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Thermophysical properties of polycaprolactone/chitosan blend membranes

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ABSTRACT

Biodegradable polycaprolactone/chiotosan blends with various proportions were prepared using concentrated acetic acid solutions as solvents. The blends were further processed into thicker membranes using a newly developed processing technique. These membranes were then investigated for their miscibility of components via thermogravimetric examinations, differential scanning calorimetric measurements, and dynamic mechanical analysis as well infrared analysis. The presence of phase separation structures inside the membranes was confirmed although very limited interactions between components were detected. In addition, it was also found that the composition ratio of the membranes did not substantially affect the interactions between the components inside the membranes.

1. Introduction

Polycaprolactone (PCL), a semi-crystalline and resorbable aliphatic polyester, has found various biomedical applications such as sutures, drug delivery systems and scaffolds in tissue engineering, due to its soft- and hard-tissue compatible properties and biodegradation characteristic [1]. Although PCL has been widely used in tissue engineering its applications are frequently limited by several its drawbacks [2–4]: (1) absence of cell recognition sites on the surface of the scaffolds; (2) hydrophobicity; (3) neutral charge distribution; (4) slow rate of degradation, and (5) acidic degradation products. In addition, like other synthetic biodegradable polyesters, PCL is costly, and therefore its applications are restricted to some extent. Numerous efforts have been focused on overcoming these drawbacks. One of common strategies is to blend PCL with other natural biopolymers, including starch [5], zein [6], cellulose [7], and chitosan [8].

Chitosan is a linear biopolymer and has been of enormous interest because of many advantages [9], including biocompatibility, biodegradability, hydrophilicity, non-toxicity, nonantigenicity, and anti-microbial activity as well as bioadherence and cell affinity. In addition, the amino groups in its backbone also make chitosan a basic characteristic. However, mechanically inferior feature of chitosan in the wet state has limited its usage. On the basis of above-mentioned characteristics, it can be seen that chitosan and PCL have mutually complementary potentials. Therefore, it is reasonable to expect that their individual deficiencies would be overcome if PCL and chitosan could be well blended together. However, some difficulties have been frequently encountered about blending PCL with chitosan due to two main troubles: (1) melting processing techniques cannot be applied since chitosan has a high glass transition temperature and will start to decompose before melting [10]; and (2) there are very few shared solvents available for chitosan and PCL. Nevertheless, several efforts have been dedicated to blending these two polymers together [8,11–14]. Sarasam et al. had prepared PCL/chitosan membranes using a 77% acetic acid solution as the solvent and they stated that the membranes were miscible based on a simplified Nishi–Wang equation using melting-point temperature as an examined variable [8]. But in another report, they pointed out that chitosan and PCL coexisted as separate phases in the blend membranes even though the same solvent and processing technique were applied [11]. Liu et al. investigated porous chitosan/PCL blend membranes following Sarasam et al.'s method, and their results supported the miscibility between chitosan and PCL components [13]. Very recently, Cruz et al. worked over chitosan/PCL blend membranes again with a method very similar to that initiated by Sarasam et al., and they demonstrated that PCL and chitosan formed phase-separated blends [14]. On the basis of these statements, it can be noticed that some confused results for PCL/chitosan blends have appeared in different reports.

In principle, glass transition temperature (T_g) is a common criterion frequently used to assess whether two polymer components are miscible in the amorphous phase of a blend. However, previous reports have not evaluated the PCL/chitosan blends over an enough broad temperature range in which the T_g of each component can

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be assessed completely. To reach a better understanding for these blends, in the present work, chitosan/PCL blend membranes were prepared using similar solvents suggested by Sarasam et al., but with a newly developed processing technique. These membranes were further examined in detail over a temperature range whose upper limit was higher than 200 °C for the T_g assessments to figure out whether the components inside the blend membranes are miscible or not.

2. Experimental

2.1. Materials

Chitosan and PCL (CAPA 6800) were supplied by Fluka and Solvay Chemicals, respectively. The degree of deacetylation and viscosity average molecular weight of chitosan were measured as 82.8 (±2.39)% and 3.72 (±0.17) × 10^5 respectively, following our previous method [15]. All other chemicals were obtained from Aldrich and used without further purification.

2.2. Preparation of chitosan/PCL blend membranes

Blend membranes were prepared using a similar solvent suggested by Sarasam et al. [11]. Typically, PCL was dissolved in the glacial acetic acid to produce some solutions with various concentrations changing from 2.0 to 10.0 wt%. Chitosan was dissolved in a 70% acetic acid solution to prepare 0.5–1.5 wt% solutions. Two types of solutions were mixed together at different weight ratios but the final concentration of the solvent in the mixtures was adjusted to around 80%. The mixtures were then concentrated in different beakers heated at around 55 °C with stirring until they became very concentrated gels. Each resultant gel-like mixture was cast into a membrane onto a Teflon dish and the dish was moved into a chamber equipped with some small windows on its wall. All membranes were allowed to be slowly dried by regulating the doors of the windows to control the evaporating rate of the solvent. Thus obtained uniform membranes had average thicknesses of around 0.8–1.0 mm. A series of PCL/chitosan blend membranes was prepared with weight ratios at 60/40, 40/60 and 20/80 (referred to as PCL/ch40, PCL/ch60 and PCL/ch80, respectively). Some pure PCL or chitosan membranes were also produced using the same technique and they were used as controls.

2.3. Characterization

The infrared (IR) spectra of membrane samples were recorded on a Nicolet 510P FTIR spectrometer with a resolution of 2 cm^{-1}, 64 scans, in a transmission mode, and the sample chamber was purged with dry nitrogen gas. The average thickness of the membrane samples was around 30 μm.

Thermogravimetric (TG) analysis was performed on TGA 2050 (TA Instruments). Each membrane sample (ca. 10 mg) was run from 30 to 500 °C at a scanning rate of 10 °C/min under a nitrogen atmosphere.

Differential scanning calorimetric (DSC) measurements were carried out on DSC 2010 (TA Instruments). The samples were heated in different temperature ranges depending on the composition of the membranes. The DSC curves were recorded under a nitrogen atmosphere by setting a heating rate at 10 °C/min.

Dynamic mechanical analysis (DMA) was conducted to observe T_g of the blend membranes. The storage modulus (E'), loss modulus (E''), and mechanical damping tangent ($\tan\delta$) of the blend membranes were recorded on a dynamic mechanical analyzer (DMA 2980, TA Instruments) from −80 to 200 °C at a frequency of 1 Hz and a heating rate of 3 °C/min under an atmosphere of 150 mL/min nitrogen.

The equilibrium water content of membranes was estimated by measuring the swelling index (SI) of samples. The dried membrane (mass = W_d) was immersed in an excess amount of deionized water at ambient temperature until swelling equilibrium was attained. The mass of wet membrane (W_w) was measured after removing the surface water with blotting paper. SI was then calculated on the basis of following formula:

$$\mathrm{SI} = \left[\frac{(W_w - W_d)}{W_d}\right] \times 100\% \quad (1)$$

3. Results and discussion

3.1. Processing condition

0.5–1.5 wt% chitosan solutions can be easily prepared by using some acetic acid solutions with various concentrations changing from 70 to 80.0%, and thus-produced chitosan solutions can be possibly well blended with designated PCL solutions. However, in all cases, a care needs to be taken for the weight ratios of components and the final concentration of the solvent in the mixtures. It was found that the concentration of the solvent should be adjusted to around 80% because otherwise chitosan or PCL components would likely be precipitated out from the mixtures during the blending procedure if the concentration of the solvent is significantly higher or lower than this value. The post-processing steps for preparing concentrated gel-like mixtures and the followed dry procedure also played an important role for producing uniform and thicker membranes. Based on many trials, it was attained that a membrane with a less (for example, <700 μm) thickness would not have enough strength for followed DMA measurements over a wider temperature span (for instance, −80 to 200 °C) if the PCL weight ratio in the membrane was significant higher than that of chitosan. On the other hand, increasing difficulties would be encountered if a very thick (for example, >1.0 mm) membrane was prepared because such a membrane was usually deformed into a tortuous shape with a crinkly surface during the drying procedure. The thickness of the membranes was therefore controlled around 0.8–1.0 mm. In addition, as described in the experimental section, although PCL/ch20 membranes could also be produced using present processing technique they had not been selected for investigations since they were not able to sustain a temperature higher than 70 °C during the DMA measurements due to the high weigh ratio of PCL component even though they had an enough thickness.

3.2. IR analysis

Fig. 1 presents IR spectra of PCL, chitosan, and blend membranes, respectively. Several characteristic bands located at 2942, 1725, 1245 and 1176 cm^{-1} are belonged to ester groups of PCL [16]. Two typical bands at 1662 (amide I: *N*-acylamide) and 1591 (amide II: amino groups) cm^{-1} for chitosan are recorded, respectively [15]. It can be observed in Fig. 1 that several clear changes occur in the spectra of the blend membranes: (1) a strong absorption band near 1725 cm^{-1} appears in the IR spectra of all blend membranes but its intensity varies, depending on the proportion of PCL component; and (2) this band should correspond to the characteristic peak of PCL originally situated at 1725 cm^{-1} but a measurable shift to relatively lower wave-numbers is registered. To more clearly observe the shifts of the bands, the same spectra shown in Fig. 1 are enlarged within a selected frequency range and represented in Fig. 2. It can be seen that the two original bands of the chitosan component at 1662 and 1591 cm^{-1} for amide I and amide II are shifted to around 1650 and 1580 cm^{-1}, respectively, except for the peak shifts of PCL originally located at 1725 and 1176 cm^{-1}. All these registered events indicate that there are possible some interactions among the

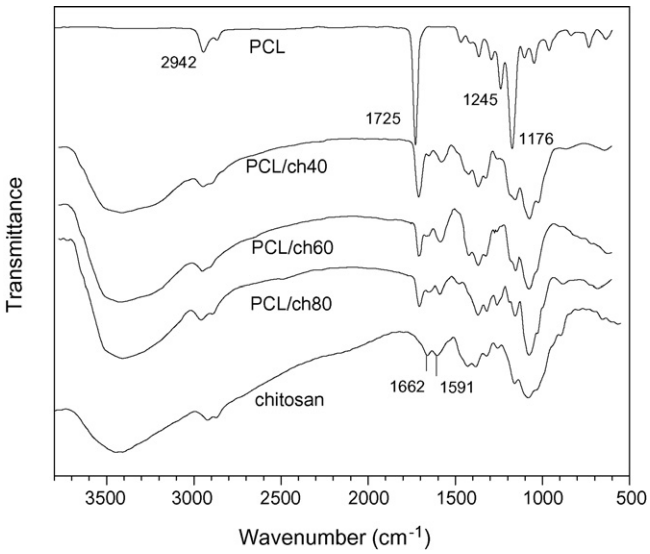

Fig. 1. FTIR spectra of PCL, chitosan, and PCL/chitosan blend membranes.

amino, carboxyl, and hydroxyl groups of two components inside the blend membrane. These interactions should be attributed to the hydrogen bonds possibly formed between amino (in chitosan) and carboxyl groups (in PCL) or hydroxyl (mainly in chitosan) and carboxyl groups, because there are no formations of new covalent bonds observed between PCL and chitosan chains based on these IR spectra.

3.3. TG analysis

Fig. 3 exhibits TG thermograms of PCL, chitosan and PCL/chitosan membranes. It can be observed that the PCL membrane discomposed completely in a single stage, pronouncedly beginning at about 379 °C. A two-stage weight loss was recorded for the chitosan membrane. The initial weight loss before ca. 109 °C should be ascribed to the moisture vaporization inside membrane, and the second stage started around 283 °C is the main thermal degradation zone corresponded to a complex process including the dehydration of the saccharide rings and followed decomposition of chitosan backbone. All blend membranes showed a three-stage degradation behavior. The first stage, before 205 °C, should be associated with

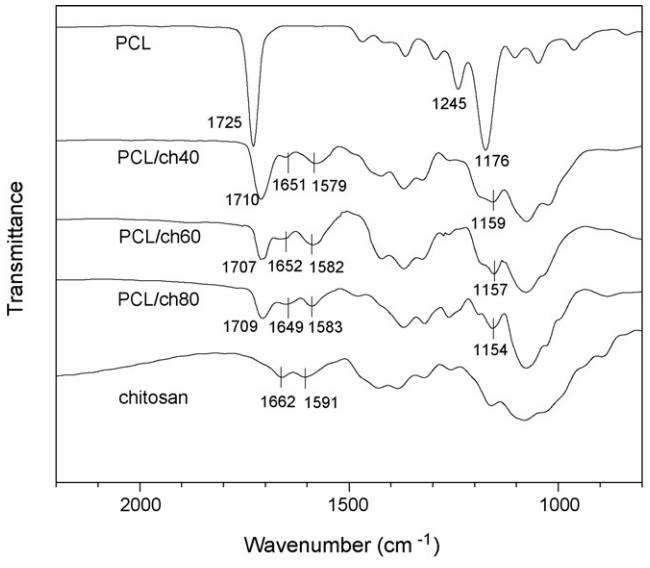

Fig. 2. FTIR spectra of different membranes in the selected frequency range.

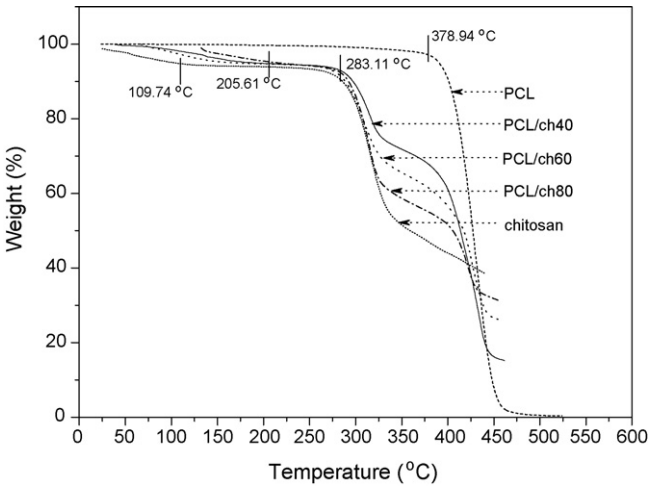

Fig. 3. TGA curves of PCL, chitosan and PCL/chitosan membranes.

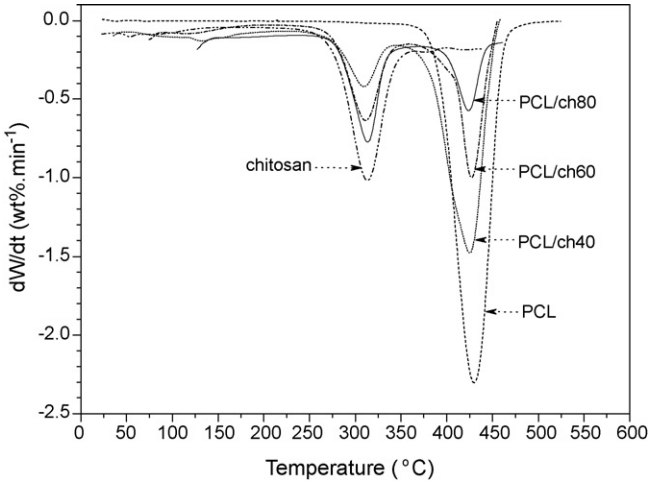

Fig. 4. The derivative curves of weigh loss percent for different samples. (□) CPC-I; (◊) PCL/ch40; (▽) PCL/ch60; (○) PCL/ch80; and (△) chitosan.

the loss of bound-water in chitosan component [17] and the elimination of the possible trace amount of acetic acid left inside the membranes. The second and the third stages reflect the typical thermal degradation characteristics of chitosan and PCL components, respectively.

To more quantificationally examine these plots, the weight-loss percent of all samples were differentiated and the derivative data are depicted in Fig. 4. Each temperature value at peaks in Fig. 4 is marked as T_{max} which corresponds to the maximum degradation rate. All blend membranes exhibit two peaks of fast thermal degradation, typically for both components. To make further comparisons among the blend membranes and controls, the peaks at a lower or higher temperature are designated as T_{max1} and T_{max2}, respectively, and the collected data are summarized in Table 1. It is clear

Table 1
Temperature at maximum degradation rate[a].

Samples	T_{max1} (°C)	T_{max2} (°C)
PCL		427.6(±0.85)
PCL/ch40	311.1(±0.88)	424.3(±0.77)
PCL/ch60	310.4(±0.79)	425.1(±0.68)
PCL/ch80	313.6(±0.81)	424.7(±0.92)
Chitosan	312.3(±0.95)	

[a] The values in table are the average values from four specimens for each sample.

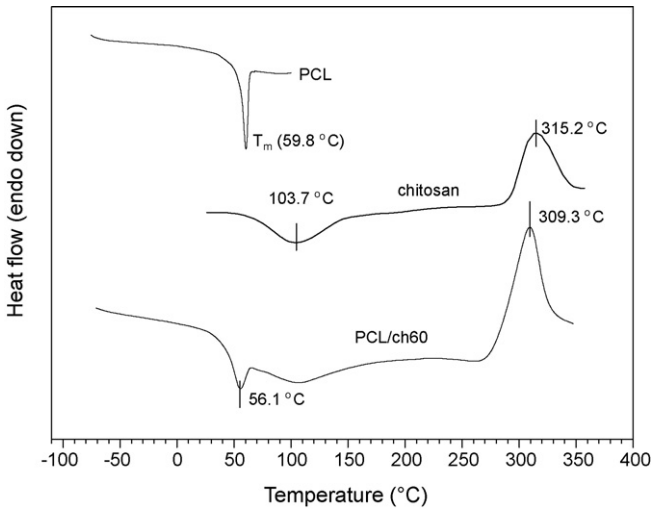

Fig. 5. DSC traces of PCL, chitosan, and PCL/ch60 membranes.

that there are no substantial differences existed among these data. In general, in a binary blend system, an improved thermal stability would be achieved for the component with a lower T_{max} if the measured T_{max} shifts to the higher T_{max} of another component due to the various interactions between two components [18]. In the present case, no evidences show that the measured T_{max} of chitosan component significantly moved towards to the T_{max} of PCL component, and the thermograms for all blend membranes do not exhibit notable changes in the degradation mechanism compared to the controls, suggesting that incorporation of PCL component does not significantly enhance the thermal stability of blend membranes, and also implying that there are no enough strong interactions between chitosan and PCL components. As defined in Fig. 4, T_{max} corresponds to the maximum degradation rate and reflects the thermal behaviors of each component during the decomposition. Accordingly, it can be extrapolated that any previously existed interactions between chitosan and PCL chains would be destroyed at such a high temperature even though those interactions do occur before. Based on above results, it can be deduced that in the present case, TG analysis is not an impactful technique to figure out whether chitosan and PCL components are miscible or not. It is generally accepted that the miscibility between molecules in a polymer blend can be effectively evaluated by T_g of components [10] and therefore, the T_gs of two components are selected for further examinations.

3.4. DSC analysis

In principle, if two components are well blended together and completely miscible each other, only one new T_g would be observed between the original T_gs of components in the DSC thermogram of the blend; if they are partially miscible, the resulting blends would have two T_gs related to the each component, but these measured T_g values corresponding to each component could be affected each other, depending on the composition ratios [19]. Fig. 5 presents several DSC thermograms for PCL, chitosan, and PCL/chitosan blend membranes. The melting point (T_m) of PCL can be easily read at around 60 °C. With respect to the DSC curve of chitosan, a wide endothermic peak centered around 104 °C over a large temperature interval can be attributed to the absorbed moisture, and an exothermic peak near 312 °C is possibly linked to decomposition procedure of chitosan, which starts at about 280 °C and is basically in agreement with the result obtained from TG analysis (see Fig. 3).

PCL and chitosan membranes did not show any features in their DSC curves with which their T_gs can be associated. Chitosan is a semi-crystalline polymer due to its strong inter- and intra-molecular hydrogen bonds, and meanwhile, it also has a rigid amorphous phase because of its heterocyclic units. As a result, when chitosan is heated within a certain temperature range below its decomposition temperature, the variations in heat capacity related to the change in specific volume near T_g are probably too small to be detected by the DSC technique [20]. It is known that the T_g of PCL is around −60 °C [21]. However, there is no any thermal event registered for the T_g of PCL in Fig. 5 although PCL membranes were scanned starting from −80 °C, revealing present DSC measurements are not sensitive enough for testing the T_g of PCL. The DSC thermogram of PCL/ch60 in Fig. 5 almost repeats similar thermal behaviors of PCL and chitosan components without any traces that can be used to locate a new T_g. Nevertheless, two clear differences are noticed: (1) the T_m of PCL component is moved to a lower value with a difference more than 3 °C; and (2) an around 6 °C decrease in the decomposition temperature (T_d) of chitosan component is registered. To figure out the effect of composition ratios on T_m or T_d, all blend membranes were examined and the collected data are summarized in Table 2. It is observed that the T_m of PCL component decreases as the weight ratio of chitosan increases; and the T_d of chitosan component increases with decreasing proportion of PCL component. These trends are basically in agreement with reported results [8,13]. Since it could be very difficult to obtain necessary T_g values through regular DSC measurements in the present cases, a more sensitive method, dynamic mechanical analysis, is therefore employed to further determine the T_g of the components in the blend membranes.

3.5. DMA analysis

DMA is a very effective technique for investigating relaxation processes in relation to the internal molecular motions associated with the possible structure changes occurred in a polymer. Fig. 6 displays the storage modulus (E') as a function of temperature for PCL, chitosan, PCL/ch40, and PCL/ch60 membranes, and Fig. 7 illustrates the temperature dependence of damping tangent ($\tan\delta$). The storage modulus shows significant changes in the overall temperature region. Chitosan membrane exhibits a higher strength and a much better elastic property compared to PCL membranes. As expected, the magnitude and varied trend of the storage modulus of PCL/ch40, and PCL/ch60 membranes are in between and significantly alter, depending on the weight ratio of PCL component. However, these plots have not shown diagnostic temperatures typically related to distinguishable thermal relaxation processes inside the membranes.

Table 2
Temperature parameter of components in blend membranes[a].

Sample	T_m (°C)	T_d (°C)	T_g of PCL (°C)	T_g of chitosan (°C)	ΔT[b]
PCL	59.82 ± 0.07		−51.4 ± 0.73		
PCL/ch40	57.5 ± 0.14	302.7 ± 0.89	−33.6 ± 1.39	152.3 ± 1.27	186.1
PCL/ch60	56.2 ± 0.13	308.4 ± 0.93	−28.4 ± 1.34	158.8 ± 1.45	185.7
PCL/ch80	54.1 ± 0.16	312.5 ± 1.14	−25.2 ± 1.62	167.3 ± 1.52	193.2
chitosan		316.1 ± 1.02		177.5 ± 1.96	

[a] The values in the table are the average values with standard deviation and collected from five specimens for each sample.
[b] $\Delta T = T_g$ (chitosan) − T_g (PCL), only average values without standard deviation are listed.

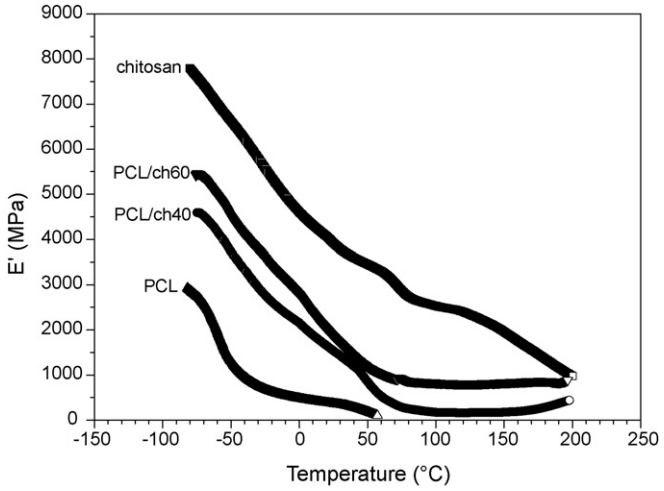

Fig. 6. Temperature dependence of storage modulus (E').

In principle, both loss modulus (E'') and tan δ can be used to measure the characteristic temperatures matched with various relaxation processes, even though a very small quantitative difference may be frequently found between the temperature values determined by E'' or tan δ [22–24]. In the present case, characteristic temperatures recorded in the plots of tan δ were selected for further investigations. In Fig. 7, the spectrum of tan δ for PCL membrane shows one relaxation peak at around −50 °C, which should correspond to an increase in the free volume of the sample with temperature and is possibly ascribed to its T_g; another temperature at about 58 °C is attributed to the T_m of PCL since the PCL membranes were already yielded at this temperature during the DMA measurements; and in addition, two peaks are registered at around 102 and 174 °C for the chitosan membrane. Several reports have suggested that the T_g of chitosan is higher than 170 °C [10,25,26] and hence, the peak at about 174 °C for the chitosan membrane should be ascribed to the α-relaxation of chitosan chains, corresponding to its T_g, and another tan δ maximum at 102 °C (β-relaxation) may be caused by partial acetamide groups attached to the C-2 position in the chitosan backbone [27].

In the case of the PCL/ch60 membrane, its DMA plot displays four detectable relaxation peaks recorded at about −27, 49, 92, and 153 °C, respectively. In comparison with the original DMA spectra of individual components, it is reasonable to believe that the peaks at −27 °C should be ascribed to the T_g of the PCL component, which is around 23 °C higher than its original T_g, and a peak at 153 °C most probably matches with the T_g of the chitosan component, which has been shifted towards a lower temperature with a difference of ca. 21 °C compared to its original T_g at 174 °C. The peak at 92 °C can be assigned to relaxation of the acetamide groups in chitosan component with an around 10 °C shift and the peak at 49 °C indicates a ca. 8 °C decrease in the T_m of PCL component. Two T_gs for this blend membrane were detected, and the difference between them is quite large (∼180 °C), suggesting the significant phase separation of two components in the membrane although this membrane did not exhibit any visible phase separation during the preparation procedure. In addition, these two T_gs reveal another fact that the tan δ spectrum of the PCL/ch60 membrane is not a simple superposition of those of the pure components.

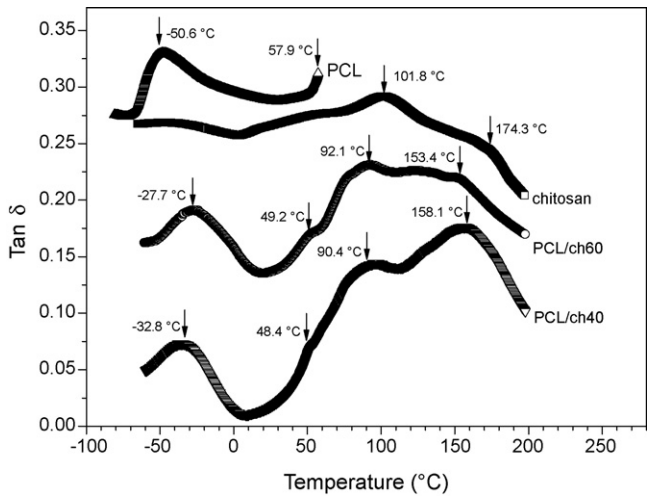

Fig. 7. Temperature dependence of tan δ.

In general, it is known that interactions between polymer chains, such as ionic interaction, hydrogen bond, and crosslinking, can cumulatively contribute to shift the T_g of a polymer. It has been reported that, in the case of two-component polymer blends, provided that the two components are not completely miscible but one component is capable of interacting with the other one, the T_gs of the components would shift to the inside of their respective original T_gs [28,29]. The fact that the two T_gs of PCL and chitosan shift to the inside, in spite of the small amounts of shifts compared to the original values, suggests that there possibly exist very limited interactions between PCL and chitosan components, probably resulting from hydrogen bonds formed between chitosan and PCL components, as revealed previously in IR analysis. A similar behavior was also observed in the case of PCL/ch40 blend membrane. The original T_g of the PCL component at ca. −50 °C has been shifted to a higher temperature at about −32 °C, and the original T_g of the chitosan component at 174 °C has been relocated at 158 °C. The presence of significant phase separation and quite limited interactions inside the blend membrane is confirmed again.

All blend membranes were measured using the DMA technique. The data focused on the T_g of each component in the blend membranes are collected in Table 2. It is seen that for each blend membrane two T_gs are recorded, and the difference between the two T_gs is very large and does not significantly alter with the composition proportions of the membranes. Hence, it can be concluded that the composition ratio of the membrane does not substantially enhance the interactions between the components inside the membranes.

To investigate the property of membranes in the wet state, their SI was measured and the collected data are depicted in Fig. 8. It

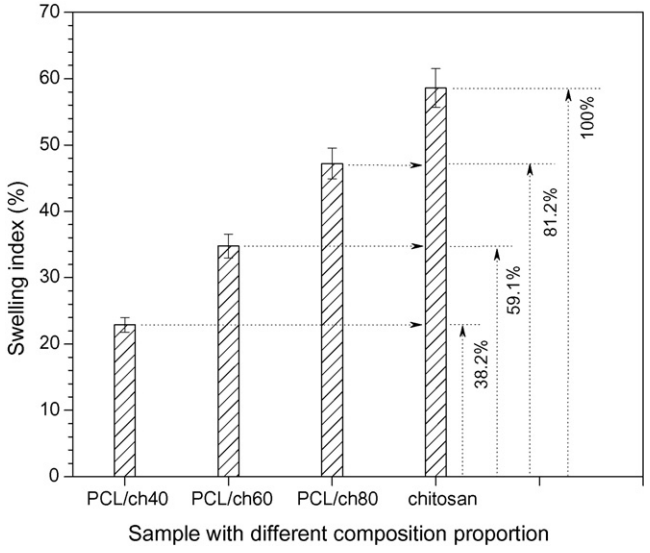

Fig. 8. The variance of SI of membranes with composition proportion of membranes (SI of pure PCL membranes is negligible).

is observed that by incorporating increasing amounts of chitosan component the SI of the blend membranes significantly increases. By rescaling SI of the chitosan membrane as 100%, SI of the blend membranes was calculated as a percentage based on the SI of chitosan membrane and the obtained data are also presented in Fig. 8. It can be noted that changes in percentages of SI of the blend membranes are basically in agreement with the weight ratio of chitosan in the blend membranes, suggesting that the equilibrium water content of blend membranes are not affected by PCL component and completely dependent on hydrophilic chitosan component. These results could further imply that two components inside the blend membranes immiscibly coexist together otherwise their SI would not quantitatively alter with the weight ratio of chitosan component.

In considering all obtained results together, it can be drawn that PCL and chitosan components inside the blend membranes are immiscible although very limited interactions between them are observed.

4. Conclusions

Many uniform and thicker polycaprolactone/chiotosan blend membranes were successfully prepared using a ca. 80% acetic acid solution as the solvent and employing a newly developed processing technique. This new processing technique made it possible to systemically investigate the thermophysical properties of the resultant membranes over a broad temperature range with an upper limit higher than 200 °C via conventional thermal analysis techniques. It was found that only very limited interactions existed between the components, and polycaprolactone and chiotosan components were basically coexisted inside the blend membranes with immiscible characteristics.

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