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Polymer 47 (2006) 7909−7917

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Surface and mechanical properties of microporous membranes of poly(ethylene glycol)−polydimethylsiloxane copolymer/chitosan

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Received 20 July 2006; received in revised form 8 September 2006; accepted 12 September 2006
Available online 4 October 2006

Abstract

Poly(ethylene glycol)−polydimethylsiloxane (PEG−PDMS) block copolymers were prepared via a condensation reaction between PEG diacid and PDMS diol. PEG diacid was synthesized from the reaction between hydroxy-terminated PEG and succinic anhydride. PDMS diol was prepared from the ring-opening polymerization of octamethylcyclotetrasiloxane (D_4) followed by hydrosilylation with allyl alcohol. The copolymers were incorporated into 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. Percent crosslinking of 66−84 was observed once 5−10 wt% of the copolymers was incorporated. As compared to the unmodified sample, the copolymer-containing chitosan exhibited the decreases in both water contact angles and the rate of water vapor permeability. The studies on tensile properties indicated that incorporation of copolymers into chitosan improved the flexibility of the films.

Keywords: Chitosan; Polysiloxane; Poly(ethylene glycol)

1. Introduction

Chitosan is a biodegradable, biocompatible and inexpensive natural polymer that has drawn extensive attractions in recent years [1]. It has thus been reported for use in various biomedical applications, such as orthopedic, periodontal, drug delivery, tissue engineering, and wound dressing applications [2−7]. Especially for use as wound dressing materials, chitosan possesses high activity as a wound healing accelerator [8,9]. However, extensive use for the particular application is limited because of its inherently rigid structure due to high degree of crystallinity, resulting in brittle materials [3,10]. Chemical modification of chitosan [5−7,11−18] or physical blending of another polymer into chitosan [19−23] has been widely studied to obtain resulting materials with desirable properties. Among those attempts, incorporation of elastomeric polymer, such as polydimethylsiloxane (PDMS) seems to be a promising method to improve its mechanical properties [24]. PDMS is a highly flexible biomaterial due to its low glass transition temperature (T_g −125 °C) and widely used in medical applications owing to its biocompatibility, high oxygen permeability and good oxidative stability [25]. Preparation and properties of chitosan modified with PDMS have recently been reported [24,26]. Incorporation of only 1 wt% PDMS into chitosan can significantly enhance flexibility of the films as compared to the unmodified samples [24]. However, a major limitation of incorporation of PDMS into chitosan is immiscibility between hydrophobic PDMS and hydrophilic chitosan, resulting in phase separation. Addition of another polymer into the solution containing PDMS and chitosan might enhance the miscibility between these two phases [27]. Chemical crosslinking or grafting of PDMS on chitosan can improve the miscibility of the system as well [28].

Chitosan modified with poly(ethylene glycol) (PEG)−PDMS copolymers is of particular interest in our research group. PEG is a water-soluble polymer that is extensively

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0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.09.028

studied for use in medical applications [29–33]. Thus, in the copolymer-modified chitosan, PEG allows the materials to retain their good water swellability, while PDMS enhances flexibility of the modified films. Due to covalent bondings of PEG and PDMS blocks, water-soluble PEG should enhance the miscibility of PDMS in chitosan phase. The molecular weights of PEG and PDMS blocks need to be adjusted to balance the hydrophobicity of PDMS and the hydrophilicity of PEG in such a way that the copolymers are soluble in chitosan phase and have microphase separation of PDMS phase during the drying process. These PDMS microphase can toughen the materials whereas good water-swelling properties are not sacrificed. Synthesis and characterization of the copolymers with various molecular weights of each block have recently reported [34].

In the current report, the studies on percent crosslinking of the copolymer-modified chitosan were discussed. Water contact angles, water vapor permeabilities, morphological and mechanical properties of chitosan containing different copolymer compositions and amounts were also reported.

2. Experimental

2.1. Materials

Chitosan from crabs (Taming Enterprise, Co.) with 98% deacetylation was used without further purification. Octamethylcyclotetrasiloxane (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. The Karstd's catalyst (Aldrich) and triflic acid (98%, Aldrich) were used as received. Poly(ethylene glycol) with molecular weights of 1000 and 8000 g/mol (Acros) were dried in a 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 of chitosan modified with PEG–PDMS/disiloxane copolymers

The synthetic method for preparing PEG–PDMS/disiloxane copolymers has been discussed in details in our previous work [34]. Briefly, the PEG–PDMS copolymers were prepared via a direct condensation between dicarboxylic acid-terminated PEG (PEG diacid) and dihydroxy-terminated PDMS (PDMS diol) in the presence of dibutyltin oxide catalyst at 180 °C under N_2 purging for 24 h without using any solvent. PEG–PDMS of molar ratio 2:1 was used to predominantly obtain PEG–PDMS–PEG triblock copolymers. PEG diacid was prepared by the reaction between dihydroxy-terminated PEG and succinic anhydride at 180 °C under N_2 atmosphere for 24 h. PEG of 1000 and 8000 g/mol was prepared to study the effect of its molecular weights on the properties of interest. PDMS diol was synthesized via a two-step reaction: (1) acid-catalyzed ring-opening polymerization of D_4 in the presence of 1,1,3,3-tetramethyldisiloxane endcapping agent to control the molecular weights and obtain PDMS with Si–H terminal, and (2) hydrosilylation of the as-synthesized PDMS with allyl alcohol in the Karstd's catalyst to obtain PDMS diol. PDMS (1000 g/mol) and siloxane dimer (only two siloxane units) were used to represent two different degrees of hydrophobicity due to siloxane component. The molecular weights of these copolymers and their corresponding homopolymers were estimated using GPC and NMR techniques (Table 1).

Chitosan (5.0 g) was dissolved in a 0.5 M acetic acid aqueous solution. Desired weight of the copolymers was introduced into the chitosan solution with rigorously stirring for 2 h. The solution was sonicated to remove air bubbles upon stirring, poured into a glass mold and kept at 50 °C for 2 days. The film was neutralized in a 0.5 M NaOH solution and dried at 50 °C for 2 days under reduced pressure.

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 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.

2.3.2. Determination of percent crosslinking

The neutralized copolymer-modified chitosan was submerged into a 0.5 M aqueous acetic acid solution with consistent stirring at room temperature for 24 h to dissolve uncrosslinked chitosan. The undissolvable part was filtered using a sinter glass and submerged again into an additional acetic acid solution. The undissolvable chitosan was again filtered and washed thoroughly with distilled water, followed by acetone to remove the unreacted PEG–PDMS/disiloxane copolymer. It was dried at 50 °C in a vacuum oven for 24 h. Percent crosslinking was calculated as follows:

$$\text{Percent crosslinking}\,(\%) = W_2 \times 100/W_1$$

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

Table 1
Molecular weights of the PEG–PDMS/disiloxane copolymers and the corresponding homopolymers

	M_n from ^1H NMR		M_n from GPC		
	Siloxane diol (g/mol)	PEG diacid (g/mol)	Siloxane diol (g/mol)	PEG diacid (g/mol)	Copolymer (g/mol)
Copolymer1	1500	1150	2900	3600	13,000
Copolymer2	1500	8200	2900	8200	18,000
Copolymer3	250	1150	900	3600	5200
Copolymer4	250	8200	900	8200	17,000

2.3.3. Scanning electron microscopy (SEM)

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

2.3.4. Water contact angles of chitosan

Contact angles (θ) between water and chitosan films were 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 commenced to swell. The reported values are the average of five different measurements.

2.3.5. Water vapor permeability of chitosan

Water vapor permeability of chitosan was investigated following the method described by Khan et al. [3]. The sample films were tightly adhered onto the top of glass vials with an approximate volume of $24\ \mathrm{cm}^3$. Each vial was filled with pre-weighed 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% 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:

$$\text{Rate of water vapor permeability (g/day/liter)} = \left[\left(T_{\mathrm{f}} - T_{\mathrm{i}}\right) - \left(C_{\mathrm{f}} - C_{\mathrm{i}}\right)\right] \times 1000/(14v)$$

where T_{i} and T_{f} are the initial and final weights (g) of the sample vials, respectively, C_{i} and C_{f} are the initial and final weights (g) 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.

2.3.6. Tensile strength and percent elongation of chitosan

Tensile strength and elongation properties were performed on a Universal Testing Machine (Instron Model 4301). The samples were cut into a dumbbell shape type IV (ASTM D638). The samples were performed at the 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:

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

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

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

3. Results and discussion

3.1. Synthesis and characterization of PEG–PDMS/disiloxane block copolymers

PEG diacid was prepared via a tin-catalyzed reaction between PEG diol and succinic anhydride (Fig. 1). PEG diacid with the molecular weights of 1000 and 8000 g/mol were used in the present work to investigate the effect of hydrophilic block lengths in the amphiphilic block copolymers on wettability, morphological and mechanical properties of the copolymer-modified chitosan. PDMS diol with the molecular weight of 1000 g/mol was prepared via acid-catalyzed ring-opening polymerization of D_4, followed by hydrosilylation with allyl alcohol (Fig. 1). In addition to preparing 1000 g/mol PDMS diol, disiloxane diol (only two siloxane units) was also synthesized. Once preparing the PEG–siloxane copolymer, the one containing this disiloxane would exhibit relatively low degree of hydrophobicity due to the presence of only two siloxane units. The chemical structures of PEG diacid and PDMS diol were characterized using ^{1}H NMR and FTIR as discussed in details previously [34].

The condensation reaction using 2:1 molar ratio of PEG diacid and PDMS/disiloxane diol, respectively, was carried out to obtain ideal triblock copolymers of PEG tail blocks and PDMS/disiloxane central blocks. The reason for adding high amount of PEG relative to siloxane component in the copolymer was to avoid macroscopic phase separation of chitosan and hydrophobic siloxane during film preparation process, and also to retain good water swellability of the films. According to GPC results, the molecular weights of the oligomers were somewhat higher than the expected values (Table 1). 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. It was reasoned that the molecular weights of these oligomers were too low that GPC technique could not determine their molecular weights precisely. However, the molecular weights of these oligomers estimated from ^{1}H NMR technique were comparable to the targeted values (Table 1). The molecular weights of the copolymers from GPC significantly increased as compared to those of the corresponding homopolymers, indicating the coupling between these two components.

Solubility test of the copolymers was performed in various solvents with a wide spectrum of polarities. According to the results in Table 2, the solutions containing copolymer1 were opaque in high polar solvents, e.g., H_2O and acetone, due to the presence of hydrophobic PDMS and low molecular weight PEG in the composition, resulting in partial miscibility. When the molecular weights of siloxane component decreased and/or those of PEG increased (copolymer2, 3 and 4), the copolymers exhibited good solubility in various polar solvents even in water. It should be noted here that PDMS and disiloxane are hydrophobic species and well soluble in non-polar solvents,

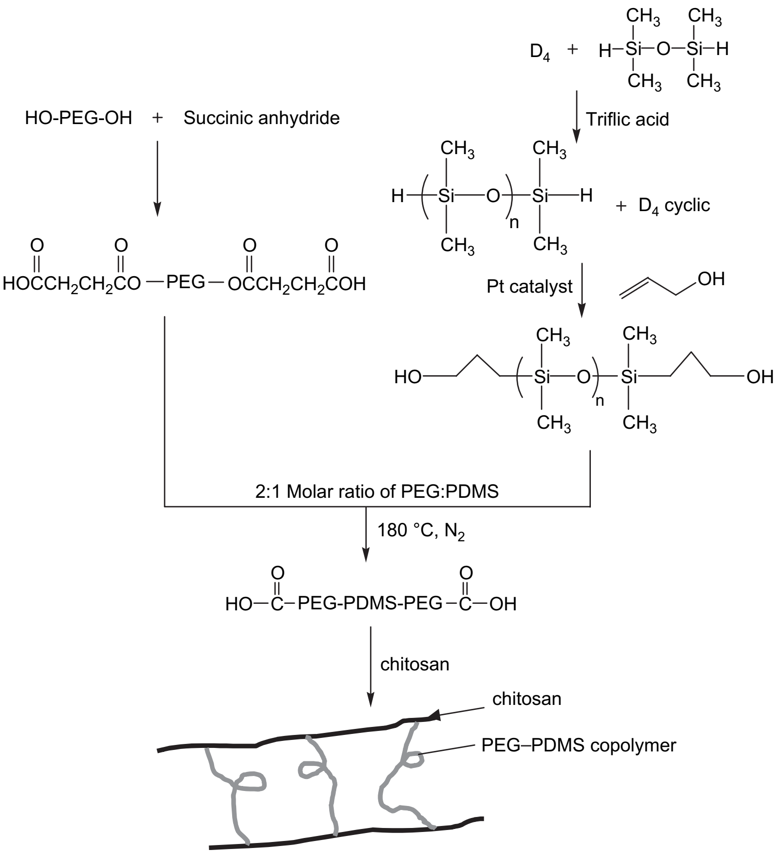

Fig. 1. Synthetic scheme for preparing chitosan modified with the PEG–PDMS copolymers.

Table 2
Solubility behavior of the PEG–PDMS/disiloxane copolymers in various solvents

	Copolymer1	Copolymer2	Copolymer3	Copolymer4
H_2O	*	**	**	**
MeOH	*	**	**	**
EtOH	*	**	**	**
Acetone	*	**	**	**
CH_2Cl_2	**	**	**	**
THF	**	**	**	**
Hexane	*	*	o	o

Definition of solubility: o – insoluble, * – dispersible or slightly soluble, and ** – completely soluble (at least 10% w/v).

whereas PEG is a hydrophilic polymer and, thus, well soluble in polar solvents. Therefore, increasing the molecular weights of PEG and/or decreasing those of siloxane components would improve solubility of the copolymers in polar solvents. Copolymer3 and copolymer4 were insoluble in hexane due to the existence of only two siloxane units in hydrophobic components, whereas partial solubility of copolymer1 and copolymer2 in hexane was observed owing to the presence of relatively high molecular weight PDMS.

3.2. Determination of percent crosslinking

Because 2:1 molar ratio of PEG diacid–PDMS/disiloxane diol was used in every composition of the copolymer, the two-fold excess of PEG can ideally serve as endcapping blocks for the PDMS/disiloxane central species, resulting in the predominant formation of triblock structure with carboxylic acid groups at each terminal. The condensation reaction between these carboxylic acid groups of the copolymers and amine functional groups in chitosan took place, allowing the formation of network structure with the copolymers as crosslinkers. Because this reaction most likely occurred via the formation of amide linkages, FTIR spectroscopy seemed to be an effective technique to confirm such formation by observing amide signals (N–H (3400 cm^{-1}) and –C=O (1650 cm^{-1}) stretching). However, this evidence is ambiguous due to the existing amide in chitosan (98% deacetylated chitosan). Determination of percent crosslinking of the copolymer-modified chitosan can confirm such interaction due to the formation of network structure. It should be noted that chitosan without copolymers was completely soluble in an acetic acid aqueous solution.

After removing unreacted copolymers and chitosan by dissolution method, the undissolvable parts were polymer networks formed due to covalent crosslinking between the copolymers and chitosan. Percent crosslinking of the copolymer-modified chitosan was ranging from 66% to 84% without significant difference of each copolymer composition (Fig. 2). In all cases, incorporation of 10 wt% copolymers into chitosan exhibited higher percent crosslinking than chitosan with only 5 wt% copolymers with the same composition due to the increase of crosslinker concentration, resulting in higher crosslink density.

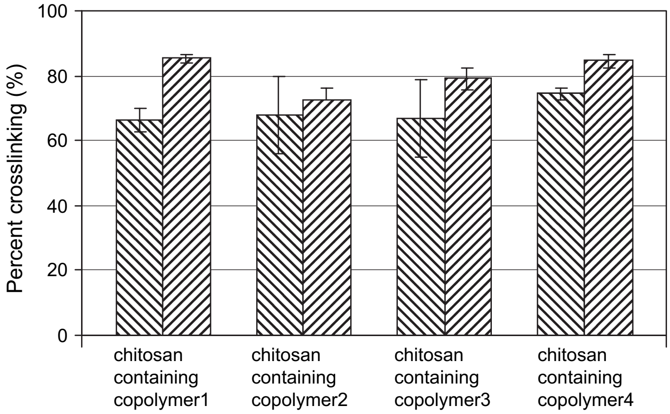

Fig. 2. Percent crosslinking as a function of the copolymer composition and amount in chitosan. ▧ is chitosan containing 5 wt% copolymer and ▨ is chitosan containing 10 wt% copolymer.

3.3. Morphological studies of the membranes

SEM micrographs of the surface and cross-section of the copolymer/chitosan membranes have been presented in Fig. 3 (5 wt% copolymer-containing chitosan) and Fig. 4 (10 wt% copolymer-containing chitosan) to observe morphological structure of their surface and in the bulk, respectively. It is apparent that micropores were observed throughout the material. These micropores were hypothesized as the hydrophobic PDMS/disiloxane components that were self-assembled and microscopically phase separated from hydrophilic chitosan during the drying process. However, these micropores were observed only in the bulk but not on its surface. It is rationalized that partial miscibility of the copolymers to chitosan took place due to the covalent bonding of the siloxane components to the hydrophilic PEG blocks. Therefore, the migration of these hydrophobic siloxanes to chitosan–air interface was limited, resulting in PEG-rich surface. This assumption was evidenced by the formation of microporous structure on the surface of chitosan containing 1 wt% PDMS homopolymer without PEG component. In good agreement with this surmise, determination of water contact angles of the copolymer-containing chitosan, which has been discussed later, also indicated that the materials possessed PEG-enriched surface.

The effect of copolymer concentration in chitosan on its morphology was also considered. The chitosan membrane without copolymer exhibited uniform and dense microstructure without any pore (Fig. 3(E)). For the copolymer-containing chitosan, the pore size increased from less than 1 μm to 1–8 μm in diameter when the percentage of the copolymers was increased from 5 wt% (Fig. 3) to 10 wt% (Fig. 4), indicating the increase of the siloxane phase size. Morphology of the cross-section of the chitosan containing 10 wt% of copolymer1 (Fig. 4(A)) exhibited significantly larger siloxane phase than others. This was attributed to the presence of relatively high molecular weight of siloxane component (1500 g/mol from NMR, Table 1) and relatively low molecular weight of PEG (1150 g/mol from NMR, Table 1) as compared to other copolymers, resulting in the enhancement of siloxane microphase separation. However, there was no significant difference in size of micropores in other cases. Interestingly, morphology of the cross-section of chitosan containing copolymer2 (Fig. 3(B′) and Fig. 4(B′)) exhibited a lamella-like structure, whereas others showed morphology with a dense structure.

3.4. Water contact angles

PDMS is a well-known hydrophobic polymer, which is prevalently used in various applications [35,36]. However, the studies in PDMS-modified chitosan are very limited due to macroscopic phase separation between these two components. Therefore, in the present work, relatively high molecular weights of PEG were covalently bonded to siloxane and, thereby, conveyed the hydrophobic siloxane to chitosan phase. PEG is a high polar polymer and, of course, well soluble in water. Addition of these copolymers into chitosan should enhance water wettability of the materials due to predominant existence of PEG in the copolymer structure. To compare the wettability of the copolymer-modified chitosan to the unmodified one, contact angles between the sample surface and water were measured in air using the sessile method [37,38]. Table 3 exhibits the results of water contact angles as a function of the copolymer composition and its content. The water contact angle of the unmodified chitosan was $64.3 \pm 1.0°$, which is significantly higher than those of the copolymer-modified chitosan ranging from $31.5 \pm 0.6°$ to $60.0 \pm 0.0°$. This indicated that incorporation of the copolymers rendered the surface more water wettable due to the presence of PEG in the copolymers, allowing the materials to have PEG-enriched surface. These results are in good agreement with the morphological studies previously discussed. Interestingly, water contact angle of chitosan modified with copolymer4 showed the highest value, although copolymer4 seemed to be the most hydrophilic copolymer in the series. This suggested additional interaction that influenced surface properties of the materials. It was rationalized that, as compared to other copolymers, disiloxane in copolymer4 possessed more mobility to migrate to the material surface due to less entanglement when compared to PDMS. In addition, a lack of crystallinity of 8200 g/mol PEG as indicated by the absence of T_c in DSC results [34] even further promoted the mobility of disiloxane to easily migrate. As a consequence, chitosan containing copolymer4 exhibited high contact angles due to hydrophobic siloxane-enriched surface. In all cases, incorporation of 10 wt% copolymers into chitosan showed lower contact angles than chitosan with only 5 wt% copolymers with the same composition, indicating the enhancement of water wettability of the materials.

3.5. Water vapor permeability

Water vapor permeability is an important property of membranes for various applications, e.g., wound healing materials, artificial skin, and packaging [8,39]. Addition of other polymers, especially PEG, to chitosan to modify this property has been widely reported [20,21]. However, modification

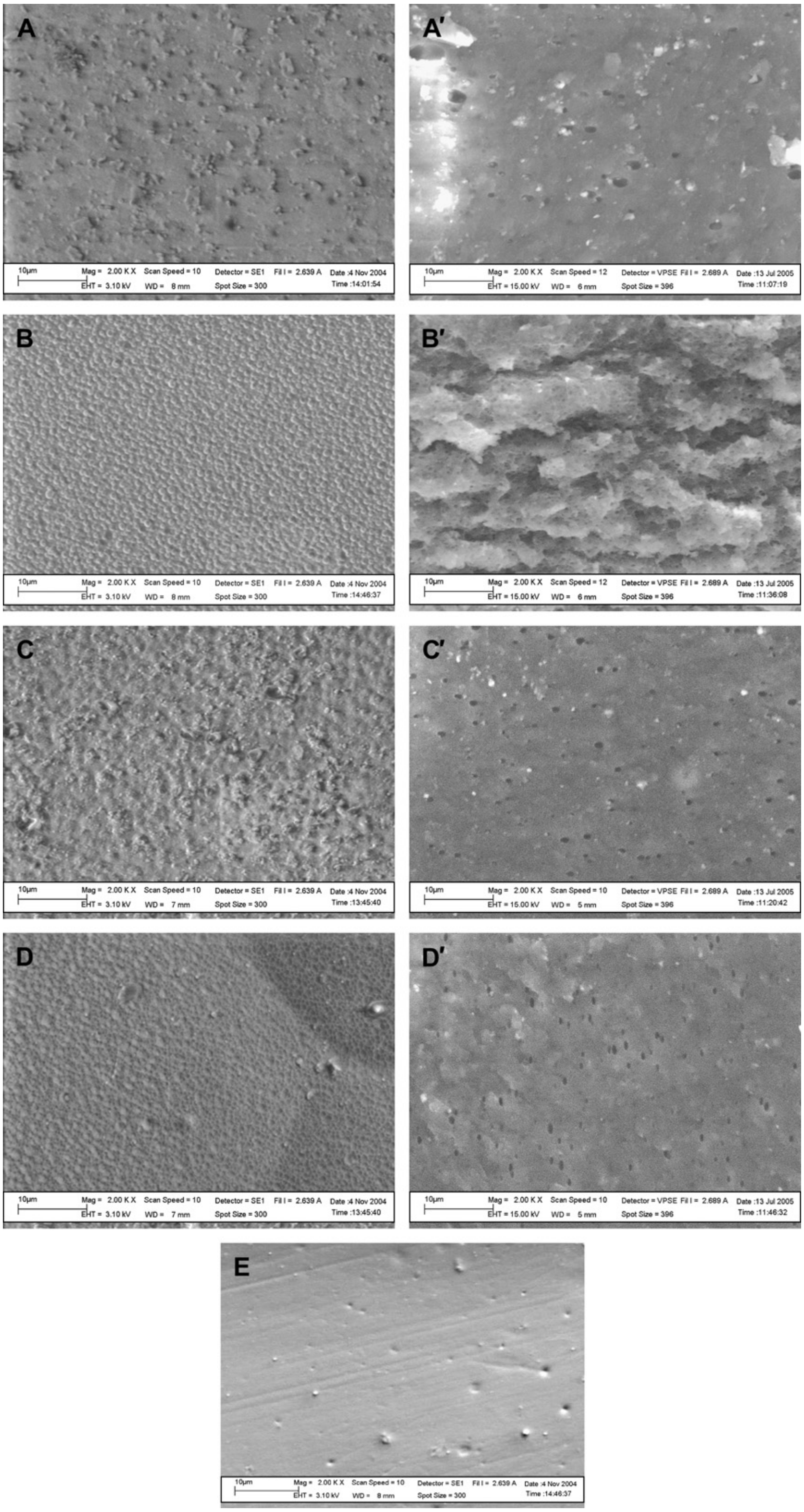

Fig. 3. Surface morphology of chitosan containing 5 wt% of (A) copolymer1, (B) copolymer2, (C) copolymer3, (D) copolymer4, (E) chitosan without copolymers, cross-section morphology of chitosan containing 5 wt% of (A′) copolymer1, (B′) copolymer2, (C′) copolymer3, and (D′) copolymer4.

of chitosan with the amphiphilic copolymers has not been prevalently studied. In this work, the presence of hydrophilic PEG is thought to enhance water vapor permeability of the modified chitosan, whereas hydrophobic siloxane components impart opposite properties. Fig. 5 exhibits the influence of the copolymers with different compositions and contents on the rate of water vapor permeability. In most cases, incorporation of 5–10 wt% copolymers lowered the rate of water vapor

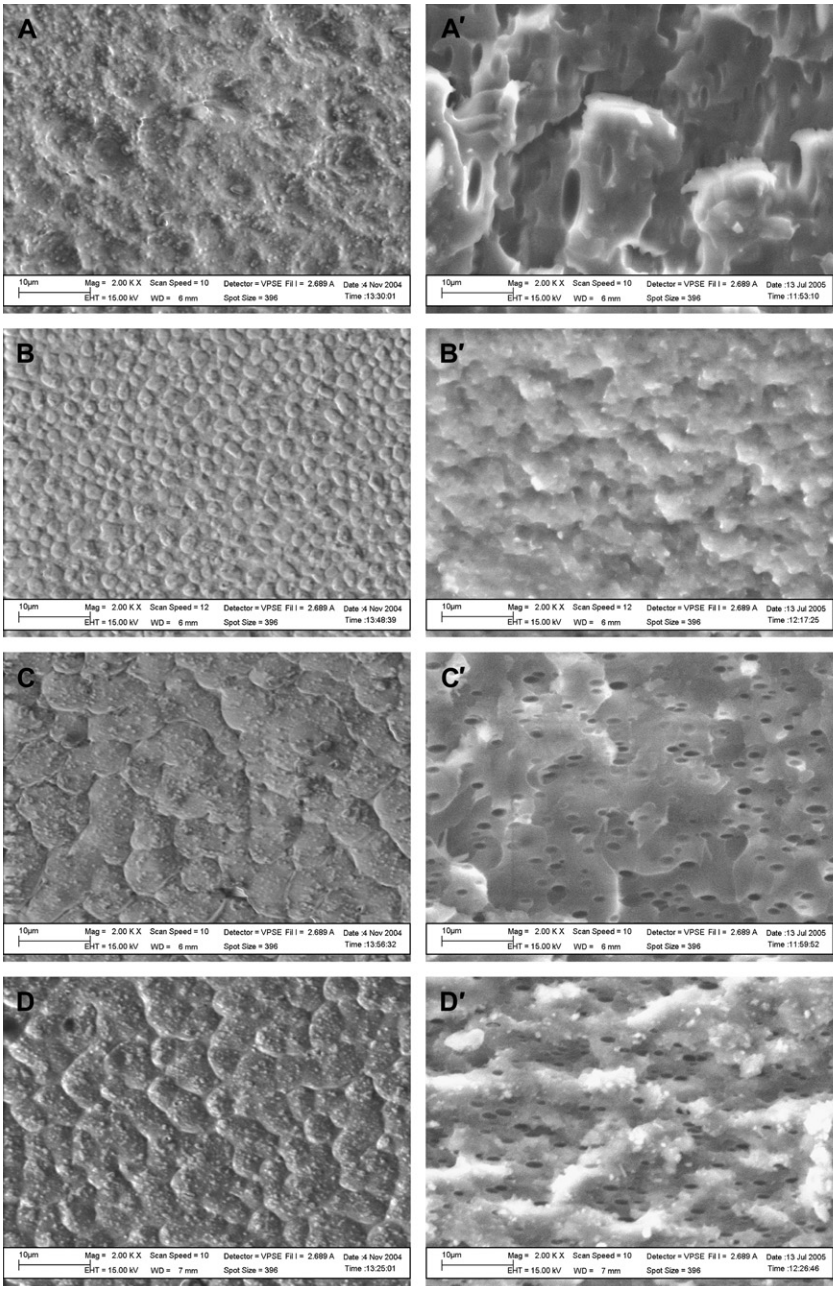

Fig. 4. Surface morphology of chitosan containing 10 wt% of (A) copolymer1, (B) copolymer2, (C) copolymer3, (D) copolymer4, cross-section morphology of chitosan containing 10 wt% of (A′) copolymer1, (B′) copolymer2, (C′) copolymer3, and (D′) copolymer4.

Table 3
Water contact angles of the copolymer-modified chitosan compared to unmodified chitosan

Chitosan containing	Water contact angle (degree)
0% copolymer	64.3 ± 1.0
5% copolymer1	39.8 ± 1.0
5% copolymer2	35.9 ± 0.6
5% copolymer3	41.3 ± 0.3
5% copolymer4	60.0 ± 0.0
10% copolymer1	31.8 ± 0.3
10% copolymer2	31.5 ± 0.6
10% copolymer3	35.8 ± 1.1
10% copolymer4	52.4 ± 0.9

permeability of materials as compared to the unmodified one. This suggested that the hydrophobic characteristics of siloxane components dominated hydrophilicity of PEG and, therefore, exhibited resistant properties to moisture. However, significant change of water vapor permeability was not observed when the copolymer concentrations in chitosan were increased from 5 wt% to 10 wt%.

3.6. Mechanical properties

PDMS is a well-known elastomer that is frequently used as a toughening modifier in glassy materials. Addition of

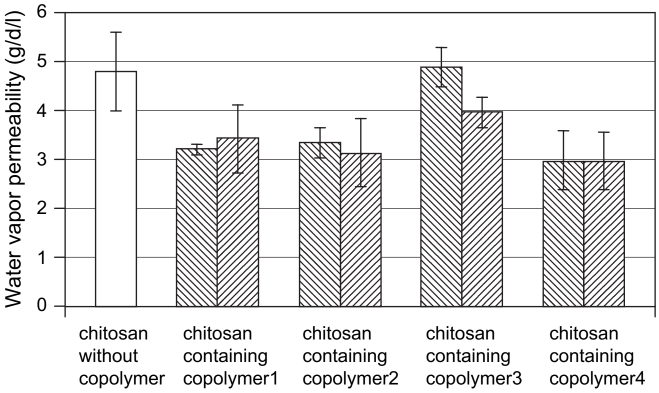

Fig. 5. Water vapor permeability of the copolymer-modified chitosan as a function of the copolymer composition and amount in chitosan. □ is chitosan without copolymers, ▧ is chitosan containing 5 wt% copolymer, and ▨ is chitosan containing 10 wt% copolymer.

the PDMS-containing copolymers to chitosan is thought to improve its toughness properties. However, PEG existed in the copolymers also of course influenced these properties of the materials. It has been reported that addition of high content of PEG to chitosan deteriorated toughness properties of the materials [19]. This has been attributed to the formation of intermolecular hydrogen bonding of PEG and chitosan. Therefore, in the current work, the molecular weights of siloxane and PEG in the copolymers needed to be optimized in such a way that, when adding the copolymers in chitosan, miscibility between these components were obtained whereas toughness properties were not sacrificed.

Fig. 6. Tensile strength and elongation as a function of the copolymer composition and amount in chitosan. □ is chitosan without copolymers, ▧ is chitosan containing 5 wt% copolymer, and ▨ is chitosan containing 10 wt% copolymer.

According to the results in Fig. 6, tensile strength and elongation at break of the unmodified chitosan were 75.4 ± 14.0 MPa and 2.5 ± 0.2%, respectively. In general, the copolymer-containing chitosan exhibited a slight decrease in tensile strength and a slight increase in elongation as compared to the unmodified films, indicating that addition of the copolymers rendered the materials tougher and more flexible. Considering the effect of percentage of the copolymers in chitosan, further increases in the copolymer content from 5 wt% to 10 wt% did not show any significant change in most cases. In addition, there was no trend in tensile strength and percent elongation observed when the composition of the copolymers changed.

4. Conclusions

The PEG–PDMS/disiloxane copolymers with different block lengths were prepared via a direct condensation of PEG diacid and PDMS diol. GPC indicated a coupling reaction of these two components. Hydrophilic PEG allowed the materials to retain their excellent water-swelling properties and wettability, whereas PDMS served as a toughening modifier and enhanced the flexibility of the materials. High degrees of crosslinking of the modified chitosan indicated the formation of network structure. Existence of microporous structures in the bulk but not on the material surface implied that siloxane phase primarily presented in chitosan. The decrease in water contact angles of the copolymer-modified chitosan showed that water wettabilities of the materials were improved due to PEG-enriched surface. On the other hand, the modified chitosan showed a decline in water transport properties as indicated by the lowered water vapor permeability. In addition, incorporation of the copolymers into chitosan exhibited a slight enhancement of toughness properties. Increasing copolymer concentrations in chitosan from 5 wt% to 10 wt% showed the enhancement of water wettability and microphase separation of the materials but not water vapor permeability and toughness properties.

Acknowledgements

The authors would like to acknowledge The Thailand Research Fund (TRF) and The Ministry of University Affairs for financial support (MRG4680090). We also acknowledge the Department of Chemistry, Faculty of Science, Mahidol University, Bangkok, Thailand for a support in contact angle measurement. MR would like to thank Assoc. Prof. Dr. Pranee Phinyocheep from the Department of Chemistry, Faculty of Science, Mahidol University, Bangkok, Thailand for the result discussion.

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