Preparation and Characterizations of Interpenetrating Polymer Network Hydrogels of Poly(ethylene oxide) and Poly(methyl methacrylate)

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ABSTRACT: Interpenetrating polymer network (IPN) hydrogels based on poly(ethylene oxide) and poly(methyl methacrylate) were prepared by radical polymerization using 2,2-dimethyl-2-phenylacetophenone and ethylene glycol dimethacrylate as initiators and crosslinkers, respectively. The IPN hydrogels were analyzed for sorption behavior at 25°C and at a relative humidity of 95% using dynamic vapor sorption. The IPN hydrogels exhibited a relatively high equilibrium water content in the range of 13–68%. The state of water in the swollen IPN hydrogels was investigated using differential scanning calorimetry. The free water in the hydrogels increased as the hydrophilic content increased. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 258–262, 2003

Key words: interpenetrating networks (IPN); poly(ethylene oxide); poly(methyl methacrylate); hydrogels; sorption

INTRODUCTION

Hydrogels are three-dimensional hydrophilic polymer networks capable of imbibing large amounts of water or biological fluids, yet insoluble in water, but swellable when immersed.[1,2] There are numerous applications of these hydrogels, particularly in the medical and pharmaceutical fields. The water-retention capacity of these materials is attributed to the presence of hydrophilic functional groups such as –OH, –COOH, –CONH$_2$, and –CONH along the polymer chains.[2] These hydrogels are being used as microbiological culture media as well.[3] Nontoxic water-soluble poly(ethylene oxide) (PEO) hydrogels have been investigated by many researchers for this reason.[2,4,5] PEO hydrogel is applied as a component of biomedical devices such as, for example, wound coverings, drug delivery systems, and hemodialysis membranes. However, PEO hydrogels possess very poor mechanical properties.[2,6–8] To solve this problem, we added poly(methyl methacrylate) (PMMA) to form an interpenetrating polymer network (IPN) structure. Our goal was to develop an important thermoplastic material possessing good mechanical properties.

An IPN is an intimate combination of two polymers both in the same network, one of which is crosslinked in the immediate presence of the other.[9] PEO/PMMA IPNs combine hydrophilic PEO with hydrophobic PMMA. It turned into a phase-separated system after the crosslinking reaction.[10,11] If the crosslinking density of PEO is small (i.e., the number of monomer units between crosslinks is high), then during the polymerization of network PMMA, the growing PMMA chains will push apart the already existing PEO chains, and a phase-separated IPN will be obtained. However, if the crosslinking density of PEO is high, the positions of the PEO chains will hardly be changed and the PMMA network will grow by interpenetrating the existing PEO network. Thus, an IPN can eventually be obtained, achieving a forced compatibilization of both polymers.[10,12,13] Previously, Sanchez et al.[10] reported synthesis of IPN in poly(methyl acrylate) with PMMA.

In the present study, PEO/PMMA IPN hydrogels by free-radical polymerization were prepared. Dynamic vapor sorption (DVS) and differential scanning calorimetry (DSC) studies were performed to understand the state of water for swollen IPN hydrogels.

EXPERIMENTAL

Materials

PEO was purchased from Aldrich Chemical Co. (Milwaukee, WI) and purified by vacuum distillation before being used. The crosslinking agents N,N-methylene bis-acrylamide (MBAA) and ethylene glycol

TABLE I
Designation in Accordance with Composition and Equilibrium Water Content of IPN Hydrogels

Polymer code	PEO : PMMA (wt %)	EWC (%)
PC1-4	1 : 4	13.82
PC1-1	1 : 1	59.49
PC4-1	4 : 1	67.83

dimethacrylate (EGDMA) were purchased from Aldrich and were used without further purification. Methyl methacrylate (MMA) was purchased from Junsei Chemical Co. (Japan). Benzoyl peroxide (BPO) and tetrahydrofuran (THF) were purchased from Duksan Pure Chemical Co. (Japan). All other chemicals were reagent grade and were used as received.

Preparation of PEO/PMMA IPN hydrogels

Hydrophilic PEO and hydrophobic MMA are immiscible. Hence, THF was employed as the common solvent because it dissolves MMA monomer, PEO, and the crosslinking agents (EGDMA, MBAA). MMA with EGDMA, whose mass was 2% of the mass of the MMA, and PEO with MBAA, whose mass was 4% of the mass of the PEO, were dissolved in THF. The amount of solvent was adjusted to avoid bubble formation and the synthetic goal was as follows[14]:

$$0.5 = (V_{reactant})/(V_{reactant} + V_{solvent})$$

where $V_{reactant}$ = (volume of PEO and MMA + volume of crosslinking agent).

BPO (0.5 wt %) was added to the mixture as an initiator and was thoroughly mixed at 40°C for over 1 h. This system was allowed to stand for 1 day at 0–4°C. The temperature was increased to 70°C while the mixture was stirred for about 2 h. The mixture was poured into a mold and kept in an air-circulated oven, initially at 80°C for 24 h and subsequently at 120°C for 4 h to facilitate complete network formation.

To remove the solvent (THF) and to eliminate homopolymers and nonreacted monomers, the IPN was first kept in a circulation oven at 40°C. This evaporated most of the solvent. Subsequently, it was placed in a vacuum oven at 60°C for 24 h to ensure complete removal of the solvent. IPN hydrogels were extracted with alcohol for 24 h to eliminate homopolymers and nonreacted monomers and was dried again to constant weight.

Samples with different weight ratios of PMMA to PEO (1 : 4, 1 : 1, 4 : 1) were synthesized. The designation and a detailed composition of each sample are listed in Table I.

Measurements

FT-IR spectroscopy (Model Magna IR 550; Nicolet Analytic Instruments, Madison, WI) was used to confirm the structure of all samples. The sorption behavior of the IPNs was analyzed at 25°C and 95% relative humidity (RH) using a dynamic vapor sorption DVS-1000 instrument (Surface Measurement Systems Ltd., London, UK). The instrument included a Cahn D200 microbalance. Before analysis, the IPN samples (~ 10 mg) were dried to constant weight under 0% RH. The equilibrium water content (EWC) was measured by conventional gravimetric methods. EWC was calculated as the weight increase with respect to the weight of the swollen sample using the following equation:

$$EWC(\%) = [(W_s - W_d)/W_s] \times 100$$

where W_s and W_d denote the weights of swollen and dry samples, respectively. It was confirmed that 24 h equilibration was enough for the swelling films to reach equilibrium. Differential scanning calorimetry (DSC; TA Instruments 2010, New Castle, DE) was employed to examine the state of water in the swollen hydrogels with different water contents. Samples sealed in aluminum pans were cooled to −25°C and then heated to 25°C at a heating rate of 5°C/min under 60 cm^3/min of nitrogen gas flow. The fraction of free water in the total water was calculated approximately as the ratio of the endothermic peak area for water-swollen hydrogels to melt the endothermic heat of fusion (334 J/g) for pure water. Bound water attributed to hydrogen bonding with the PEO chains was expressed as the difference between the total water and the free water.
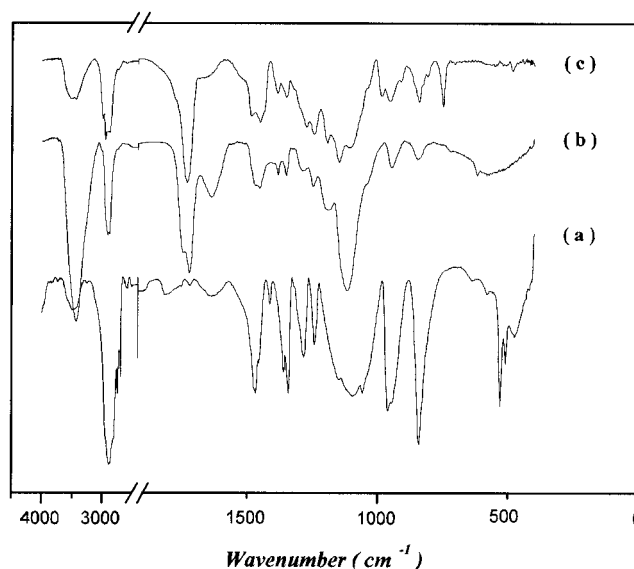
Figure 1 The FT-IR spectra of hydrogels: (a) PEO, (b) c-PEO, (c) IPN.
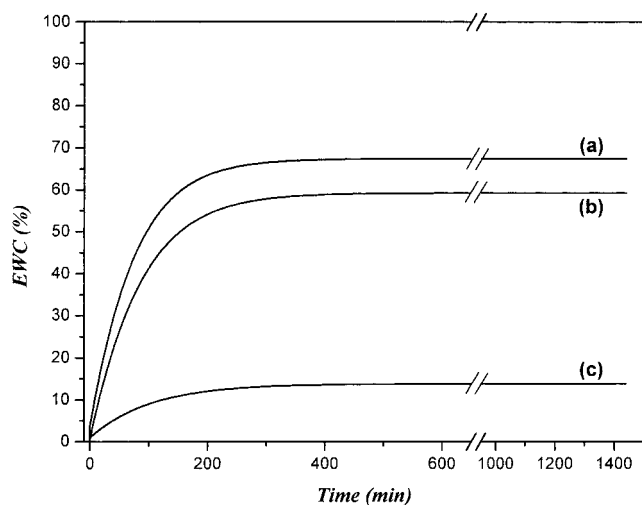
Figure 2 Sorption behavior at 25°C: (a) PC4-1, (b) PC1-1, (c) PC1-4.

RESULTS AND DISCUSSION

FT-IR spectroscopy (Nicolet Model Magma IR 550) was used to confirm the structure of the PEO/PMMA IPN hydrogels. Figure 1 shows the FT-IR spectra of the IPN hydrogel. The characteristic C—O—C stretching vibrations of the repeat unit –OCH$_2$CH$_2$ appeared at 1150 cm^{-1}, and for the crosslinking agents (MBAA, EGDMA), a C=O stretching vibration of the ester carbonyl group occurred at 1745 cm^{-1}.[15] Peaks around 1097 cm^{-1} in PEO were assigned to the C—O stretching of the polyether. In the case of crosslinked PEO homopolymer (c-PEO) and the IPN, a new peak appeared at 1722 cm^{-1}, which can be attributed to the crosslink of a urethane bond from the crosslinking agent MBAA. There is a characteristic aldehyde peak (1385 cm^{-1}) of c-PEO and IPNs. Peaks at 1487 and 1639 cm^{-1} were attributed to amide I and III bands caused by the remaining acrylamide groups in MBAA.[16]

Figure 2 shows the effect of the PEO component on the sorption behavior of PEO/PMMA IPN hydrogels. All IPN hydrogels swelled rapidly and reached equilibrium within 6 h. With increasing PEO content, the EWC of the IPN hydrogels increased, and the sorption time to equilibrium also lengthened. This was attributed to the hydrophilicity of PEO and hydrophilic functional groups capable of hydrogen bonding, such as –CONH and –CONH$_2$. In general, the swelling of hydrogels based on PMMA was reported to occur within 10 h.[9,17] The EWC of IPN hydrogels was 13–68%, which increased with PEO content. As seen in Table I, sample PC1-4 possessed fewer hydrophilic functional groups than the other IPN hydrogels. Accordingly, PC1-4 retains the smallest amount of water among the samples. No large differences can be seen between PC1-1 and PC4-1. This behavior may be at-

tributed not only to the amount of the PEO network but also to the amount of the crosslinking agent having a large number of water-binding sites, which are attributed to the high crosslinking degree of PEO. Water states of the IPN hydrogels are listed in Table I.

Free and bound water were measured from the DSC melting thermograms of swollen hydrogels and calculated as previously described.[18,19] The following equation assumes that the heat of fusion of free water in the hydrogel is the same as that of ice[20]:

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

where W_t is the total water (%); W_b is the amount of the bound water (%); and W_f and W_{fb} are the amounts of free water and freezing bound water, respectively. Q_{endo} and Q_f are the heat of fusion of free water in the IPN hydrogel and that of the ice (334 J/g),[21] respectively. Generally, the state of water in a polymer can be divided into free water, freezing bound water, and nonfreezing bound water. Free water is the water that does not take part in hydrogen bonding with polymer molecules. It has a transition temperature, enthalpy, and DSC curves similar to those of pure water. Freezing bound water is the water that interacts weakly with polymer molecules. Nonfreezing water is the water molecules that are bound to polymer molecules through hydrogen bonds. This kind of water shows no endothermic peak in the temperature range of −70 to 0°C.

Figure 3 shows the DSC thermograms of water-swollen IPN hydrogels. Two melting peaks in the IPN hydrogels can be seen in the DSC curve, indicating that free water and freezing bound water exist in the IPN hydrogels. As a rule, DSC is used to determine the amount of free water that is not bound by hydrogen
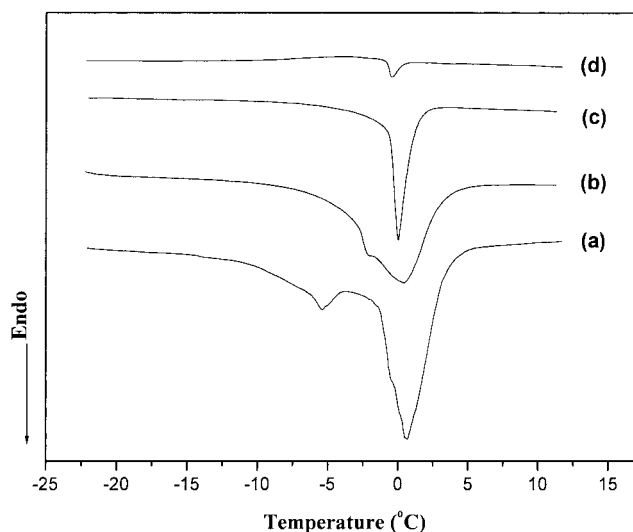
Figure 3 DSC thermograms of swollen IPN hydrogels: (a) c-PEO, (b) PC4-1, (c) PC1-1, (d) PC1-4.

IPN (PEO : PMMA)	Total water (%)	Free water (%)	Bound water (%)
1 : 4	13.82	0	13.82
1 : 1	59.49	31.08	28.41
4 : 1	67.83	37.39	30.44

[a] All samples were fully swollen in distilled water for 24 h at 25°C.

bonding. The fraction of free water of the total water is listed in Table II. Bound water attributed to hydrogen bonding with the PEO chains is expressed as the difference between the total water and the free water. The endothermic peaks appearing around 0–4°C, shown in Figure 3, were attributed to the presence of free water in the hydrogels. As can be seen in Table II, the bound water contents of PC1-4 to PC4-1 range between 13 and 31% of the total water. However, the amount of free water increased with PEO content in the hydrogel. This indicates that the increase of EWC with PEO content is attributed mainly to the free water content in the hydrogel. Corkhill and Tighe[22] prepared high EWC (>70%) semi-IPN hydrogels based on cellulose ester and N-containing hydrophilic monomers. They also reported that the hydrogels could be used as wound coverings and implant materials requiring high EWC. In this respect, PEO/PMMA IPN hydrogels in the present work have useful EWCs.[23]

The sorption data were analyzed by use of the following equation:

$$M_t/M_\infty = kt^n$$

where M_t and M_∞ represent the amount of water uptake at times t and ∞, respectively; k is a characteristic constant of the hydrogel; and n is a characteristic exponent of the mode of transport of the penetrating molecule.[24] It is noted that for Fickian kinetics, where the rate of diffusion of the penetrant is rate limiting, $n = 0.5$. For non-Fickian processes, where contributions from other processes such as polymer relaxation are important, $n = 0.5–1$.[25] Plots of $\ln(M_t/M_\infty)$ against $\ln t$ using the present experimental sorption data yielded $n = 0.653$ and $k = 0.0426$ for PC4-1, $n = 0.0639$ and $k = 0.0403$ for PC1-1, and $n = 0.597$ and $k = 0.0344$ for PC1-4. Because the sorption exponent for the three hydrogels studied were all above 0.5, it can be concluded that the overall process is non-Fickian because of polymer relaxation. Diffusion coefficients of IPN hydrogels in pure water at 25°C were calculated and the diffusion coefficients for thin films were calculated by utilizing diffusion equations first developed by Crank and Park.[26] A sample of thin film was sus-

pended in the sorption apparatus and the kinetics of sorption for a single step in humidity was recorded in the usual manner. For a single step in a controlled humidity, a double-sided thin film of thickness d, the initial kinetics of sorption into the bulk may be described by the following equation:

$$\frac{M_t}{M_\infty} = \frac{4}{d}\sqrt{\frac{Dt}{\pi}}$$

where M_t is the amount adsorbed at time t, M_∞ is the amount adsorbed when thermodynamic equilibrium was reached, and D is the diffusion coefficient. The above equation is typically valid for values of $M_t/M_\infty < 0.4$, where a plot of M_t/M_∞ against $\sqrt{t}/d$ should be linear. The diffusion coefficients of IPN hydrogel samples may then be calculated from the slope of this line, as shown in Figure 4. The diffusion of water vapor into 3- to 10-mg samples of PEO/PMMA IPN hydrogel film with thicknesses between 20 and 30 microns was studied using a dynamic sorption instrument. The thin film was exposed to humidity increasing in steps from 0% relative humidity, such that both sorption and desorption were measured for each discrete humidity above 0% RH. The data-acquisition interval was set at 2 s, given that the kinetics was expected to be fast. The water diffusion coefficients (cm^2/s) of each IPN film were calculated from the slope of the linear line below $M_t/M_\infty < 0.4$ (Fig. 4). The water diffusion coefficient of PC4-1 film was 3.32×10^{-7} cm^2/s. This value is higher than those of PC1-1 and PC1-4 films (2.03×10^{-7} and 2.01×10^{-8} cm^2/s) at 25°C and 95% RH. Generally, PEO has a high affinity for water because of the hydrophilic groups and, depending on its degree of crystallinity, may or may not be water soluble. With an increase in the hydrophilic content of the IPN hydrogels, the values of diffusion
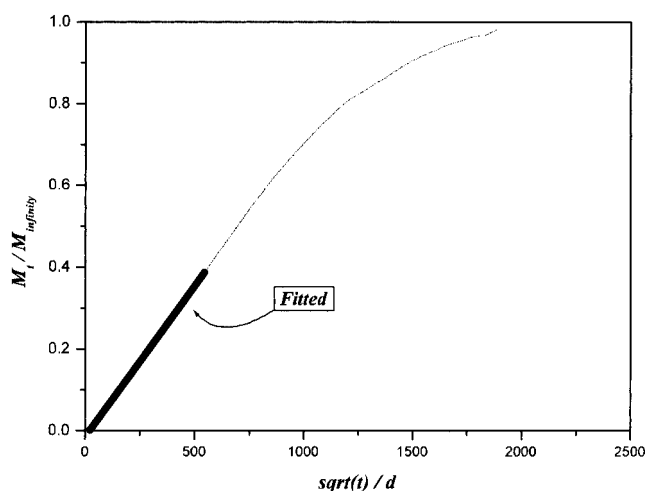
Figure 4 Water sorption isotherm of sample PC4-1 at 25°C.

coefficients were found to increase as a result of greater penetration of water into the hydrogels.

CONCLUSIONS

Hydrogels based on PEO and PMMA were prepared using the simultaneous IPN method. Free-radical polymerization was used to promote IPN formation within the crosslinked PEO network with the MBAA and PMMA networks with EGDMA. FT-IR spectroscopy confirmed the structure of PEO/PMMA IPN hydrogels. DSC measured water and bound water for the IPN hydrogel. From the results of DVS, EWC values of IPN hydrogels were in the range of 13–68%. All IPN hydrogels exhibited a relatively high swelling ratio that increased with PEO content and reached equilibrium within 6 h. The water diffusion coefficient of the PC4-1 value is higher than those of PC1-1 and PC1-4.

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