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Interpenetrating polymer network hydrogels based on poly(ethylene glycol) macromer and chitosan

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Abstract

Interpenetrating polymer network (IPN) hydrogels were prepared by UV irradiation of solutions in mild aqueous acid media of poly(ethylene glycol) macromer (PEGM) with chitosan in the presence of glutaraldehyde as a crosslinking agent. Hydrogels obtained were characterized by using FT-IR, FT-Raman, wide angle X-ray diffractometry (WAXD), differential scanning calorimetry (DSC) and dielectric analysis (DEA). Equilibrium water content (EWC) of these hydrogels was in the range of 74–97%. Photocrosslinked PEGM segments within the IPNs had considerably reduced crystallinities compared to PEGM itself. All the IPNs revealed two glass transition temperatures (T_g), indicating the presence of phase separation in the IPNs. In addition, T_g values of PEGM segments were reduced with decreasing crosslinking degree. The tensile strength and elongation at break of IPNs hydrogels in the swollen state ranged from 0.06 to 0.18 MPa and 18–48%, respectively. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Interpenetrating polymer networks; Poly(ethylene glycol); Hydrogels

1. Introduction

Chitin is the second most abundant natural polymers having β(1-4)-linked *N*-acetylglucosamine repeat units. In spite of its availability, chitin has limited applications because of strong inter- or intramolecular hydrogen bonding caused by acetamide groups in glucopyranose residues. However, solubility, reactivity and processability of chitin has been improved by chemical modification (Kim, Kim & Lee, 1994a). Deacetylation of chitin, the most facile chemical alteration gives a useful derivative, named chitosan. Chitosan is more readily processable into films and membranes from most aqueous acid solutions than chitin (Kim & Lee, 1993; Lee & Shin, 1991; Lee, Nam & Kim, 1992). It has already been reported to be suitable for biomedical applications such as sutures, controlled release of drugs and wound dressings (East & Qin, 1993; Wei, Hudson, Mayer & Kaplan, 1992; Yao, Peng, Goosen, Min & He, 1994). Moreover, wound dressings based on chitin or chitosan are long known to more than double the rate of wound-healing, from 30 to 75% (Balassa & Prudden, 1978). Recently, there have been many reports on the preparation of hydrogels from natural polymers for biomedical applications (Kamath, Kincaid & Mandal, 1996; Singh & Ray, 1994).

We prepared of hydrogel films from β-chitin and poly(ethylene glycol) diacrylate macromers (PEGM) for use in wound dressing (Kim, Lee & Cho, 1995). These hydrogels have a semi-interpenetrating polymer network (semi-IPN) structure. Although β-chitin is more soluble in many organic solvents such as formic acid, dimethylacetamide–lithium chloride and trichloroacetic acid than α-chitin, it should be carefully treated to minimize degradation of the polymer backbone in some cases (Kim, Kim & Lee, 1996). In addition, when it is applied to wounded human skin or tissue, even very small quantities of residual solvent may be harmful. More recently, therefore, semi-IPN hydrogels composed of β-chitosan and PEGM were prepared from weak aqueous acetic acid solution (Lee, Kim & Kim, 1997). In this case however, the mechanical strength of PEGM/β-chitosan hydrogels was much lower than that of PEGM/β-chitin hydrogels. Since hydrogels have a large amount of water in their network structure, they show the characteristic properties of natural tissues.

Most hydrogels, have low mechanical strengths particularly at high water contents. Hydrogels for contact lenses, articular cartilage and wound dressings require relatively good mechanical properties (Corkhill & Tighe, 1990).

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Table 1
Sample preparation, water contents, thermal properties and mechanical properties of IPN hydrogels

Sample code	PEGM (wt%)	Chitosan (wt%)	EWC (%)	Free water (%)	Bound water (%)	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	ΔH_f (J/g)	Crystallinity (%)	Tensile strength (MPa)		Elongation (%)	
											Dry	Wet	Dry	Wet
PEGM	100	0	–	–	–	-50[a]	–	59	177	81	–	–	–	–
IPN-1	50	50	74	37	37	15	134	42	13	6	5.16	0.18	20.7	47.9
IPN-2	33	67	75	37	38	13	133	43	5	2	5.69	0.08	23.0	32.1
IPN-3	25	75	97	79	18	5	133	42	2	< 1	4.98	0.06	10.1	18.2
Chitosan	0	100	–	–	–	–	150	–	–	–	–	–	–	–

[a] Observed from DSC. All other T_gs are from DEA at 100 Hz.

Corkhill, Fitton and Tighe (1993) prepared hydrogels for synthetic articular cartilage. They reported that semi-IPNs including cellulose acetate butyrate as a reinforcing agent improved their mechanical properties.

There are two basic synthetic routes for IPNs; sequential and simultaneous IPNs (Sperling, 1994). PEGM/chitosan hydrogels in the present study are prepared by the simultaneous IPN method. Crosslinked chitosan is produced via Schiff's base reaction of amino groups in chitosan and aldehyde groups in glutaraldehyde. Since PEGM is a water-soluble and non-toxic prepolymer that can be crosslinked, a PEGM network can be prepared simply by UV irradiation. In addition, intermolecular association through hydrogen bonding between amino hydrogen in chitosan and oxygen in PEGM contributes to interpenetration of PEGM within a crosslinked chitosan network (Yao, Peng, Goosen, Min & He, 1993).

In this paper, preparation and properties of simultaneous IPN hydrogels based on PEGM and commercially available chitosan from shrimp are described for possible application to transdermal drug delivery matrix or wound dressing materials.

2. Materials and methods

2.1. Materials

Chitosan (degree of deacetylation was 0.76 and viscosity-average molecular weight was 5×10^5) was purchased from Tokyo Kasei Organic Chemicals. PEG ($M_n = 6000$) was purchased from Showa Chemical Inc. and used after azeotropic distillation with benzene (Junsei Chemical Co., Ltd.). Acryloyl chloride and 2,2-dimethoxy-2-phenyl acetophenone as a photoinitiator were supplied by Aldrich and used without further purification. Glutaraldehyde (25% solution) and acetic acid were obtained from Junsei Chemical Co., Ltd. and J.T. Baker Inc., respectively. All other reagents were of extra pure grade and used as received.

2.2. Synthesis of PEGM/chitosan IPNs

PEGM was synthesized by the previously reported method (Kim et al., 1995) and dissolved in 2 wt% acetic acid to give 10 wt% PEGM solution. Chitosan was also dissolved in 2 wt% acetic acid and the solid content in solution was 1.5 wt%. A given amount of PEGM/chitosan mixed solution was obtained by mechanical stirring for 2 h. To this was added 2,2-dimethoxy-2-phenyl acetophenone (0.45 wt% based on the weight of PEGM) and 5×10^{-5} mol of glutaraldehyde under agitation. The mixed solution was poured into a circular glass mould and was maintained at room temperature. Then, UV irradiation was performed to polymerize and crosslink PEGM within the crosslinked chitosan network using a 450 W UV lamp (Ace Glass Co.) placed above the mould at a height of 20 cm for 1 h until gelation occurred. Finally, IPN samples obtained were washed with deionized water and dried under high vacuum for 2 days. Table 1 lists the composition of PEGM/chitosan used for preparing IPNs.

2.3. Measurements

Fourier transform infrared (FT-IR) with a Raman module were used to obtain spectra of all the samples (Nicolet Model Magna IR 550). To investigate the crystalline characteristics of IPNs as well as PEGM and chitosan, a wide-angle X-ray diffractometer (WAXD, Rigaku Denki) was employed. WAXD patterns were recorded by the reflection method with nickel-filtered CuKα radiation operated at 50 kV, 180 mA in the 2θ scanning mode between 5 and 35°. Equilibrium water content (EWC) was measured by the conventional gravimetric method. Preweighed dry samples were immersed in deionized water and excess surface water was blotted out with absorbent paper. The weight of swollen samples was measured at a given time interval. The swelling procedure was repeated until there was no further weight increase. EWC was calculated as the weight increase with respect to the weight of swollen sample using the following equation:

$$\mathrm{EWC}\ (\%) = \frac{W_s - W_d}{W_s} \times 100$$

where, W_s and W_d denote the weights of swollen and dry samples, respectively. Differential scanning calorimetry (DSC, Du Pont Instruments 910) was employed to examine the crystallinities of IPN hydrogels by observing the melting endotherms. Measurement was carried out from 20 to 70°C with a heating rate of 10°C/min under 50 cc/min of nitrogen flow. DSC melting thermograms of samples were obtained from the second run. The state of water in the swollen hydrogels with different water content was also evaluated from DSC analysis. Samples sealed in aluminium pans were cooled down to −25°C and then heated to 25°C at a heating rate of 5°C/min under 50 cc/min of nitrogen flow. The fraction of free water in total water was approximately calculated as the ratio of endothermic peak area for water-swollen hydrogel to melting endothermic heat of fusion (334 J/g) for pure water. Bound water due to hydrogen bonding with the PEG chains was expressed as the difference between the total water and the free water. Glass transition of IPNs was investigated by dielectric analysis using TA Instruments DEA 2970 with a parallel plate ceramic sensor. The experiment was done from −60 to 200°C at a rate of 3°C/min with dry nitrogen adjusted to a flow rate of 500 cc/min. Applied frequencies were 1, 10, 100 and 1000 Hz. Mechanical properties of IPN hydrogels were measured on a universal testing machine (UTM, Hounsfield 10 KM) with a crosshead speed of 2 mm/min under 50 kg load cell. Reported values are the mean of five specimens and the deviation from the mean is within ±5%.

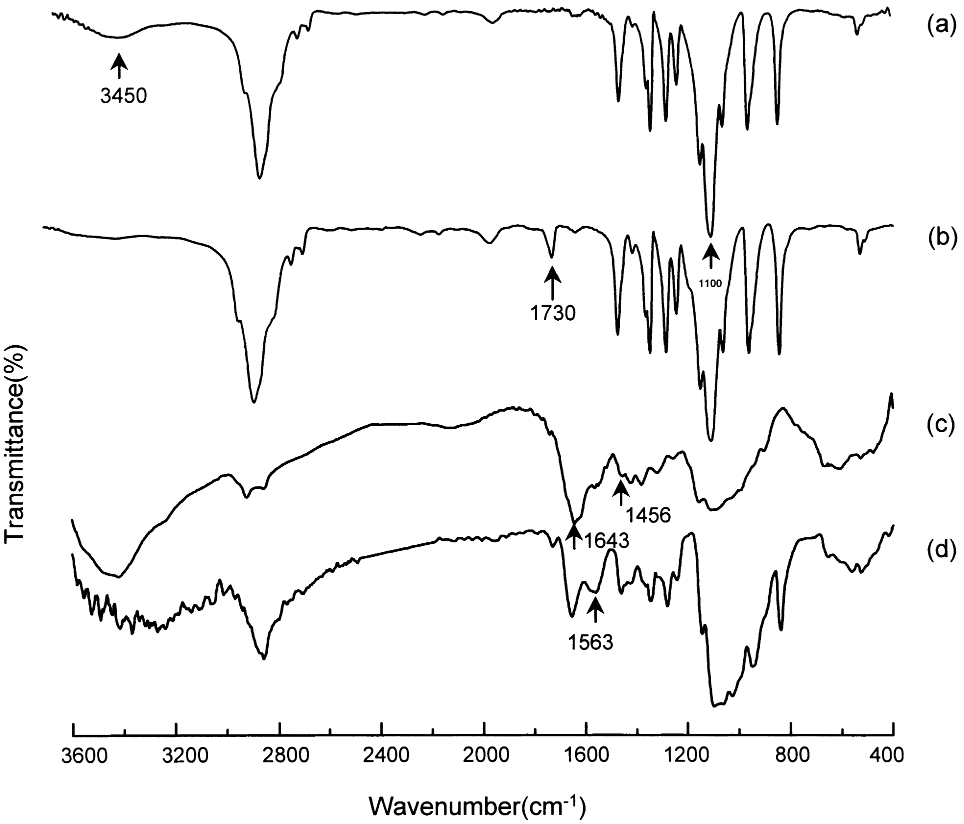

Fig. 1. FT-IR spectra of (a) PEG; (b) PEGM; (c) chitosan and (d) PEGM/chitosan IPN.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the FT-IR spectra of PEG, PEGM, chitosan and PEGM/chitosan IPN. Peaks at around 3450 and 1110 cm^{-1} in PEG are assigned to the terminal hydroxyl group and C–O stretching of polyether, respectively. In the case of PEGM, a new peak appears at 1730 cm^{-1}, that can be attributed to the formation of an ester carbonyl bond due to the reaction between acryloyl chloride and hydroxyl group in PEG. In comparison with spectra of PEG, –OH stretching vibration peak at around 3400 cm^{-1} disappears in the PEGM. There is a characteristic amino peak (1456 cm^{-1}) of chitosan as seen in Fig. 1(c). A peak at 1643 cm^{-1} is attributed to amide I band caused by the remaining acetamide group in chitosan. Fig. 1(d) shows a significant peak at 1563 cm^{-1} due to imine bonds (C=N) formed by crosslinking reaction between amino groups in chitosan and aldehyde groups in glutaraldehyde.

Fig. 2 shows the FT-Raman spectra of PEG and PEGM. In comparison with FT-IR spectra, stronger Raman peaks could be obtained for non-polar vibration than for polar one. A new peak appeared at 1630 cm^{-1} in Fig. 2(b) for PEGM indicates conjugated C=C bonds of dimethacrylate in PEGM, which did not appear in PEG (Fig. 2(a)) and were not identified in the FT-IR spectra (Fig. 1). From FT-IR and Raman spectroscopy, it can be deduced that the crosslinked polymers are present as interpenetrating networks.

The crystalline characteristics of IPNs as well as PEGM and chitosan are shown in Fig. 3. PEGM exhibits sharp crystalline peaks at around $2\theta = 18.9$ and 23.0° in the WAXD patterns. Although PEGM is a modified PEG where the terminal hydroxyls are converted into dimethacrylate, as might be expected, highly crystalline structure of PEGM is not much changed compared with PEG. It has been reported that the crystallinity of chitosan depends on the degree of deacetylation (Kurita, Tomita, Tada, Ishii, Nishimura & Shimoda, 1993). The crystalline structure of shrimp chitosan is retained up to a deacetylation degree of 70%. On further deacetylation, the chitosan has less ordered structure resulting in lower crystallinity. At more than 90% degree of deacetylation, however, crystallization of chitosan takes place again. Chitosan (76% degree of deacetylation) used in the present work shows small but wide peaks due to crystalline regions as shown in Fig. 3(f). On the other hand, the crystallinity of PEGM network in IPNs remarkably decreases with increasing chitosan content. Crystallinity changes of chitosan network upon crosslinking were not shown by the X-ray diffraction pattern because of the low degree of crystallinity of chitosan as a starting material.

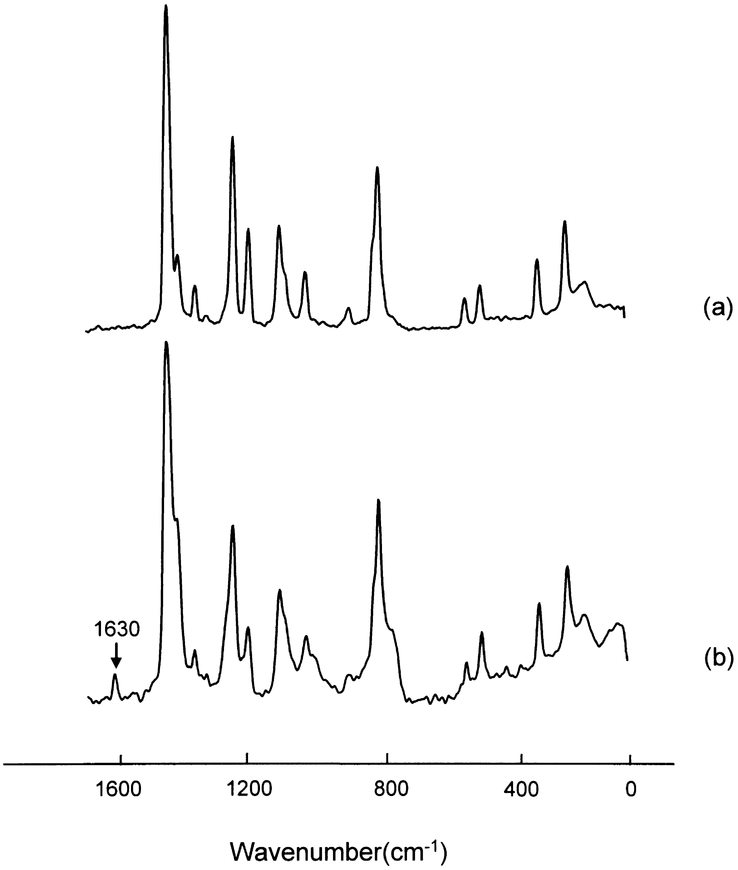

Fig. 2. Raman spectra of (a) PEG and (b) PEGM.

3.2. Swelling behaviour

Fig. 4 shows the water content of IPN hydrogels measured at various time intervals. These samples reveal a rapid increase in water content and reach an equilibrium within 40 min. All the hydrogels have a high EWC, in the range of 74–97%, even if reliable swelling kinetics data are not obtained on account of the very rapid swelling process. In general, swelling of hydrogels based on PEG has been reported within tens of minutes (Vyavahare & Kohn, 1994). In order to verify the equilibrium state, we immersed the gels in distilled water for 2 h before the swelling measurements were carried out. IPN hydrogels from the combination of hydrophilic PEGM and chitosan give a high EWC. IPN-3 possesses less crosslinkable double bonds compared to the other IPNs. Accordingly, IPN-3 retains the largest amount of water among the samples studied. No large differences can be seen between IPN-1 and IPN-2. This behaviour may be due not only to the crosslinking degree of PEGM network but also to the content of chitosan having a large number of water-binding sites. Water contents in IPN hydrogels are listed in Table 1. Free water and bound water contents are measured from the DSC melting thermograms of swollen hydrogels and calculated as previously described (Kim et al., 1995; Sawhney, Pathak & Hubbell, 1993). Corkhill and Tighe (1990) 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 dressing and implant materials requiring high EWC. In this respect, PEGM/chitosan IPNs hydrogels in the present work have useful EWCs.

3.3. Thermal characterization

Fig. 5 shows the DSC melting thermograms of PEGM and IPN hydrogels. PEGM reveals a sharp melting endothermic peak at 59°C, whereas broader and weaker melting peaks of PEGM within IPNs are observed at around 42°C. While the photocrosslinking reaction was performed in the solution, the reorientation of PEGM segments was limited, resulting in a further decrease in the crystallinity of the IPNs as compared to the linear PEGM. Subsequently, the melting temperature of the PEGM segments in the IPNs was significantly lower than that of the linear PEGM. This result is in agreement with previous reports on the degree of crystallinity of a polymer and its melting temperature (Lee & Kim, 1997; Vyavahare & Kohn, 1994). On the other hand, the decrease in crystallinity of chitosan network cannot be determined from DSC analysis. Although chitosan has crystalline regions, the crystalline melting temperature (T_m) is not found because of rigid-rod polymer backbone having

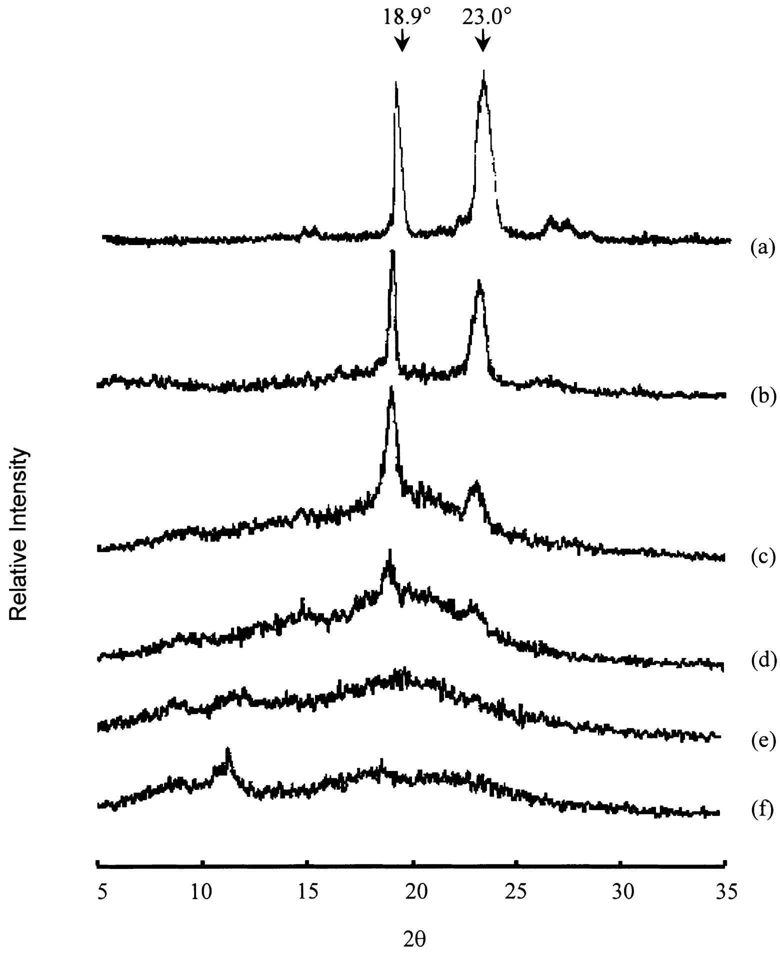

Fig. 3. WAXD patterns of (a) PEG; (b) PEGM; (c) IPN-1; (d) IPN-2; (e) IPN-3 and (f) chitosan

strong inter- and/or intra-molecular hydrogen bonding. This behaviour is frequently detected in many polysaccharides such as cellulose and chitin derivatives (Kim, Kim, Moon & Lee, 1994).

As a rule, the crystallinity of a polymer is calculated from the ratio of heat of fusion (ΔH_f) measured at T_m for the polymer sample and corresponding 100% crystalline polymer. Melting endothermic areas of PEGM network in IPNs are reduced in comparison with the linear PEGM. Endothermic peak patterns of IPNs are obviously caused by crosslinking reaction of PEGM network. The decrease in crystallinity is a typical feature for a crosslinked polymer. T_m, ΔH_f and crystallinity of each sample are listed in Table 1.

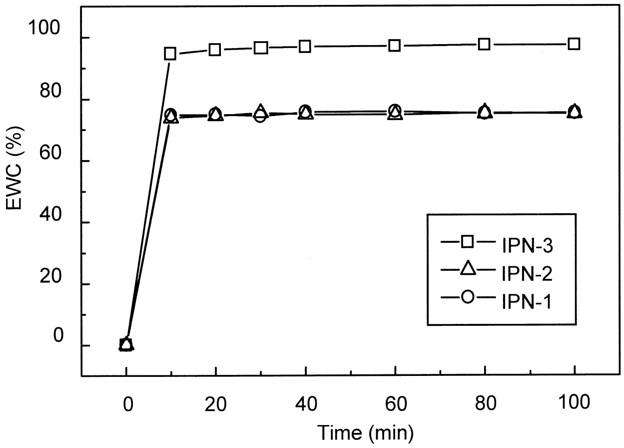

Fig. 4. Swelling kinetics of IPN hydrogels.

3.4. Dielectric properties

Dielectric thermal analysis was conducted and shown in Fig. 6. These curves exhibit log tan δ dissipation factor, obtained from ε' (dielectric constant) and ε'' (loss factor) for each sample. All IPNs have three relaxation transition peaks. In Fig. 6(a), the peak in each of the tan δ curves between -13 and 25°C, is assigned to a glass transition temperature (T_g) of PEGM in IPN-1. Since uncrosslinked PEGM shows glass transition behaviour at around -50°C (Lee et al., 1997), it can be confirmed that the T_g shifts to higher temperature due to the presence of a crosslinked network. In addition, the T_g of PEGM segment becomes higher as the DEA measurement frequency is increased.

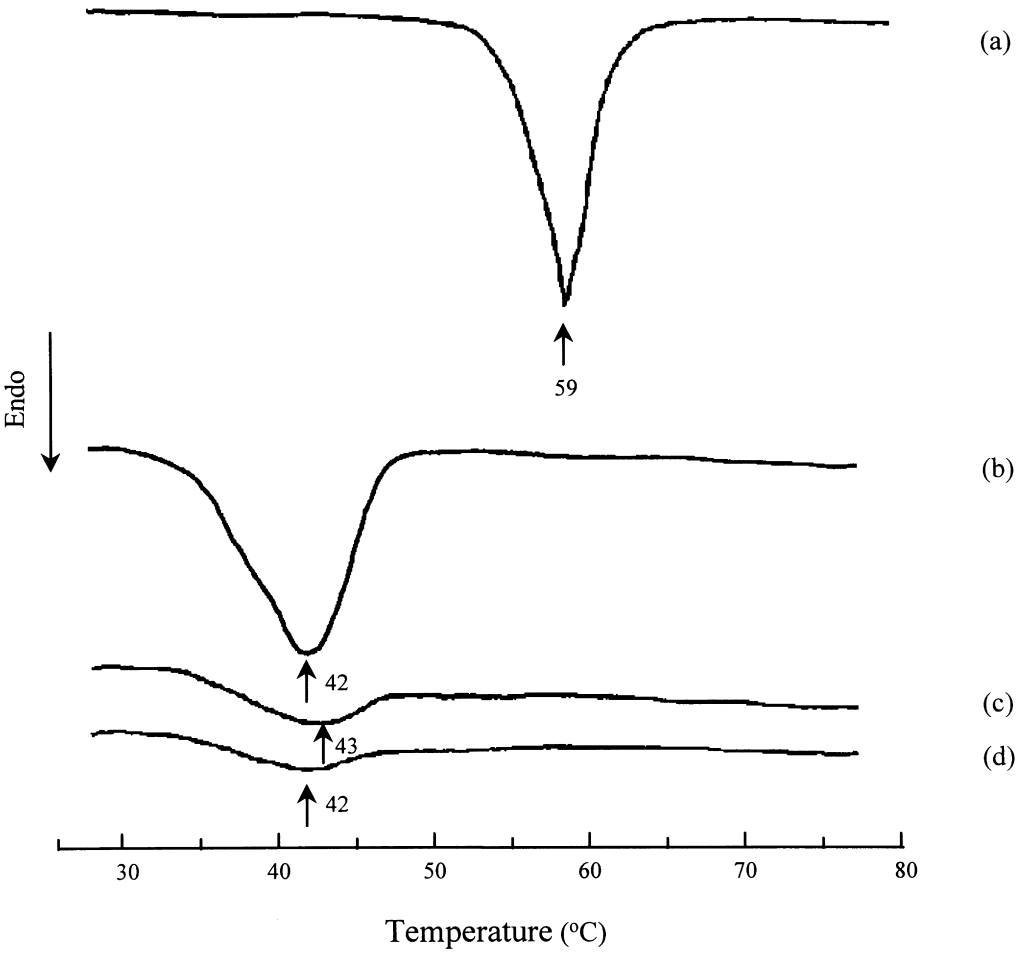

Fig. 5. DSC melting endotherms of dry hydrogels: (a) PEGM; (b) IPN-1; (c) IPN-2 and (d) IPN-3.

This is a general consequence attributed to a decrease in the steric effects hindering the micro-Brownian motion of the main chain (Woo, 1993). A slight decrease in T_g of IPN-2 (Fig. 6(b)) and IPN-3 (Fig. 6(c)) compared to IPN-1 may be due to the lower degree of crosslinking. Another relaxation transition at around 50°C was thought to be the T_m of the PEGM segments in the IPNs as was found from DSC analysis.

The other T_g event, even if not resolved at all analysis frequencies, is observed at around 130°C. It is considered to be main chain relaxation of chitosan network in the IPNs because T_g of chitosan appears at above 150°C (Maeko, Hiromasa, Tatsuya & Teruo, 1988; Nam & Lee, 1997). In particular, tan δ peaks at 100 Hz show two well-defined transitions associated with T_g of PEGM at approximately 25°C and chitosan at 130°C, indicating the presence of phase separation in IPNs. Table 1 also summarizes the thermal properties and relaxation temperatures.

3.5. Mechanical properties

Mechanical properties of IPN hydrogels in the dry and swollen states are listed in Table 1. IPN hydrogels in the dry state are somewhat brittle having low elongation-at-break. IPN-2 shows slightly higher value of tensile strength than that of IPN-1, probably due to the higher rigidity or stiffness of the polymer chain with increased chitosan content (Kim et al., 1996; Shinichi & Noriko, 1996; Yoshiyuki & Naoto, 1992). Nevertheless the tensile strength of IPN-3 in the dry state is the lowest of the three samples. Although the chitosan content is high, the low crosslinking degree results in a much weaker hydrogel. This tendency is also clearly seen in the swollen state. The crosslinking degree in the network plays a major role in enhancing the tensile strength of IPN hydrogels. The tensile strengths of samples in the swollen state are rather low, even if these values are higher than that of PEGM/β-chitosan semi-IPN hydrogels. It might be expected that tensile strength of these hydrogels can be improved by controlling the crosslinking degree and chitosan content. On the other hand, elongation-at-break in the swollen state ranges from 18 to 48% as the chitosan content affects the decrease in flexibility in the IPNs.

4. Conclusions

Hydrogels based on PEGM and chitosan were prepared

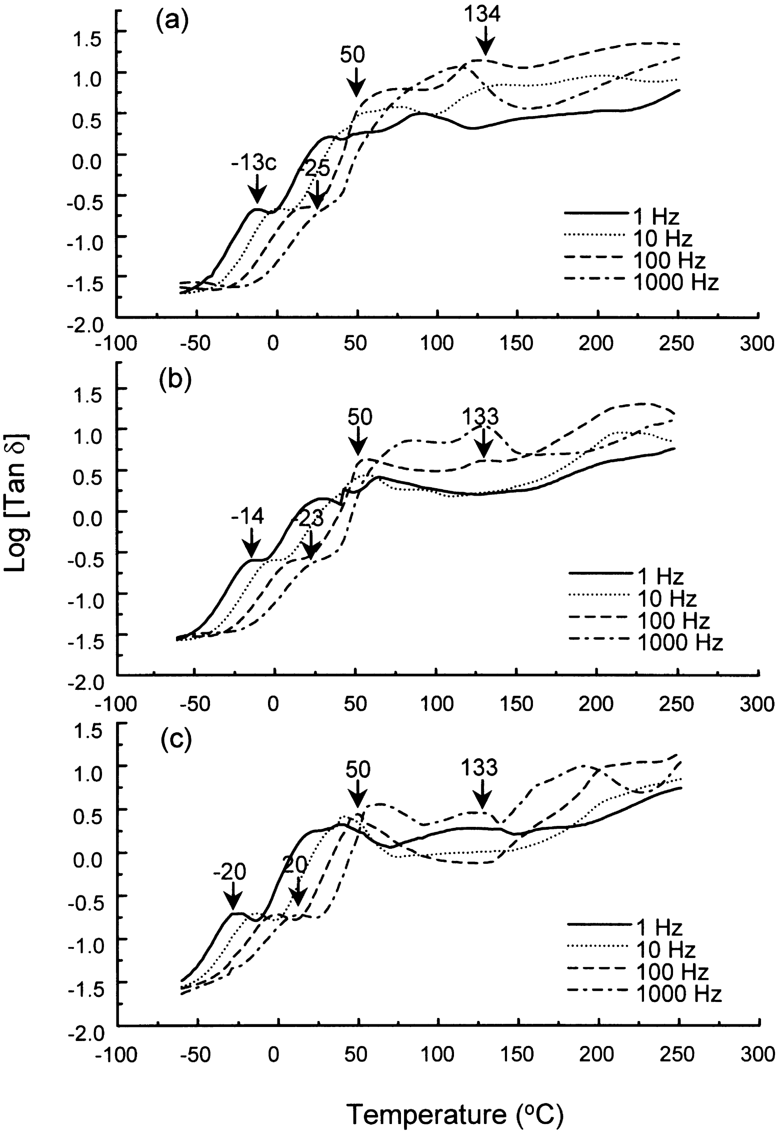

Fig. 6. Relaxation behaviours observed by DEA: (a) IPN-1; (b) IPN-2; and (c) IPN-3.

by the simultaneous IPN method. UV irradiation was used to promote IPN formation within the crosslinked chitosan network with glutaraldehyde. FT-IR spectroscopy and WAXD patterns confirmed the structure of PEGM/chitosan IPNs. Photocrosslinked PEGM segments within IPNs had considerably reduced crystallinities in comparison with uncrosslinked PEGM. EWC of hydrogels was in the range of 74–97%. From the result of DEA, all the IPNs exhibited two T_gs, which appeared in the middle of two respective T_gs of PEGM and chitosan, indicating the presence of phase separation in the IPNs. A slight decrease in T_g of PEGM within IPN-2 and IPN-3 compared to IPN-1 might be due to the lower crosslinking degree. Mechanical properties of hydrogels depended upon the crosslinking degree of the network and the chitosan content.

Acknowledgements

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