

# Glass transition temperature of chitosan and miscibility of chitosan/poly(*N*-vinyl pyrrolidone) blends

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## Abstract

There are a few communications concerning the relaxation temperature corresponding to the glass transition temperature of chitosan. We succeeded in observing the  $T_g$  of chitosan (to be ca. 203°C) by the direct and careful measurement of differential scanning calorimetry (DSC), which had been assumed not to be sensitive enough to detect it. In addition to this observation, the dynamic mechanical analysis (DMA) measurement in the second heating run showed the  $\alpha$ -relaxation at the same temperature as the glass transition temperature observed in DSC. The peak in the  $\tan \delta$  curve appeared at about 150°C in the first heating run as if it were the  $\alpha$ -relaxation and might be due to the secondary molecular motion when the chitosan molecules were in the pseudo-stable state.

Chitosan was blended with poly(*N*-vinyl pyrrolidone) in acetic acid solution and this solution was cast to prepare the blend film. The miscibility and the phase structure in the binary blend films were studied using DSC measurements and the wide-angle X-ray diffraction (WAXD) method. The glass transition temperature of the binary blend films decreased with increase of PVP content and the relation obeyed Fox's theory. This implies that the blend system of chitosan and PVP is able to form a miscible phase. It was supported by WAXD observations of the binary blend films. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Chitosan; Glass transition temperature; Miscibility of blends

## 1. Introduction

Nowadays, earth-environmental pollution or disruption is becoming a serious problem in the world. Needless to say, the polymer industry has numerous problems regarding recycling or disposal of polymeric wastes at present. Therefore, material developments without an accompanying disruption of the earth-environment are getting much more important even in the polymer industry. Among them, the natural polymers have undergone a reevaluation regarding their ability to biodegrade. Chitosan is a deacetylated product of chitin, which is obtained from the cuticle of the marine crustaceans such as crabs and shrimps, and it is also classified as a natural polymer because of the presence of a degradable enzyme, chitosanase. Both chitin and chitosan have been widely investigated for the last two decades on their industrial and biomedical applications [1–3]. In addition, chitosan is expected to be useful in the development of composite materials such as blends or alloys with other polymers, since chitosan has many functional properties

[4]. When chitosan is blended with a polymer, the miscibility between their molecules is a very significant factor especially for a mechanical property of the blend. In order to estimate the miscibility, we can utilize the variation of the glass transition temperature,  $T_g$ , of the blends against the blend ratio. For this reason, the glass transition temperature of pure chitosan must be known. However, there are only a few communications about the relaxation temperatures corresponding to the glass transition temperature of chitosan based on dynamic mechanical analysis [5,6]; the glass transition temperature of chitosan has not been definitely determined yet.

In this study, first the glass transition temperature of chitosan was determined and then the miscibility at molecular level of the composite of chitosan blended with poly(*N*-vinyl pyrrolidone) (PVP) is discussed, by analyzing the change of the glass transition temperatures of blends as a function of the blend ratio.

## 2. Experimental

### 2.1. Samples

Chitosan was kindly supplied by Katakura Chikkarin Ltd

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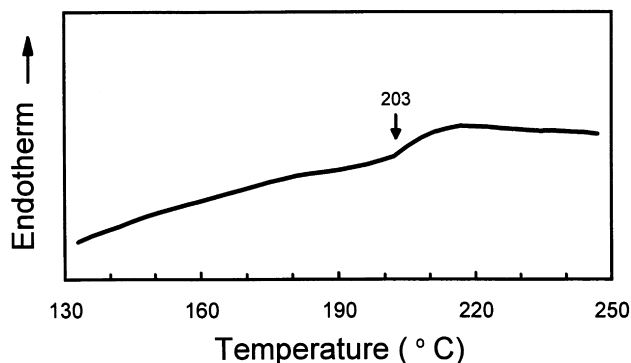


Fig. 1. DSC thermogram of chitosan in the second heating run.

Co., Tokyo, having a degree of deacetylation of 96%. Poly(*N*-vinyl pyrrolidone) of extra pure grade with  $M = 90,000$  was purchased from Nacalai Tesque Inc., Kyoto. Other chemical reagents used were of guaranteed pure grade and used without purification.

### 2.2. Film preparation

Chitosan was dissolved in a 2.0 wt% aqueous acetic acid solution at a concentration of 1.5 wt%. The 1.5 wt% chitosan solution was cast in a plastic dish at 60°C for 5 h. Then the cast film, which still contained a small quantity of the solvent, was lyophilized, rinsed with diethyl ether and dried under reduced pressure at room temperature for 24 h to eliminate the solvent thoroughly and obtain the chitosan film. PVP was dissolved in the same solvent at the same concentration as chitosan. A series of chitosan/PVP blended solutions with different weight ratios was prepared from different amounts of the 1.5 wt% chitosan and 1.5 wt% PVP solutions. Each blend film was made from the blended solution in the same way as the chitosan film. All the prepared films were kept under the dry condition.

### 2.3. Measurements

Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer DSC7. DSC curves of each film were obtained from the second heating run at a rate of 10 K/min, after the first run of heating up to 190°C and cooling to 25°C at the same rate of 10 K/min, under nitrogen atmosphere, in order to estimate the glass transition temperature. The details about the method of determination of glass transition temperature from a DSC curve are, for example, provided in our earlier paper [7] or in Ref. [8]. The weight of each sample film was about 5 mg. Dynamic mechanical analysis (DMA) measurements were carried out on a chitosan sample with a Rheometric Science RSA II at 1 Hz and a heating rate of 2 K/min under nitrogen atmosphere, in order to characterize the dynamic mechanical spectra, mechanical damping  $\tan \delta$ , storage modulus  $E'$  and loss modulus  $E''$ . In this measurement, the dynamic mechanical spectra were observed in two cycles of heating:

the first heating up to 180°C and the second heating up to 250°C after holding at 180°C for 5 min and then the first cooling to 30°C at a cooling rate of 2 K/min. The samples were 22.4 mm long between clips, 5.0 mm wide, and about 0.1 mm thick. Wide-angle X-ray diffraction (WAXD) photographs of samples were obtained with a Rigaku D-IA, using nickel-filtered  $\text{CuK}\alpha$  radiation (40 kV, 20 mA).

## 3. Results and discussion

It is well known that the miscibility [9] of the molecules in a blend of polymers can be judged by the morphological methods and/or the properties of the solid state such as the glass transition temperature, the mechanical relaxation and so on. Glass transition temperature can be measured by various methods [10] such as dilatometry, DSC or DTA, spectroscopy, diffraction, rheological, dielectric methods. Among them, the DSC method is one of the convenient ones. A baseline step in a DSC curve appears due to the different heat capacity below and above the glass transition temperature of a polymer [11]. Many investigators have used the DSC method for its convenience and we have also utilized it to determine the glass transition temperatures of some synthetic polymers [7,12]. Generally, the glass transition temperature is read at the initial change in the slope of the heat capacity of the DSC thermogram, i.e. the temperature at the onset of a baseline step in the DSC curve.

First, the DSC thermogram of chitosan was measured. Special care must be taken during DSC measurements since chitosan is apt to absorb moisture, which should strongly affect the DSC measurements, and moreover the thermal degradation of chitosan [13] begins at about 250°C. To eliminate the effect of moisture, two cycles of heating and cooling runs were adopted, considering the temperature region so as not to bring about the thermal degradation in the first heating run. The result in the second heating run is shown in Fig. 1. Here, the glass transition temperature could be estimated to be 203°C, though the baseline step was somewhat small. Chitosan is not a completely amorphous polymer but a partially crystalline polymer, as some diffraction rings due to the crystallites of chitosan can be seen in the WAXD pattern. In addition, the change of the heat capacity corresponding to that of the specific volume might be small at the glass transition temperature, because the chitosan molecules consist of the rigid 2-amino-2-deoxy-D-glucopyranose (or glucosamine residues). These are the reasons why the small baseline step was found in the DSC curve.

Fig. 2 shows the temperature dependence of the dynamic mechanical spectra on storage modulus,  $E'$ , loss modulus,  $E''$  and damping,  $\tan \delta$  of chitosan, obtained from the DMA measurement in the first and second heating, respectively. The large peak near 153°C can be seen in the  $\tan \delta$  curve in the first heating (Fig. 2a), which coincides with the results reported by Ogura et al. [6] and Pizzoli et al. [14], who

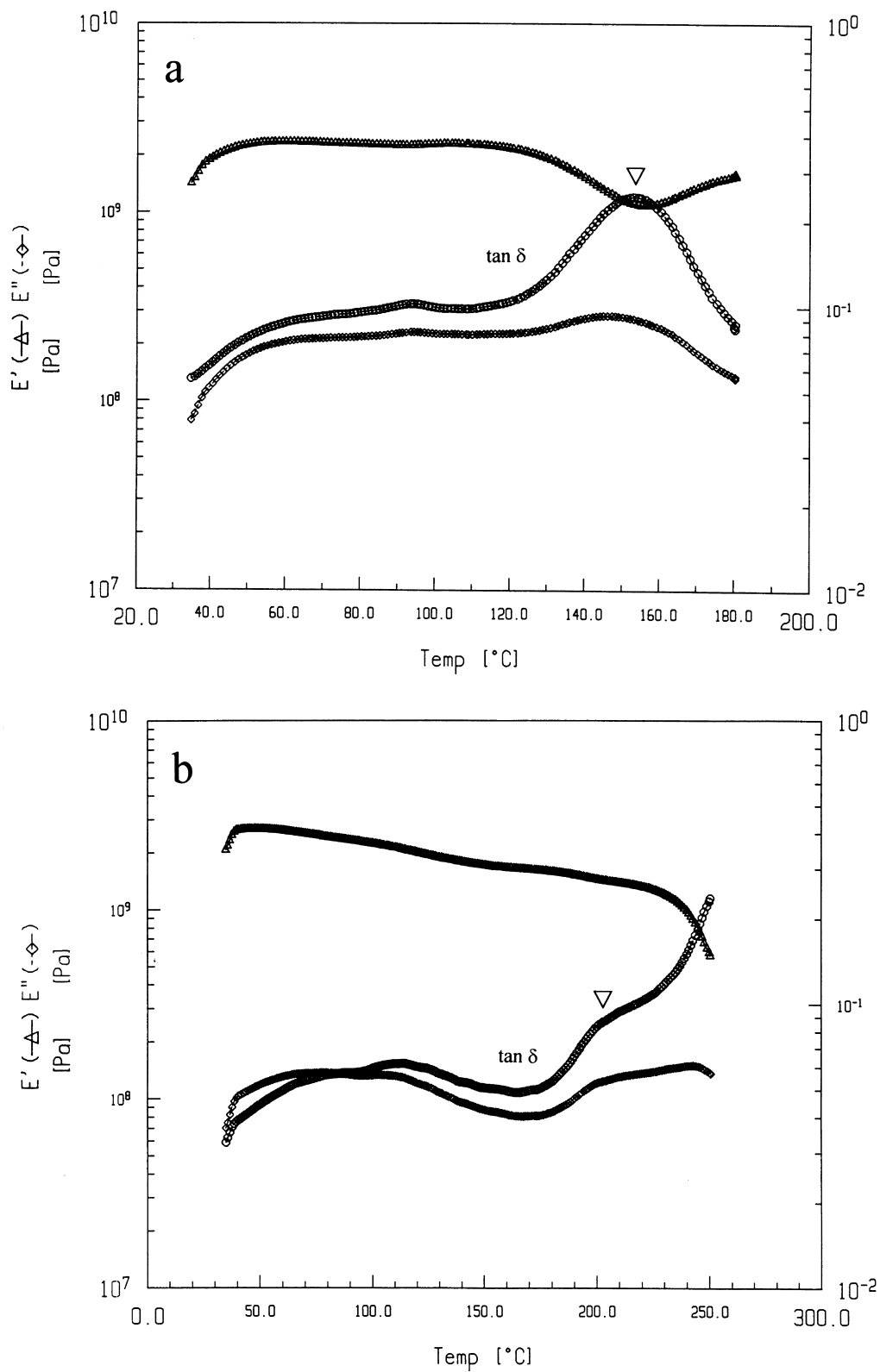


Fig. 2. Dynamic mechanical spectra of chitosan: (a) in the first heating up to 180°C; and (b) in the second heating up to 250°C after first cooling from 180 to 30°C.

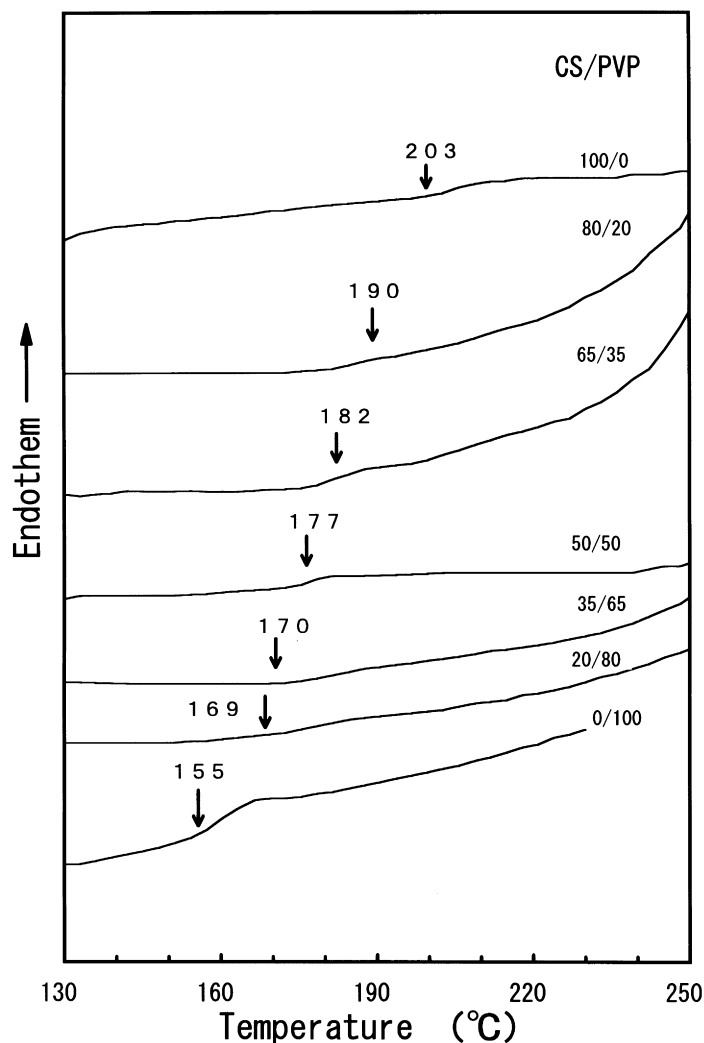


Fig. 3. DSC thermograms of chitosan/PVP blends in the second heating run. The arrow indicates the glass transition temperature.

measured the dynamic mechanical spectra of chitosan only in the first heating up to 180°C. However, it should be noted that the  $\tan \delta$  curve drastically changed in the second heating, which is shown in Fig. 2b; a large shoulder appears at about 205°C, while the peak near 153°C almost disappears. This must be the result for the annealed chitosan that underwent the heat treatment by holding at 180°C for 5 min. The relaxation temperature that appeared at 205°C for chitosan has not been reported so far. This temperature is in good agreement with the glass transition temperature estimated from the DSC measurement, mentioned above. Ogura et al. assigned the relaxation at 150°C in the first heating to be attributed to a glass transition but it does not seem correct, judging from these results. Pizzoli et al. suggested it to be a secondary relaxation and presumed that chitosan should have  $T_g$  close to that of dextran of 220°C. Recently, Miyashita et al. [15] suggested that  $T_g$  of chitin should be higher than 200°C, from the result of a series of DSC measurements in the chitin and PVP binary blend system. Kim et al. [16] estimated  $T_g$  of chitin to be 236°C from the

$\tan \delta$  curve based on DMA. When the molecular structures of chitin and chitosan are compared, chitin has many *N*-acetyl groups while chitosan used here has fewer *N*-acetyl groups because of its high degree of deacetylation (96%). It implies that chitosan is more flexible than chitin in the amorphous regions, leading to the assumption that chitosan is expected to have a lower  $T_g$  than chitin. Taking these considerations into account, it can be concluded that the relaxation at about 205°C should be assigned to the  $\alpha$ -relaxation, corresponding to the glass transition of pure chitosan. In the higher temperature region of the second heating,  $E'$  rapidly decreased at about 250°C, which corresponded to the beginning of the degradation.

In contrast, the  $\tan \delta$  peak at 153°C in the first heating accompanies the  $E''$  peak as well as a relatively large reduction in the storage modulus,  $E'$ . It seems as if it were an  $\alpha$ -relaxation, but our result showed that it was not correct. In fact, the chitosan annealed at 180°C for 1 h, which is not shown here, gave almost the same dynamic mechanical spectra as those observed in the second heating.

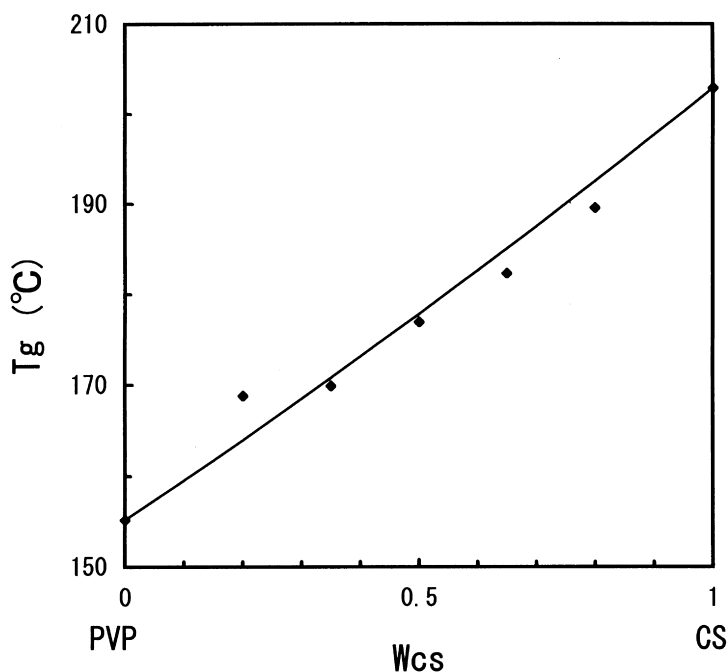


Fig. 4. Glass transition temperature of chitosan/PVP blends versus weight fraction of chitosan.

Therefore, the dispersion at 153°C in the first heating might be due to the local molecular motion in the pseudo-stable state. Alternatively, a plasticizing effect on the glass transition temperature may be considered; it is well known that the glass transition temperature decreases with increase of plasticizer, including water molecules in case of hydrophilic polymers [17,18]. However, this effect cannot be admitted in our case since the moisture content of chitosan used here was very low. Therefore, there is no other idea than the former presumption, i.e. the local mode of molecules in the pseudo-stable state.

Now let us consider the miscibility of chitosan and PVP. DSC thermograms were measured for a series of chitosan and PVP blend films with a different weight ratio. The glass transition temperatures of the blend films and the sole PVP film were determined on DSC curves in the second heating run as shown in Fig. 3. Since these films were heated up to 190°C and cooled down to 30°C in the first heating and

cooling cycle, they were subjected to the heat treatment in the first heating. The estimated  $T_g$  of the PVP film was 155°C, which was lower by about 20°C than the  $T_g$  of the original PVP specimen. The similar depression of  $T_g$  for PVP was found by Miyashita et al. [4]. As pointed out by them, it may be due to the reduction of the molecular weight of PVP when it was dissolved in the acetic acid solution. As for the  $T_g$  of the blend estimated from DSC curves shown in Fig. 3, it should be noted that there was the only one  $T_g$  in any blend film with a different composition ratio. Fig. 4 shows the relation between  $T_g$  and the weight fraction of chitosan, where the solid line gives the theoretical curve proposed by Fox [19], expressed by the following equation:

$$\frac{1}{T_g} = \frac{W_{CS}}{T_{g,CS}} + \frac{W_{PVP}}{T_{g,PVP}} \quad (1)$$

where  $W_{CS}$  and  $W_{PVP}$  are the weight fractions of chitosan and PVP, respectively; and  $T_{g,CS}$  and  $T_{g,PVP}$  are the glass transition

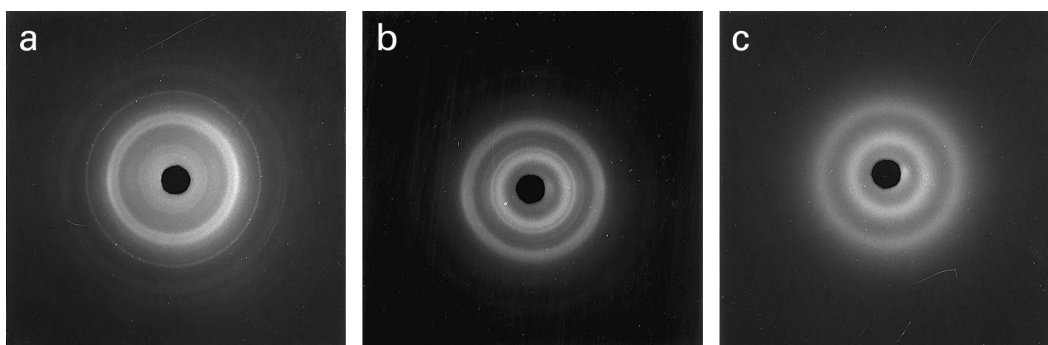


Fig. 5. WAXD photographs: (a) chitosan; (b) PVP; and (c) chitosan/PVP (50/50) blend.

temperatures of chitosan and PVP, respectively. The  $T_g$  of the blend increases with increase of chitosan content and their relation is well expressed by the theoretical curve. These facts imply that a miscible phase at a molecular level is formed in the chitosan and PVP blend system. This is supported by the results of WAXD. Fig. 5 shows the WAXD photographs of three samples of chitosan, PVP and the blend film with a weight ratio of 50:50. These three films were prepared under the same condition without further heat treatment.

It is known that the WAXD method is one of the morphological methods [9] which give us the information available to judge the miscibility of crystalline polymers. In general, if the micro phase separation occurs in the blend of crystalline polymers owing to the bad miscibility, the individual domain consisting of a separate polymer appears and the crystalline regions are to be formed in the domains. In the case of good miscibility, on the contrary, the molecular chains of both crystalline polymers are mixed so well that the domains of each component are scarcely formed. As a result, the molecular chains of each polymer cannot crystallize, since the molecular chains must be arranged regularly in the three-dimensional space in order to crystallize.

In the present study, both chitosan and PVP gave some crystalline diffraction rings on WAXD photographs shown in Fig. 5, though they were not strong or very sharp. This means that both polymers are crystalline and their own chain molecules partially crystallize to some extent in the individual chitosan or PVP film. In the blend film, such crystalline diffraction rings could no longer be seen but only the two diffused scatterings appeared: the outer scattering due to the halo and the inner diffused scattering probably due to the PVP crystallites with a large distortion. From these facts, it is suggested that chitosan and PVP are mixed well at a molecular level and consequently the molecules of the individual polymer cannot crystallize to result in an increase of the amorphous regions with mixed molecules. In other words, a miscible phase of the two polymers, which cannot crystallize, may be newly formed.

Finally, if attention is paid again to the relationship between the glass transition temperature of the blend and a weight fraction of chitosan, shown in Fig. 4, the  $T_g$  of 203°C determined for chitosan would be quite reasonable.

#### 4. Conclusion

The glass transition temperature,  $T_g$ , of chitosan, which had not been clear, was determined to be 203°C based on the careful DSC and DMA measurements.

The blend films were prepared from the chitosan and PVP solution, and the glass transition temperatures of the blends were estimated by DSC analyses. The  $T_g$  of the blend increased with increase of a weight fraction of chitosan and their relation satisfied the Fox equation, using the  $T_g$  of 203°C determined for chitosan. It implies that a miscible phase was newly formed in this blend system, which was also supported by the WAXD result. On the contrary, this relation itself confirms that the  $T_g$  of chitosan determined to be 203°C is reasonable.

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