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Semi-interpenetrating polymer network hydrogels between polydimethylsiloxane/polyethylene glycol and chitosan

Nantharak Rodkate, Uthai Wichai, Boonjira Boontha, Metha Rutnakornpituk*

Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand

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ABSTRACT

Synthesis and properties of semi-interpenetrating polymer networks (semi-IPNs) based on polydimethylsiloxane (PDMS)/poly(ethylene glycol) (PEG)-modified chitosan were studied. 1–20 wt% of PDMS or PEG was interpenetrated into chitosan hydrogels having 10 wt% of hexamethylene-1,6-di-(aminocarboxysulfonate) (HDA) as a water-soluble crosslinker. PDMS prepolymer was synthesized *via* acid-catalyzed ring-opening polymerization of octamethylcyclotetrasiloxane (D_4), followed by hydrosilylation reaction with allyl alcohol to obtain hydroxyl-terminated PDMS. Effect of PDMS/PEG contents (1–20 wt%) and their molecular weights (2000 and 8000 g/mol) in chitosan semi-IPNs on percent crosslinking, water swelling properties, thermal stability, surface properties, water vapor permeability and tensile properties were investigated. Percent crosslinking of the PDMS/PEG-chitosan semi-IPNs ranged between 42% and 74% depending on molecular weight and percent of PDMS/PEG added. PDMS and PEG in the semi-IPNs enhanced water swellability and water vapor permeability of the films. Also, PDMS/PEG in chitosan semi-IPNs enhanced their thermal stability and surface hydrophobicity, while their tensile properties were sacrificed.

1. Introduction

Chitosan, prepared by alkaline deacetylation of chitin, is a biodegradable, biocompatible, and inexpensive natural polymer which comprises of β-(1,4)-2-amino-2-deoxy-D-glucopyranose units (Mao et al., 2005; Wu et al., 2005; Zeng, Fang, & Xu, 2004). It has gained marked attraction in last few decades owing to its potential applications in medicine, cosmetics, agriculture and biomaterials. In particular, excellent activity as a wound healing accelerator (Ishihara et al., 2002; Khan, Peh, & Ch'ng, 2000; Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domb, 2004) combined with antibacterial capability and good tissue compatibility of chitosan, made it become an excellent wound dressing material (Mi, 2005; Mi, Tan, Liang, & Sung, 2002; Mi, Sung, Shyu, Su, & Peng, 2003). However, limited solubility of chitosan in water and common organic solvents inhibited its extensive studies and utilization (Morita, Sugahara, Ibonai, & Takahashi, 1999). Modifications of chitosan with polymers have been widely investigated to tune its properties to acquire some requirements for specific applications. These were carried out either by physical blending, chemical grafting, or crosslinking (Gibson, Walls, Kennedy, & Welsh, 2003; Welsh, Schauer, Qadri, & Price, 2002; Zeng et al., 2004; Zeng & Fang, 2004).

Graft copolymer of chitosan and L-lactic acid (CL) was prepared by grafting L-lactic acid onto the amino groups in chitosan without using any catalyst to improve tensile strength and water uptake properties of the CL films (Yao et al., 2003). Semi-interpenetrating polymer network (semi-IPN) microspheres of acrylamide grafted on dextran (AAm-*g*-Dex) and chitosan (CS) crosslinked with glutaraldehyde were prepared by a water-in-oil emulsion method for controlled release of acyclovir (Ajit, Sangamesh, & Tejraj, 2006). The cumulative release of the entrapped drug in the microspheres ranged from 20% to 40% with an in vitro release within 12 h. PEG-crosslinked chitosan hydrogel film was prepared by crosslinking chitosan with diepoxy PEG (Tanuma et al., 2010). The swelling ratio increased when decreasing pH of the solution or decreasing $\overline{M}_n$ of PEG. Crosslinked chitosan (CS) membrane with sub-micrometer porous structure was prepared by extraction of PEG phase from CS/PEG semi-IPN membrane (Zeng & Fang, 2004). The membrane showed reversible and rapid responses in swelling as the solution pH changed. It also showed good mechanical strength both in dried and swollen states. In our previous paper, PEG-PDMS block copolymer, prepared by a condensation reaction between PEG diacid and PDMS diol, was incorporated to chitosan in order that good water swellability and wettability of chitosan were retained due to hydrophilic PEG blocks, whereas PDMS block in the copolymers functioned as a toughening modifier (Rutnakornpituk, Ngamdee, & Phinyocheep, 2005a; Rutnakornpituk & Ngamdee, 2006). However, some macroscopic phase separation between the copolymer and chitosan was still observed when high percent of the copoly-

* Corresponding author. Tel.: +66 55 96 3464; fax: +66 55 96 3401.
E-mail address: methar@nu.ac.th (M. Rutnakornpituk).

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mer was applied due to the absence of chemical bonding between these two phases.

In the current report, PDMS or PEG representing hydrophobic and hydrophilic polymers, respectively, was interpenetrated in chitosan networks. PDMS is of particular interest in this work owing to their unique properties, e.g. low toxicity, high oxygen permeability, good flexibility, good thermal and oxidative stability (Guo, Han, Wang, Xiao, & Dai, 2007; Rutnakornpituk, Ngamdee, & Phinyocheep, 2005b; Wang, Xu, & Chen, 2007). It is also widely used in medical applications due to its biocompatibility, good oxidative stability and high oxygen permeability (Akimoto, Aoyagi, Minoshima, & Nagase, 1997). Turning now to the hydrophilic polymer representative, PEG is a well-known nontoxic polymer, which is favorable for most of medical applications (Nikolova, Manolova, & Rashkov, 1998; Ouchi, Nishizawa, & Ohya, 1998). PEG is widely used as precipitants and crystallization agent for protein (Kumar, Sharma, & Kaloni, 2009; Price, Cornelius, & Brash, 2001; Shu, Zhang, Teng, Wang, & Li, 2009; Shulgin & Ruckenstein, 2006; Zhang, Li, Gong, Zhao, & Zhang, 2002). One can also vary its $\overline{M_n}$ to adopt the optimal value for the precipitation of a particular protein. Therefore, incorporation of PDMS/PEG into chitosan hydrogel was focused herein. However, a major limitation of adding PDMS/PEG into chitosan is their immiscibility, resulting in phase separation. Chemical crosslinking of PDMS/PEG in chitosan should improve the miscibility of the system. PDMS/PEG-modified chitosan semi-IPNs were prepared using a water-soluble diisocyanate derivative as a crosslinker. Effect of molecular weight ($\overline{M_n}$) and concentration of PDMS/PEG in the networks on the properties such as percent crosslinking, water swelling behavior, surface morphology, tensile strength, water contact angle, and water vapor permeability, were investigated.

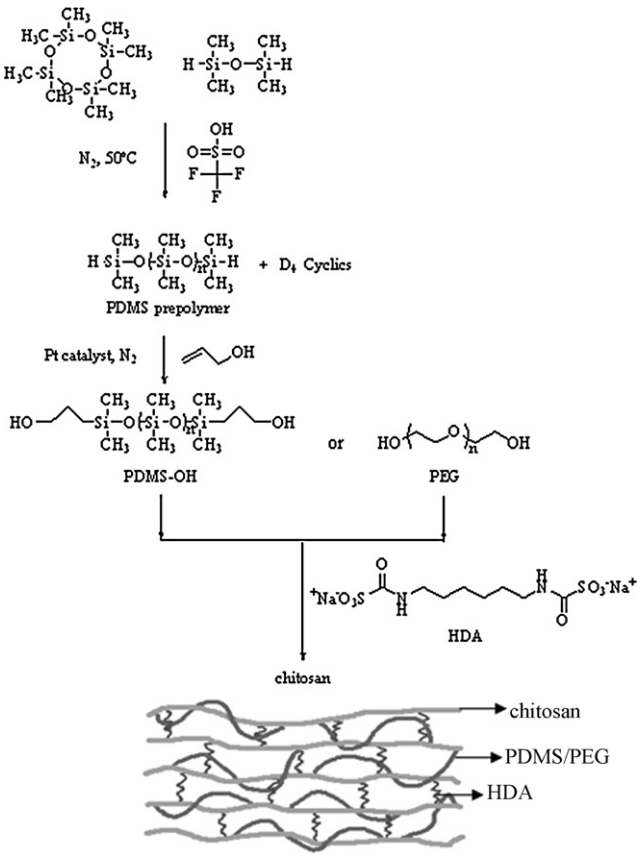

Fig. 1. Semi-IPNs of chitosan hydrogels modified with PDMS/PEG.

2. Experimental

2.1. Materials

Chitosan from crabs (Taming Enterprise, Co.) with 98% deacetylation and poly(ethylene glycol) ($\overline{M_n}$ 2000 and 8000 g/mol) (Acros), were used as received. Octamethyl cyclotetrasiloxane (D_4), 99% (Fluka) was stirred in CaH_2 and distilled prior to use. 1,1,3,3-Tetramethyldisiloxane, 97% (Acros) and allyl alcohol, 99% (Acros) were fractionally distilled before used. Karstd's catalyst (Aldrich), triflic acid, 98% (Aldrich), 1,6-hexamethylene diisocyanate (HDI), 99% (Acros) and sodium metabisulphite, $Na_2S_2O_5$ (Carlo Erba reagent) were used as received.

2.2. Synthesis

2.2.1. Synthesis of dihydrogen-terminated polydimethylsiloxane (PDMS prepolymer)

Synthesis of PDMS prepolymer with targeted $\overline{M_n}$ of 2000 g/mol (PDMS 2K) is provided. The PDMS prepolymer was synthesized *via* a ring-opening polymerization of D_4 (20 g, 0.068 mol) with 1,1,3,3-tetramethyl disiloxane (1.77 ml, 0.01 mol) as an endcapping agent to control $\overline{M_n}$ and obtain PDMS with Si–H terminal (Fig. 1). When the solution temperature was increased to 55 °C, triflic acid (0.13 ml, 0.65 wt% based on siloxane monomers) was slowly added *via* a syringe. The reaction was allowed for 72 h at 55 °C under N_2 blanket. After the reaction completed, diethyl ether was added into the solution and it was then washed with distilled water repeatedly to neutralize the solution. The solution was dried with anh. $MgSO_4$ and the solvent was then evaporated. D_4 monomers remaining from the equilibrium were removed under reduced pressure at 100 °C overnight. PDMS prepolymer with targeted $\overline{M_n}$ of 8000 g/mol (PDMS 8K) was synthesized in the similar fashion with the use of an appropriate molar ratio of D_4 monomer to the endcapper.

2.2.2. Synthesis of dihydroxy-terminated polydimethylsiloxane (PDMS diol)

PDMS diol was synthesized *via* hydrosilylation reaction of PDMS prepolymer with allyl alcohol (Fig. 1). PDMS 2K prepolymer (20 g, 0.01 mol) was slowly added into an excess of allyl alcohol (2.04 ml, 0.03 mol) in the presence of Karstd's catalyst (0.08 ml) with stirring at 65 °C under filled N_2 for 2 h. After the reaction completed, an excess of allyl alcohol was removed under reduced pressure at 100 °C for 4 h. ^{1}H NMR and FT-IR were used to verify its chemical structure and functional groups.

2.2.3. Synthesis of hexamethylene-1,6-di-(aminocarboxysulfonate) (HDA) as a crosslinking agent

In a round-bottom flask containing a magnetic bar, HDI (10 g, 0.06 mol) was added to $Na_2S_2O_5$ (12 g, 0.06 mol) dissolved in water and the solution was then stirred for 24 h at room temperature. The product was precipitated in acetone and filtered. Insoluble polymeric by-product was removed by dissolving HDA in water, followed by filtration. HDA product was re-precipitated in acetone, dried in vacuum, and resulted in white powder.

2.2.4. Formation of PDMS/PEG-chitosan semi-IPNs

In a 100 ml round-bottom flask containing HDA dissolved in a mixed solvent of THF:H_2O (50:50, v/v), a given amount of PDMS diol solution (THF:H_2O 50:50, v/v) was slowly added and stirred at 40 °C for 1 h. The PDMS/HDA mixture was added into acidic aqueous solution of chitosan and stirred for 5 min. The solution was then cast

in a glass mould and dried at 30 °C for 2 days. PEG-chitosan semi-IPNs were prepared in H_2O as a solvent for HDA and PEG with the same condition described above.

2.3. Characterization

2.3.1. Characterization of polymers

Proton nuclear magnetic resonance (^{1}H NMR) was performed on a 400 MHz Bruker NMR spectrometer using $CDCl_3$ as a solvent. Fourier transform infrared spectroscopy (FT-IR) was performed on a PerkinElmer Spectrum GX0 Series FT-IR spectrophotometer. Neat samples were directly cast onto potassium chloride plates. Thermal analyses were conducted on a PerkinElmer Pyris-1 differential scanning calorimeter (DSC). The samples were heated from −140 to 90 °C at 10 °C/min heating rate. DSC thermograms of the second scan were reported. Thermogravimetric analysis (TGA) was performed on SDTA 851 Mettler-Toledo at temperature ranging between 25 and 700 °C at 20 °C/min heating rate under nitrogen atmosphere.

2.3.2. Determination of percent crosslinking

To determine percent crosslinking, sample films with the dimension of 1 cm × 1 cm were submerged into 1 M acetic acid and stirred at room temperature for 48 h to dissolve uncrosslinked chitosan and HDA. The undissolvable hydrogels were filtered and washed with distilled water and acetone to remove uncrosslinked portion. The swollen gels were then dried at 30 °C for 24 h. Percent crosslinking was calculated as following:

$$\text{percent crosslinking}\,(\%) = \left(\frac{W_2}{W_1}\right) \times 100$$

where W_1 and W_2 are the weights of the dried samples before and after dissolution, respectively. The reported values are the average of at least three different measurements.

2.3.3. Equilibrium water content measurement

The pre-dried samples were precisely weighed and immersed in 1 M NaOH aqueous solution for 1 h and then submerged in distilled water at room temperature for 48 h. The swollen samples were then removed from water, wiped off excess water on their surface and weighed. Percent of equilibrium water content was calculated as following:

$$\text{Percent of equilibrium water content}\,(\%\text{EWC}) = \frac{W_s - W_d}{W_d} \times 100$$

where W_s and W_d are the weights of the swollen and dried samples, respectively.

2.3.4. Surface morphology studies

Surface morphology of sample surface was performed on LEO 1455 VP scanning electron micrometer (SEM) with an accelerating voltage of 5 kV. Sample films were dried at 30 °C for 1 day. They were cut into 1 cm × 1 cm in size, adhered onto an aluminum stub and coated with gold.

2.3.5. Determination of tensile properties

Tensile strength and elongation properties were performed on a Universal Testing Machine (model WDW-5E). The sample films were cut into a rectangular shape with 1.0 cm width and 5.0 cm length (ASTM D882). The samples were performed at the 30 mm gage length with the crosshead rate of 10 mm/min and 1 kN load cell. The reported values are the average of five different measurements. Tensile strength and percent elongation at break were calculated as follows:

$$\text{percent elongation at break}(\%) = \frac{\text{the increase in length at breaking point (mm)}}{\text{original length (mm)}} \times 100$$

2.3.6. Water contact angle measurement

Contact angles (θ) between water and sample films were measured using the sessile method on a ramé-hart Model 200 Standard Contact Angle Goniometer at room temperature. A drop of water was carefully applied on a sample film and the contact angle was quickly determined before the film commenced to swell. The reported values are the average of five different measurements.

2.3.7. Determination of water vapor permeability

A measurement procedure of water vapor permeability was described by Khan et al. (2000). A glass vial with an approximate volume about 25 cm^3 was filled with anhydrous calcium chloride ($CaCl_2$) with a precise weight. The sample film was cut in a round shape and tightly adhered onto the top of a vial, while a control vial contained glass beads having the weight approximately identical to that of the sample vials. The vials were kept in a close desiccator containing saturated NaCl aqueous solution at 30 ± 3 °C and 70 ± 5% RH for 14 days. Rate of water vapor permeability was reported in gram/day/liter unit and calculated as follows:

$$\text{rate of water vapor permeability}\,(\text{g/d/L}) = \frac{[(S_f - S_i) - (C_f - C_i)]}{14\nu} \times 1000$$

where S_i and S_f are initial and final weights (g) of the sample vials, C_i and C_f are initial and final weights (g) of the control vials and ν is volume (cm^3) of the vials. The reported values are average of three different measurements.

3. Results and discussion

3.1. Synthesis and characterization of polydimethylsiloxane (PDMS)

PDMS prepolymer was synthesized *via* acid-catalyzed ring-opening polymerization of D_4 to obtain Si–H terminated PDMS. $\overline{M_n}$ s of PDMS prepolymer (2K and 8K) were targeted by adjusting the molar ratio of D_4 monomer to 1,1,3,3-tetramethyl disiloxane endcapper. One mole of the endcapper was used for every mole of PDMS prepolymer. $\overline{M_n}$ of the as-synthesized PDMS were estimated from ^{1}H NMR spectroscopy. According to the ^{1}H NMR spectrum, the signal at 0.1 ppm corresponding to methyl protons along the PDMS backbone (Si–C$\underline{H}_3$, signal *a*) relative to the signal at 4.7 ppm corresponding to the protons at the chain ends (Si–$\underline{H}$, signal *b*) was used to determine their $\overline{M_n}$ (Fig. 2A). The calculated results revealed that 2500 and 7500 g/mol of PDMS were obtained, respectively. They were hereafter referred to as simply PDMS 2K for the lower $\overline{M_n}$ and PDMS 8K for the higher one. An FT-IR spectrum of PDMS 2K showed the characteristic signal of Si–H stretching at 2127 cm^{-1} (Fig. 2B), indicating the existence of Si–H bonds at the PDMS chain terminal. An FT-IR spectrum of PDMS 8K prepolymer exhibited a similar pattern to Fig. 2B. Hydrosilylation of the PDMS prepolymers with allyl alcohol was carried out to obtain PDMS with hydroxyl functional groups at both terminals. One and a half molar excess of allyl alcohol were used in the reaction to ensure that all Si–H bonds in the prepolymer were fully reacted. Excess allyl alcohol was easily stripped from the mixture at 80 °C under reduced pressure. According to the ^{1}H NMR spectrum of PDMS 2K, it indicates

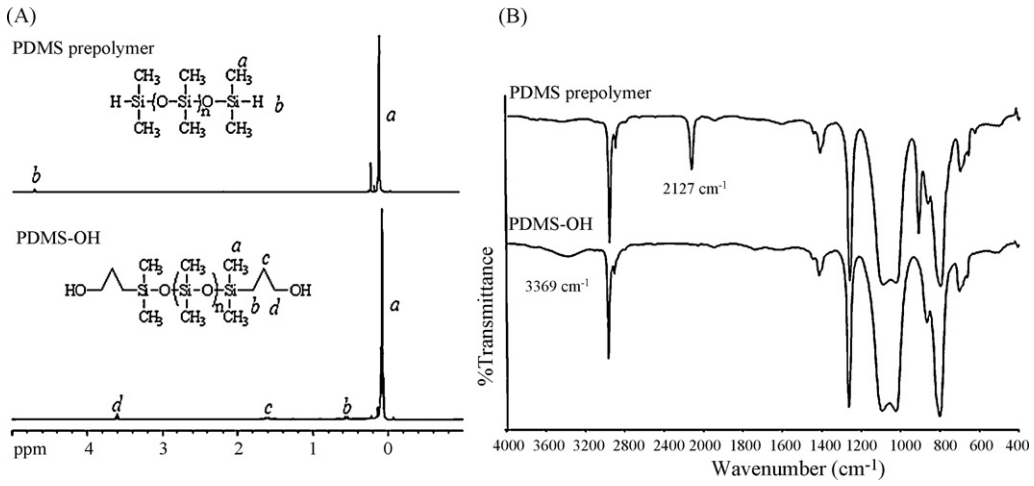

Fig. 2. (A) ^{1}H NMR and (B) FT-IR spectra of PDMS prepolymers and hydroxyl-terminated PDMS (PDMS-OH).

the formation of the linkage corresponding to the coupling reaction of Si–H bonds to allyl alcohol (0.6 ppm, signal *b* and 1.7 ppm, signal *c*) (Fig. 2A). Fig. 2B shows FT-IR spectra of PDMS diol and their corresponding prepolymer. The signal at 2127 cm^{-1} corresponding to Si–H stretching disappeared, indicating that all Si–H in the prepolymer were fully reacted after hydrosilylation. Instead, it appeared a weak signal of hydroxyl group (–OH) at 3369 cm^{-1} due to the formation of hydroxyl-terminated PDMS.

3.2. Synthesis of hexamethylene-1,6-di-(aminocarboxysulfonate) (HDA) as a crosslinking agent

HDA crosslinking agent was prepared *via* a reaction between HDI and $Na_2S_2O_3$ in water. After the reaction, the characteristic signal of isocyanate group of HDI (2277 cm^{-1}) disappeared (supporting information). In addition, the spectrum exhibited the signals of carbonyl group (C=O) at 1678 cm^{-1} and amino group (N–H) at 3330 cm^{-1} of aminocarboxy sulfonate, indicating the formation of HDA. In good agreement with FT-IR results, the ^{1}H NMR signal at 3.3 ppm corresponding to methylene protons adjacent to aminocarboxy sulfonate groups indicated the formation of HDA (supporting information).

3.3. Preparation and properties of PDMS/PEG-chitosan semi-IPNs

3.3.1. Functional group characterization of PDMS/PEG-chitosan semi-IPNs

PDMS/PEG was interpenetrated into chitosan using 10 wt% of HDA as a water-soluble crosslinker. FT-IR was used to evaluate the presence of PDMS and PEG in the chitosan semi-IPN structure. As compared to an FT-IR spectrum of PDMS homopolymer (Fig. 3a), the PDMS-chitosan semi-IPNs exhibited strong Si–O bands, the characteristic signals of PDMS, in the range of 1092–830 cm^{-1} (Fig. 3b), indicating the presence of PDMS in the chitosan network. In Fig. 3c, the most characteristic absorption of PEG is a strong band in the 1150–1089 cm^{-1} range due to asymmetrical C–O–C stretching (Fig. 3c). Likewise, the band was observed in PEG-chitosan semi-IPNs; the peak occurred at 1125 cm^{-1} (Fig. 3d), indicating the presence of PEG in chitosan hydrogel.

3.3.2. Percent crosslinking and water swelling properties

HDA, a water-soluble derivative of HDI, was used to effectively crosslink chitosan due to the reaction between bisulfite protected diisocyanate groups of HDA with amino groups in chitosan structure. A minimal amount of crosslinker just enough to form chitosan networks was determined to avoid formation of dense network structure. 10 wt% of HDA was used in every composition of the hydrogels because, when less than 10 wt% of HDA was used, the semi-IPNs were not fully cured as indicated by the presence of detached fragment after immersing the samples in water.

According to the plots in Figs. 4 and 5, % crosslinking and % EWC of HDA-crosslinked chitosan (0% PDMS/PEG) were 98 ± 5% and 126 ± 16%, respectively. Addition of PDMS or PEG, even only 1 wt%, to chitosan semi-IPNs obviously lowered % crosslinking in both systems. PDMS/PEG presenting in the networks might somewhat inhibit effective crosslinking reaction of HDA in chitosan structure. Considering chitosan semi-IPNs containing hydrophobic polymer, increasing % and $\overline{M_n}$ of PDMS in the networks enhanced % crosslinking probably due to the increase in network density. % EWC of PDMS-chitosan semi-IPNs was first anticipated to drop as increasing PDMS concentrations in the hydrogels because of hydrophobic nature of PDMS combined with the formation of dense network structure. Surprisingly, % EWC of PDMS-modified chitosan was rather enhanced as compared to the unmodified hydrogel. This was attributed to the existence of microphase separation of PDMS phase in chitosan matrix. The presence of PDMS microphase resulted in a significant increase in polymer–air interface chitosan owing to porous-like morphology. The existence of PDMS microphase was confirmed by SEM technique, which was shown in the latter description (Fig. 6). Increasing $\overline{M_n}$ of PDMS from 2K to 8K even

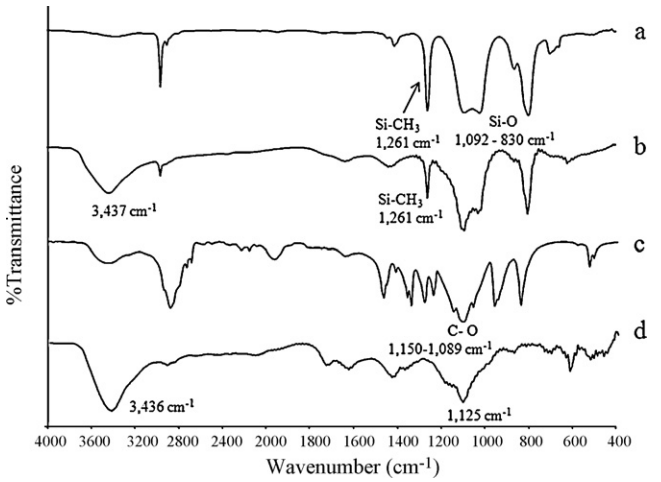

Fig. 3. FT-IR spectra of (a) PDMS 8K, (b) 20 wt% PDMS 8K-chitosan semi-IPNs, (c) PEG 8K, and (d) 20 wt% PDMS 8K-chitosan semi-IPNs.

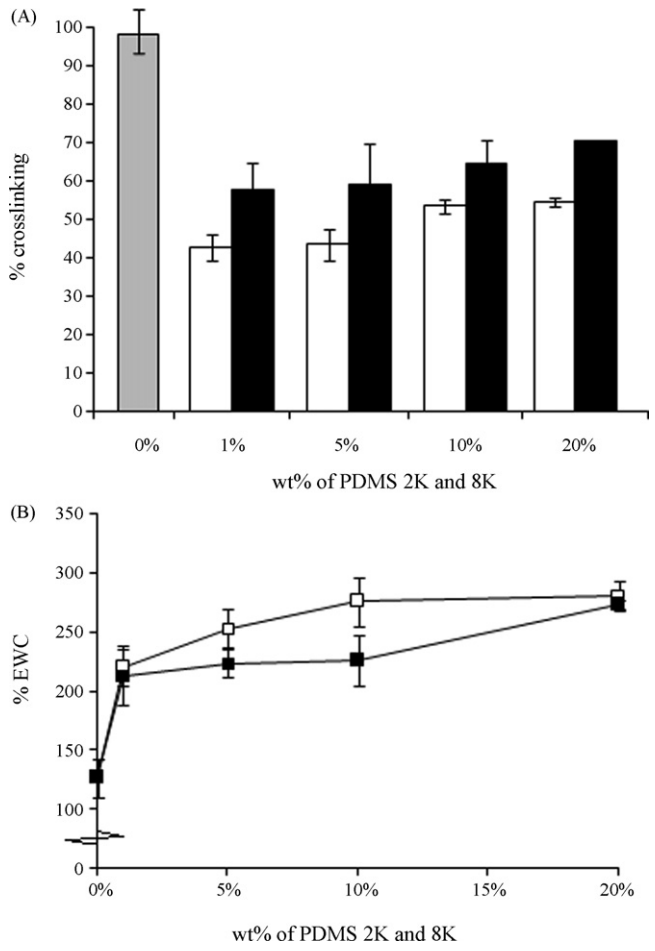

Fig. 4. (A) Percent crosslinking and (B) percent EWC of PDMS 2K-chitosan semi-IPNs (□) and PDMS 8K-chitosan semi-IPNs (■).

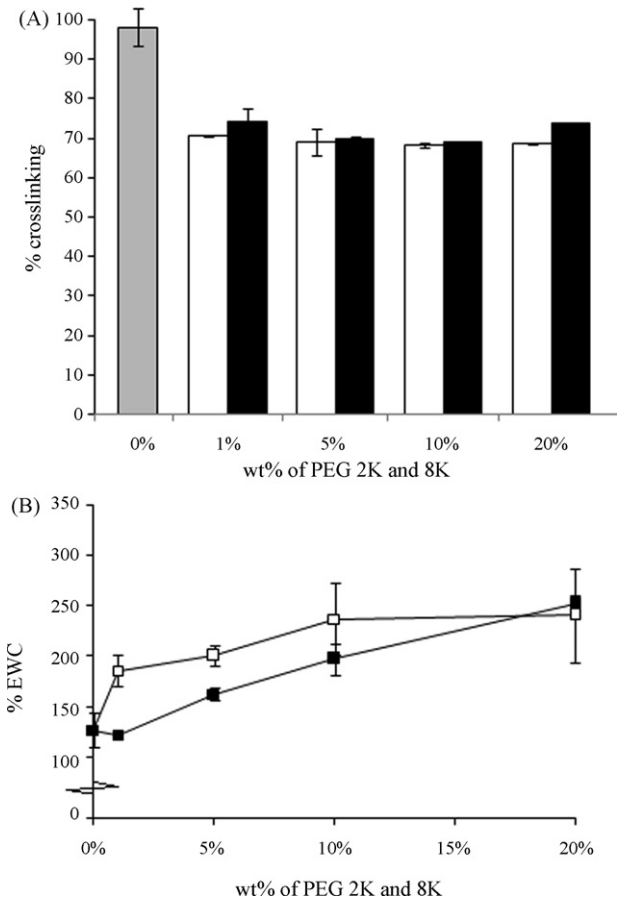

Fig. 5. (A) Percent crosslinking and (B) percent EWC of PEG 2K-chitosan semi-IPNs (□) and PEG 8K-chitosan semi-IPNs (■).

further promoted the degree of entanglement in the networks, resulting in the enhancement of percent of crosslinking and suppressing percent EWC.

Turning now to the case of hydrophilic polymer, % crosslinking of PEG-chitosan semi-IPNs was slightly higher that those of PDMS-chitosan ones; it was approximately 70% regardless of the concentration and $\overline{M_n}$ of PEG used (Fig. 5). Their % EWC slightly increased (from 126% to 250%) upon increasing PEG content, similarly to the case of PDMS-chitosan networks (from 126% to 280%). This was attributed to partial hydrophilic nature of PEG, which somewhat promoted water swellability of the materials. However, similarly to the PDMS-chitosan semi-IPNs, increasing $\overline{M_n}$ of PEG generally lowered their % EWC. Long chain length of PEG 8K might, to some extent, influence water swelling competency of the hydrogels due to high degree of entanglement and eventually suppressed % EWC.

3.3.3. Surface morphology of PDMS/PEG-chitosan semi-IPNs

Surface morphology of chitosan modified with PDMS or PEG was studied *via* SEM. Fig. 6 depicts representative images of chitosan semi-IPN containing 20 wt% PDMS or PEG, comparing with chitosan physically blended with PDMS or PEG (without HDA crosslinker) at the same concentrations.

In the case of PDMS-chitosan blend, shringkage of PDMS thin layer on the top of the film was observed due to macroscopic phase separation (Fig. 6A). Once HDA crosslinking agent was incorporated, PDMS phase separation no more existed (Fig. 6A'). This indicated that miscibility between chitosan and hydrophobic PDMS was enhanced due to the formation of semi-IPN structure. Similarly, incorporation of HDA crosslinker also promoted their miscibility between chitosan and PEG as indicated by the improvement of material homogeneity (Fig. 6B and B'). The dimples thoroughly dispersed on PEG/chitosan blend belonged to PEG microphase due to partial miscibility of high $\overline{M_n}$ PEG (8K) in chitosan continuous phase (Fig. 6B). Lowering $\overline{M_n}$ of PDMS or PEG from 8K to 2K even further promoted its miscibility in chitosan as evidenced by the improved microphase separation in PDMS/PEG 2K/chitosan blends (Fig. 6C and D).

3.3.4. Thermal properties of PDMS/PEG-chitosan semi-IPNs

3.3.4.1. Differential scanning calorimetry (DSC) studies. Fig. 7 shows DSC thermograms of PDMS/PEG-chitosan semi-IPNs (20 wt% of PDMS or PEG in chitosan semi-IPNs) in comparison with those of unmodified chitosan and the corresponding homopolymers (PDMS 8K and PEG 8K). Considering the DSC thermogram of PDMS-chitosan semi-IPNs (Fig. 7A), its thermal behavior was similar to that of chitosan; no phase transition was observed, while three phase transitions of PDMS 8K homopolymer were apparent. Although PDMS microphases (2–10 μm) were observed in PDMS-chitosan semi-IPNs (Fig. 6A'), an effective entrapment of PDMS chains in chitosan network might inhibit their mobility in the structure, resulting in no transition observed. On the other hand, in the case of PEG-chitosan semi-IPNs, a melting temperature (T_m) at 58 °C was observed and this corresponds to T_m of PEG presenting in the networks. A slight decrease of the T_m as compared to that of PEG homopolymer (68 °C) suggested that semi-IPN structure might influence crystalline structure of PEG in the networks and consequently affect its T_m.

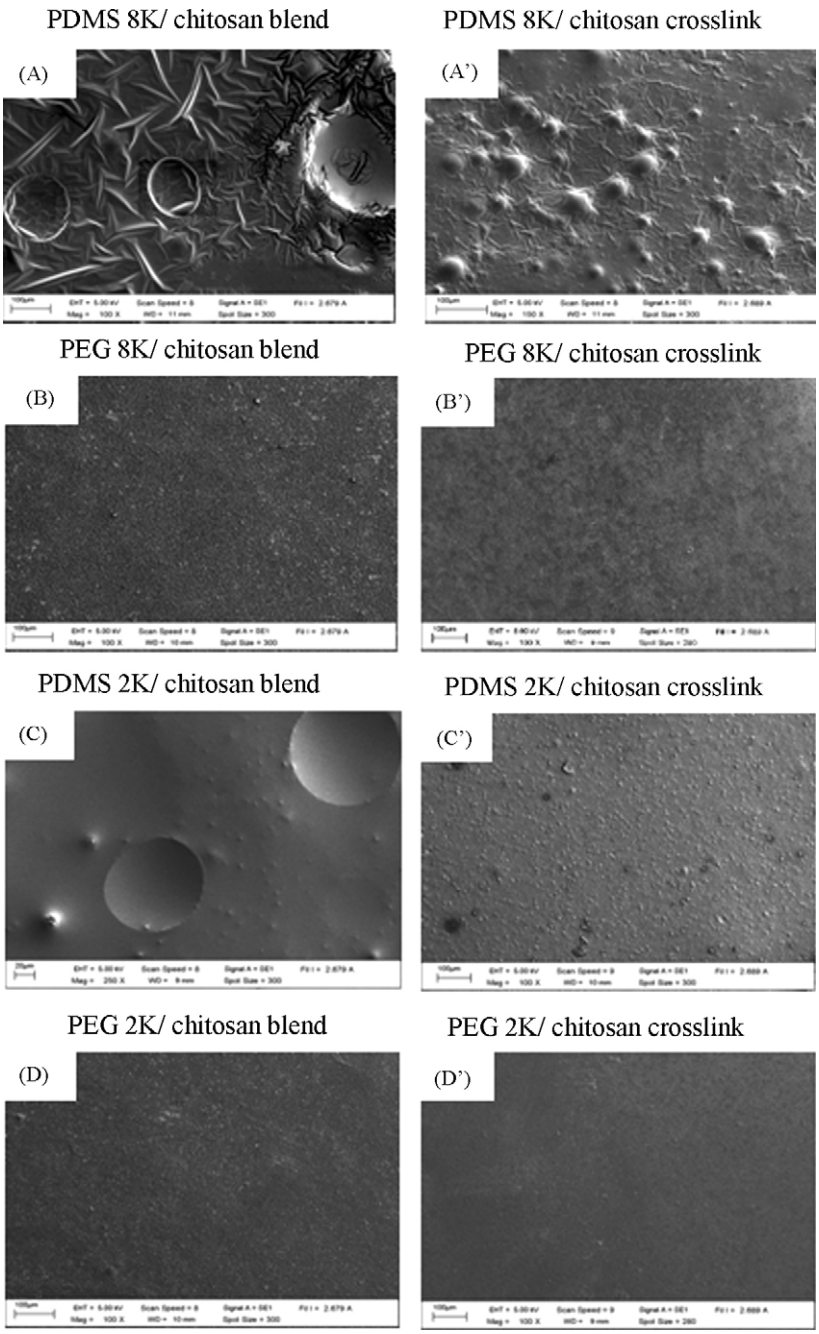

Fig. 6. (A–D) Chitosan physically blended with 20% PDMS/PEG 8K and 2K and A'–D') chitosan chemically crosslinked with 20% PDMS/PEG 8K and 2K.

3.3.4.2. Thermogravimetric analysis (TGA) studies. TGA was conducted to investigate the effect of PDMS and PEG on thermal stability of the modified hydrogels. 20 wt% PDMS/PEG was used in every sample. In the case of PDMS-chitosan semi-IPNs (Fig. 8A), % weight reduction seemed to be retarded as compared to HDA-crosslinked chitosan (without PDMS), indicating the improved thermal stability upon addition of PDMS in their structure. Increasing $\overline{M_n}$ of PDMS did not further promote their thermal stability. Similarly, slight improvement of thermal stability was also observed in PEG-chitosan semi-IPNs (Fig. 8B), while increasing $\overline{M_n}$ of PEG from 2K to 8K did not enhanced their thermal stability. In both cases, two decomposition steps of PDMS/PEG-chitosan semi-IPNs appeared at the ranges of 230–300 and 380–410 °C, whereas only single decomposition step was observed in HDA-crosslinked chitosan (without PDMS or PEG).

3.3.5. Tensile properties

Fig. 8 shows tensile properties of uncrosslinked chitosan, HDA-crosslinked chitosan and PDMS/PEG-chitosan semi-IPNs. The increase in tensile strength and the decrease in % elongation of the HDA-crosslinked chitosan as compared to the uncrosslinked one indicated the loss in flexibility of the materials and this was attributed to the formation of network structure.

PDMS-chitosan semi-IPNs networks showed a decrease in both tensile strength and elongation, indicating that addition of PDMS into chitosan networks deteriorated their strength and flexibility (Fig. 9). Increasing $\overline{M_n}$ of PDMS in the networks from 2K to 8K slightly diminished their tensile properties. The decrease in tensile properties was attributed to the formation of network structure. Similarly, the presence of PEG in chitosan network also deteriorated their tensile properties comparing with the HDA-crosslinked

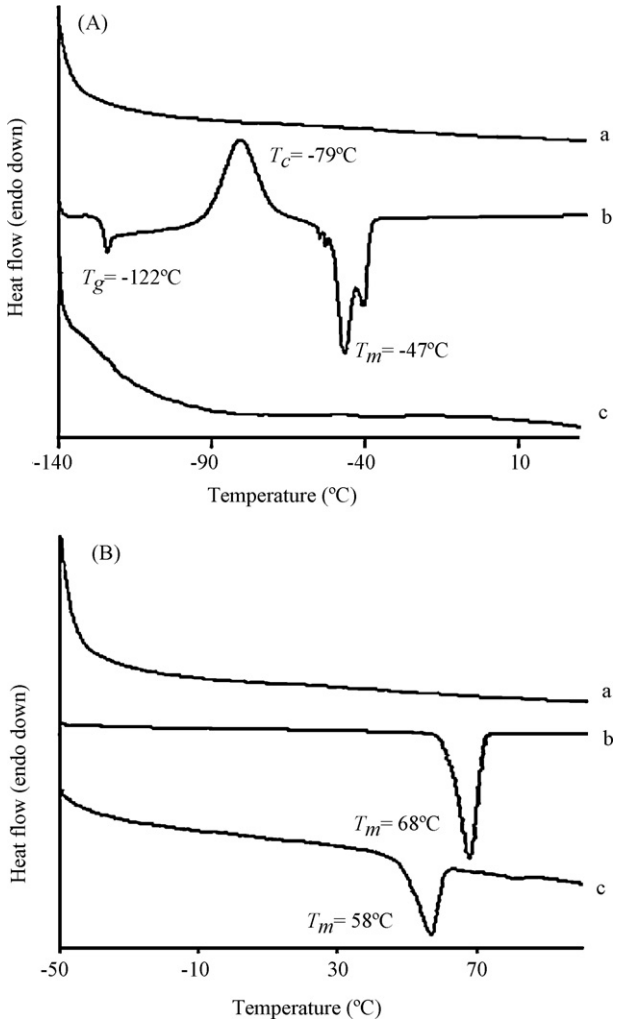

Fig. 7. DSC thermograms of (A) chitosan (a), PDMS 8K (b), and 20 wt% PDMS 8K-chitosan semi-IPNs (c) and (B) chitosan (a), PEG 8K (b) and 20 wt% PEG 8K-chitosan semi-IPNs (c).

chitosan. Both tensile strength and % elongation were higher than those of the PDMS cases, indicating that they were more resistant upon stretching. Increasing $\overline{M_n}$ of PEG from 2K to 8K also enhanced their tensile properties.

3.3.6. *Water contact angle of PDMS/PEG-chitosan semi-IPNs*

Effect of PDMS/PEG on surface wettability of chitosan semi-IPNs was investigated by measuring their water contact angle compared with those of uncrosslinked and HDA-crosslinked chitosan. Water contact angles of uncrosslinked chitosan (Chit) was $114.78 \pm 4.66^\circ$ and those of HDA-crosslinked chitosan (Chit-HDA) was $57.18 \pm 0.51^\circ$ (Fig. 9). The significant decrease in water contact angle upon crosslinking was attributed to the presence of aminocarboxysulfonate groups of HDA on their surface, resulting in the enhancement of their surface hydrophilicity.

Addition of only 1 wt% PDMS to the hydrogels displayed insignificant effect on their surface properties (Fig. 10A). Increasing PDMS concentration in the hydrogels lowered their surface hydrophilicity (an increase in water contact angles from 50° to 80°) due to inherently hydrophobic characteristics of PDMS. In addition, low surface energy of PDMS should also promote the samples to have PDMS-enriched surface (Rutnakornpituk & Ngamdee, 2006). However, increasing $\overline{M_n}$ of PDMS from 2K to 8K showed no significant impact to their surface properties. Considering the system containing hydrophilic polymer, addition of PEG in semi-IPNs was expected

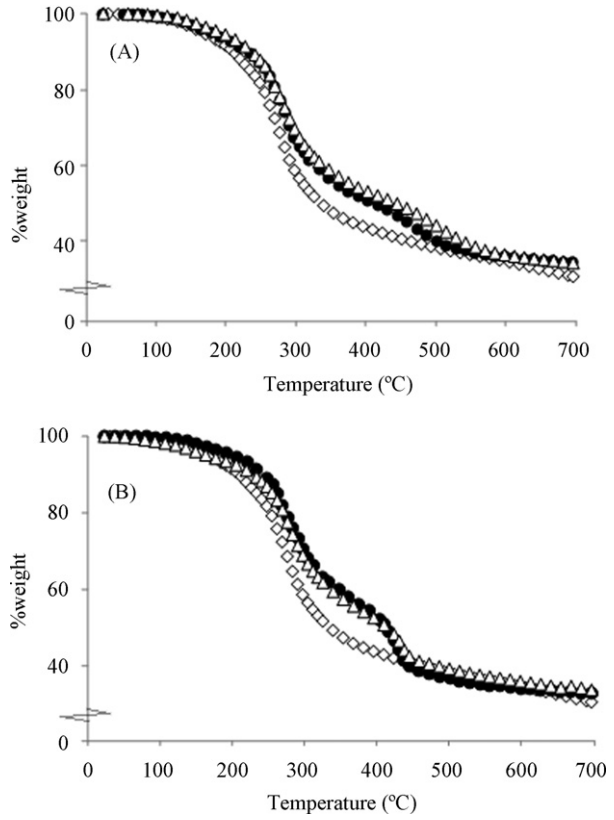

Fig. 8. TGA thermograms of (A) chitosan semi-IPNs modified with 20 wt% PDMS 2K (●), 20 wt% PDMS 8K (△), HDA-crosslinked chitosan (◊), and (B) chitosan semi-IPNs modified with 20 wt% PEG 2K (●), 20 wt% PEG 8K (△), HDA-crosslinked chitosan (◊).

to enhance surface wettability of the samples. Surprisingly, it was found that increasing PEG concentration in the semi-IPNs lowered their surface hydrophilicity (an increase in water contact angles from 38° to 70°) (Fig. 10B). It was reasoned that PEG might not be able to express its hydrophilic properties because it was tightly

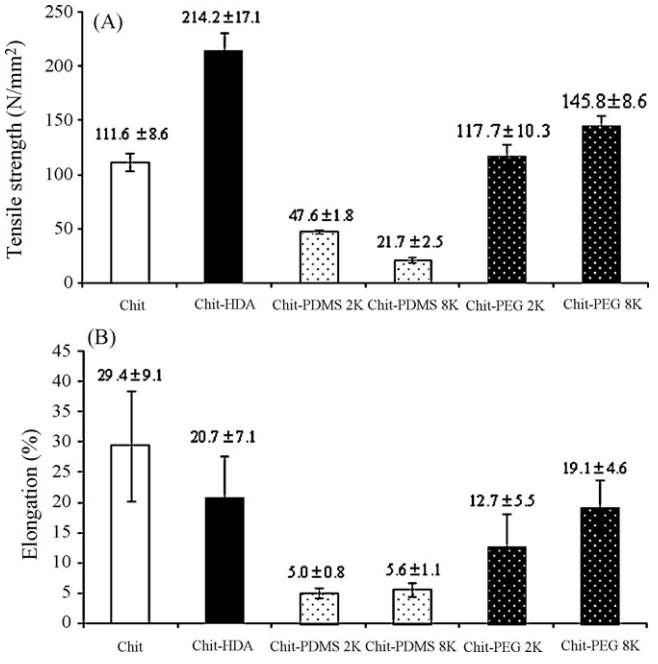

Fig. 9. (A) Tensile strength and (B) elongation of uncrosslinked chitosan, HDA-crosslinked chitosan and 20 wt% PDMS/PEG (2K and 8K)-chitosan semi-IPNs.

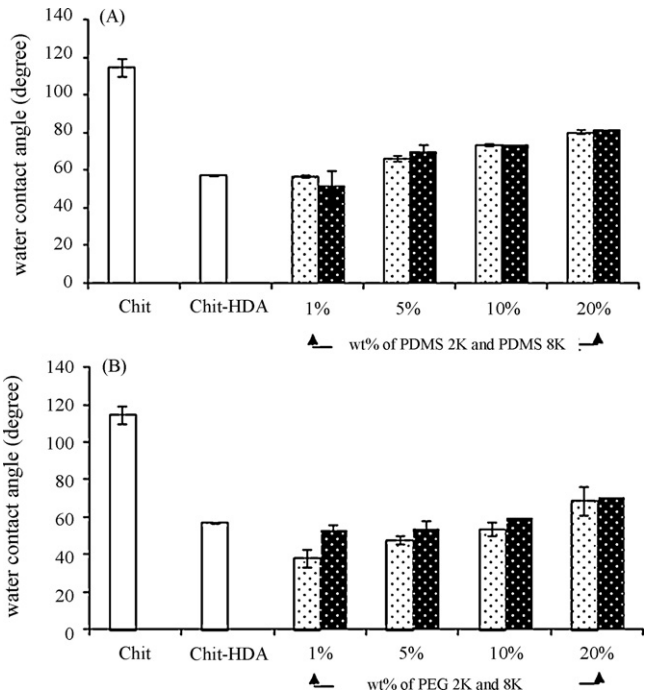

Fig. 10. Water contact angles of (A) PDMS-chitosan semi-IPNs containing 1–20 wt% PDMS 2K (⁙) and PDMS 8K (▩), and (B) PEG-chitosan semi-IPNs containing 1–20 wt% PEG 2K (⁙) and PEG 8K (▩).

locked in place in the semi-IPN structure. Their water contact angles were thus increased upon addition of PEG due to the dense network structure. Increasing $\overline{M_n}$ of PEG from 2K to 8K did not show significant difference in their surface wettability.

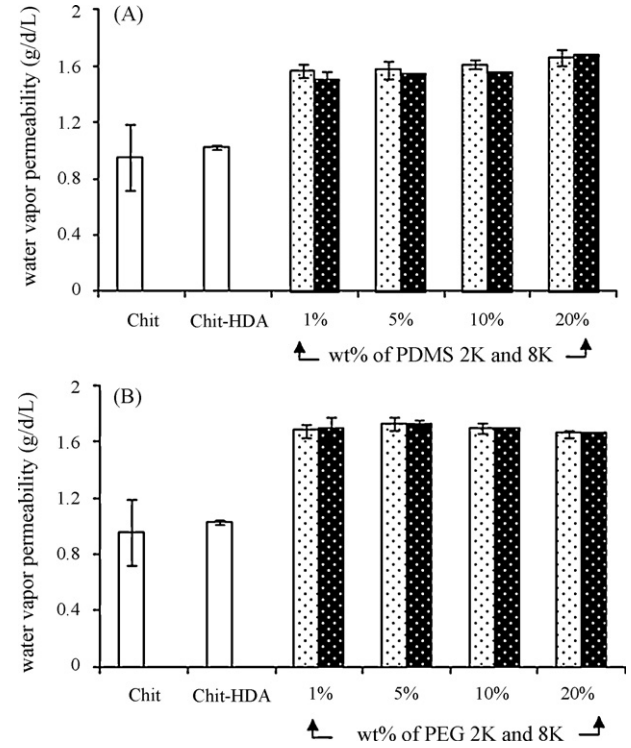

Fig. 11. Water vapor permeability of (A) PDMS-chitosan semi-IPNs containing 1–20 wt% PDMS 2K (⁙) and PDMS 8K (▩), and (B) PEG-chitosan semi-IPNs containing 1–20 wt% PEG 2K (⁙) and PEG 8K (▩).

3.3.7. *Water vapor permeability of PDMS/PEG-chitosan semi-IPNs*

From Fig. 11, water vapor permeability of uncrosslinked chitosan (Chit) was 0.60 ± 0.10 g/d/L and those of HDA-crosslinked chitosan (Chit-HDA) was 0.67 ± 0.01 g/d/L. In the case of chitosan semi-IPNs containing hydrophobic polymer, increasing PDMS concentrations from 1 to 20 wt% enhanced their water vapor permeability (0.98–1.42 g/d/L) probably due to the formation of PDMS microphase, which, to some extent, increased its porosity and thereby promoted water vapor permeability of the PDMS-modified semi-IPNs. Water swelling behavior and surface morphology studies also supported this premise that % EWC was significantly increased upon addition of PDMS in chitosan hydrogels (Fig. 4B) and the appearance of PDMS microphase on their surface (Fig. 6A'). In the case of chitosan semi-IPNs containing hydrophilic polymer, incorporation of PEG into chitosan promoted water vapor permeability of the hydrogels, regardless of PEG concentrations and $\overline{M_n}$ used (1.09–1.14 g/d/L). This was attributed to the presence of hydrophilic PEG in the semi-IPN structure, which thus facilitated transportation of moisture through the films.

4. Conclusions

Preparation of PDMS/PEG-chitosan semi-IPNs was described herein. PDMS and PEG were selected to represent hydrophobic and hydrophilic polymers, respectively, to investigate their effect on the properties of chitosan hydrogels. They were interpenetrated and locked in place in chitosan structure, so that up to 20 wt% PDMS/PEG with high $\overline{M_n}$ (8000 g/mol) can be incorporated. Without the formation of semi-IPNS structure, hydrophobic PDMS with high $\overline{M_n}$ and high content tended to macrophase separate from chitosan continuous phase. PDMS and PEG in the chitosan semi-IPNs generally promoted water swellability and water vapor permeability of the modified chitosan films. It was hypothesized that PEG enhanced these properties due to its hydrophilic characteristics, while, in the case of PDMS-chitosan semi-IPNS, this was attributed to the formation of PDMS microphase, allowing the materials having more polymer–air interfaces and more contact with water. Addition of PDMS/PEG to chitosan semi-IPNs slightly enhanced their thermal stability and surface hydrophobicity, while their tensile properties were sacrificed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2010.03.023.

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