Characterization and Diffusion Behavior of Chitosan–POSS Composite Membranes

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ABSTRACT: Four types of polyhedral oligosilsesquioxanes (POSS) were incorporated into chitosan by solution blending to fabricate composite membranes. The thermal stability of the composite membranes was improved compared with the neat chitosan membrane. For the mechanical properties, the stiffness of the composite membranes was weakened by the presence of POSS. However, the effects of POSS on the strength and elongation at break of the composite membranes depended on the type of POSS incorporated. Hydrophilic POSS increased the ductility of the composite membranes and maintained their strength, while hydrophobic POSS made the membranes more brittle and less rigid compared with the neat chitosan membranes. These significant differences were due to the different compatibility and interfacial adhesion between POSS and chitosan. The permeation of sodium chloride and riboflavin in the composite membranes was also influenced by the type and content of POSS in the membranes. Composite membranes containing hydrophilic POSS showed higher partition coefficients but lower diffusion coefficients of riboflavin, compared with the composite membranes containing hydrophobic POSS. This indicates that the transport of riboflavin is retarded by the interactions between riboflavin and the membrane. This study suggests that the structure and physical properties of chitosan membrane can be modified by the incorporation of a small amount of POSS molecules. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 427–435, 2011

Key words: chitosan; polyhedral oligosilsesquioxanes; thermogravimetric analysis; mechanical properties; diffusion

INTRODUCTION

Inorganic/organic composite materials prepared by incorporating inorganic segments into polymers have attracted overwhelming interests in recent years. The synergistic combination of individual inorganic/organic components provides promising potential to tune the resulting structure and to design or tailor the resulting properties for extended applications in many areas, such as packaging, electronics, optical devices, aerospace, automotive engineering, biomaterials, etc.[1] In particular, nanosized inorganic fillers, such as layered silicate, precipitated silica, and carbon nanotubes are widely studied because of their effective reinforcement at very low loadings.[2]

Organosilicate molecules with the basic formula $R_nSi_nO_{1.5n}$ (where R can be hydrogen, alkyl, alkylene, aryl, arylene, etc.) are referred to silsesquioxanes. The molecular architecture of silsesquioxanes can be random, ladder, partial-cage, or cage structure. Silsesquioxanes with cage-like structures, also known as polyhedral oligosilsesquioxanes (POSS), are widely studied due to their well-defined and highly symmetric structure. A POSS molecule has an approximate linear dimension of 1.5 nm taking into account the R vertex groups.[3] The inorganic silica core of POSS is thermally and chemically robust while the diversity of the R groups makes them compatible with various polymer systems. Therefore, POSS, regarded as the smallest possible particles of silica,[4] are widely used as nanofillers in polymers and can be incorporated into polymers through copolymerization,[5,6] grafting,[7,8] or blending.[9–11] The resulting reinforcements in thermal stability and mechanical properties of the composite materials have been reported in many papers.[12–14] Furthermore, through tuning the microstructure of the polymers, POSS are able to impart unique rheological,[6] solubility, and diffusion[9,15] properties to the composite materials. However, the modifications of POSS fillers on the material properties depend substantially on the interactions between POSS and the polymer matrix. The same POSS molecule can serve as a reinforcing agent or a plasticizer when introduced into different polymer systems.[16] For the same polymer system, POSS with different R groups can have very

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different effects on the glass transition temperature, rheological and mechanical properties.[6] Hence, by varying the R groups of POSS, it is possible to tailor the structure and bulk properties of POSS/polymer composites.[10,17]

Most of the current research focus on the POSS-reinforced synthetic polymer systems. Very few studies have been conducted to examine the effect of POSS fillers on natural polymers.[7,18] Chitosan is an N-deacetylation derivative of chitin which is the second most abundant natural polymer in the world.[19] The notable properties of chitosan include biocompatibility, biodegradability, and good film-forming property. Chitosan also contains large quantities of hydroxyl and amino groups which can be easily modified. Therefore, it is a versatile material which is widely applied in areas such as packaging,[20] biomedical,[21] metal adsorption,[22] separation,[23] and so on. In this study, four types of POSS with different R groups were introduced into chitosan membranes through solution blending. The X-ray diffraction patterns, morphologies, thermal stability, swelling behavior, mechanical properties, as well as the permeability behavior of the chitosan–POSS composite membranes were investigated.

EXPERIMENTAL

Materials

Chitosan flakes with a degree of deacetylation (DD%) of 90% and $M_w \sim 180{,}000$ was obtained from Bio21 Co., Pattaya, Thailand. Octaanion (OA), octaaminophenyl (OAPS), octanitrophenyl (ONPS) POSS were purchased from Mayaterials, Ann Arbor, USA and octaammonium (OAS) POSS was provided by Hybrid Plastics^{TM}, Hattiesburg, USA. Their chemical structures are shown in Figure 1. Among them, OA and OAS are water soluble, whereas ONPS and OAPS are soluble in tetrahydrofuran and chloroform. Analytical grade sodium chloride (Fluka, Singapore), riboflavin (Sigma-Aldrich, Singapore), and acetic acid (Merck, Singapore) were used as received.

Fabrication of neat chitosan and chitosan–POSS composite membranes

Chitosan–POSS composite membranes were fabricated by solution blending. Chitosan solution (1 wt %) was prepared by dissolving chitosan flakes in 1 wt % acetic acid aqueous solution. After stirring for 4 h, varying amounts of POSS (1, 5, and 9 wt % based on chitosan weight) were added and stirred for another 20 h followed by filtration. The resulting bubble free solution was cast into Petri dishes and dried in an oven at 40°C for $\sim$ 12 h. The resulting membranes were neutralized with 1M

(a) OA, R = $O^- N(CH_3)_4^+$ (b) OAS, R = $\diagup\!\!\diagdown NH_3^+ Cl^-$

(c) ONPS, R = $\langle\text{aryl}\rangle-NO_2$ (d) OAPS, R = $\langle\text{aryl}\rangle-NH_2$
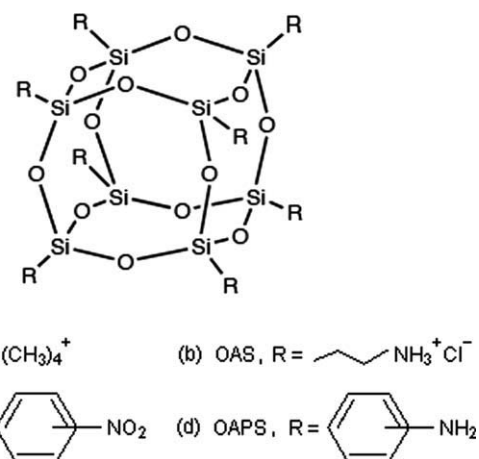
Figure 1   Chemical structures of POSS.

NaOH solution for 15 min and thoroughly washed with deionized water until neutral. After drying at room temperature, the membranes were peeled off and dried at 40°C under vacuum for 24 h. The neat chitosan membrane was prepared following the same procedure except for the absence of the addition of POSS. The thickness of the membranes was 20–30 µm.

Characterization

X-ray diffraction (XRD) spectra of POSS powder, neat chitosan, and chitosan–POSS composite membranes were obtained by a Siemens D5005 X-ray diffractometer. The measurement was operated at 40 kV, 40 mA (Cu Kα radiation) with a 2θ range of 3–36°. The macrographs of the surface and cross section of the membranes were taken by a JEOL JSM-6390LA analytical scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was conducted with a TA SDT Q600 thermogravimetric analyzer at a heating rate of 10°C/min under a nitrogen atmosphere. The mechanical properties of the membranes were measured by an Instron model 5543. Films with a gauge length of 50 mm and width of 10 mm were stretched at a crosshead speed of 2 mm/min at 20°C. The resulting data were taken from the average of at least five samples.

To measure the degree of swelling, the vacuum-dried membranes were weighed and immersed in deionized water for 48 h until equilibrium was reached. The fully swollen membranes were taken out, carefully wiped with tissue paper to remove the surface water, and quickly weighed. The percent degree of swelling (DS) was calculated as follows:

$$\%DS = \frac{W_s - W_d}{W_d} \times 100 \qquad (1)$$

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

Diffusion measurements

A homemade horizontal glass diffusion cell consisting of two cylindrical half cells with a volume of 60 cm^3 each were employed for permeation studies. The membrane was placed between the two compartments of the diffusion cell. The contact area was 1.78 cm^2. Permeation studies were conducted for both NaCl and riboflavin aqueous solutions. The feed compartment was filled with $1M$ NaCl or 50 mg/L riboflavin aqueous solution, whereas the receiving compartment was filled with deionized water and stirred at 500 rpm with a magnetic bar. For NaCl permeation, the concentration of NaCl solution in the receiving compartment was measured continuously by a Thermo Orion 3 Star conductivity meter. For riboflavin permeation, 1 mL of receiving solution was taken out at certain time intervals and analyzed by a Nicolet evolution 500 UV–Visible spectrophotometer at 267 cm^{-1} and returned to the receiving compartment immediately after measurement. The permeability coefficient, P, was calculated from the flux, J, during the steady state period of the diffusion when Fick's law was applicable (e.g., a high constant concentration of feed on one side and negligible concentration on the other side). Hence, P was determined from the following equations[24]:

$$J = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \qquad (2)$$

$$P = J \times \frac{l}{C_0} \qquad (3)$$

where V is the volume of water in the receiving compartment, A is the membrane contact area, $\Delta C/\Delta t$ is the slope of the concentration versus time during steady state, l is the thickness of the membrane and C_0 is the initial concentration of the feed solution.

Adsorption of riboflavin

Fifty milligrams of the membrane was added into 50 mg/L riboflavin solution and shaken at 150 rpm for 48 h. The concentration of the resulting solution was analyzed by the UV spectrophotometer at 267 cm^{-1}. The partition coefficient, K_d, was calculated as follows:

$$K_d = \frac{C_m}{C_s} = \frac{V_{\text{sol}}(C_0 - C_e)}{V_m C_e} \qquad (4)$$

where C_m is the concentration of riboflavin in the membrane, C_s is the concentration in the solution, C_e
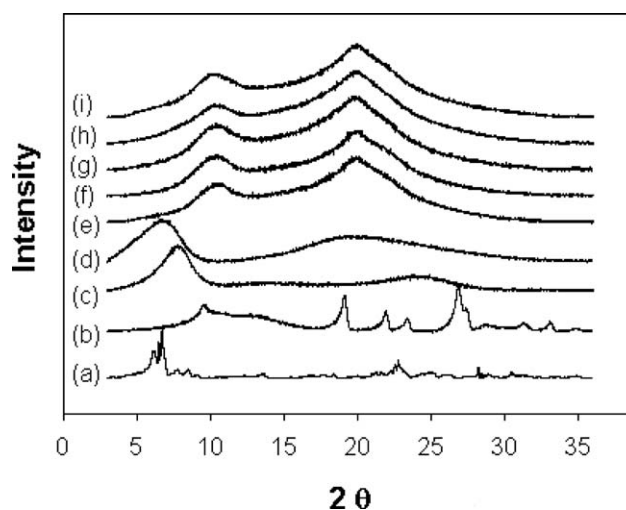
Figure 2 X-ray diffraction patterns of POSS powders: (a) OA, (b) OAS, (c) ONPS, (d) OAPS; (e) neat chitosan membrane; and chitosan–POSS composite membranes with 9 wt % POSS: (f) chitosan–OA, (g) chitosan–OAS, (h) chitosan–ONPS, (i) chitosan–OAPS.

is the equilibrium concentration, V_{sol} and V_m are the volumes of the solution and the membrane, respectively. The diffusion coefficient, D, was calculated according to the equation as follows:

$$D = \frac{P}{K_d} \qquad (5)$$

RESULTS AND DISCUSSION

XRD studies

X-ray diffractograms of the neat chitosan membrane, four types of POSS and chitosan–POSS composite membranes containing 9 wt % POSS are shown in Figure 2. The neat chitosan membrane has two broad peaks around 10° and 20° indicating the semicrystalline nature of the polymer. After the incorporation of POSS, all the composite membranes show crystalline profiles very similar to the neat chitosan membranes regardless of the type of POSS. For chitosan–OA and chitosan–OAS composite membranes, their XRD patterns do not contain any sharp peaks which are the characteristics of pure OA and OAS POSS. This suggested that OA and OAS are well dispersed in the chitosan matrix. For chitosan–ONPS and chitosan–OAPS composite membranes, as the XRD peaks of pure ONPS and OAPS POSS are fairly broad, it is difficult to determine the dispersion state from XRD results.

Morphologies

Figure 3 displays the macrographs of the surface and cross section of neat chitosan and chitosan–POSS composite membranes containing 9 wt %
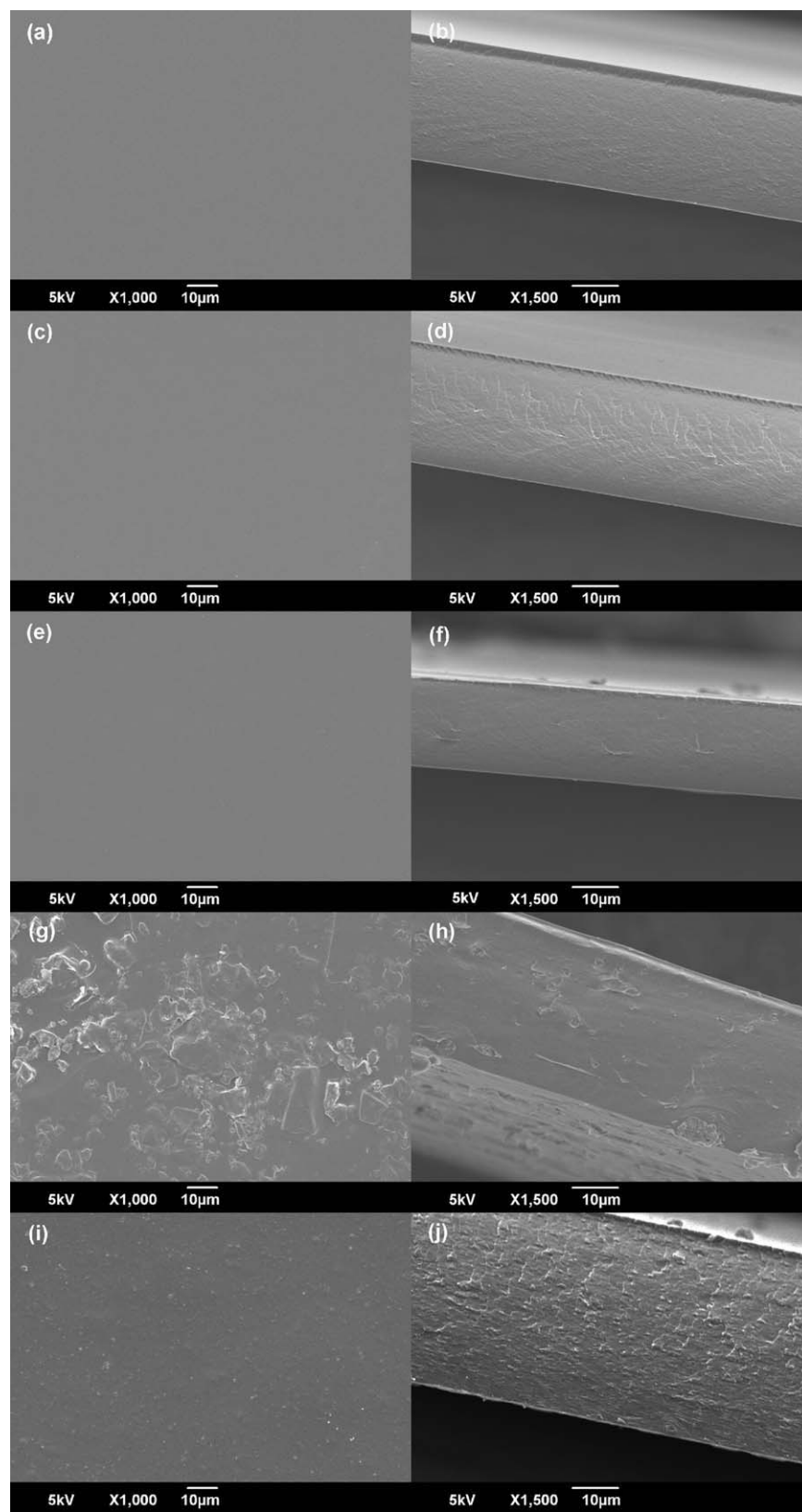
Figure 3   SEM images of the CS and CS-POSS composite membranes containing 9 wt % POSS. (a) CS membrane surface; (b) CS membrane cross section; (c) CS-OA membrane surface; (d) CS-OA membrane cross section; (e) CS-OAS membrane surface; (f) CS-OAS membrane cross section; (g) CS-ONPS membrane surface; (h) CS-ONPS membrane cross section; (i) CS-OAPS membrane surface; (j) CS-OAPS membrane cross section.
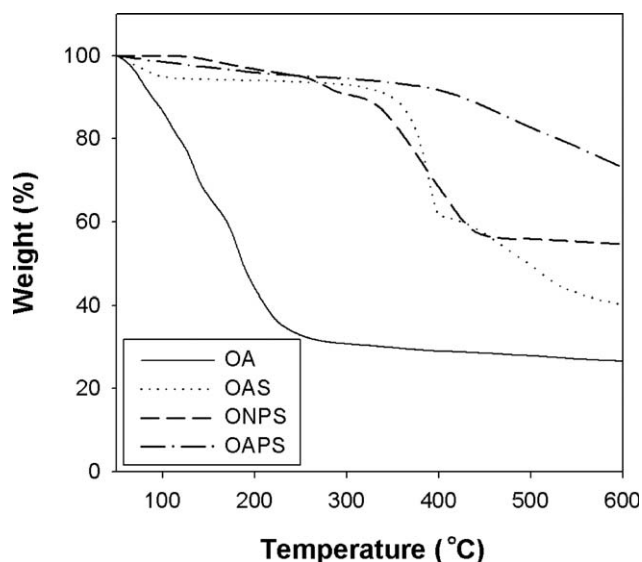
Figure 4   TGA curves of POSS.

POSS taken by SEM. Within the detection limit of the SEM, the neat chitosan membrane has a dense and smooth surface without defects. The surface morphologies of the composite membranes containing hydrophilic OA and OAS POSS are similar to the neat chitosan membrane, without any aggregate or particle of POSS being detected. However, in chitosan–OAPS composite membrane, a uniform dispersion of OAPS particles around 1 μm is observed. In chitosan–ONPS composite membrane, macroaggregates of ONPS with various sizes are seen to be heterogeneously dispersed within the chitosan matrix. This indicates that hydrophilic POSS molecules have good compatibility with chitosan and can be well dispersed in the chitosan matrix which is in accordance with the XRD data. On the other hand, hydrophobic POSS molecules, particularly ONPS, have poor interaction with chitosan and tend to aggregate leading to the macrophase separation between POSS and chitosan.

TGA studies

The TGA curves in Figure 4 show that four types of POSS have very different thermal degradation profiles. OAPS has the greatest thermal stability with an initial thermal decomposition temperature, T_d, at around 415°C, whereas OA has the poorest stability with the lowest char yield of 26%. However, despite the large differences in the thermal stability of different POSS molecules, all the composite membranes containing 9 wt % POSS display very similar degradation behaviors to that of the neat chitosan membrane as shown in Figure 5. This indicates that the degradation mechanism of the chitosan matrix has not been significantly altered by the presence of

the POSS fillers. However, compared with the neat chitosan membrane, all the composite membranes show slightly lower T_d and higher char yields. The reduction of T_d is ascribed to the poor stability of the organic R side groups around the Si-O cage of POSS. The inorganic Si-O framework of POSS, which has good thermal stability, could form a protective layer on the composite membranes preventing further degradation. This would contribute to the increased char yields observed in chitosan–POSS composite membranes.[25]

Mechanical properties

Table I shows the mechanical properties of the neat chitosan and chitosan–POSS composite membranes. Compared with the neat chitosan membrane, the Young's modulus of all the composite membranes decrease regardless of the type and amount of POSS molecules. For example, when the POSS loading is 9 wt %, the reduction in modulus is around 23%, 50%, 65%, and 56% for the composite membranes containing OA, OAS, OAPS, and ONPS, respectively, compared with the neat chitosan membrane. Baldi et al.[26] proposed that when POSS with a siliceous hard core surrounded by a hydrocarbon soft shell were dispersed in the polymer matrix, they acted as soft, rubber-like particles which were unable to reinforce stiffness. They also pointed out that the reduction effect depended on the thickness of the shell which was determined by the length of the R side groups of POSS molecules.

It is also observed in Table I that the addition of OA and OAS has little impact on the tensile strength of membranes, while the introduction of ONPS and
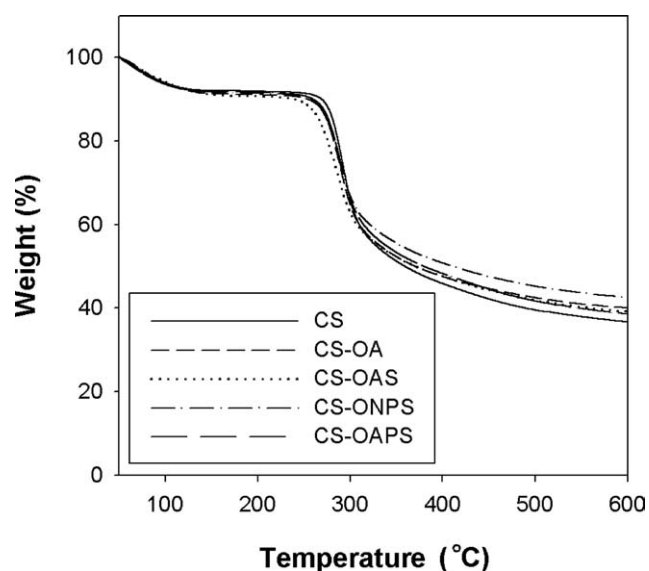

Figure 5   TGA curves of the neat chitosan and chitosan–POSS composite membranes with 9 wt % POSS.

TABLE I
The Mechanical Properties of the Neat Chitosan and
Chitosan–POSS Composite Membranes

Membranes	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
Chitosan	43.2 ± 4.8	15.5 ± 3.0	59.1 ± 5.3
Chitosan–OA			
1 wt %	23.4 ± 0.8	14.2 ± 2.7	52.2 ± 4.5
5 wt %	25.2 ± 2.4	18.2 ± 3.4	62.2 ± 6.7
9 wt %	33.2 ± 2.0	23.1 ± 2.3	60.9 ± 3.1
Chitosan–OAS			
1 wt %	23.7 ± 2.8	14.1 ± 6.4	49.6 ± 9.4
5 wt %	23.7 ± 0.7	25.6 ± 2.4	59.7 ± 3.0
9 wt %	21.7 ± 1.4	26.5 ± 4.2	50.3 ± 7.1
Chitosan–ONPS			
1 wt %	22.3 ± 2.9	17.4 ± 2.5	47.7 ± 6.5
5 wt %	17.5 ± 2.8	14.1 ± 4.7	33.0 ± 6.3
9 wt %	18.9 ± 2.6	9.0 ± 4.2	33.9 ± 3.6
Chitosan–OAPS			
1 wt %	26.7 ± 1.7	13.9 ± 5.3	50.2 ± 2.9
5 wt %	24.8 ± 0.7	13.5 ± 3.4	40.2 ± 3.4
9 wt %	15.2 ± 0.9	14.0 ± 4.6	34.0 ± 6.4

OAPS decrease the strength. It is known that tensile strength is influenced by the stress transfer between the fillers and the matrix.[27] Hydrophobic POSS molecules, which tend to form aggregates and have very poor interfacial adhesion with the matrix, can cause inefficient stress transfer. On the other hand, hydrophilic POSS molecules with good compatibility with the chitosan matrix have little effect on the stress transfer mechanism.

The incorporation of hydrophilic POSS or hydrophobic POSS also have different effects on the elongation at break of the membranes. The composite membranes with OA and OAS exhibit largely improved elongation at break at high loadings of POSS compared with the neat chitosan membrane (at 9 wt % loading of OA and OAS composite membranes, the elongation at break increase by 49 and 71%, respectively). However, the addition of 9 wt % ONPS and OAPS result in a decrease of 42 and 9%, respectively, for the elongation at break compared with the neat chitosan. These differences are attributed to the different interactions of POSS with the chitosan matrix. On one hand, the nonchemical interactions such as hydrogen bonding and van der Wals forces provide strong interfacial adhesion between hydrophilic POSS and chitosan which enhances the ability of the membranes to resist deformation. On the other hand, the interactions between hydrophilic POSS molecules and chitosan may also lead to a loose packing structure of polymer—the so called plasticization effect[28]—resulting in increased mobility of the polymer chains. In contrast, hydrophobic POSS molecules, which form aggregates in the polymer matrix, could not only hinder the

stress transfer, but also increase the number of defects[29] thus making the composites more brittle.

In summary, the composite membranes containing hydrophilic POSS become less stiff and more ductile without loss of strength, whereas the composite membranes with hydrophobic POSS have worse overall mechanical properties compared with the neat chitosan membrane. Unlike other nanofillers such as nanoclay and carbon nanotubes which tend to increase the modulus and strength of polymers via reinforcement mechanism,[24,30] POSS can either embrittle materials or act as plasticizers depending on the interactions between POSS and polymers. When POSS are grafted to the polymer chain or copolymerized with other monomers, nanodispersion of POSS molecules in the matrix is facilitated by the strong covalent bonds between POSS and the polymer. Therefore, the nanoscale reinforcement on the polymer matrix is significant.[17,31] Furthermore, POSS may act as crosslinking agents between polymer chains and hence reduce ductility by increasing the crosslinking density.[12] However, when POSS are blended with polymers as in this study, the modification effects on polymer mechanical properties are largely dependent on the physical interactions between POSS and the polymer matrix. Edward T. Kopesky et al.[32] have reported that trisilanol-phenyl-POSS could better retain the modulus and yield stress of poly(methyl methacrylate) (PMMA) than methacryl-POSS due to hydrogen bonding between the hydroxyl group of trisilanol-phenyl-POSS and the ester group of PMMA. Owing to the specific core-shell molecular structure of POSS, the structure of the R groups, which mediates the interaction between POSS molecules and polymers, plays a significant role on the effects of POSS as fillers. Furthermore, the length of the R groups, which determines the thickness of the soft shell around POSS, also affects the stress transfer within the materials.[25] In general, the modification effects of POSS fillers on polymers are multifaceted depending on the complex interactions between POSS and polymers.

Swelling behavior

Figure 6 shows the effects of the type and loading amount of POSS on the degree of swelling of the composite membranes in deionized water. Generally, the degree of swelling of the composite membranes is lower than the neat chitosan membrane. For composite membranes containing hydrophobic OAPS and ONPS, the degree of swelling gradually decrease with increasing POSS content. On the other hand, for the composite membranes with hydrophilic OA and OAS, the degree of swelling first decrease, then increase with increasing POSS loading. However, even for the composite membranes
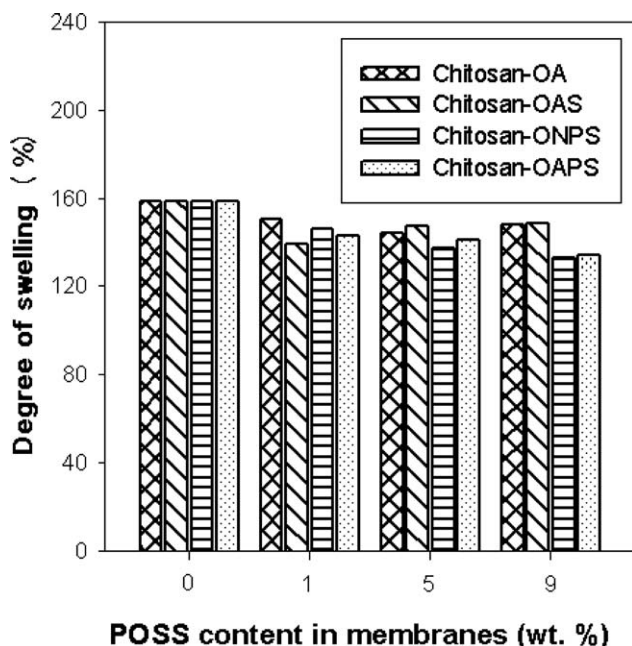
Figure 6 Degree of swelling of the neat chitosan and chitosan–POSS composite membranes in deionized water.

with the highest OA and OAS loadings, the degree of swelling are still lower than the neat chitosan membrane. It is known that the swelling of membranes in water depends on the chemical composition, microstructure, the incorporated moiety and the degree of crystallinity. XRD data have shown that there was little change in the degree of crystallinity of membranes when POSS were incorporated. Therefore, the swelling behavior of chitosan composite membranes is mainly influenced by the properties of POSS. As expected, the incorporation of hydrophobic POSS reduces the hydrophilicity of membranes, thus decreasing the water affinity. The decrease in the degree of swelling of composite membranes with hydrophilic POSS is likely due to the reduction of water absorption sites owing to the competition between POSS and water for such sites in the chitosan matrix.

Permeability of NaCl and riboflavin

In the time interval of the permeability experiment, the relationship between concentration and time is found to be linear during steady state. Hence, eqs. (2) and (3) can be applied to determine the permeability coefficient. Figure 7 shows the permeability coefficients of NaCl in chitosan–POSS composite membranes. For chitosan–OA and chitosan–ONPS composite membranes, at only 1 wt % loading, the permeability coefficient increases by 18 and 16%, respectively, compared with that of the neat chitosan membrane. However, as the amount of embedded OA and ONPS further increases, the permeability

coefficient decreases in value. With the addition of OAPS into chitosan, the permeability coefficient increases and a maximum value is reached when the loading is 5 wt %. For the chitosan–OAS composite membranes, the permeability coefficient is almost unchanged when the loading of OAS is low (1 and 5 wt %), whereas an increase of around 6.80% is obtained when 9 wt % OAS is introduced.

Figure 8 shows the permeability coefficients of riboflavin in chitosan–POSS composite membranes. It is observed that the variation trend of the permeability coefficients of riboflavin in membranes is similar to that of NaCl. For chitosan–OA composite membranes, the permeability coefficient reaches a maximum value at 1 wt % of OA loading and starts to decrease with increasing amount of OA. In chitosan–OAPS composite membranes, the permeability coefficient of riboflavin reaches a maximum value at 5 wt % loading. In chitosan–OAS and chitosan–ONPS composite membranes, as the content of ONPS and OAS increased, the permeability coefficient decreases monotonously. However, except for the composites with 1 and 5 wt % loading of OA, the permeability coefficients of riboflavin in all the other composite membranes are lower than that in the neat chitosan membrane. Such a trend is different from the NaCl permeability behavior.

It is known that the permeability of a solute in a hydrogel membrane is significantly influenced by the size of solute, degree of hydration of the membrane and the interaction between the solute and the
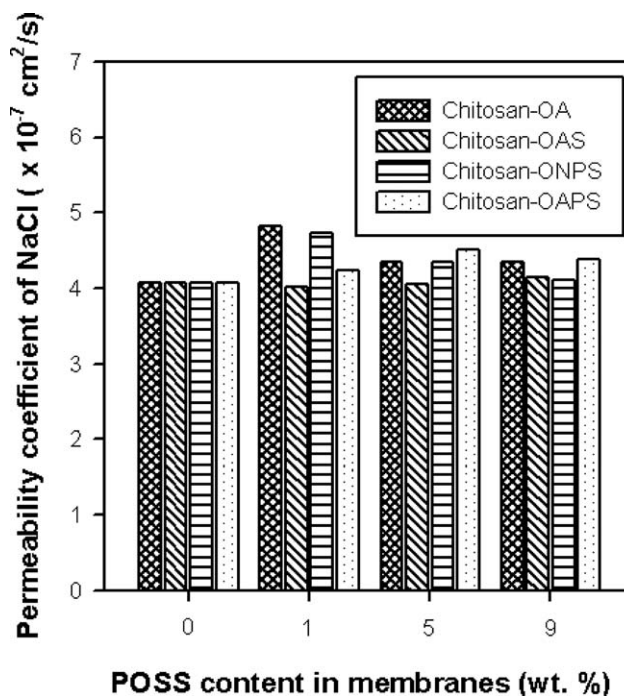

Figure 7 Permeability coefficients of sodium chloride in the neat chitosan and chitosan–POSS composite membranes.
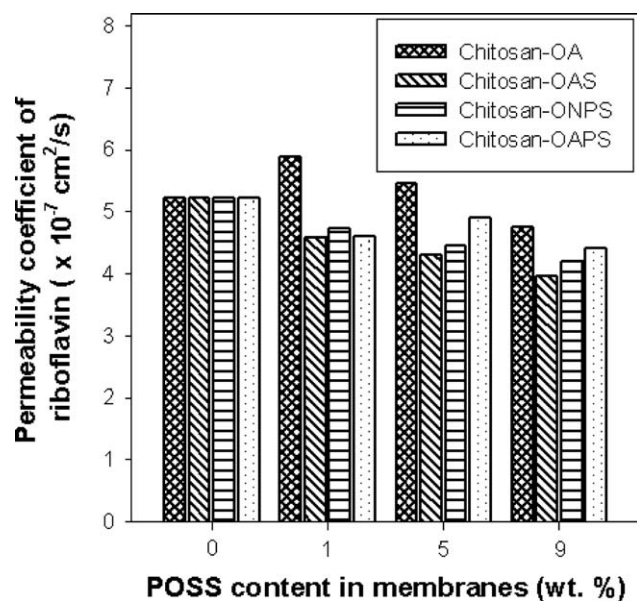
Figure 8 Permeability coefficients of riboflavin in the neat chitosan and chitosan–POSS composite membranes.

membrane (ionic, hydrophilic/hydrophobic interaction, etc.). Riboflavin, which has a pK_a of 10.2, is positively charged at pH 7.0. Therefore, riboflavin ions and Na^+ are likely to favor negatively charged membranes such as chitosan–OA and chitosan–ONPS composite membranes which are embedded with negatively charged OA and ONPS. However, chitosan–OA and chitosan–OAS composite membranes have relatively high degree of swelling in water owing to the hydrophilic nature of OA and OAS. Therefore, the permeability of the solutes in the composite membranes depends on the synergetic effect of electrostatic force and the hydration of the membranes.

Partition coefficients and diffusion coefficients of riboflavin

According to the free volume theory, the permeability of a solute in a membrane comprises of sorption of the solute into the membrane and diffusion within the membrane.[32] Therefore, adsorption experiments were carried out to investigate the interaction between riboflavin and the composite membranes. Table II shows the partition coefficients and diffusion coefficients of riboflavin for the neat chitosan and chitosan composite membranes loaded with 9 wt % POSS calculated from eqs. (4) and (5), respectively. It is observed that the partition coefficients of the neat chitosan and chitosan–POSS composite membranes are much larger than unity. This phenomenon has been reported for PVA and chitosan membranes[33,34] and was attributed to the existence of bound water that connected the solute to the membrane. The

enrichment of riboflavin in the membranes is likely due to the good affinity of the chitosan matrix toward riboflavin. Furthermore, the partition coefficients of riboflavin decrease in the order: chitosan–OA > chitosan–OAS > chitosan > chitosan–OAPS > chitosan–ONPS. Because of the hydrophilicity of riboflavin, it is expected that high affinity and good distribution can be obtained in more hydrophilic membranes containing hydrophilic OA and OAS. It is also worth noting that chitosan–OA has much higher affinity to riboflavin than chitosan–OAS. This can be explained by the electrostatic attraction between the negative charged OA and the positively charged riboflavin. However, the hydrophobic nature of chitosan–OAPS and chitosan–ONPS composite membrane makes it difficult for riboflavin molecules to get close enough to the polymer chains for electrostatic interactions to play a role. Therefore, the higher partition coefficient of riboflavin in chitosan–OAPS is attributed to the greater degree of swelling of chitosan–OAPS compared with chitosan–ONPS composite membranes. Because riboflavin is soluble in water, more water inside the membranes provides more accommodation for riboflavin.

The diffusion coefficients of riboflavin decrease in the order: chitosan–ONPS > chitosan–OAPS > chitosan > chitosan–OAS > chitosan–OA, which is opposite to that of the partition coefficients. According to the free volume theory, the diffusion of a solute in polymer membrane depends on the probability of a solute to find a mesh formed by the polymeric network having a volume with at least the dimensions of the solute. The interaction between the solute and the polymer makes it difficult for the solute to leave the present mesh and move to the next one, but it also offers more opportunities for the solute to find other sites.[35] The former effect decreases the probability of the solute to diffuse while the latter effect increases this probability. Our result suggests that the former effect is predominant for the studied membranes. Therefore, the adsorption of riboflavin in the membranes reduces the interfacial velocity, causing riboflavin molecules to take a long time to be transported through the membranes.[36] Hence,

TABLE II
The Partition Coefficients and Diffusion Coefficients of the Neat Chitosan and Chitosan–POSS Composite Membranes with 9 wt % POSS

Membranes	Partition coefficient	Diffusion coefficient ($\times 10^{-8}$, cm^2/s)
Chitosan	24.4	2.1
Chitosan–OA	44.4	1.0
Chitosan–OAS	30.3	1.3
Chitosan–ONPS	15.8	2.7
Chitosan–OAPS	21.2	2.2

riboflavin would have a low diffusion rate in hydrophilic membranes with high partitioning effect.

CONCLUSIONS

Hydrophilic and hydrophobic POSS with different charges were added into chitosan matrix to form composite membranes. Phase separation was observed in composite membranes containing hydrophobic POSS, whereas no phase separation was observed in the membranes containing hydrophilic POSS. The thermal stability of all the chitosan–POSS composite membranes was improved as the decomposition was retarded. With the introduction of POSS, significant losses in modulus were observed, while the effects on elongation at break and tensile strength depended on the type of POSS. Composite membranes containing hydrophilic POSS presented good mechanical properties due to good compatibility and strong interactions between POSS and the chitosan matrix. However, hydrophobic POSS with poor interfacial interaction with chitosan made the composite membranes more brittle.

The diffusion permeability of NaCl and riboflavin in the composite membranes depended on the interactions between the solutes and the membranes, as well as the hydration of the membranes. Membranes incorporated with hydrophilic POSS displayed higher partition coefficients, but lower diffusion coefficients of riboflavin, compared with that of the membranes containing hydrophobic POSS.

In conclusion, with the incorporation of a small amount of POSS, the structure and properties of chitosan membrane can be modified. Furthermore, the modifications are largely dependent on the R side groups of POSS suggesting a great potential to tune the polymers for extended applications.

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