Available online at www.sciencedirect.com

Carbohydrate Polymers 63 (2006) 229–237

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Preparation and properties of polydimethylsiloxane-modified chitosan

Metha Rutnakornpituk [a,*], Paradorn Ngamdee [a], Pranee Phinyocheep [b]

[a] Department of Chemistry, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand
[b] Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

Received 30 June 2005; received in revised form 16 August 2005; accepted 24 August 2005
Available online 8 November 2005

Abstract

Preparation and properties of polydimethylsiloxane (PDMS)-modified chitosan are discussed herein. A series of PDMS with systematically varied molecular weights were first prepared via acid-catalyzed ring opening polymerization of octamethylcyclotetrasiloxane (D_4) to obtain PDMS prepolymers. They were subsequently functionalized with allyl glycidyl ether to obtain epoxy functional groups at PDMS terminals. Their chemical structures and molecular weights were characterized using ^{1}H NMR, ^{13}C NMR and FTIR, and thermal properties were determined by DSC. The reaction of the epoxidized PDMS and chitosan was carried out in an acidic aqueous solution. Increasing the molecular weights of PDMS and/or its concentrations improved flexibility and water swellability due to the formation of PDMS microphase. Water contact angle and water vapor permeability measurements indicated that incorporation of the PDMS enhanced its hydrophobicity as compared to the unmodified one.

Keywords: Chitosan; Polydimethylsiloxane; Modification

1. Introduction

In recent years, chitin and chitosan have drawn a lot of attention due to their unique properties such as biocompatibility, biodegradability and economical advantages (Khor & Lim, 2003; Tanodekaew, Prasitsilp, Swadison, Thavornyutikarn, Pothsree and Pateepasen, 2004). Chitin is*N*-acetyl-D-glucosamine repeating unit linked by β-(1→4) linkage and chitosan is 2-amino-2-deoxy-(1→4)-β-D-glucan (Prashanth & Tharanathan, 2003). Chitin is difficult to dissolve in water or any organic solvents whereas chitosan is well soluble in various acidic aqueous solutions, e.g. formic and acetic acids (Kweon, Ha, Um, & Park, 2001). Chitosan has thus been widely studied for use in various applications such as pharmaceutics, medicine, textiles, agriculture and other industrial applications.

Modifications of chitosan with polymers have been markedly studied to tailor its properties to satisfy basic requirements for particular applications. These were accomplished either by physical blending, chemical grafting, or crosslinking (Zeng & Fang, 2004; Zeng, Fang, & Xu, 2004). For instance, incorporation of poly(ethylene glycol) into chitosan to improve their swelling properties and blood compatibility has been investigated for biomedical applications (Amiji, 1995; Gupta, Majeti, & Kumar, 2001; Zhang, Li, Gong, Zhao, & Zhang, 2002). Chitosan grafted with acrylonitrile or methylmethacrylate using potassium persulfate as an initiator was studied for feasible use as packaging materials (Prashanth and Tharanathan, 2003). The influence of glutaraldehyde crosslinking reagent on the transport properties of chitosan was investigated for the packaging application as well (Tual, Espuche, Escoubes, & Domard, 2000).

Because the inherent brittleness and stiffness of chitosan have limited many possible applications, polydimethylsiloxane (PDMS) was thus incorporated into chitosan in the present studies to improve their toughness properties. PDMS is of particular interest for this purpose owing to their low glass transition temperature (T_g) and high flexibility as it is typically used as an elastomeric modifier in various applications. In addition to that, other unique properties of PDMS, e.g. low toxicity, good biocompatibility, high oxygen permeability, good thermal and oxidative stability, are also suitable for use as biomaterials (Rutnakornpituk, 2005; Schulze Nahrup, Gao, Mark, & Sakr, 2004). However, only a few precedents have incorporated PDMS into chitosan probably due to immiscibility between hydrophobic PDMS and hydrophobic chitosan. Kweon has reported in grafting PDMS homopolymer onto chitosan and investigated their surface and mechanical properties (Kweon, 1998). Preparation of PDMS-grafted chitosan

---

* Corresponding author. Tel.: +66 55 261 000x3464; fax: +66 55 261 000x3401.

E-mail address: methar@nu.ac.th (M. Rutnakornpituk).

0144-8617/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2005.08.063

(Kim, Kim, Shin, Lee, Shin and Kim, 2002) and PDMS/poly(vinyl alcohol)-chitosan hydrogel (Shin, Kim, Kim, Kim, Song and Kim, 2002) as well as their swelling behavior were previously reported.

In the current work, synthesis of PDMS with epoxy functional groups has been discussed. Its chemical structures and molecular weights were elucidated by^{1}H NMR,^{13}C NMR and FTIR, and thermal properties were studied by DSC. The study on percent of extractable portions of the PDMS-modified chitosan was also discussed. Mechanical properties, water swelling behavior, water vapor permeability and surface properties of chitosan containing PDMS as a function of PDMS molecular weights and contents compared with the unmodified chitosan were also reported.

2. Experimental

2.1. Materials

Chitosan from crabs (Taming Enterprise, Co.) with 98% deacetylation and approximate number average molecular weight (M_n) of 1.4×10^5 g/mol was used as received. Octamethylcyclotetrasiloxane, D_4, 99+% (Fluka), was stirred in CaH_2 and distilled prior to use. 1,1,3,3-Tetramethyldisiloxane, 97% (Acros), was fractionally distilled and stored under N_2 until used. Karstd's catalyst (Aldrich) and triflic acid, 98% (Aldrich), were used as received. Allyl glycidyl ether, 99+% (Acros), was dried in activated molecular sieves, fractionally distilled and stored in a freezer until used.

2.2. Synthesis

The first part of the synthesis of epoxy-terminated PDMS involved the preparation of controlled molecular weight PDMS prepolymers with Si–H terminals. The PDMS prepolymers were then subsequently hydrosilylated with allyl glycidyl ether to obtain epoxy-terminated PDMS.

2.2.1. Synthesis of PDMS prepolymers with controlled molecular weights

A procedure for preparing PDMS prepolymer with a targeted molecular weight of 1000 g/mol is provided. The PDMS prepolymers with other molecular weights were prepared in a similar fashion but with different ratios of octamethylcyclotetrasiloxane (D_4) to the endcapping reagent. D_4 (20 g) and 1,1,3,3-tetramethyldisiloxane (3.54 ml, 0.02 mol) were charged into a round-bottom flask filled with N_2. The temperature was increased to 55 °C and trifluoromethane sulfonic acid catalyst (triflic acid) (0.13 ml, 0.65 wt% based on siloxane monomers) was slowly added via a syringe. The reaction was equilibrated at 55 °C for 72 h. Gel permeation chromatography (GPC) was used to monitor the molecular weights of the polymer during the reaction and thereby confirm that the reaction reached equilibrium after 72 h period. The acidic mixture was cooled to room temperature, dissolved in diethyl ether, then neutralized by repeatedly extracting with water. The mixture was dried over sufficient anhydrous magnesium sulfate with continuously stirring for 30 min, and subsequently filtered through a filter paper. Diethyl ether was evaporated using a rotary evaporator for 30 min. The cyclic monomers remaining upon the equilibration were removed by vacuum stripping at 120 °C overnight.

2.2.2. Synthesis of epoxy-terminated PDMS

Allyl glycidyl ether (0.34 ml, 0.03 mol), toluene (10 ml) and the Karstd's platinum catalyst (0.07 ml) were charged into a the 4-neck reaction flask with a dropping funnel, a magnetic stir bar, thermocouple and nitrogen inlet. A PDMS prepolymer terminated with Si–H groups with molecular weight of 1000 g/mol (10 g, 0.01 mol) was charged to a dropping funnel. It should be noted that the amount of allyl glycidyl ether used was one and a half moles for every mole of Si–H bonds in the prepolymers. After the temperature was raised to 55 °C, the PDMS prepolymer were slowly dropped to the reaction mixture due to highly exothermic reaction. After the reaction was complete, the temperature was increased to 65 °C for 2 h. The mixture was cooled to room temperature, and then filtered. The excess of allyl glycidyl ether was removed by distillation at 100 °C for 3 h. Preparation of epoxy-terminated PDMS with different molecular weights was carried out in the same procedure and the same 1.5:1 molar ratio of allyl glycidyl ether to Si–H group.

2.2.3. Preparation of PDMS-modified chitosan films

Chitosan (5.0 g) was dissolved in 100 mL of a 0.5 M acetic acid aqueous solution. Desired weight and molecular weight of the epoxidized PDMS was dissolved in 10 mL of isopropanol and was introduced into the chitosan aqueous solution with continuous stirring for 2 h. Sonication was applied to remove air bubbles in the reaction mixture for 4 h. The solution was then poured into a glass mold to obtain a square sample film with 10×10 cm^2 and kept at 50 °C for 2 days. The films were neutralized in a 0.5 M NaOH solution and dried at 50 °C for another 2 days under reduced pressure. The PDMS-modified chitosan was somewhat opaque as compared to the unmodified chitosan.

2.3. Characterization

2.3.1. Characterization of PDMS

Proton (^{1}H NMR) and carbon magnetic resonance (^{13}C NMR) were performed on a 400 MHz Bruker NMR Spectrometer and $CDCl_3$ used as a solvent. Fourier transform infrared spectrometer (FTIR) spectra were measured from Perkin–Elmer Spectrum GX0 Series FTIR Spectrophotometer. GPC data was conducted on PLgel 10 μm mixed B2 columns and a refractive index detector. Tetrahydrofuran (THF) was used as a solvent with a flow rate of 1 mL/min at 30 °C. Thermal analyses were performed on a Perkin–Elmer Pyris-1 differential scanning calorimeter (DSC). The samples were heated from −140 to 0 °C with a 10 °C/min heating rate.

2.3.2. Measurement of the percent of dissolvable parts

The neutralized PDMS-modified chitosan was submerged into a 0.5 M aqueous acetic acid solution with consistently stirring at room temperature for 24 h. to dissolved uncrosslinked chitosan. The undissolvable chitosan was filtered using a sinter glass and submerged again into an additional acetic acid solution. The undissolvable chitosan was again filtered and washed with distilled water followed by acetone to remove uncrosslinked PDMS. It was dried at 50 °C in a vacuum oven for 24 h. Percent of extractable parts was calculated as follows:

$$\text{Percent of extractable part }(\%) = \frac{(W_1 - W_2)100}{W_1}$$

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

2.3.3. Water swelling properties of chitosan

The pre-dried samples were precisely weighed (70–80 mg) and submerged into water at room temperature. At a given time interval, the swollen samples were removed from water, wiped off excess water on surface and weighed. Percent of water swelling was calculated as follows:

$$\text{Percent of water swelling }(\%) = \frac{(W_s - W_d)100}{W_d}$$

where W_s and W_d are the weights of the swollen and dry samples, respectively. The reported values are the average of three different measurements.

2.3.4. Scanning electron microscopy (SEM)

The morphology of the sample surface was carried out through LEO 1455 VP scanning electron microscopy (SEM) with an accelerating voltage of 20 kV. The neutralized chitosan with different submerging times in water were dried in a vacuum oven at 50 °C for 2 days. They were cut into $1 \times 1\ \text{cm}^2$ in size and adhered onto an aluminum stub.

2.3.5. Water contact angle of chitosan

Contact angle (θ) between water and chitosan films was measured on a Krüss DSA 10 contact angle meter at room temperature. Water was carefully dropped on chitosan films and contact angles were quickly determined before the films started to swell. The reported values are the average of five different measurements.

2.3.6. Water vapor permeability of chitosan

Water vapor permeability of chitosan was investigated following the method described by Khan, Peh, and Chang (2002). The sample films were tightly adhered onto the top of glass vials with an approximately volume of 24 cm^3. Each vial was filled with preweighed anhydrous calcium chloride, whereas glass vials for control contained small glass beads of approximately identical weights to that of the sample vials. They were kept in a desiccator with 75 ± 3% relative humidity (RH) maintained with a saturated sodium chloride solution at 28 ± 3 °C. The vials were weighed again after 14 days after kept in the close desiccator. Rate of water vapor permeability was calculated as follows:

$$\text{Rate of water vapor permeability(g/day/liter)} = \frac{[(T_f - T_i) - (C_f - C_i)]1000}{(14v)} x$$

where T_i and T_f are the initial and final weights of the sample vials, respectively, C_i and C_f are the initial and final weights of the control vials, respectively, and v is the volume (cm^3) of each vial. The reported values are the average of three different measurements.

2.3.7. Tensile strength and percent elongation of chitosan

Tensile strength and elongation properties were performed on a universal testing machine (Instron Model 4301). The samples free from air bubbles were cut into a dumbbell shape type IV (ASTM D638). The samples were performed at 25 mm gage length with the speed of 50 mm/min and 1 kN load cell. Tensile strength and percent elongation at break were calculated as follows:

$$\text{Tensile strength(N/mm}^2) = \frac{\text{Breaking force(N)}}{\text{Cross} - \text{sectional area of the sample(mm}^2)}$$

$$\text{Percent elongation at break }(\%) = \frac{\text{The increase in length at breaking point(mm) 100}}{\text{Original length(mm)}}$$

The results presented were the average numbers of five independent measurements.

3. Results and discussion

3.1. Synthesis of epoxy-terminated PDMS

PDMS containing epoxy functional groups at the ends was prepared following a two-step synthesis: (1) preparation of PDMS prepolymers containing Si–H terminals, and (2) epoxidation of the PDMS prepolymers with allyl glycidyl ether to obtain PDMS with diepoxy end groups (Fig. 1). In the first step, PDMS prepolymers with systematically varied molecular weights (1000, 5000 and 10,000 g/mol) were synthesized through the acid-catalyzed ring opening equilibrium polymerization of octamethylcyclotetrasiloxane (D_4) using 1,1,3,3-tetramethyldisiloxane as the endcapping reagent. One mole of the endcapping agent was used for every mole of the polymer in order to control the molecular weight of the polymer. GPC indicated the existence of cyclic species remaining after the reaction equilibrium. These cyclics were removed by evaporation under reduced pressure at 120 °C overnight. The molecular weight of the prepolymer was estimated from a ^{1}H NMR spectrum. The peak at 0.1 ppm corresponding to methyl protons along the PDMS backbone (Si–CH_3) relative to the peak at 4.7 ppm corresponding to the protons at the chain ends (Si–H) was used for the molecular weight determination. The observed molecular weights were

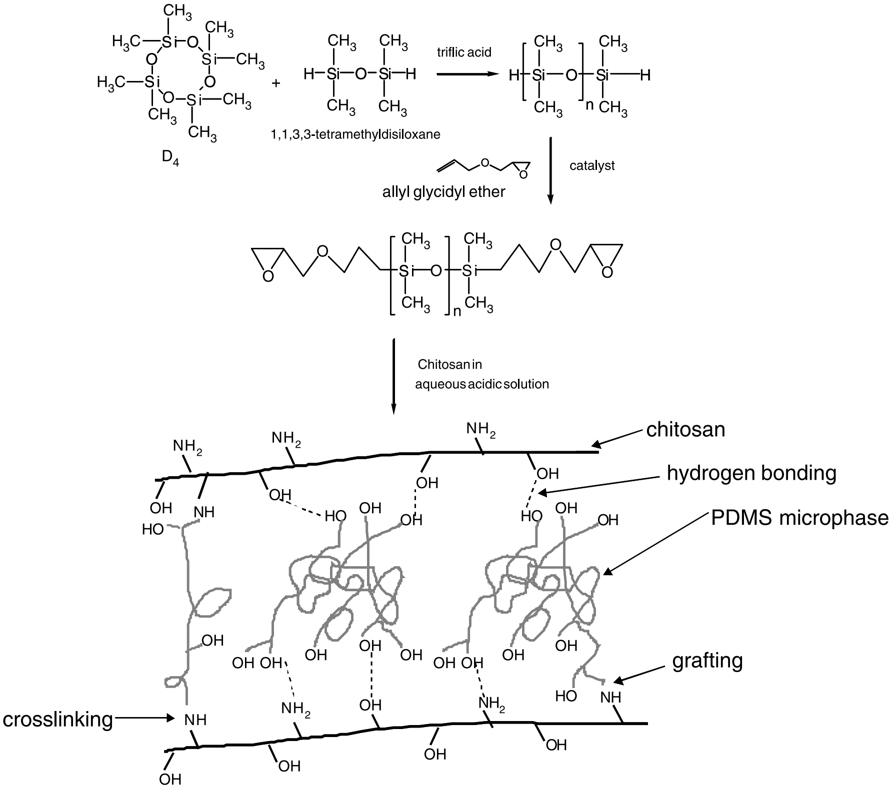

Fig. 1. Synthetic scheme for preparation of chitosan modified with PDMS.

1300, 5300 and 10,700 g/mol, respectively, which are slightly higher than the targeted values. This is probably owing to the partial loss of low molecular weight linear species during vacuum stripping off the equilibrium cyclics.

Si–H groups at each end on the PDMS prepolymers were hydrosilylated with allyl glycidyl ether to obtain epoxidized PDMS. One and a haft mole of allyl glycidyl ether per mole of Si–H group were incorporated to provide sufficient allyl groups to completely react with Si–H ends of the prepolymers. An excess of allyl glycidyl ether was quantitatively removed once the reaction was complete. Because this hydrosilylation reaction was highly exothermic, it was important to add the PDMS prepolymers into an excess of allyl glycidyl ether dropwise. FTIR was used to observe the disappearance of the strong Si–H stretching peak at 2150 cm^{-1} (Fig. 2). In addition to FTIR, the reaction progress was also investigated via proton NMR by observing the disappearance of the signal at 4.7 ppm corresponding to Si–H in the prepolymers (Spectrum A inFig. 3). Proton NMR of the complete reaction before purification indicated the existence of toluene and the remaining allyl glycidyl ether (Spectrum B inFig. 3). The signals corresponding to these residues were completely disappeared after purification by vacuum stripping off whereas the signals corresponding to the hydrosilylated products appeared (signal*b–i* in Spectrum C,Fig. 3).

Molecular weights of the epoxidized PDMS were calculated based on^{1}H and^{13}C NMR. In^{1}H NMR, the molecular weights were determined based on the integration ratio of the signal at 3.15 ppm (peak*g*) corresponding to the protons in the epoxy ring to the signal at 0.1 ppm corresponding to Si–CH_3 (methyl protons on Si) (Fig. 3). In^{13}C NMR, the methylene carbons attached to the terminal silicons (peak*b* at 14 ppm) were used in conjunction with methyl peaks in the repeating units (peak*a*) to calculate its molecular weights (Fig. 4). In all cases, the molecular weights of the epoxidized PDMS were slightly higher than those of the PDMS prepolymers due to the incorporation of two epoxy functional groups at both ends (Table 1). In addition to that, determination of the molecular weights and polydispersity index of the polymers was carried out using GPC. The molecular weights of 5000 and 10,000 g/mol PDMS estimated from GPC were comparable to the targeted numbers and also close to the molecular weights determined from^{1}H and^{13}C NMR techniques. However, the

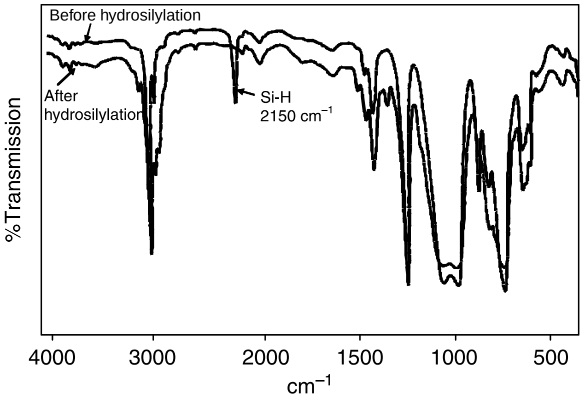

Fig. 2. FTIR spectra of PDMS before and after hydrosilylation with allyl glycidyl ether.

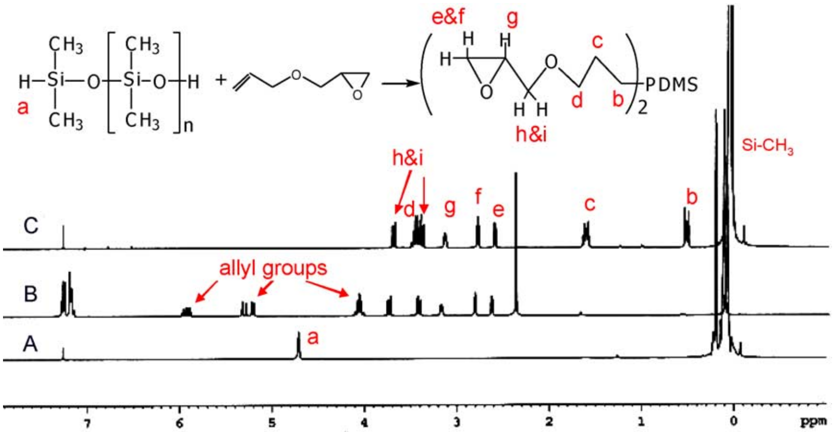

Fig. 3. ^{1}H NMR spectrum of 1000 g/mol PDMS, (A) prepolymer with Si–H terminal, (B) after hydrosilylation with allyl glycidyl ether before purification, and (C) after purification.

molecular weight of 1000 g/mol PDMS oligomer estimated from GPC was significantly higher than the targeted value. This is likely due to the molecular weight of the oligomer was so small that GPC could not determine their molecular weights precisely. Polydispersity indexes of PDMS were decreased as increasing the molecular weights of the polymers. The thermal behavior of the polymers was investigated using DSC. TheT_g's of epoxidized PDMS were approximately -125 °C regardless of the molecular weights of the polymers.

3.2. Preparation of PDMS-modified chitosan films

To prepare the PDMS-modified chitosan films, approximately 10% by volume of isopropanol were used to dissolve PDMS and added into the chitosan aqueous solution to enhance the miscibility between PDMS and chitosan. Addition of isopropanol more than 10% by volume resulted in aggregation of chitosan in the mixture. One to ten weight percent of PDMS in chitosan were prepared. Phase separation during drying process was troublesome when mixing more than 10 wt% of hydrophobic PDMS into hydrophilic chitosan. Moreover, it is thought that a small quantity of PDMS should enhance flexibility and modify surface of the chitosan-based films without sacrificing their swelling properties. This might be important in some applications, e.g. wound healing materials, which need to retain excellent water swellability of chitosan. Incorporation of the functionalized PDMS into chitosan in an acidic aqueous solution is thought to essentially open the epoxy rings and form vicinal diols (1,2-diols) at each PDMS terminal. The amphiphilic characteristics due to the formation of hydrophilic hydroxyl terminals and hydrophobic PDMS backbone apparently enhanced the miscibility between PDMS and chitosan. This phenomenon was evidenced by the significantly lower concentration of the unfunctionalized PDMS that can be introduced into chitosan solutions without phase separation. It is hypothesized that the hydroxyl terminals formed hydrogen bonding with chitosan and left PDMS backbone to aggregate microscopically. Crosslinking and/or grafting reactions of the difunctionalized PDMS with chitosan were also possible (Fig. 1). Extraction of the dissolvable portions was carried out in acetic aqueous solutions to remove uncrosslinked chitosan followed by acetone to remove uncrosslinked PDMS. It should be noted that chitosan without PDMS is well soluble in acetic aqueous solution. Lower percent of extractable portion implies that there is higher degree of crosslinking. Chitosan containing 1000 and 5000 g/mol PDMS did not show any significant difference in percent of extractable parts (Fig. 5). On the other hand, chitosan containing 10,000 g/mol PDMS exhibited more than 90% extractable parts, which indicated that there were less PDMS crosslinked with chitosan than those of the low molecular weight ones. This was likely because high degree of hydrophobicity of the high molecular weight PDMS enhanced microphase separation, allowing less PDMS to react with

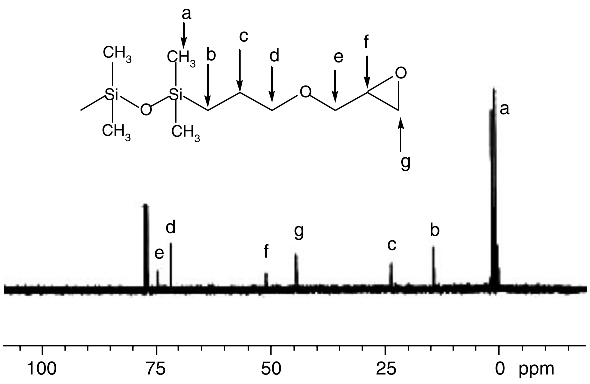

Fig. 4. ^{13}C NMR spectrum of 1000 g/mol epoxidized PDMS.

Table 1
Number average molecular weights and polydispersity index of PDMS

Mn of the PDMS pre-polymer (g/mol)		Mn of the epoxidized PDMS (g/mol)			Polydispersity Index*
Targeted Mn	^{1}H NMR	^{1}H NMR	^{13}C NMR	GPC	
1000	1300	1500	1600	2600	1.70
5000	5300	5700	5500	6000	1.60
10,000	10,700	11,500	11,000	12,000	1.35

Based on GPC.

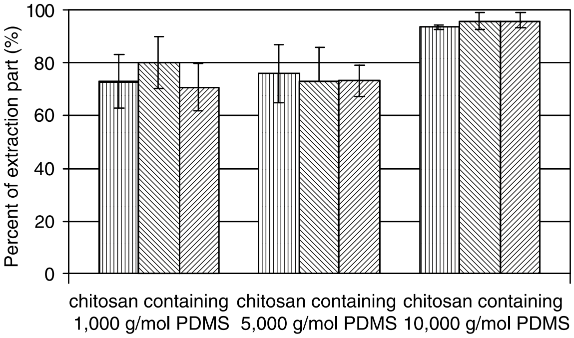

Fig. 5. Percent extraction part of PDMS-modified chitosan as a function of molecular weights and percent of PDMS in chitosan. ▥ is chitosan containing 1 wt% PDMS. ▧ is chitosan containing 5 wt% PDMS. ▨ is chitosan containing 10 wt% PDMS.

chitosan. Incorporating different amounts of PDMS in chitosan in each sample did not exhibit any significant difference in percent extractable portions. This might imply that the increment of the PDMS crosslinker did not enhance percent crosslinking between PDMS and chitosan but enhanced microphase separation instead.

3.3. Water swelling properties

Fig. 6 exhibits swelling behavior of unmodified chitosan and chitosan containing 1, 5 and 10 wt% of 10,000 g/mol PDMS. The unmodified chitosan reached the equilibrium rapidly within 10 min with equilibrium water content (EWC) of approximately 120%. Percent of water swelling of modified chitosan in all cases reached equilibrium within the first hour of the investigation. These swollen chitosan remained intact without observed debris throughout the investigation. Increase of PDMS content in chitosan from 1 to 10 wt% resulted in a significant increase of EWC.Fig. 7 exhibits the effect of molecular weight and content of PDMS on EWC. EWC was consistently increased as increasing the molecular weight or/and content of PDMS in chitosan. This dramatic increases of EWC were probably due to the presence of microphase separation of PDMS amphiphile in chitosan matrix. Namely, hydrophobic segments of PDMS backbone might microscopically aggregate and leave hydrophilic parts due to hydroxyl endgroups hydrogen bonding with chitosan. The presence of microphase separation resulted in significant increase of surface area of chitosan owing to porous-like morphology. The existence of PDMS microphase could be confirmed by scanning electron microscopy (SEM) technique.Fig. 8A–C show SEM images of chitosan containing 10 wt% of 5000 g/mol PDMS in various stages of swelling test andFig. 8D shows the cross-section of the same sample. Chitosan containing different PDMS molecular weights and contents exhibited similar results. Before submerging the film into water, the sample contained spherical PDMS phase with size ranging from 15 to 25 μm in diameter (Fig. 8A). These spheres became smaller after prolonged swelling for 1 h (Fig. 8B) and became even smaller (less than 20 μm) after 24 h of the experiment (Fig. 8C). This indicated that chitosan absorbed water at the PDMS-chitosan interface resulting in enhanced water absorbability of PDMS-containing chitosan as compared to the unmodified one. The existence of the spherical PDMS phase throughout the materials even further enhanced water swellability due to the significant increase of the PDMS-chitosan interface (Fig. 8D). However, the sizes of these spherical PDMS (2–3 μm) were significantly smaller than those at the surface (15–25 μm). It is hypothesized that, due to its inherently low surface tension, PDMS can exhibit microphase separation in chitosan during the drying process and then slowly migrate to chitosan-air interface, resulting in PDMS-rich surface and large PDMS phase sizes. Incorporation of higher molecular weight and content of PDMS resulted in a larger PDMS phase size, and, thereby, increased EWC, as shown inFig. 7. However, addition of PDMS more than 10 wt% resulted in phase separation between hydrophobic PDMS and hydrophilic chitosan as observed by the presence of PDMS on chitosan surface after the film preparation process.

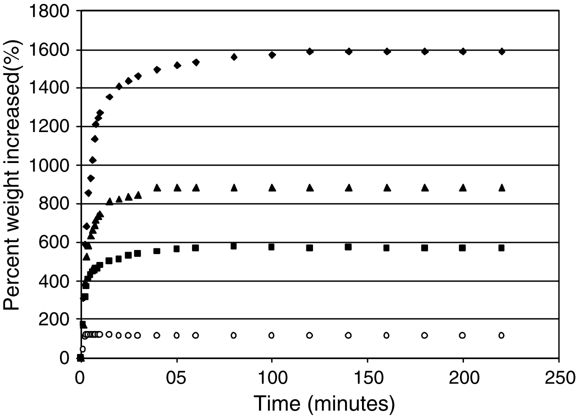

Fig. 6. Swelling behavior of chitosan without PDMS (○), containing 1 wt% (■), 5 wt% (▲), and 10 wt% (◆) of 10,000 g/mol PDMS.

3.4. Water contact angle

It is well known that PDMS is a hydrophobic polymer with extremely low surface tension, and therefore it has been used as a surface modifier in various applications (Huang, Yao, Huang, & Yunzhao, 2001; Janocha, Hegemann, Oehr, Brunner, Rupp and Geis-Gerstorfer, 2001). Therefore, in the present work, incorporation of small amount of PDMS into chitosan was not only aimed to improve their toughness properties, but also to

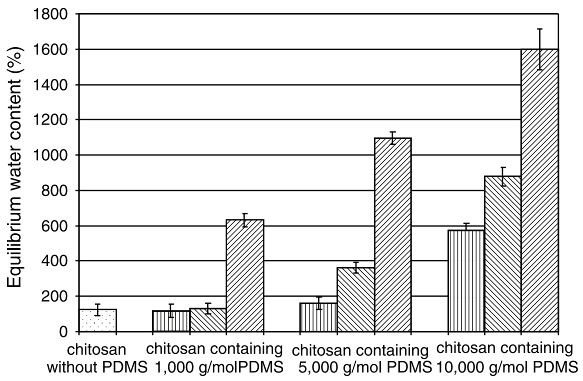

Fig. 7. Swelling behavior of PDMS-modified chitosan as a function of molecular weights and percent of PDMS in chitosan. ⬚ is chitosan without PDMS. ▥ is chitosan containing 1 wt% PDMS. ▩ is chitosan containing 5 wt% PDMS. ▨ is chitosan containing 10 wt% PDMS.

modify its surface. To compare the wettability of PDMS-modified chitosan to the unmodified one, contact angles between sample surface and water were measured in air using the sessile method (Huh, Kang, Lee, Kim, Lee and Park, 2001; Ishihara, Iwasaki, Ebihara, Shindo, & Nakabayashi, 2000).Fig. 9 exhibits the results of water contact angles as a function of PDMS molecular weights and contents. The water contact angle of the unmodified chitosan was 66.2 ± 3.9 °, which is significantly lower than those of the PDMS modified chitosan ranging from 80 to 105 °, meaning that incorporation of PDMS rendered the surface less water wettable. The result is in agreement with SEM images (Fig. 8), showing the presence of the large PDMS phase on the surface, indicating the PDMS-enriched surface. However, there was no significant change in water contact angles as the molecular weights or/and contents of PDMS increased (Fig. 9). Although incorporating small amount of PDMS into chitosan enhanced surface hydrophobicity of the materials, good water swelling properties of the materials still retained due to the significantly increase of PDMS-chitosan interface in the bulk. This might be a good candidate for some applications that require materials with hydrophobic surfaces and good water swelling properties.

3.5. Water vapor permeability

Permeability of moisture through membranes is an important property for various applications, e.g. wound healing materials, artificial skin, and packaging materials (Mi, Shyu, Wu, Lee, Shyong and Huang, 2001; Tual et al., 2000). Incorporation of other components to materials in order to modify their properties has been extensively studied (Kweon et al., 2001). In the present work, addition of PDMS was not only to improve its mechanical properties and modified its surface, but also modified its transport properties, e.g. water swelling and water vapor permeability.Fig. 10 exhibits the influence of PDMS with various molecular weights and contents on water vapor permeability. Small amount of PDMS can significantly lower water vapor permeability of chitosan. This suggests that the hydrophobic characteristics of PDMS presented in chitosan, especially at the surface, rendered the films resistant to moisture, resulting in inhibiting water vapor to permeate through the membranes. Increasing the molecular weight of PDMS tended to increase water vapor permeability of the films. This is probably due to low miscibility of high molecular weight PDMS in chitosan,

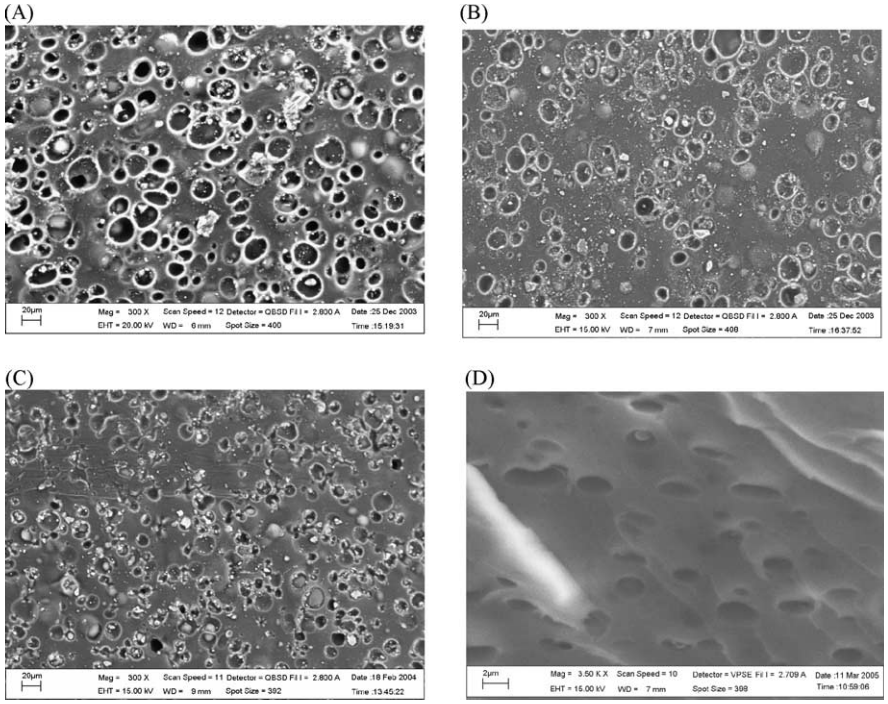

Fig. 8. Scanning electron micrographs (SEM) of chitosan containing 10 wt% of 5000 g/mol PDMS, (A) before submerging in water, (B) after submerging in water for 1 h, (C) after submerging in water for 24 h, and (D) cross section of the material before submerging in water.

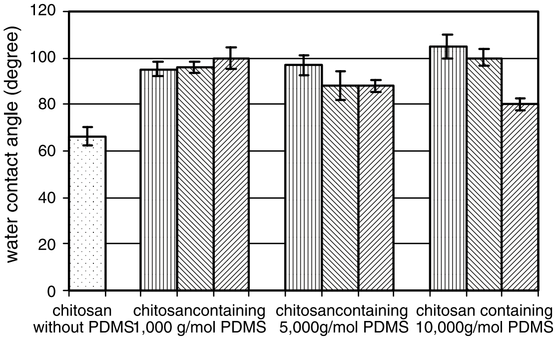

Fig. 9. Water contact angle of PDMS-modified chitosan as a function of molecular weights and percent of PDMS in chitosan. ⬚ is chitosan without PDMS. ▥ is chitosan containing 1 wt% PDMS. ▧ is chitosan containing 5 wt% PDMS. ▨ is chitosan containing 10 wt% PDMS.

which might enhance hydrophobic PDMS to separate microscopically from chitosan. As a result, chitosan contained less PDMS and exhibited higher water vapor permeability. However, significant change of water vapor permeability was not observed when PDMS contents in chitosan were increased from 1 to 10 wt%.

3.6. Mechanical properties

Measurement of tensile strength and elongation at break provides an indication of the strength and elasticity of materials. Tough and flexible properties of materials are preferable for some applications, e.g. wound dressing material and skin scaffold (Khan, Peh, & Chang, 2002). Since PDMS is a well-known elastic polymer, incorporating PDMS into chitosan-based films is thought to toughen the materials, and thereby improve their flexibility. According to the mechanical measurement, tensile strength and elongation at break of the unmodified chitosan were 75.6 ± 3.2 MPa and 1.6 ± 0.7%, respectively. A low percent elongation value indicated that the material was rather brittle because it was in a dry state. In all cases, the PDMS-containing chitosan films exhibited a low tensile strength and high elongation at break as compared to the unmodified chitosan films, indicating that the PDMS-modified films were tougher and more flexible (Fig. 11). Further increases in the molecular weights of PDMS from 1000 to 5000 and 10,000 g/mol did not show any significant change in tensile strength but exhibited an increase in percent elongation. Considering the effect of percent PDMS in chitosan on its mechanical properties, further increases in PDMS content tended to lower their tensile strength in all cases and increase percent elongation only in 1000 g/mol PDMS-containing chitosan. There was no trend observed upon increasing amounts of 5000 and 10,000 g/mol PDMS in chitosan.

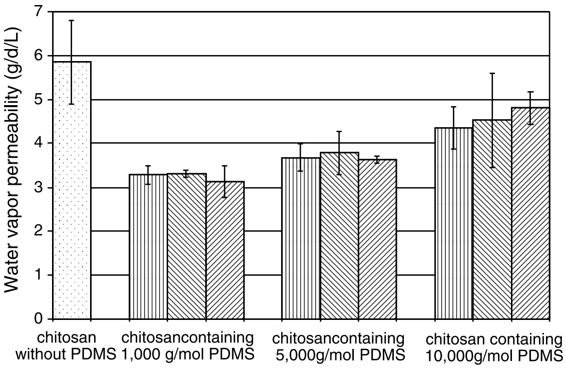

Fig. 10. Water vapor permeability of PDMS-modified chitosan as a function of molecular weights and percent of PDMS in chitosan. ⬚ is chitosan without PDMS. ▥ is chitosan containing 1 wt% PDMS. ▧ is chitosan containing 5 wt% PDMS. ▨ is chitosan containing 10 wt% PDMS.

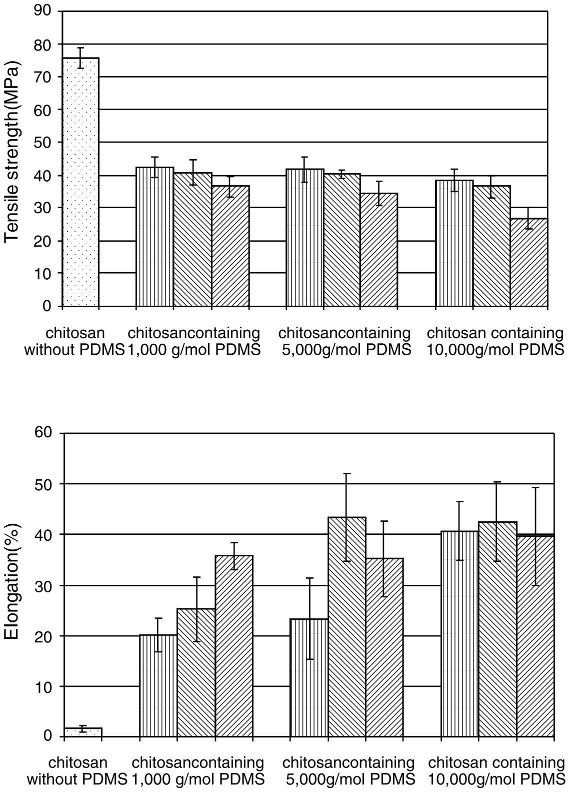

Fig. 11. Tensile strength (A) and elongation (B) properties of PDMS-modified chitosan as a function of molecular weights and percent of PDMS in chitosan. ⬚ is chitosan without PDMS. ▥ is chitosan containing 1 wt% PDMS. ▧ is chitosan containing 5 wt% PDMS. ▨ is chitosan containing 10 wt% PDMS.

4. Conclusions

PDMS with controlled molecular weight was prepared via the cationic ring opening polymerization of D_4 followed by hydrosilylation with allyl gylcidyl ether to obtain epoxy-functional endgroups. Mixing the functionalized PDMS with chitosan in an acidic aqueous solution allowed the formation of hydroxyl PDMS terminals, which improved solubility between the hydrophobic PDMS and hydrophilic chitosan. The extraction of the uncrosslinked portion implied that chitosan containing lower molecular weight PDMS exhibited higher degree of crosslinking. Incorporation of the PDMS into chitosan rendered the films more flexible as compared to the unmodified ones. Equilibrium water content (EWC) increased as the PDMS contents and molecular weights increased due to the presence of PDMS microphase as indicated by SEM. In addition, it was found that addition of the PDMS into chitosan enhanced hydrophobicity of chitosan as indicated by the increase of water contact angles and the decrease in water vapor permeability of the PDMS-containing chitosan when compared to the unmodified one.

Acknowledgements

The authors would like to acknowledge The Thaland Research Fund (TRF) and The Ministry of University Affairs (MRG4680090), and the National Metal and Materials Technology Center (MTEC) (MT-S-46-BMD-26-070-G) for financial support.

References

Amiji, M. M. (1995). Permeability and blood compatibility properties of chitosan–poly(ethylene oxide) blend membranes for haemodialysis. *Biomaterials*, *16*, 593–599.

Gupta, K. C., Majeti, N. V., & Kumar, R. (2001). pH dependent hydrolysis and drug release behavior of chitosan/poly(ethylene glycol) polymer network microspheres. *Journal of Materials Science: Materials in Medicine*, *12*, 753–759.

Huang, W., Yao, Y., Huang, Y., & Yu, Y. (2001). Surface modification of epoxy resin by polyether–polydimethylsiloxanes–polyether triblock copolymers. *Polymer*, *42*, 1763–1766.

Huh, M. W., Kang, I. K., Lee, D. H., Kim, W. S., Lee, D. H., Park, L. S., et al. (2001). Surface characterization and antibacterial activity of chitosan-grafted poly(ethylene terephtharate) prepared by plasma glow discharge. *Journal of Applied Polymer Science*, *81*, 2769–2778.

Ishihara, K., Iwasaki, Y., Ebihara, S., Shindo, Y., & Nakabayashi, N. (2000). Photoinduced graft polymerization of 2-methacryloxyethyl phosphorylcholine on polyethylene membrane surface for obtaining blood cell adhesion resistance. *Colloid and Surfaces B: Biointerfaces*, *18*, 325–335.

Janocha, B., Hegemann, D., Oehr, C., Brunner, H., Rupp, F., & Geis-Gerstorfer, J. (2001). Adsorption of protein on plasma-polysiloxane layers of different surface energies. *Surface and Coatings Technology*, *142–144*, 1051–1055.

Khan, T. A., Peh, K. K., & Chang, H. S. (2002). Mechanical, bioadhesive strength and biological evaluations of chitosan films for wound dressing. *Journal of Pharmacy and Pharmaceutical Science*, *3*, 303–311.

Khor, E., & Lim, L. (2003). Implantable applications of chitin and chitosan. *Biomaterials*, *24*, 2339–2349.

Kim, I. Y., Kim, S. J., Shin, M., Lee, Y. M., Shin, D., & Kim, S. I. (2002). pH- and thermal characterization of graft hydrogels based on chitosan and poly(dimethylsiloxane). *Journal of Applied Polymer Science*, *85*, 2661–2666.

Kweon, D. K. (1998). Preparation and characteristics of chitosan-g-PDMS copolymer. *Polymer Bulletin*, *41*, 645–651.

Kweon, H., Ha, H. C., Um, I. C., & Park, Y. H. (2001). Physical properties of silk fibroin/chitosan blend films. *Journal of Applied Polymer Science*, *80*, 928–934.

Mi, F. L., Shyu, S. S., Wu, Y. B., Lee, S. T., Shyong, J. Y., & Huang, R. N. (2001). Fabrication and characterization of a sponge-like asymmetric chitosan membrane as a wound dressing. *Biomaterials*, *22*, 165–173.

Prashanth, K. V., & Tharanathan, R. N. (2003). Studies on graft copolymerization of chitosan with synthetic monomers. *Carbohydrate*, *54*, 343–351.

Rutnakornpituk, M. (2005). Modification of epoxy-novolac resins with polysiloxane containing nitrile functional groups: Synthesis and characterization. *European Polymer Journal*, *41*, 1043–1052.

Schulze Nahrup, J., Gao, Z. M., Mark, J. E., & Sakr, A. (2004). Poly(dimethylsiloxane) coatings for controlled drug release-polymer modifications. *International Journal of Pharmaceutics*, *270*, 199–208.

Shin, M., Kim, S. I., Kim, I. Y., Kim, N. G., Song, C. G., & Kim, S. J. (2002). Characterization of hydrogels based on chitosan and copolymer of poly(dimethylsiloxane) and poly(vinyl alcohol). *Journal of Applied Polymer Science*, *84*, 2591–2596.

Tanodekaew, S., Prasitsilp, M., Swadison, S., Thavornyutikarn, B., Pothsree, T., & Pateepasen, R. (2004). Preparation of acrylic chitin for wound dressing application. *Biomaterials*, *25*, 1453–1460.

Tual, C., Espuche, E., Escoubes, M., & Domard, A. (2000). Transport properties of chitosan membranes: Influence of crosslinking. *Journal of Polymer Science, Part B: Polymer Physics*, *38*, 1521–1529.

Zeng, M., & Fang, Z. (2004). Preparation of sub-micrometer porous membrane from chitosan/polyethylene glycol semi-IPN. *Journal of Membrane Science*, *245*, 95–102.

Zeng, M., Fang, Z., & Xu, C. (2004). Effect of compatibility on the structure of the microporous membrane prepared by selective dissolution of chitosan/synthetic polymer blend membrane. *Journal of Membrane Science*, *230*, 175–181.

Zhang, M., Li, X. H., Gong, Y. D., Zhao, N. M., & Zhang, X. F. (2002). Properties and biocompatibility of chitosan films modified by blending with PEG. *Biomaterials*, *23*, 2641–2648.