

# Synthesis and Dynamic Mechanical Behavior of Glucose-Mediated Poly(Ethylene Glycol/Chitosan) Membrane

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**ABSTRACT:** The pH-dependent chitosan/PEG membrane was prepared by a surface-mediated process with glucose as a source. Swelling study shows that the glucose-mediated membrane is more stable in a neutral environment than an acidic one and the stability in all soaking environments generally increases with increasing glucose concentration because of an increase in Schiff's reaction product as demonstrated by a mediated degree analysis. DMA analysis shows that as the glucose concentration increases, the rubber plateau of the glucose-mediated membrane is prolonged and keeps a higher storage modulus, and the tangent  $\delta$  peak shifts to a high temperature as the temperature increases. In

an isothermal mode, as the glucose concentration increases to 10 wt %, the storage modulus shows a small change in frequency dependence, indicating that the mediating effect is obviously affected by glucose addition. It can also be found that surface-mediated membrane has a higher complex viscosity than chitosan/PEG membrane at high frequencies. Thus, a new way was found to use glucose to produce stable biomaterial. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 809–820, 2004

**Key words:** chitosan; blending; glucose; glass transition; viscoelastic property

## INTRODUCTION

Polymeric membranes contacting with tissue fluid may result in one of the following<sup>1</sup>: (1) no chemical effect; (2) little swelling, membrane may be compatible for a short term use; (3) extensive swelling and slow dissolution of membrane; (4) complete dissolution or disintegration of membrane; or (5) relaxation of polymer chains due to plasticization and swelling with subsequent pore size reduction. Because of the presence of certain functional groups along the polymer chain, membrane is sensitive to the surrounding environment, which is referred as intelligent materials. Therefore, it is of interest to prepare a pH-dependent membrane for biomedical application such as drug delivery system, muscle, and implants.<sup>2</sup> Many studies have prepared membranes by using chitosan (Ch) and other polymers as pH-dependent materials. Illum et al.<sup>3</sup> prepared Ch film by reversible physical crosslinking and Park et al. used tetraethyl orthosilicate (TEOS) as an inorganic material and Ch as an organic com-

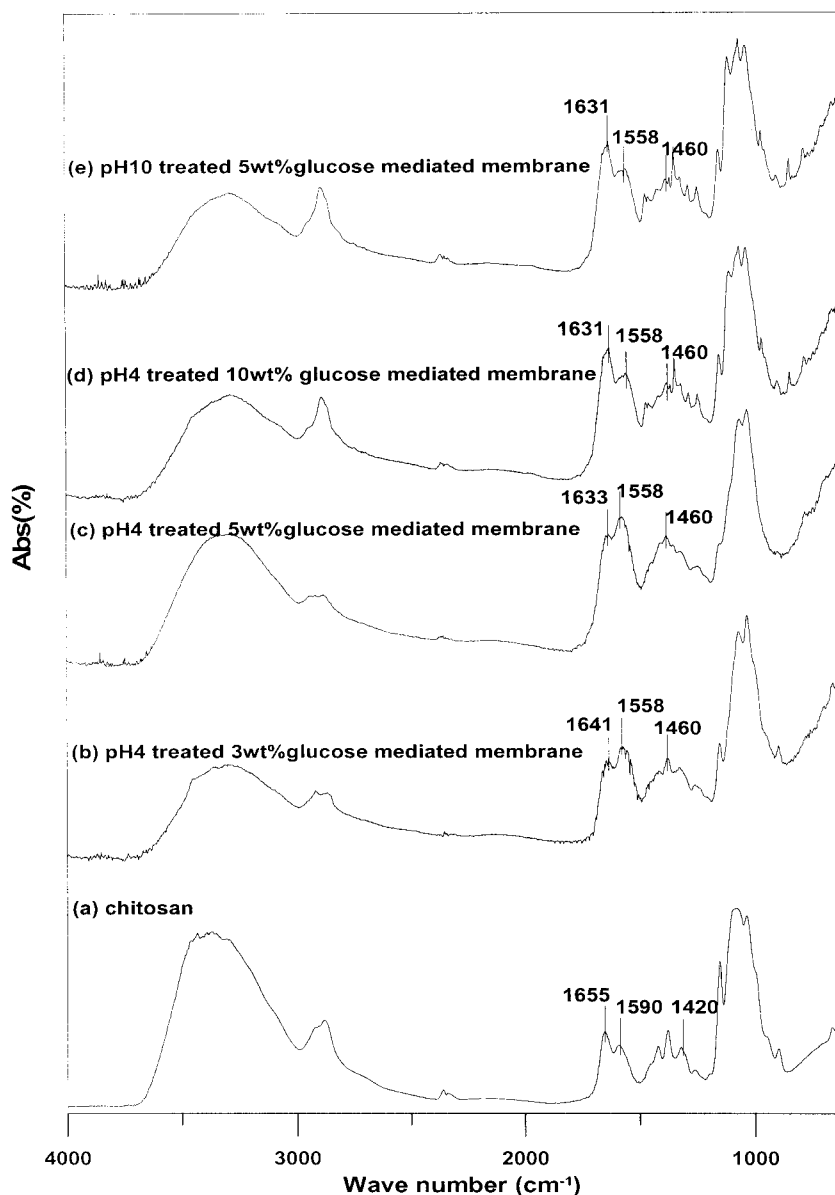
pound by sol-gel process to prepare a novel pH-sensitive membrane for drug delivery.<sup>4</sup>

Ch is a typical biological macromolecule derived from the cuticle of marine crustaceans such as crabs and shrimps and is made of glucosamine and *N*-acetylglucosamine units linked by 1–4 glycosidic bonds. Ch is also a natural polycationic polymer that possesses useful properties such as nontoxicity, high biocompatibility, and non-antigenicity that offer advantages for possible clinical uses.<sup>5</sup> Polycationic property of Ch along with its possession of potentially reactive amino functional group has given it unique possibilities for utilization in different fields. In particular, the ability of Ch to form films has found application in various fields such as drug development, obesity control, and tissue engineering.<sup>6</sup>

To improve the hydrophilic character of Ch derivatives, some approaches were made by blending hydrophilic polymers such as poly(vinyl alcohol) (PVA) and poly(ethylene glycol) (PEG).<sup>7</sup> PEG is a non-charged polymer and is widely used as pharmacological product with hydrophilicity, biocompatibility, and low biodegradability. Jiang and Han<sup>8</sup> indicated that Ch/PEG blend is compatible and the attractive intermolecules interact at various PEG-6000 concentrations. Therefore, applying a suitable amount of PEG and polymer would increase biocompatibility or solubility to tissue.

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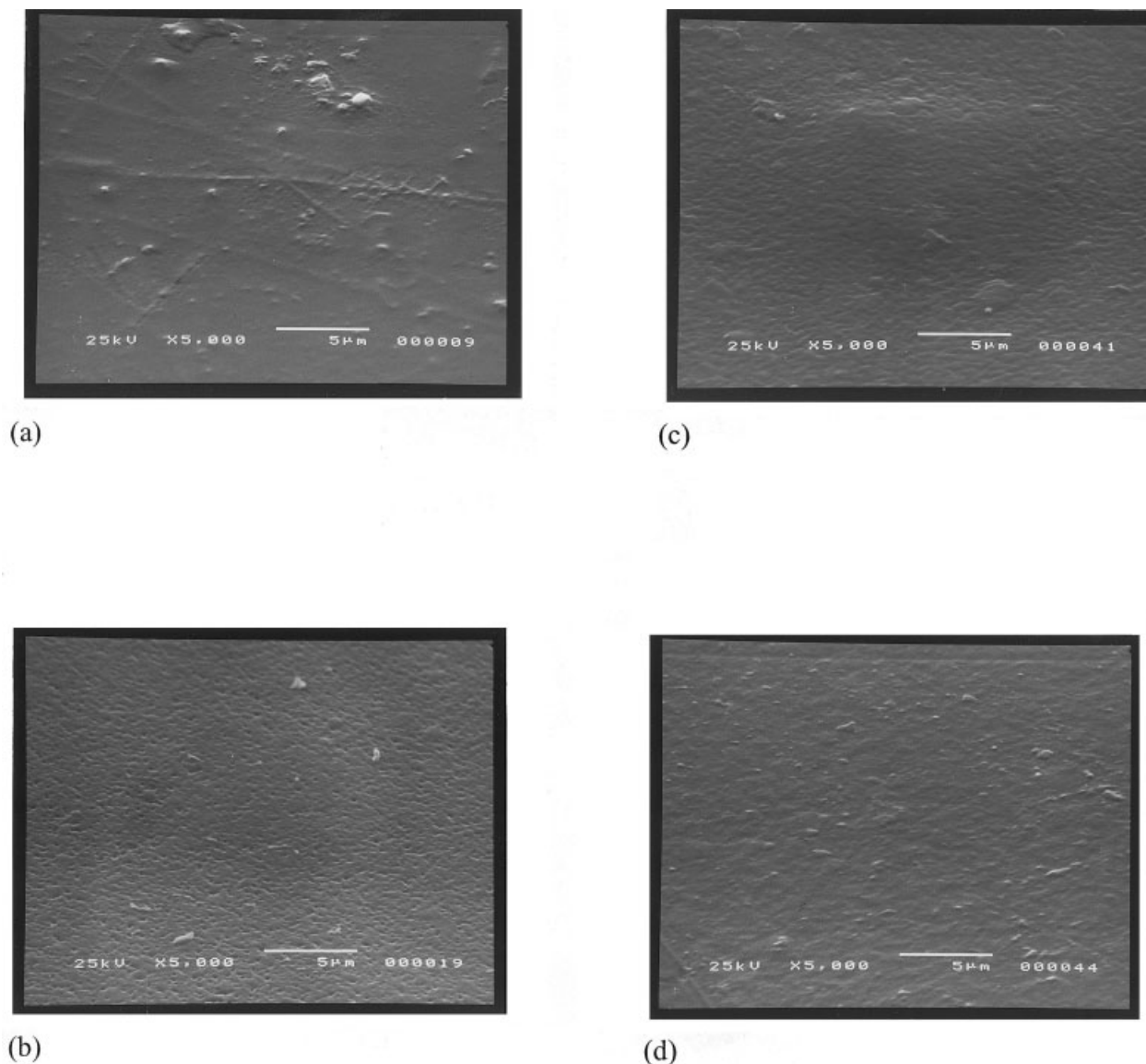


**Figure 1** FTIR spectra of (a) chitosan, (b) pH 4 treated 3 wt % glucose-mediated membrane, (c) pH 4 treated 5 wt % glucose-mediated membrane, (d) pH 4 treated 10 wt % glucose-mediated membrane, (e) pH 10 treated 5 wt % glucose-mediated membrane.

Ch/PEG polyblends were usually prepared by chemical crosslinking with formaldehyde, epichlorohydrin, and glutaraldehyde.<sup>9</sup> This material swells under acidic conditions because of the ionization of amino groups but remains in a shrunken state under neutral conditions. However, the chemical crosslinking agents possibly induce toxicity and may have a negative influence on tissue. The use of reduced sugar such as fructose or glucose that has aldehydes in end group as a stabilizer was developed in our group.<sup>10</sup> The reaction between Ch amino group and aldehydes as described<sup>11</sup> involves the formation of a Schiff base, which is accompanied by color formation and is called maillard reaction. However, the reactivity and stabil-

ity of maillard reaction end product are highly influenced by the pH of the reaction system. The open-chain form of the sugar and the unprotonated form of the amino group are favored at a higher pH, but the stability of the end products is still a controversial issue. Tressl et al.,<sup>12</sup> using <sup>13</sup>C-labeled sugars, have given a new reaction mechanism and found that a degraded melanoidin was formed at low pH, which will increase the solubility of the polymer with free amino group.

In the present study, pH-dependent membranes were prepared by a surface-mediated process with glucose as a natural source to stabilize the Ch/PEG polyblend. The properties of Ch and glucose-medi-



**Figure 2** Scanning electron micrographs of surfaces of (a) chitosan, (b) chitosan/PEG, (c) 5 wt % pH 4 treated glucose-mediated membrane, (d) 5 wt % pH 10 treated glucose-mediated membrane.

ated Ch/PEG polyblend were investigated by FTIR analysis, equilibrium swelling studies, mediating degree analyses, dynamic mechanical analysis (DMA), and scanning electronic microscopy (SEM).

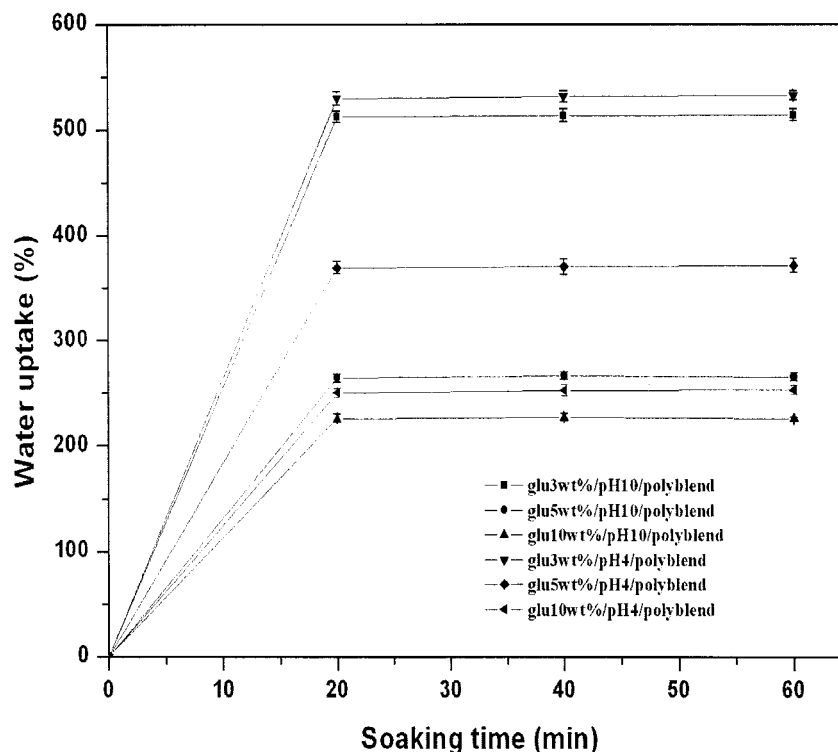
## EXPERIMENTAL

### Materials

Ch with high molecular weight (degree of deacetylation is 53%,  $M_w \sim 4 \times 10^5$ ) was obtained in flake form from Fluka (Buchs, Switzerland). PEG ( $M_n = 6000$ ) was purchased from Rideld-dehaen (Germany). Dextrose anhydrous was used as mediating agent and supplied by J. T. Baker Inc. (USA). All other reagents were extra pure grade and used as received.

### Preparation of surface-mediated Ch/PEG membrane

Ch (3 g) was dissolved in 100 mL of 2% aqueous acetic acid. The mixture was stirred for 4 h to obtain a perfectly transparent solution. Ch/PEG blend was prepared by mechanical stirring the filtered Ch and PEG flake in a percentage of 70 : 30 at room temperature. The films of the resulting polymer blend were obtained by casting into polystyrene Petri dishes for 40 min in an oven at 68°C. The membrane was neutralized with 10% (w/v) sodium hydroxide followed by rinsing with deionized distilled water (DDW) and dried in an oven at 30°C for 60 min. The polyblend was placed in desiccators and allowed for further mediating. The mediating solution was prepared by



**Figure 3** Swelling behavior of glucose-mediated chitosan/PEG membrane as a function of glucose concentration in acidic environment (0.1N HCl) as prepared by different pH conditions (pH 4, 10).

dissolving 3, 5, and 10 wt % glucose in DDW and adjusting the pH value to 4  $\times$  0.5M hydrochloride acid, to 10  $\times$  1M sodium hydroxide, respectively, and then thermal treated at 120°C in an oven for 1 h. After drying, the membrane was soaked in mediating solution at 68°C for 2 days and the final glucose-mediated polyblend was obtained. After further rinsing twice by DDW, the membrane was dried at room temperature overnight and stored in desiccators.

#### FTIR spectrum analysis

FTIR spectra were measured by a Jacob FTIR 8100 spectrometer to determinate the chemical interaction between glucose and Ch/PEG. The pH-treated glu-

cose-mediated Ch/PEG membrane was mixed with KBr and pressed to a plate for measurement.

#### Extent of mediating of ch/PEG with pH-treated glucose solution

The primary amine content of mediated and nonmediated membranes, expressed as the mediated percentage of free amino groups in the treated membranes related to the nonmediated membrane, was determined by using 2,4,6-trinitrobenzenesulfonic acid (TNBS) as reaction solution as described by Sheu et al.<sup>13</sup> The resulting solution was diluted with 5 mL DDW and the absorbance was measured at 345 nm. The degree of mediating was calculated as

The extent of mediating

$$= 1 - (\text{absorbance}_{\text{mc}}/\text{mass}_{\text{mc}}) \times (\text{absorbance}_{\text{nmc}}/\text{mass}_{\text{nmc}})^{-1} \quad (1)$$

where the subscripts mc and nmc stand for the mediated Ch/PEG membrane and nonmediated Ch/PEG, respectively.

#### Morphologic observation

The surface morphology of Ch, Ch/PEG, and pH-treated glucose-mediated Ch/PEG membranes were

**TABLE I**  
Degree of Mediating of Chitosan/PEG with Different Glucose Concentrations and Mediating Conditions

Concentration of glucose (wt %)	Mediating condition	
	pH = 4	pH = 10
	Degree of mediating (%)	
3	61.55 $\pm$ 1.21 <sup>a</sup>	82.03 $\pm$ 1.41
5	65.58 $\pm$ 1.04	84.61 $\pm$ 1.47
10	78.13 $\pm$ 1.74	105.42 $\pm$ 2.03

<sup>a</sup> Data represent mean  $\pm$  SD from three independent experiments.

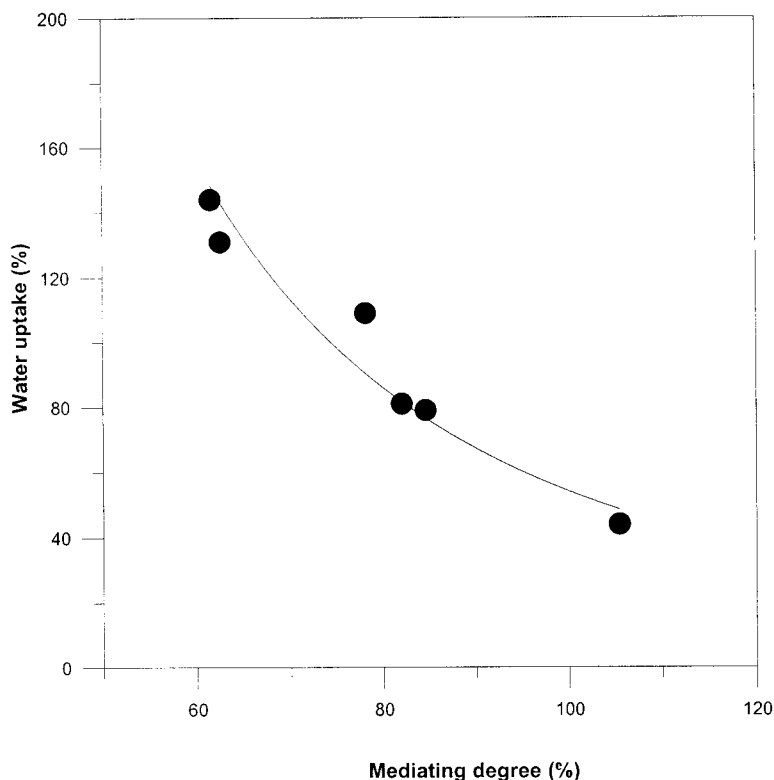


Figure 4 Effect of mediating degree on the water uptake ability of glucose-mediated membranes in pH 7.4 medium.

observed by using a JEOL 5120 SEM conducted at 25 kV on platinum-coated surface of the membrane under an argon atmosphere.

#### Equilibrium swelling studies

Blank glucose-mediated polyblend was suspended in a glass bottle containing 20 mL of swelling media and incubated in a water-bath at 37°C. After soaking for 24 h, the polyblend was taken out, and the excess water was removed carefully with filter paper from polyblend surface and then weighed immediately. The swelling percentage of the polyblend at equilibrium was calculated from the formula

$$\text{Water uptake} = [(W_w - W_0)/W_0] \times 100 \quad (2)$$

where  $W_w$  is the weight of the polyblend at the swelling equilibrium and  $W_0$  is the initial weight of the polyblend. The media for the swelling studies were 0.1N HCl (pH 1.2) and 0.1M phosphate buffer (pH 7.4), respectively. The ionic strength of the above buffered solution was adjusted to 0.145M by adding an appropriate amount of sodium chloride.

#### Dynamic mechanical properties of the glucose-mediated polyblend

Dynamic mechanical analysis (DMA) was performed in tension by using a TA Instruments 2980, applying

sufficient force to produce a deformation strain  $< 2\%$  in the sample. Strips in dimensions of  $15 \times 6 \times 0.1$  mm were used as specimens for glucose-mediated polyblend. The storage ( $E'$ ) and loss modulus ( $E''$ ) were measured at a frequency of  $1 \text{ rad s}^{-1}$  over a temperature range of 25 to 300°C at a heating rate of 5°C/min. For comparison, measurements were also conducted isothermally at 37°C and a frequency scan mode from 0.1 to 100 Hz. The tangent of the phase angle ( $\tan \delta$ ) and the magnitude of the complex viscosity ( $\eta^*$ ) were determined from  $E'$  and  $E''$  as

$$\tan \delta = E'/E'' \quad (3)$$

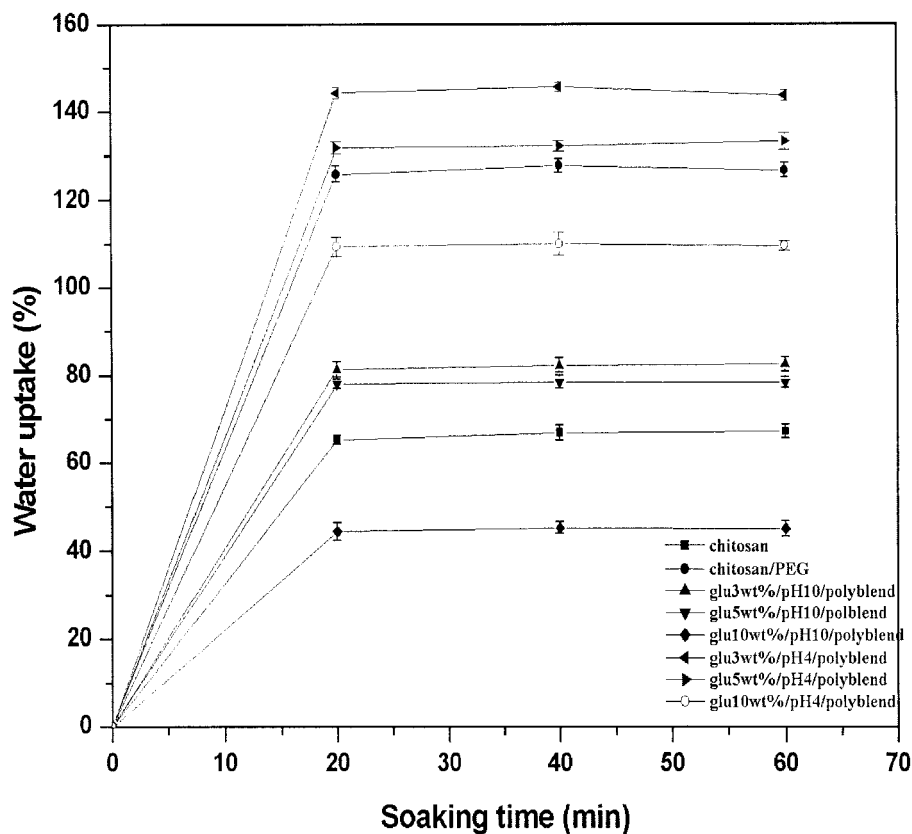
$$\eta^* = \sqrt{(E'/\omega)^2 + (E''/\omega)^2} \quad (4)$$

where  $\omega$  is the angular frequency.

## RESULTS AND DISCUSSION

#### FTIR analysis and swelling study

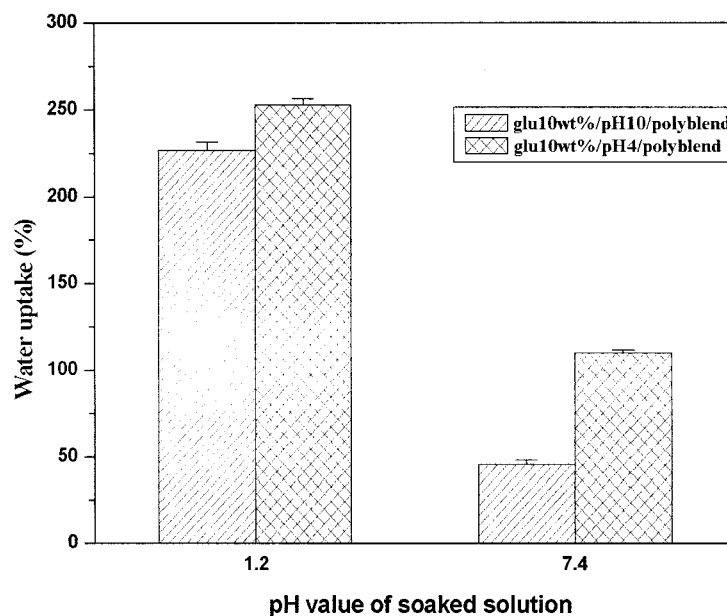
In our first study,<sup>10</sup> we demonstrated that the glucose could react Ch/PEG gel solution and form a Schiff base product, which has C=N presented in the structure by FTIR analysis. It is proposed that the mechanism of mediating between the aldehyde and the free amine on Ch follows the Schiff's base reaction that results in C=N formation. This result was similar to Ch crosslinking with glutaraldehyde.<sup>14</sup> Figure 1 shows



**Figure 5** Swelling behavior of glucose-mediated chitosan/PEG membrane as a function of glucose concentration in PBS solution (pH 7.4) as prepared by different pH conditions (pH 4, 10).

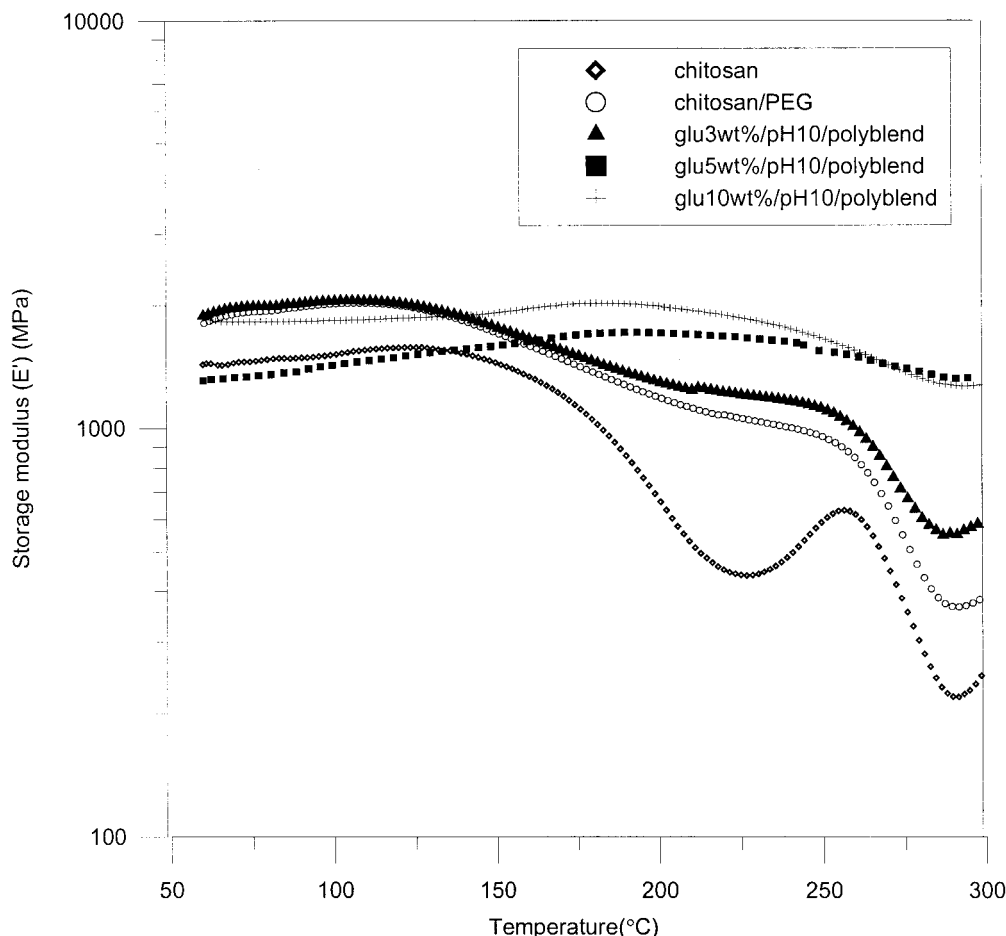
the FTIR spectra of Ch, pH 4 treated 3, 5, and 10 wt %, pH 10 treated 5 wt % glucose-mediated membrane. The spectrum of the Ch film exhibits an absorption

around 1655 and 1590  $\text{cm}^{-1}$ , which represents the amide I and amide II bands, respectively. There are bands at 1420, 1380, and 1320  $\text{cm}^{-1}$ , in addition to the



**Figure 6** Swelling behavior of 10 wt % glucose-mediated chitosan/PEG membrane as a function of soaked solution pH.





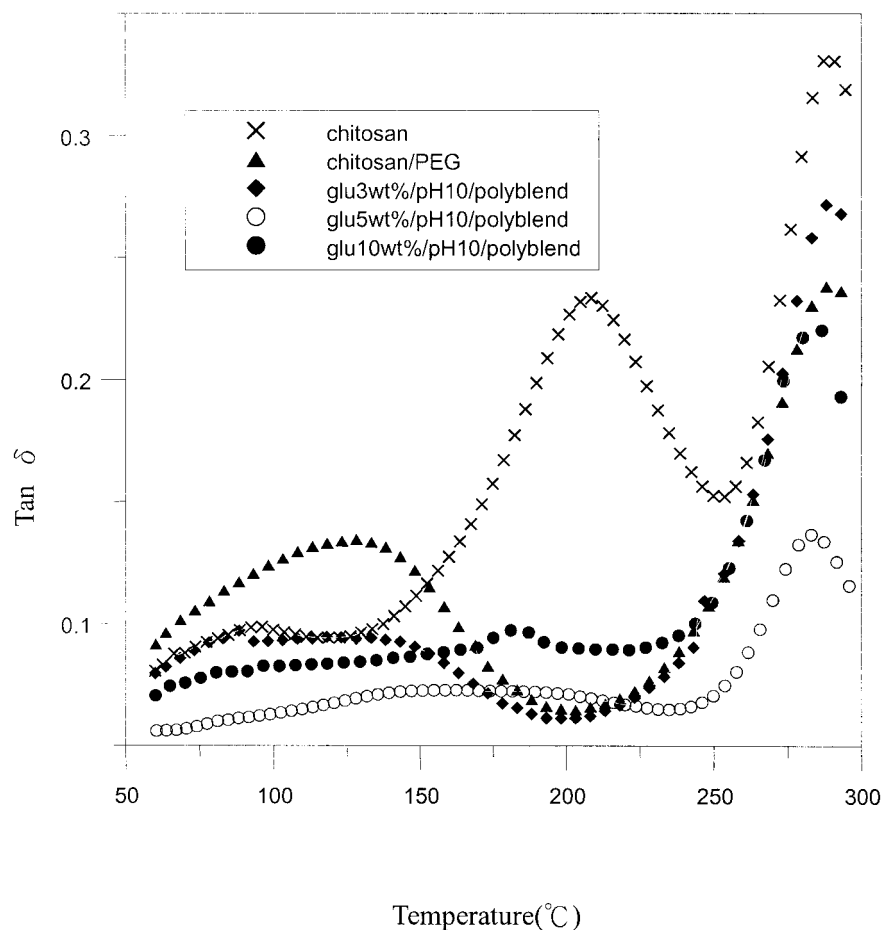
**Figure 7** Change in storage modulus ( $E'$ ) with different glucose concentrations for membrane prepared by surface-mediated process as performed at the frequency of 1 Hz.

usual C—H aliphatic band at  $2880\text{ cm}^{-1}$ . The OH and  $\text{NH}_2$  overlapping bands are found around  $3310\text{--}3450\text{ cm}^{-1}$ . It is important to note that the peaks at  $3310\text{--}3450\text{ cm}^{-1}$  corresponding to stretching vibrations of OH and  $\text{NH}_2$  groups moved to lower wave numbers and became broader, which indicates the strong interaction between these groups and glucose. This interaction mechanism seems to be mainly hydrogen bonding, because generally glucose in solution has a lot of OH groups on their backbone, which are active sites that interact via hydrogen bonding with the surroundings.<sup>15</sup> There were slight differences between Ch and pH 4 treated 3 wt % glucose-mediated Ch/PEG membrane spectra except that the peak at  $1650$  and  $1590\text{ cm}^{-1}$  moved to a lower wave number,  $1641$  and  $1558\text{ cm}^{-1}$ , as shown in Figure 1(b). The effects of glucose concentration on the Ch/PEG is also shown in Figure 1. On increasing the glucose concentration, the peak corresponding to  $1641\text{ cm}^{-1}$  gradually narrows because of the formation of more C=N formation. It is implied that as the glucose concentration increases, more aldehyde groups of glucose in linear form resulted in more Schiff's base product. In contrast with

spectra of pH 4 and pH 10 treated 5 wt % glucose-mediated membrane, a significant peak at  $1631\text{ cm}^{-1}$  and coupled with the decrease of peaks at  $1558\text{ cm}^{-1}$  in the spectra is due to the formation of C=N and this is because of the Schiff's base reaction between amino groups from Ch and aldehyde group in glucose. It also implied that the reaction between Ch and glucose was favored in the pH 10 environment.

#### Morphology of pH treated glucose-mediated membrane

The surface morphologies of Ch, Ch/PEG membrane, and pH-treated glucose-mediated membrane are shown in Figure 2. The top surface of Ch membrane was very smooth [Fig. 2(a)], whereas the Ch-PEG [Fig. 2(b)] membrane surface was rough. The small round voids were distributed uniformly throughout the membrane surface. The small circular-shaped voids in Ch-PEG membrane possibly formed by leaching out the low molecular weight PEG oligomer during the membrane rinsing process.<sup>16</sup> The pH value and glucose concentration had little effect on the surface mor-



**Figure 8** Change in loss tangent ( $\delta$ ) with different glucose concentrations for membrane prepared by surface-mediated process as performed at the frequency of 1 Hz.

phology of Ch/PEG membrane. For example, the pH 4 treated 5 wt % glucose-mediated membrane was relatively smooth in comparison with Ch/PEG membrane. Otherwise, the increase of pH media has significant influence on surface structure and the color of the sample became much deeper, which indicates that the maillard reaction between Ch and glucose are favored in high pH environment.

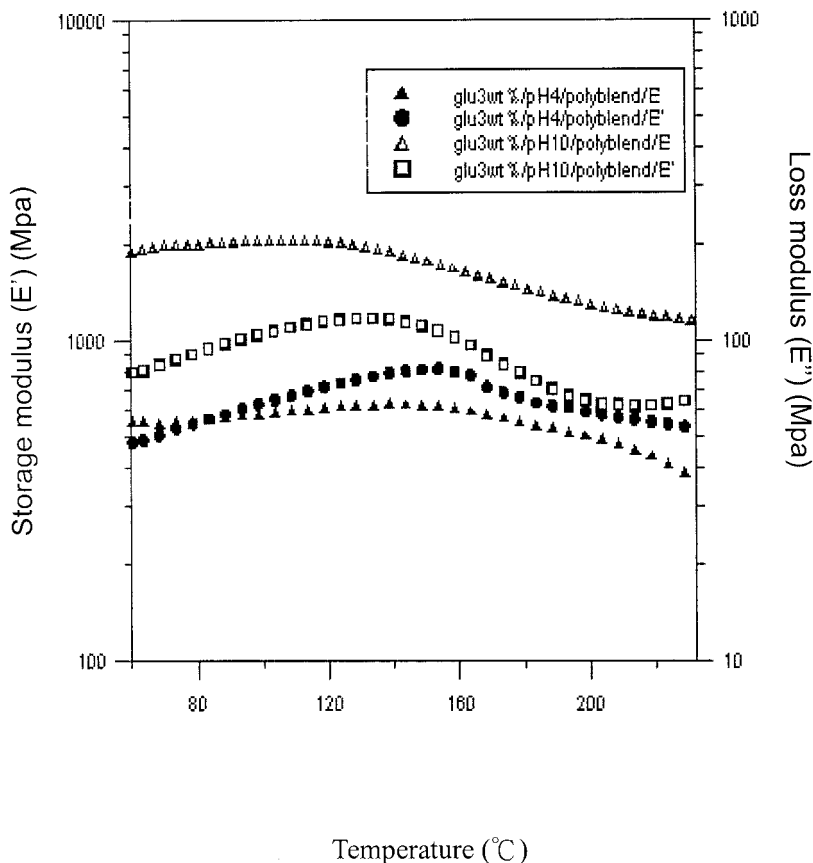
The pH-dependent swelling behavior and kinetics of films for Ch have been already reported in many articles.<sup>12</sup> In this study, the Ch and Ch/PEG membranes were rapidly dissolved in 0.1N HCl (pH 1.2) in 20 min because of the protonation of  $\text{NH}_2$  groups of Ch and hydroxyl groups of PEG, the mediating conditions, and processes of Ch/PEG polyblend are expected to reduce the numbers of  $-\text{NH}_2$  groups of Ch, and hence, reduce the solubility at pH 1.2.

The typical data for swelling of surface-mediated Ch/PEG membrane as a function of glucose concentration in pH 1.2 environments and various mediating conditions (pH 4 and 10) are shown in Figure 3. In the surface-mediating process, as the glucose concentration increases, the swelling ratio of membrane pre-

pared by pH 4 and 10 decreases. It also can be found that the acidic-treated glucose-mediated membrane has higher water uptake ability than the basic-treated one. Importantly, the surface-mediated glucose-mediated membrane still keeps the original integrity, which demonstrates that the chemical reaction occurs between glucose and Ch.

According to Sheu et al.,<sup>13</sup> the mediating degree of membranes can be expressed as the mediated percentage of free amino groups in the treated membranes related to the nonmediated membrane. Therefore, the increase of mediating degree infers that the decrease of the free amine groups can easily explain the swelling test result. As shown in Table I, it can be easily found that in surface-mediating mode, with increasing the glucose concentration, the mediating degree increased, which demonstrates that the Schiff's reaction occurs. Otherwise, the basic mediated membrane has a higher mediating degree, indicating that for the membrane prepared in more basic mediating solution, the Schiff's reaction is more distinct. According to Hofmann's report,<sup>17</sup> an increase in temperature leads to an increase in the reactivity between the reduced





**Figure 9** A comparison of  $E'$  and  $E''$  between low (pH 4) and high mediating conditions (pH 10) for 3 wt % glucose-mediated membrane at a frequency of 1 Hz.

sugar and amino group. Martins et al.<sup>18</sup> indicated that glucose or fructose is much easier to transform into linear open-chain molecules from stable chair ring structure in basic solution. Thus, there will be more aldehyde groups presented in basic solution than in acidic solution for  $\text{NH}_2$  groups of Ch to react and the reduced numbers of the amino groups of Ch will be much less in acidic mediating condition. Figure 4 also shows the swelling results with the variations of the mediating degree between the Ch/PEG membrane and the glucose. It can be found that, as the mediating degree increases, the water uptake ability decreases in pH 7.4 medium, which demonstrated that the main factor for the difference of swelling ratio between the acidic- and basic-treated membrane was the reaction between the aldehyde and the  $\text{NH}_2$  group, leading to the decrease in the amino group number of Ch. Therefore, a higher swelling ratio is favored in acidic mediating condition.

At pH 7.4 phosphate buffer saline (PBS) environments, the water uptake of the pH 4 treated glucose-mediated membranes are also higher than the pH 10 treated one, as shown in Figure 5. The difference in water uptake ability may be due to the greater stability of Schiff base formation product in neutral environ-

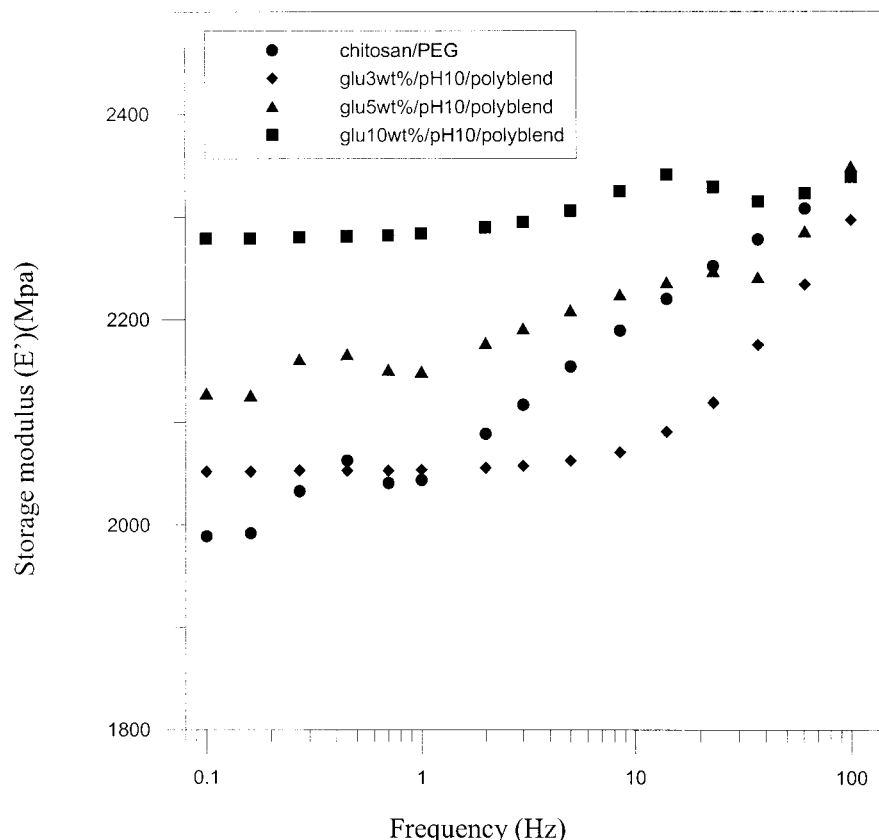
ment. Hence, in the range of pH 1.2 to pH 7.4 environment, the water uptake ability of pH 4 treated glucose-mediated membrane is higher than the pH 10 treated one. The water uptake ability of 10 wt % glucose-mediated Ch/PEG membrane as a function of pH for soaked solution is shown in Figure 6. It is apparent that all of the membrane swelled at pH 1.2 and shrunk at pH 7.4. As expected, glucose can improve the stability of Ch/PEG membrane, especially in an acidic environment.

**DMA analysis for the glucose-mediated membrane**

A theoretical equation proposed by Fox<sup>19</sup> for calculating the glass transition temperature ( $T_g$ ) value of a composite is expressed as

$$1/T_g = W_{cs}/T_{gcs} + W_{PEG}/T_{Gpeg} \tag{5}$$

where  $W_{cs}$  and  $W_{PEG}$  are the weight fractions of Ch and PEG, respectively, and  $T_{gcs}$  and  $T_{gPEG}$  are the glass transition temperatures of Ch and PEG with 212 and 45°C, respectively. The  $T_g$  of the experimental value of 125°C matches well with the theoretical value (121.27°C), implying that a miscible phase at a molec-

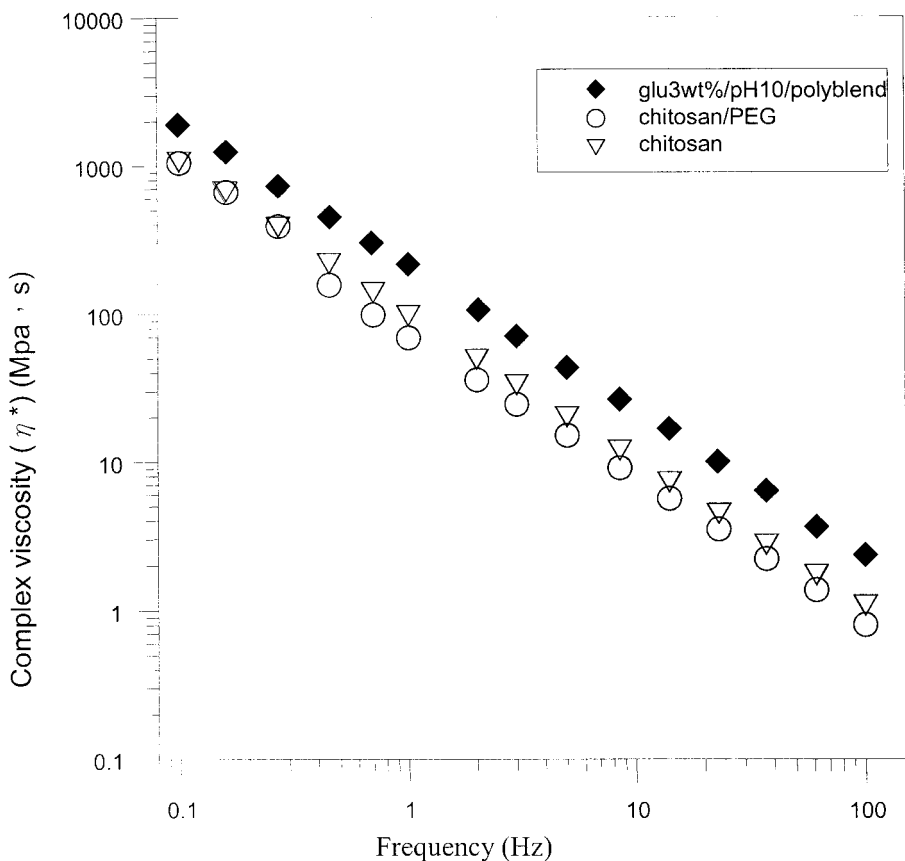


**Figure 10** Frequency dependence of glucose-mediated membrane prepared by surface-mediated process with different glucose concentrations at 37°C.

ular level is formed in the Ch/PEG blend system. Figure 7 shows the change in storage modulus with different glucose concentrations for Ch/PEG polyblend prepared by surface-mediated process. Although the drop in modulus from  $10^9$  to  $10^8$  Pa is observed in all cases, the initial modulus is not the same. At temperatures lower than 150°C, the storage modulus is over  $10^6$  Pa. According to the Crankshaft model,<sup>20</sup> as the temperature and the free volume increase, the side chains and localized groups of Ch begin to have enough space for moving and the materials start to develop some toughness. This transition, called the  $\beta$ -transition,  $T_{\beta}$ , about 100°C in this case, is defined as glassy region. After the sharp drop of the storage modulus in the glass transition region, the behavior of Ch moves to the rubbery plateau region. With blending with PEG polymer, the glass transition region becomes broadened as the temperature increases. As the glucose concentration increases, the glass transition region becomes broadened and the rubber plateau of the material is prolonged and keeps at a higher storage modulus with increasing temperature. As the glucose concentration increases, the tangent  $\delta$  peak amplitude decreases and the position shifts to a high temperature, as shown in Figure 8. It indicates that  $T_g$  shifts to a high temperature and the

crystallinity increases. The DMA property of glucose-mediated polyblend behaves similar to a crosslinking product. For a crosslinking product, as the temperature increases, the storage modulus would not drop sharply because the crosslinks can prevent the chains from slipping past each other; therefore, the viscous flow is not obvious and the storage modulus increases in the rubber region as the crosslinking density increases.<sup>21</sup> Otherwise, the  $T_g$  will increase because the crosslinking effect restricts the chain relaxation in the high-temperature region and the crosslinking also has an insignificant effect on the glass region. From the above analysis, it demonstrates that the mediating density of glucose-mediated membrane increases as the glucose concentration increases.

Figure 9 shows a comparison of the modulus of storage and loss between low (pH 4) and high (pH 10) mediating conditions for 3 wt % glucose-mediated membrane at a frequency of 1 Hz. The initial storage modulus of basic mediated membrane is higher than the acidic mediated one, but both of them have a broader glass transition region and prolonged rubber plateau as the temperature increases. It indicates that a mediating product is also formed in low pH mediating condition, although they have higher water uptake ability. The difference in initial storage modulus



**Figure 11** Frequency dependence of 3 wt % glucose-mediated chitosan/PEG membrane at 37°C.

between basic- and acidic-mediated membranes may be attributed to the glucose activity in different pH conditions.

In an isothermal DMA study of membrane, the frequency dependence of glucose-mediated membrane prepared by the surface-mediating process with different glucose concentrations at 37°C is shown in Figure 10. For Ch/PEG membrane, a continuous decay in the storage modulus is observed as the frequency changes from 100 to 2 Hz, but for 3 wt % glucose-mediated membrane, the decay range changes from 100 to 10 Hz. At higher frequencies, both of them are relatively stiff, whereas at a low frequency, the rubbery behavior is observed. However, at frequencies lower than 1 Hz, the 3 wt % glucose-mediated membrane shows a higher storage modulus. It is well known that the storage modulus of a permanent network shows almost independent frequency characteristics, but for 3 wt % glucose-mediated membrane, a sort of glass-to-rubber transition type of process in Figure 10 indicates that the membrane behaves as an amorphous elastomer. It may be due to the presence of a weakly structured network of self-associated Ch, further restricted by a few covalent crosslinking points provided by glucose addition.<sup>22</sup> As the glucose concentration increases, the membrane possesses a higher

storage modulus at a frequency lower than 10 Hz. At glucose concentrations up to 5 wt %, the form of storage modulus shows the viscoelastic behavior of a weak network in the frequency range of 0.1–1 Hz with that of Ch/PEG polymer chain dominated by entanglements of a greater lifetime than 1 Hz. It suggests that with more linear glucose addition, the existence of a chemical crosslinked network formed by Ch chains restricts the mobility. As the glucose concentration increases to 10 wt %, the storage modulus shows a small change in frequency dependence with respect to an ideal crosslinked polymer and stays at a higher value. According to Arguelles-Monal et al.,<sup>11</sup> for the Ch/glutaraldehyde chemical gel system with a higher crosslinking density, the storage modulus of polymer shows almost independence on frequency, implying the mediating effect by glucose addition.

The frequency dependence of 3 wt % glucose-mediated Ch/PEG membrane at 37°C is shown in Figure 11. At low-frequency scan ( $\omega = 0.1$ ), the initial complex viscosity is about 1000 MPa s for all of the samples. With the frequency increasing, the complex viscosity of all samples decreases in a linear decay from 1000 to 1 MPa s, which is a characteristic of pseudoplastic behavior. The weak film behavior of the Ch and Ch/PEG may be due to a weak network-forming as-

sociation.<sup>23</sup> The surface-mediated membrane possesses a higher complex viscosity than the Ch/PEG membrane, especially at a high frequency. The high-frequency dependence of the sample coincides with the results in increasing temperature mode. According to fundamental rule of polymer behavior,<sup>24</sup> with the frequency scan in isothermal state, the high-frequency or short-time dynamic mechanical property of the sample can be superior at low temperature. Therefore, the Ch/PEG polyblend prepared by surface-mediated membrane possesses a good mechanical property for biomedical applications.

### CONCLUSION

pH-dependent Ch/PEG membranes were prepared by a surface-mediating process with glucose as a source. The glucose-mediated membrane is more stable at pH 7.4 than at pH 1.2 medium, and the stability at all pH values generally increases with increasing glucose concentration due to an increase in mediating and thus fewer number of NH<sub>2</sub> groups of Ch remained available for protonation and subsequent dissolution at pH 1.2.

Mediating degree measurement shows that in the surface-mediating mode, with increasing the glucose concentration, the mediating degree increased, which demonstrates that the Schiff's reaction occurs. Otherwise, the basic mediated membrane has a higher mediating degree, indicating that for the membrane prepared in more basic mediating solution, the Schiff's reaction is more distinct. As the glucose concentration increases, the glass transition region becomes broadened and the rubber plateau of the material prolongs and keeps at a higher storage modulus with the increasing temperature; also, the tangent  $\delta$  peak amplitude decreases and the position shifts to a high temperature, demonstrating that the mediating density of glucose-mediated membrane increases as the glucose concentration increases.

In an isothermal DMA study of membrane, as the glucose concentration increases to 10 wt %, the storage modulus shows a small change in frequency dependence with respect to an ideal crosslinked polymer and stays at a higher value, implying the mediating effect by glucose addition. The frequency dependence of 3 wt % glucose-mediated Ch/PEG membrane at

37°C shows that the surface-mediated membrane possessed a higher complex viscosity than Ch/PEG membrane, especially at high frequency. The glucose can be used as a natural source to stabilize the Ch/PEG structure.

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