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Polymer 46 (2005) 9742–9752

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Synthesis, characterization and properties of chitosan modified with poly(ethylene glycol)–polydimethylsiloxane amphiphilic block copolymers

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Received 5 June 2005; received in revised form 16 August 2005; accepted 17 August 2005
Available online 6 September 2005

Abstract

Synthesis of poly(ethylene glycol)-polydimethylsiloxane amphiphilic block copolymers is discussed herein. Siloxane prepolymer was first prepared via acid-catalyzed ring-opening polymerization of octamethylcyclotetrasiloxane (D_4) to form polydimethylsiloxane (PDMS) prepolymers. It was subsequently functionalized with hydroxy functional groups at both terminals. The hydroxy-terminated PDMS can readily react with acid-terminated poly(ethylene glycol) (PEG diacid) to give PEG–PDMS block copolymers without using any solvent. The PEG diacid was prepared from hydroxy-terminated PEG through the ring-opening reaction of succinic anhydride. Their chemical structures and molecular weights were characterized using ^{1}H NMR, FTIR and GPC, and thermal properties were determined by DSC. The PEG–PDMS copolymer was incorporated into chitosan in order that PDMS provided surface modification and PEG provided good water swelling properties to chitosan. Critical surface energy and swelling behavior of the modified chitosan as a function of the copolymer compositions and contents were investigated.

Keywords: Chitosan; Polydimethylsiloxane; Poly(ethylene glycol)

1. Introduction

Chitosan, *N*-deacetylated derivative of chitin, has extensively studied in recent years for feasible use in pharmacological, agricultural and biomedical applications, e.g. orthopedic, periodontal, tissue engineering, wound healing, drug delivery applications [1–6]. Use of chitosan as wound healing materials is of particular interest not only due to its biocompatibility, but also its excellent water absorbability, hemostatic properties and economical advantages [2]. Although these intriguing properties seem favorable to use chitosan for the wound healing purpose, its limited solubility only in acidic aqueous solutions due to highly crystalline and rigid structure has inhibited its studies for extensive applications [7]. In addition to that, its relatively high surface energy might induce thrombogenicity to occur and inhibit potential applications of the materials [8]. This phenomenon takes place when polymeric biomaterials possessing high surface energy directly contact with blood, followed by adsorption of blood cells and protein onto the surfaces, platelet adhesion and coagulation eventually [9].

Incorporation of low surface energy polymers into chitosan films has been proposed to minimize these disadvantages [8]. Polydimethylsiloxane (PDMS) is of particular interest for this purpose owing to their low surface energy [10]. In addition to that, other unique properties of PDMS, e.g. low toxicity, high oxygen permeability, good thermal and oxidative stability, are also suitable for use as biomaterials [11]. Medical devices made of polyurethane (PU) containing PDMS soft segment has been reported to exhibit better blood contact properties

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doi:10.1016/j.polymer.2005.08.051

relative to commercially available PU [12–14]. Another advantage of adding PDMS into chitosan is to improve their mechanical properties. Because hardness and brittleness are major drawbacks of chitosan which limit their use as wound healing materials [2], incorporation of elastomeric PDMS (glass transition temperatures ≈ −120 °C) should somewhat soften the materials [15]. Kweon has reported in grafting PDMS homopolymer onto chitosan by chemical modification. Slight decreases in its critical surface energy were observed whereas tensile strength and elongation were insignificantly changed as compared to the unmodified chitosan [8]. Swelling behavior of PDMS-grafted chitosan [16] and of PDMS/poly(vinyl alcohol)-chitosan hydrogel [17] were reported by Kim et al. It was found that equilibrium water content (EWC) of the materials in these two systems decreased as PDMS content increased in time-dependent, temperature-dependent, and pH-dependent behavior. The depression in EWC, which is unfavorable for would healing application, is attributed to the hydrophobic characteristics of PDMS. Moreover, immiscibility of hydrophobic PDMS and hydrophilic chitosan is also limiting the studies. Addition of amphiphilic block copolymers containing PDMS and another hydrophilic segment into chitosan is an interesting approach to surmount these limitations.

Amphiphilic block copolymer, an important class of block copolymers, contains both hydrophobic and hydrophilic segments. This dualistic character has drawn a lot of attentions due to self-assembly of copolymers in a selective solvent, resulting in formation of micelle structure. There are a number of applications of amphiphilic block copolymers that take advantage of the difference in chemical composition, e.g. surfactants, colloid stabilizers and drug carriers [18,19].

Incorporation of poly(ethylene glycol) (PEG)–PDMS amphiphilic copolymers into chitosan is of particular interest in the current studies. PEG is a well-known non-toxic and excellent water-soluble polymer, which is favorable for would healing materials [20–23]. PEG allows the materials to retain their excellent water swelling properties, whereas PDMS modifies its surface to inhibit protein adsorption. Because of covalent bonding of these two phases, soluble PEG segment should bring PDMS segment into chitosan-based matrix, and then PDMS segment exhibits microphase separation [24]. PDMS microphase provides not only surface modification to chitosan, but also should allow the material to possess better oxygen permeability, which is favorable for would dressing application. Only a few studies have reported reaction procedures to achieve PEG–PDMS amphiphilic copolymer [9,25–28].

In the present work, a reaction procedure to prepare PEG–PDMS amphiphilic copolymers has been reported. Their chemical structures and molecular weights were elucidated by ^{1}H NMR, FTIR and GPC, and thermal properties were studied via DSC. Swelling behavior and critical surface energy of chitosan containing these copolymers as a function of copolymer compositions and their contents compared with the unmodified chitosan were also reported.

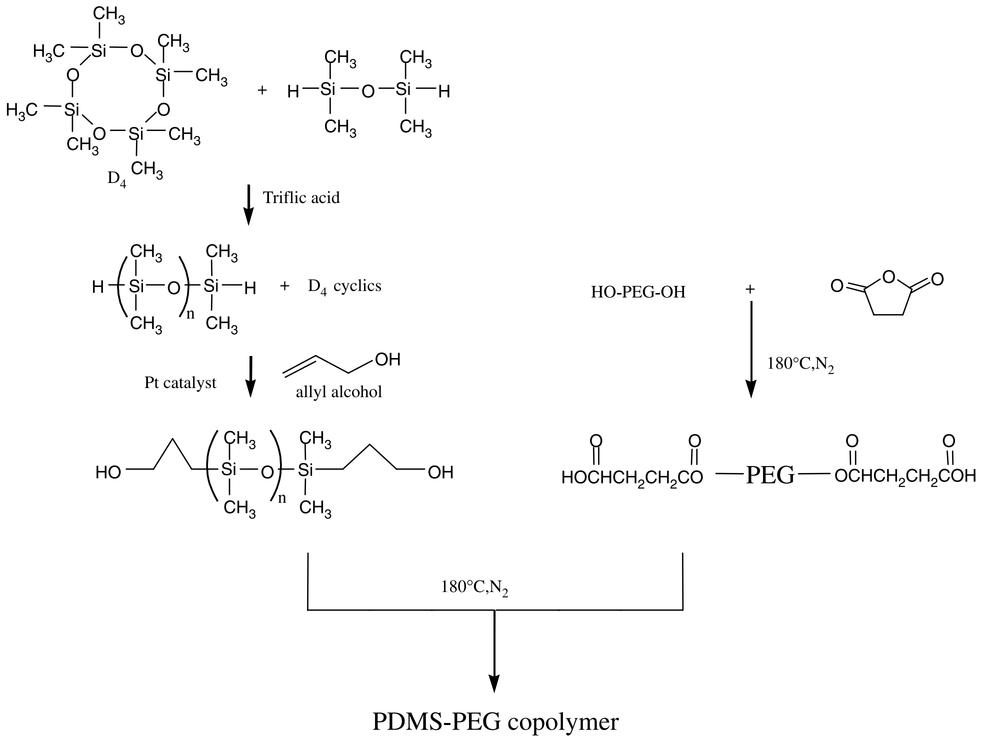

Fig. 1. Synthetic scheme for preparing the PEG–PDMS amphiphilic block copolymers.

2. Experimental

2.1. Materials

Chitosan from crabs (Taming Enterprise, Co.) with 98% deacetylation was used as received. 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 and stored under N_2 until used. Karstd's catalyst (Aldrich) and triflic acid, 98% (Aldrich) were used as received. Poly(ethylene glycol) with M_n 1000 and 8000 g/mol (Acros) were dried in vacuum oven at 60 °C under phosphorus pentoxide for 48 h. Succinic anhydride, 97% (Aldrich) and dibutyltin oxide were used as received.

2.2. Synthesis

The first part of the synthesis of PEG–PDMS block copolymer involved the preparation of PDMS prepolymer with Si–H terminals. The PDMS prepolymer was subsequently hydrosilylated with allyl alcohol to obtain difunctional hydroxy-terminated PDMS (PDMS diol). They were then condensed with PEG diacid to form PEG–PDMS copolymers (Fig. 1).

2.2.1. Synthesis of poly(dimethylsiloxane) prepolymer with M_n of 1000 g/mol (PDMS prepolymer)

D_4 (20 g, 0.068 mol), 1,1,3,3-tetramethyldisiloxane (3.54 ml, 0.02 mol) and triflic acid (0.13 ml, 0.65 wt%) were charged into a round-bottom flask filled with N_2. The mixture was stirred at 55 °C for 72 h to reach thermodynamic equilibrium. Upon the equilibrium, 60 ml of ethyl ether were added into the mixture and it was then washed with deionized water repeatedly to neutralize the mixture. The solution was dried with anhydrous magnesium sulfate and then filtered through a filter paper. D_4 monomers remaining from the equilibrium were removed under reduced pressure at 120 °C overnight.

2.2.2. Synthesis of dihydroxy-terminated poly(dimethylsiloxane) (PDMS diol)

Allyl alcohol (2.04 ml, 0.03 mol), toluene (10 ml) and the Karstd's catalyst (0.08 ml) were charged into a reaction flask with stirring at 50 °C. Thousand grams per mole PDMS prepolymer (10 g) was then slowly introduced into the reaction flask via a dropping funnel. The reaction temperature was raised to 65 °C for 2 h. An excess of allyl alcohol was removed under reduced pressure at 100 °C for 3 h.

2.2.3. Synthesis of 1,3-di(3-hydroxylpropyl)-1,1,3,3-tetramethyldisiloxane (disiloxane diol)

Allyl alcohol (2.04 ml, 0.03 mol), toluene (10 ml) and a platinum catalyst (0.08 ml) were charged into a reaction flask with consistently stirring at 50 °C. 1,1,3,3-Tetramethyldisiloxane (3.54 ml, 0.02 mol) was then slowly introduced into the reaction flask via a dropping funnel. The reaction temperature was raised to 65 °C for 2 h. An excess of allyl alcohol was removed under reduced pressure at 100 °C for at least 3 h.

2.2.4. Synthesis of dicarboxylic acid-terminated poly(ethylene glycol) (PEG diacid)

An example procedure is for preparing 1000 g/mol PEG diacid. Eight thousand grams per mole PEG diacid was prepared in a similar manner but using hydroxy-terminated PEG with M_n 8000 g/mol as a prepolymer. Dry hydroxy-terminated PEG (10 g), succinic anhydride (2.4 g, 0.024 mol) and dibutyltin oxide (0.0020 g) were charged into a two neck 100 ml round bottom flask. A slight excess of succinic anhydride was used to ensure that hydroxy terminals were completely reacted. The reaction mixture was maintained at 180 °C under N_2 for 24 h. Once the reaction was cool down, the mixture was dissolved in 50 ml of cold CH_2Cl_2. Because the unreacted succinic anhydride is insoluble in cold methylene chloride, it was easily removed by filtration. Methylene chloride in the mixture was removed using a rotary evaporator. The polymer was dried at 60 °C under reduced pressure over night.

2.2.5. Synthesis of PEG–PDMS block copolymer

Carboxylic acid-terminated PEG with M_n 1000 g/mol (10 g), hydroxy-terminated PDMS with M_n 1000 g/mol (5 g) and dibutyltin oxide were charged into a three-neck round bottom flask adapted with a mechanical stirrer. The mixture was kept at 180 °C under N_2 purge for 24 h without using any solvent. After the reaction, the mixture was slowly cool down at room temperature under nitrogen purge. Copolymers with different block lengths were prepared in the same procedure but using the corresponding functionalized homopolymers.

2.2.6. Preparation of chitosan modified with PEG–PDMS/disiloxane copolymers

Chitosan (5.0 g) was dissolved in a 0.5 M acetic acid aqueous solution. Desired weight of copolymers was introduced into the chitosan solution with continuous stirring for 2 h. The solutions were then poured into a glass mold 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 2 days under reduced pressure. The copolymer-modified chitosan was somewhat opaque as compared to the unmodified chitosan.

2.3. Characterization

2.3.1. Characterization of polymers

^1H NMR was performed on a 400 MHz Bruker NMR spectrometer using $CDCl_3$ as a solvent. FTIR spectra were measured using a KBr disk method via a Perkin–Elmer Spectrum GX0 Series FTIR Spectrophotometer. GPC data was conducted on PLgel 10 μm mixed B2 columns and a refractive index detector. 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 DSC. The PEG–PDMS/disiloxane copolymers were heated from −140 to 50 °C with a 10 °C/min heating rate, whereas the PDMS-containing chitosan was heated from 25 to 200 °C with a 20 °C/min heating rate. The T_g values taken from the midpoints of the curves were determined from the second scans.

2.3.2. Measurement of swelling properties of chitosan

The pre-dried samples were precisely weighed (70–80 mg) and immerged in a phosphate buffer saline (PBS) solution with pH 7.4 at room temperature. At a given time interval, the swollen samples were removed from the solution, wiped off an excess solution on surface and weighed. Percent of water swelling was calculated as follows:

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

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

2.3.3. Measurement of critical surface energy of chitosan

Contact angle (θ) between a series of solvents and chitosan films was measured on a KRUSS DSA 10 Contact Angle Meter at room temperature. Six organic solvents with different surface tensions were used in this investigation: THF ($\gamma = 26.40$ dyn/cm), CH_2Cl_2 ($\gamma = 27.20$ dyn/cm), *o*-xylene ($\gamma = 29.76$ dyn/cm), DMF ($\gamma = 37.10$ dyn/cm), ethylene glycol ($\gamma = 47.99$ dyn/cm), and glycerol ($\gamma = 64.00$ dyn/cm) [10]. According to the Zisman method, critical surface energy, γ_c, of the films can be determined from the plot between cosine of contact angles (θ) and surface tensions (γ) of each solvent where cosine of contact angles (θ) was equal to one (Cos $\theta = 1$). The reported values are the average of three different measurements.

3. Results and discussion

3.1. Synthesis of PDMS diol and disiloxane diol

PDMS diol with M_n 1000 g/mol was prepared following a two-step synthesis (Fig. 1). In the first step, PDMS prepolymer was synthesized via the acid-catalyzed ring-opening equilibrium polymerization of D_4 using 1,1,3,3-tetramethyldisiloxane as the endcapping reagent. To control the molecular weight of the polymer, one mole of the endcapping agent was used for every mole of the polymer. During the reaction, the concentration of the polymer relative to cyclic species and its molecular weight were determined using GPC. In addition to control the molecular weight, 1,1,3,3-tetramethyldisiloxane endcapping reagent also allowed the polymer to have Si–H terminals, which would be needed in the second step of the synthesis. According to GPC result, the ratio of linear to cyclic species at equilibrium was 85 wt% linear chains and 15 wt% small cyclics. The cyclics remaining upon the reaction equilibrium were removed by evaporation under reduced pressure at high temperature.

The molecular weight of the prepolymer was estimated using ^1H NMR technique. The peak at 0.1 ppm corresponding to methyl protons along the 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 molecular weight determination. The observed molecular weight was approximately 1500 g/mol, which is somewhat higher than the targeted value. This is likely attributed to the loss of low molecular weight linear species during vacuum stripping off the equilibrium cyclics.

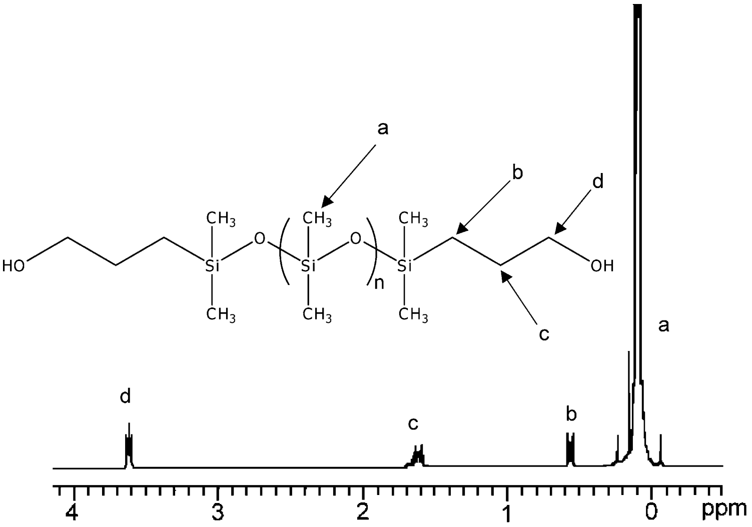

Fig. 2. ^1H NMR spectrum of hydroxy-terminated PDMS in $CDCl_3$.

In the second step, the Si–H terminals of the prepolymer were then hydrosilylated with allyl alcohol to produce PDMS diol. The reaction was carried out in toluene due to phase separation of the mixture. One and a half moles of allyl alcohol were used for every mole of Si–H bonds in the prepolymer to ensure that the polymer ends were fully capped. The reaction progress was monitored by observing the decrease of an integration ratio of a Si–H signal (4.7 ppm) to a Si–CH_3 signal (0.1 ppm) in ^{1}H NMR spectra. The presence of methylene proton signals (peaks *b*, *c* and *d*) in combination with the complete disappearance of a Si–H signal (4.7 ppm) in ^{1}H NMR spectra after purification process indicated that the prepolymers were fully capped (Fig. 2). In addition to ^{1}H NMR, FTIR technique also showed the disappearance of a Si–H stretching signal at 2128 cm^{-1} of the prepolymer and the existence of a hydroxy functional group at 3334 cm^{-1} of the PDMS diols (Fig. 3).

Disiloxane diol was prepared in a similar fashion to the PDMS diol but using 1,1,3,3-tetramethyldisiloxane instead of PDMS prepolymer. Upon preparing the amphiphilic block copolymer, this disiloxane diol would allow the copolymer to have high polarity due to the existence of only two siloxane units in the hydrophobic moiety. Similar to the preparation of the PDMS diol, the disappearance of Si–H signals in ^{1}H NMR (4.7 ppm) and FTIR spectra (2128 cm^{-1}) indicated that Si–H bonds in 1,1,3,3-tetramethyldisiloxane were completely reacted with allyl alcohol.

3.2. Synthesis of carboxylic acid-terminated PEG

Carboxylic acid-terminated PEG was synthesized from commercially available hydroxy-terminated PEG via a tin-catalyzed ring-opening polymerization of succinic anhydride. Dibutyltin oxide has been reported as an effective catalyst for the condensation reaction [29]. One mole of tin was used for every 20,000 mol of hydroxy functional groups. In the present work, hydroxy-terminated PEG with M_ns of 1000 and 8000 g/mol were used as PEG prepolymers to investigate the effect of hydrophilic block lengths in the amphiphilic block copolymers on swelling properties and critical surface tension of the copolymer-modified chitosan. To prepare PEG with carboxylic acid terminals, 2.4 mol of succinic anhydride were used for every mole of PEG (two moles of hydroxy groups). The slight excess of succinic anhydride introduced in the reaction was to allow the hydroxy functional groups in PEG to completely react. During the reaction, it was observed that the excess of succinic anhydride sublimed inside the reaction vessel. Upon the reaction, PEG diacid was dissolved in cold methylene chloride and the unreacted succinic anhydride was easily removed by filtration.

Structural characterization of PEG diacid was performed by ^{1}H NMR technique to observe the disappearance of the signals corresponding to succinic anhydride (3.00 ppm) and methylene protons adjacent to hydroxy groups in PEG prepolymer (–OCH$_2$CH_2OH, 3.75 ppm). In addition to that, the signals corresponding to the methylene protons in PEG diacid (peak *b* and *c*, Fig. 4) appeared upon the reaction. Molecular weights of PEG diacid were estimated from the signal at 2.55 ppm (peak *b*) corresponding to the methylene protons between two carbonyl groups at the chain terminals in conjunction with methylene peaks in the repeating units (peak *a* at 3.60 ppm) (Fig. 4). It was found that the molecular weights of PEG diacid prepared from 1000 and 8000 g/mol PEG diols were approximately 1150 and 8200 g/mol, respectively. These numbers are comparable to the molecular weights of 1 mol of PEG diol combined with two moles of succinic anhydride.

The signal at 1735 cm^{-1} in the FTIR spectrum corresponding to the carbonyl group of carboxylic acid also confirmed the formation of PEG diacid (Fig. 5). It should be noted that the signals corresponding to the carbonyl group of succinic anhydride are approximately 1865 cm^{-1} due to an asymmetric C=O stretching mode and 1782 cm^{-1} due to a symmetric C=O stretching mode [30] and both did not appear. These indicated that there was no unreacted succinic anhydride remaining after purification.

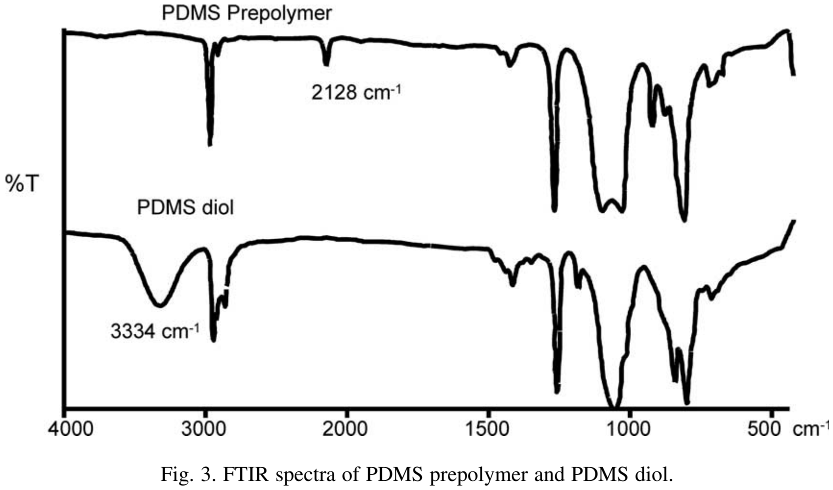

Fig. 3. FTIR spectra of PDMS prepolymer and PDMS diol.

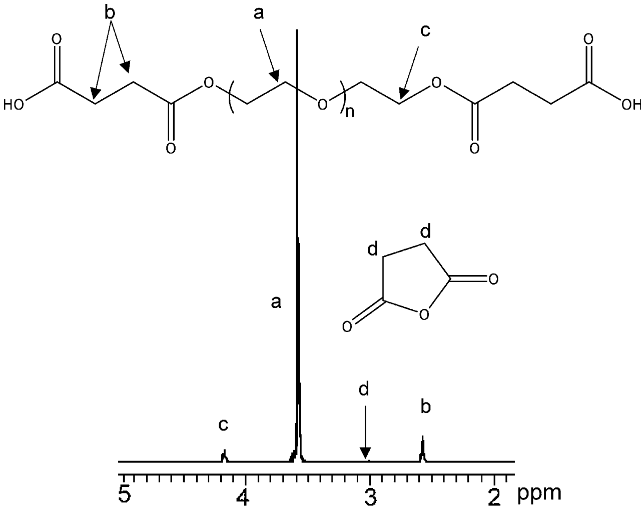

Fig. 4. ^{1}H NMR spectrum of carboxylic acid-terminated PEG in $CDCl_3$.

As depicted in Fig. 5, the signal corresponding to the hydroxy group in carboxylic acid terminals of PEG diacid (3506 cm^{-1} in spectrum B) exhibited significantly less intensity than that of PEG diol (3408 cm^{-1} in spectrum A). This is probably due to inherently labile protons of carboxylic acid functional groups allowing, to some extent, the formation of dicarboxylate-terminated PEG.

3.3. Synthesis of PEG–PDMS block copolymers

The condensation reaction between PEG diacid and PDMS diol was carried out at 180 °C under nitrogen atmosphere without using any solvent. In addition to high reaction temperature, it is believed that nitrogen purging during the reaction can continuously remove water by-product and enhance the reaction equilibrium to the condensation products. Although phase separation was observed at the early stage of the reaction, continuously stirring the reaction mixture combined with a high reaction temperature rendered the mixture homogeneous within 2 h. 2:1 Molar ratio of PEG:PDMS were used in the reaction to obtain ideal triblock copolymers of PEG tail blocks and PDMS or disiloxane central blocks. The purpose of incorporating high content of PEG relative to PDMS in the copolymer was to retain good water swelling properties of PEG, while allowing small amount of PDMS or disiloxane to migrate to the surface of the films when mixing with chitosan without sacrificing water swelling properties. The evidence of ester linkages from the coupling reaction between PDMS/disiloxane diol and PEG diacid, however, was not observed by FTIR and ^{1}H NMR techniques. This is attributed to a small number of ester linkages from the coupling reaction. In addition, the ester linkages existed in PEG diacid also rendered them difficult to be distinguished.

An increase of size or molecular weight of copolymers as compared to PDMS/disiloxane and PEG homopolymers was evidenced by GPC technique. Fig. 6 shows the increment of the molecular weight of the copolymer2 (chromatogram A) as compared to the molecular weight of the corresponding PEG and PDMS homopolymers physically blended together (chromatogram B). In chromatogram B, the small peak at 18 min retention time corresponds to the PDMS diol, whereas the large peak at 16 min retention time corresponds to PEG diacid. In all cases, the molecular weights of the copolymers were significantly higher than the corresponding homopolymers, indicating that the coupling reaction of these two components took place (Table 1). More interestingly, the molecular weights of copolymer2 and copolymer4 were approximately the sum of two moles of PEG diacid and one mole of PDMS/disiloxane diol, indicating the predominant formation of PEG–PDMS/disiloxane–PEG triblock copolymers. The driving force for producing mainly triblock structure in the condensation reaction was the presence of the large excess of PEG diacid species (2:1 molar ratio of PEG:PDMS/disiloxane), which can ideally serve as endcapping blocks for the PDMS/disiloxane central species. The molecular weight of

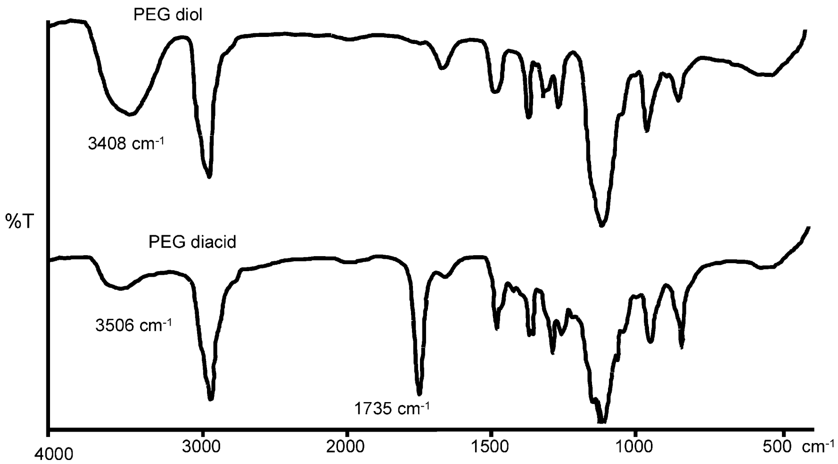

Fig. 5. FTIR spectra comparing between hydroxy-terminated PEG and carboxylic acid-terminated PEG.

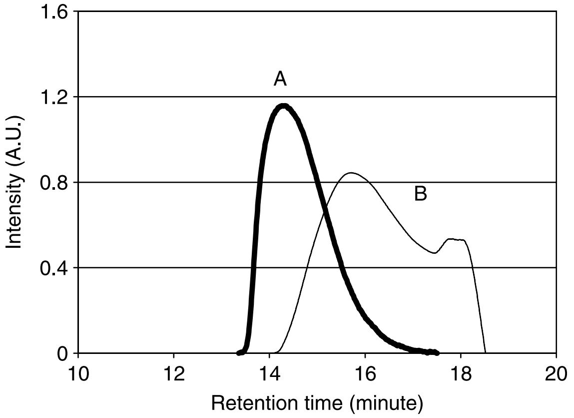

Fig. 6. Representative GPC chromatograms showing the increment of the molecular weights of the copolymer as compared to the corresponding homopolymers, (A) a chromatogram of copolymer2 (M_n 18,000 g/mol), and (B) a chromatogram of the blend between 8200 g/mol PEG diacid and 2900 g/mol PDMS diol.

copolymer1 was slightly higher than the expected number, which was 10,000 g/mol of PEG–PDMS–PEG triblock copolymer. This is attributed to the partial formation of multiblock copolymers, e.g. PEG–PDMS–PEG–PDMS tetrablock copolymer. On the other hand, the molecular weight of copolymer3 was somewhat lower than expecting value, which was 8000 g/mol of PEG–disiloxane–PEG triblock copolymer. Once again, this is probably due to partial formation of PEG–disiloxane diblock copolymer.

According to Table 1, the molecular weights of the oligomers were somewhat higher than expected values. Namely, the molecular weights of 1000 g/mol PDMS diol, disiloxane diol and 1000 g/mol PEG diacid, were 2900 g/mol PDMS diol, 900 g/mol disiloxane diol and 3600 g/mol PEG diacid, respectively, as indicated by GPC chromatograms. This is probably due to the molecular weights of these oligomers were so small that GPC technique could not determine their molecular weights precisely. However, estimation of the molecular weights of these oligomers from ^{1}H NMR technique indicated that their molecular weights were comparable to the expected values as discussed earlier. In all cases, polydispersity indexes of the copolymers were less than two, which are typical for the condensation reaction. In general, the molecular weight distributions of these copolymers were slightly broader than the corresponding PEG and PDMS homopolymers.

Table 1
Molecular weights and molecular weight distributions of the PEG–PDMS/disiloxane copolymers compared to molecular weights of the corresponding homopolymers determined from GPC technique

	M_n of PDMS or disiloxane diol (g/mol)	M_n of PEG diol (g/mol)	M_n of copolymer (g/mol)	Polydispersity of the copolymer
Copolymer1	2900	3600	13,000	1.75
Copolymer2	2900	8200	18,000	1.94
Copolymer3	900	3600	5200	1.92
Copolymer4	900	8200	17,000	1.54

Thermal behavior of the copolymers as well as their corresponding homopolymers was investigated using DSC. Fig. 7 shows the representative thermograms comparing between copolymer1 and its corresponding PDMS and PEG homopolymers. Two glass transition temperatures (T_g) were observed in copolymer1 (thermogram C). The higher transition temperature corresponds to the PEG phase (T_g −65 °C), whereas the lower transition temperature corresponds to the PDMS phase (T_g −125 °C). The crystalline temperature (T_c) of copolymer1 was observed at −38 °C corresponding to the PEG phase. While the melting temperature (T_m) of the PEG phase in the copolymer retained (−17 °C), both T_g and T_c of the PEG phase in the copolymer significantly decreased (thermogram C) as compared to those of the PEG homopolymer (thermogram B). These depressions indicated partial miscibility between PEG and PDMS blocks due to chemical bonding. In the other word, the PEG phase contained some of the PDMS elastomer. PDMS possesses extremely low T_g (T_g −125 °C in thermogram A) and, thereby, enhances mobility of the PEG phase in the copolymer relative to the PEG homopolymer. The depression of T_g of the PEG phase in copolymers was observed in all cases (Table 2). However, there was no observed increment of T_g corresponding to the PDMS phase in the copolymer. It should be emphasized that only 3600 g/mol PEG in copolymer1 and copolymer3 showed T_c and both exhibited the depression in the copolymers as well (Table 2(A) and (C)). Molecular length of 8200 g/mol PEG might be so long that it was difficult to crystallize. Two thousand and nine hundred grams per mole PDMS showed T_g at −125 °C (Table 2(A) and (B)) indicating the existence of amorphous region, whereas T_g of 900 g/mol siloxane oligomer was not observed due to only a few siloxane units existing (Table 2(C) and (D)).

3.4. Swelling behavior

High equilibrium water content (EWC) observed in PEG-containing chitosan system was previously contributed to the existence of the intermolecular hydrogen bonding between chitosan and PEG, and the abundance of amorphous region in polyether, which facilitated molecules of water to penetrate into the materials [7]. However, in the present work, hydrophobic PDMS or siloxane oligomers existing in copolymers would definitely play an important role and influence their swelling behavior.

EWC of chitosan containing 5 wt% copolymers as a function of copolymer compositions was shown in Fig. 8. Incorporation of 10 wt% copolymers into chitosan exhibited a similar trend without significant change in EWC of each sample. As seen in Fig. 8, it was apparent that percent of water swelling rapidly increased in all cases. The unmodified chitosan reached the equilibrium within 30 min with EWC of approximately 500%. However, after

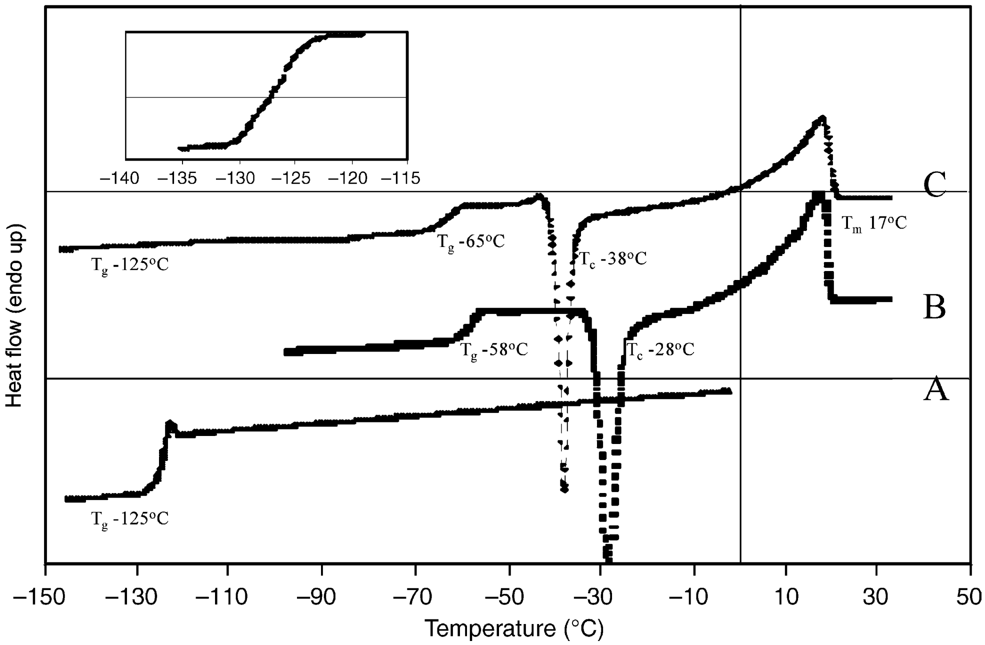

Fig. 7. The second scan DSC thermograms of (A) 2900 g/mol PDMS diol, (B) 3600 g/mol PEG diacid, and (C) copolymer1, obtained at 10 °C/min scan rate from −140 to 50 °C. The inset is the expansion of −140 to −115 °C region of thermogram C.

prolonged swelling for 2 h, small pieces were found to detach from the unmodified chitosan, whereas the copolymer-containing chitosan still remained intact throughout the investigation. This is probably due to a trace of carboxylic acid remaining upon film preparation process, although neutralization was thoroughly made to remove acidic residue. After the swelling test of copolymer-containing chitosan was carried on for 5 days, no detached debris was observed. This result indicated that copolymer existing in chitosan sustained the material in place without any detachment for a long period of time as compared to the unmodified chitosan in the same condition. It is hypothesized that the copolymers might partially crosslink to chitosan due to the existence of dicarboxylic acid functional groups at both ends of the copolymers, resulting in formation of network structures of the materials.

As shown in Fig. 8, chitosan containing copolymer1 or copolymer2 reached equilibrium within one day, while the ones containing copolymer3 or copolymer4 took 4 days. At the initial, rapid increases of percent of water swelling of the chitosan containing copolymer3 or copolymer4 were comparable to that of the unmodified chitosan. It should be noted that these two copolymers were comprised of low molecular weight siloxane (900 g/mol siloxane oligomers based on GPC). It is thought that hydrophobicity due to

Table 2
Glass transition temperatures (T_g) and crystalline temperatures (T_c) of (A) copolymer1, (B) copolymer2, (C) copolymer3, and (D) copolymer4, and their corresponding homopolymers

	T_g (°C)	T_c (°C)
(A)		
PDMS	−125	–
PEG	−58	−28
Copolymer1	−125 and −65	−38
(B)		
PDMS	−125	–
PEG	−47	–
Copolymer2	−125 and −59	–
(C)		
PDMS	–	–
PEG	−58	−28
Copolymer3	−67	−37
(D)		
PDMS	–	–
PEG	−47	–
Copolymer4	−59	–

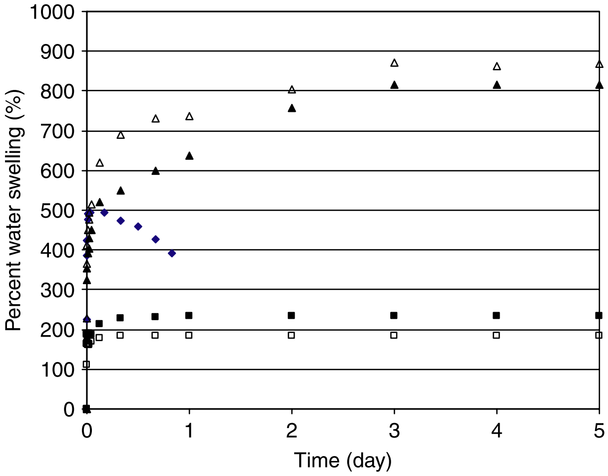

Fig. 8. Swelling behavior of chitosan, (1) without copolymer (♦), containing 5 wt% of (2) copolymer1 (■), (3) copolymer2 (□), (4) copolymer3 (▲), and (5) copolymer4 (△).

siloxane moiety and hydrophilicity due to PEG moiety balanced out the swelling properties, resulting in the similar swelling behavior to the unmodified chitosan at the initial. Interestingly, these materials exhibited more than 800% water swelling at the equilibrium. This is likely owing to the existence of low $M_n$siloxane oligomers allowing chitosan to have PEG as a majority and resulting in high polar materials.

In the cases of chitosan containing 2900 g/mol PDMS (copolymer1 and copolymer2), the materials exhibited significant decrease of EWC as compared to the unmodified chitosan. Although the molecular weights of PDMS (2900 g/mol based on GPC) presented in the copolymers were somewhat lower than that of PEG (3600 g/mol in copolymer1, and 8200 g/mol in copolymer2 based on GPC), the swelling behavior suggested that hydrophobicity of PDMS can overcome hydrophilicity of PEG, resulting in the depression in EWC (190–240%) as compared to the unmodified materials (500%). The influence of the molecular weights of PEG on EWC was also considered. Considering chitosan containing identical 2900 g/mol PDMS, it was expected to observe the greater EWC in chitosan containing copolymer2 (8200 g/mol PEG) than those containing copolymer1 (3600 g/mol PEG) due to the existence of the crystalline structure of low M_n PEG (T_c −38 °C in Table 2). It was, however, apparent that they exhibited insignificant difference in EWC of these two samples. Likewise, there was no significant difference in EWC in case of the ones containing copolymer3 and copolymer4 (the same 900 g/mol siloxane oligomers). This is most likely due to the absence of the crystalline structure of PEG when it was incorporated into chitosan as indicated by the lack of T_c due to the PEG phase in DSC.

3.5. Studies of critical surface energy

In the current work, small amount of PDMS or disiloxane was incorporated into chitosan to suppress critical surface energy of the materials without impairing their good swelling properties. It is thought that, due to its inherently low surface tension, PDMS or siloxane oligomer can exhibit microphase separation in chitosan during the drying process and then slowly migrate to chitosan-air interface, resulting in siloxane-rich surface. Therefore, incorporating small amount of PEG–PDMS/disiloxane copolymers into chitosan should decrease the overall critical surface energy of chitosan whereas good water swelling properties of chitosan still retain due to the presence of hydrophilic PEG components. However, PEG is well known as a polar polymer, which can of course affect surface properties of chitosan. Therefore, molar ratio of PEG to siloxane as well as its content in chitosan need to be optimized.

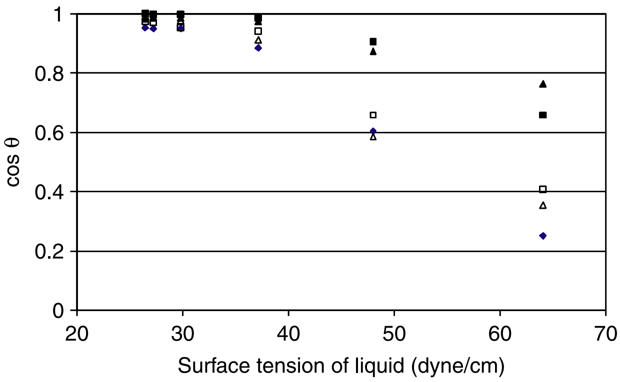

Fig. 9. Typical Zisman plots of chitosan, (1) without copolymer (♦), containing 10 wt% of (2) copolymer1 (■), (3) copolymer2 (□), (4) copolymer3 (▲), and (5) copolymer4 (△).

Critical surface energy is defined as the maximum surface tension of the solvent that can completely wet the surface of a solid film. In the other word, any solvents that have surface tension below the critical surface energy of a solid film will theoretically completely wet the film ($\theta = 0$). In the present paper, the critical surface energy of the copolymer-modified chitosan was determined using the Zisman method. Cosine of contact angle (θ) between a series of solvents and chitosan (y-axis) was plotted against the surface tension of each solvent (x-axis). Critical surface energy of a solid film is determined from the intercept between this plot and the straight line where cosine of contact angle is equal to one ($\cos \theta = 1$ or $\theta = 0$). A series of solvents used in the present investigation were chosen due to a good distribution of their surface tensions ranging from 26.40 to 64.00 dyn/cm and lack of interaction with chitosan. Typical Zisman plots were depicted in Fig. 9. Contact angle between chitosan and solvents decreased (increasing of $\cos \theta$) when surface tension of solvents decreased.

Influence of copolymer compositions and copolymer contents in chitosan on its critical surface energy was shown in Table 3. It should be noted that the R-square values of every reported results are higher than 0.90. As compared to the unmodified chitosan (0% copolymer), increases of critical surface energy of modified chitosan were observed in most cases except in case where copolymer3 was incorporated. Namely, in both cases of 5 and 10 wt% copolymer introduced, copolymer3-containing chitosan exhibited lowest critical surface energy, whereas only slight increases of critical surface energy were found in copolymer1-containing chitosan. Chitosan containing copolymer2 and copolymer4 showed relatively high critical surface tensions in both cases (5 and 10 wt%). The significant increment of critical surface energy in these cases was probably due to inherently high polarity of high M_n of PEG (8200 g/mol PEG based on GPC). Increasing percent of copolymer2 in chitosan from 5 to 10 wt% did not significantly change its critical surface energy. On the other hand, critical surface energy of chitosan containing copolymer4 increased significantly from 28.2 to 29.7 dyn/cm as percent of the copolymer increased from 5 to 10 wt%. It should be noted that copolymer2 and copolymer4 contained the same 8200 g/mol PEG but different M_ns of siloxane (2900 g/mol PDMS in copolymer2 and 900 g/mol

Table 3
Critical surface energy of copolymer-containing chitosan as a function of copolymer composition and copolymer contents

Chitosan containing	Critical surface energy (dyn/cm)
0% copolymer	26.3
5% copolymer1	27.4
5% copolymer2	28.3
5% copolymer3	25.8
5% copolymer4	28.2
10% copolymer1	27.0
10% copolymer2	28.4
10% copolymer3	22.2
10% copolymer4	29.7

siloxane oligomers in copolymer4). Hydrophobic and hydrophilic characteristics of PDMS and PEG might be balanced in case of chitosan containing copolymer2, resulting in an insignificantly change in critical surface energy as the copolymer content increased. In contrary, when percent of the copolymer4 in chitosan increased, surface properties might be governed by hydrophilic component of PEG, resulting in an increase of critical surface energy.

Likewise, it was expected to observe lower critical surface energy in case of copolymer1-containing chitosan than that of copolymer3-containing chitosan due to relatively high molecular weight of siloxane component in copolymer1. It was, however, apparent that critical surface energy of chitosan containing copolymer3 was the lowest values in both 5 and 10 wt% copolymer-containing chitosan. The result suggested an additional interaction that affected surface properties of the materials. It should be addressed once again that 3600 g/mol PEG in copolymer1 and copolymer3 crystallized as indicated by the existence of crystalline temperatures (T_c) in DSC. Crystallinity of PEG might inhibit mobility of PDMS in copolymer1 in such a way that it could not easily migrate to the chitosan surface, resulting in PEG-rich surface and thereby slight increases of critical surface energy relative to unmodified chitosan were observed. Instead of having microphase separation, the molecular weights of 900 g/mol siloxane oligomer in copolymer3 might be low enough to induce miscibility to PEG and chitosan, resulting in microscopic homogeneity of the material. As a result, further increase in copolymer3 content from 5 to 10 wt% even further suppressed critical surface energy of chitosan. This assumption can be confirmed by DSC experiments by observing the decrease of T_gs of the copolymer3-containing chitosan due to the miscibility of siloxane moiety in chitosan. As expected, the T_gs of the copolymer3-containing chitosan (141.6 °C for chitosan containing 5 wt% copolymer3 and 138.0 °C for chitosan containing 10 wt% copolymer3) were significantly lower than those of the unmodified one ($T_g = 147.2$ °C).

4. Conclusions

PEG–PDMS block copolymers were successfully prepared through the condensation reaction between the prepolymers of the carboxylic acid-terminated PEG and the hydroxy-terminated PDMS without using any solvent. DSC showed the depression of T_g and T_c of the PEG phase indicating partial miscibility between PDMS and PEG phases. GPC exhibited the increase of the molecular weights of the copolymers, indicating the formation of PEG–PDMS block copolymer. The copolymer-modified chitosan was prepared by mixing the copolymers in acetic acid aqueous solution of chitosan and casting the film. Chitosan containing low molecular weight siloxane tended to have higher EWC relative to the unmodified chitosan, whereas EWC was not dependent on molecular weight of PEG. Most of critical surface energy of the copolymer-modified chitosan were higher than the unmodified chitosan except the one containing copolymer3 (3600 g/mol PEG-900 g/mol PDMS). Increasing copolymer contents in chitosan from 5 and 10 wt% did not show any significant change in both swelling behavior and critical surface energy. The feasibility to use these materials for wound dressing application is warranted to study in the future.

Acknowledgements

The authors would like to acknowledge The Thai Research Fund (TRF) and The Ministry of University Affairs for financial support (MRG4680090). The authors would also like to thank Dr Rakchart Traiphol for discussion in DSC results.

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