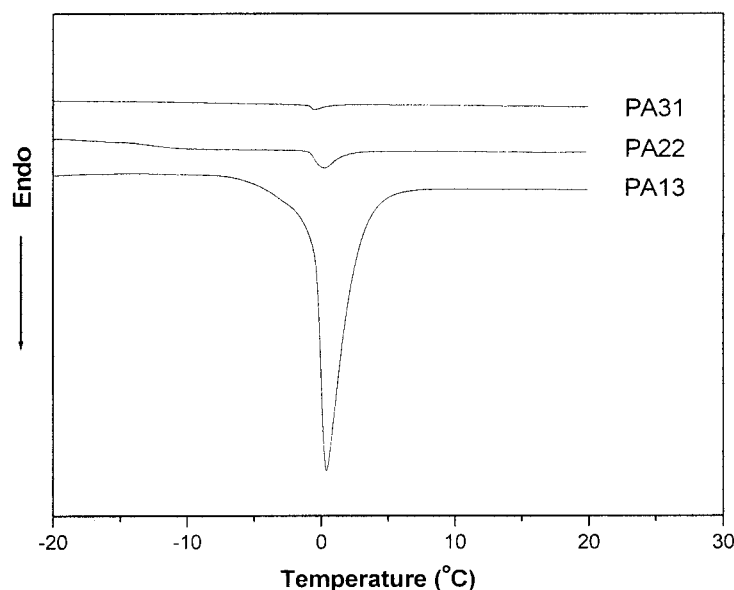
Figure 4 DSC thermograms of swollen PPGM/PAAc IPNs.

indicates that the increase in the swelling ratio is attributed mainly to the free water content in the IPN hydrogels.

CONCLUSIONS

IPN hydrogels composed of PAAc and PPGM were synthesized by UV irradiation and their properties were studied. Hydrophobic PPGM segments and PAAc segments were crosslinked and formed. All hydrogels exhibited EWC in the range of 9.5–36.7%. The IPN hydrogels exhibited a relatively higher swelling ratio as the PAAc content increased. The PA13 sample with the highest PAAc content among the samples showed the highest swelling ratio in temperature-dependent swelling behavior, but the PA31 sample showed a decrease in the swelling ratio. DSC was used for the quantitative determination of the amounts of freezing bound water. The free water content in the IPN hydrogels increased with increasing PAAc content.

TABLE II
Water State of PPGM/PAAc IPN Hydrogels
Estimated by DSC Analysis

Sample	EWC (%)	Free water (%)	Bound water (%)
PA31	9.50	7.52	1.98
PA22	11.77	10.40	1.37
PA13	36.69	33.39	3.3

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