Studies on Glass Transition Temperature of Chitosan with Four Techniques

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ABSTRACT: Studies on the glass transition temperature (T_g) of chitosan are difficult to pursue because of the difficulty in sample preparation and the hydroscopicity of samples. There are a few works concerning this principal relaxation of chitosan. Among them, several quite different values (150°C, 161°C, and 203°C) have been reported. In this paper, the T_g of chitosan (140 ~ 150°C) was determined by means of four techniques, namely, dynamic mechanical thermal analysis (DMTA), differential scanning calorimetry (DSC), thermally simulated current spectroscopy (TSC), and dilatometry (DIL).

DSC measurement has been assumed not to be sensitive enough to detect the relaxation temperature of polysaccharides. We propose a new method to improve the sensitivity of the DSC measurement. After a physical aging treatment of samples, the transition in DSC traces became much more distinct because of the enthalpy relaxation. This technique was also used to distinguish the T_g from other relaxations.

The T_g of chitosan with different degree of deacetylation (D.D.) was examined by DSC. No influence of D.D. on T_g was found. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 1553–1558, 2004

Key words: chitosan; glass transition; ageing; DSC

INTRODUCTION

Chitin, which has a repeating structure unit of 2-acetamido-2-deoxy-β-D-glucose, is the most abundant naturally occurring amino polysaccharide and easily accessible from shells of arthropods such as crabs and shrimps.[1,2] Chitosan is the *N*-deacylated chitin. Since chitosan is soluble in acidic solvents, it can be applied more widely compared with chitin. Chitosan possesses unique functional and biomedical properties. Some of the well known applications of chitosan include its use for prevention of water pollution, medicine against hypertension, antimicrobial and hypocholesterolemic activity, flavor encapsulation, immobilization of whole cells or enzymes, recovery and removal of undesirable compounds from wastes, seed coatings, film-forming, and controlled release of food ingredients, nutrients, and drugs.[3]

However, relatively few basic studies have been conducted on the molecular motion and thermal relaxation behavior of chitosan. Although it is important to understand the physical state and physicochemical and applied properties of chitosan by investigating the glass transition temperature (T_g), studies on the T_g of chitosan are difficult to pursue due to the difficulty in sample preparation and the hydroscopicity of samples. There are a few works concerning the T_g measurement of chitosan. Ogura et al.[4] reported the T_g of chitosan to be around 150°C using the dynamic mechanical analysis (DMA) technique in the temperature range from −150 to 180°C.

Ko et al.[5] and Ahn[6] observed a peak at 161°C in dynamic mechanical thermal analysis (DMTA) curve, and assigned it to be attributed to α-relaxation. At the same time, some authors reported a much higher temperature value of T_g. Pizzoli et al.[7] suggested it close to that of dextran at 220°C. Sakurai et al.[8] estimated the T_g of chitosan to be 203°C from both the differential scanning calorimetry (DSC) trace and tan δ curve based on DMA. It is rather confusing that there exist two kinds of T_g value (~ 150°C and ~ 200°C), with a difference as large as 50°C.

In our present research the T_g of chitosan was detected by means of four techniques. Then a physical aging treatment was performed to improve the sensitivity of the DSC measurement, which is also used to distinguish the T_g from other relaxations.
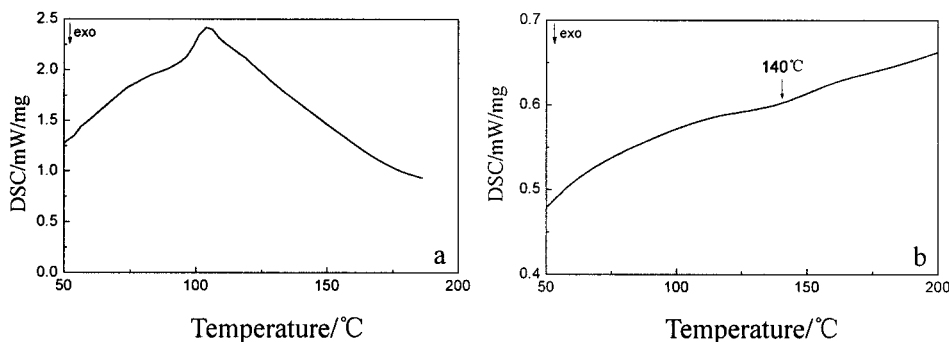
EXPERIMENTAL

Material

Commercial chitosan powder (100 mesh) with a viscosity-average molecular weight (M_V) of 4.5×10^5 ([η]

Figure 1 DSC traces of chitosan film: (a) first and (b) second heating runs, respectively.

= 623 mL/g) and a degree of deacetylation of 91% (measured with acid-base titration) was supplied by Shandong Chitin Powder Factory (China). The M_V was determined in 0.1 mol/L CH_3COONa + 0.2 mol/L CH_3COOH at 30°C, according to the Mark-Houwink equation with k = 6.589 × 10^{-3}, α = 0.88.[9] Other chemical reagents used were of guaranteed pure grade and used without purification.

Preparation of solution cast film[8]

Chitosan was dissolved in a 2.0wt % aqueous acetic acid solution at a concentration of 1.5wt %. The 1.5wt % chitosan solution was cast in a Teflon vessel at 60°C for 24h. Then the cast film was rinsed with diethyl ether and dried under reduced pressure at room temperature for 24h to evaporate the solvent thoroughly and obtain the chitosan film.

Characterization

DSC measurements were carried out on a Netzsch DSC 204 (Germany). DSC traces of each film were obtained from the second heating run at a constant rate of 20 K/min, after the first run of heating up to 190°C and cooling naturally to room temperature under nitrogen atmosphere.[8] The weight of each sample film was 5–10mg. DMTA measurements were performed on a Rheometric Scientific IV instrument (USA) at 1 Hz and a heating rate of 2 K/min. DMTA curves were also obtained from the second heating run, after the first run of heating up to 180°C and cooling naturally to room temperature. The recorded temperature range was from 30 to 250°C. Thermally simulated current spectroscopy (TSC) was determined with an American Radiant Technologies Inc. Pyroelectric Test System (USA). The chitosan film (1 × 1cm², thickness 0.14mm) was sandwiched between two aluminum plate electric polars. After polarizing on 500v at 100°C for 10 min, the sample was cooled down to room temperature. The current-temperature curves were then recorded at a heating rate of 2 K/min and in

the temperature range from 30 to 220°C. Dilatometry (DIL) measurements were performed on a Netzsch DIL 402C at a heating rate of 5 K/min under nitrogen atmosphere. DIL curves were also obtained from the second heating run, after the first run of heating up to 190°C and cooling naturally to room temperature. The recorded temperature range was from 30 to 250°C. Parallel experiments were performed for every DSC, TSC, DMTA, and DIL determination to ensure reproducibility. Infrared spectra were carried out on a Nicolet Avatar 360 FTIR spectrometer (USA). KBr pellets were used as samples.

RESULTS AND DISCUSSION

DSC measurements

It is well known that T_g can be measured by DSC. A baseline step in a DSC trace occurs due to the different heat capacity below and above the T_g of a polymer. The onset of the step is normally adopted as T_g.

Figure 1 shows DSC traces of the chitosan film in the first and second heating runs. The first heating run gives a single endothermic peak at about 100°C (Fig. 1a), which attributes to absorbed moisture. To eliminate the effect of moisture on T_g measurement, the second heating run was used. In the second heating run (Fig. 1b), the endothermic peak appeared no longer but only the change of inclination of the baseline at 140°C, which corresponded to the T_g for chitosan film. The change of inclination of the baseline was small, because chitosan is a partially crystalline polymer and also due to the small specific volume of rigid chain.[8]

The best condition to detect the T_g by DSC was studied, and the results are shown in Figure 2 and Figure 3. From Figure 2, it can be noticed that the sensitivity was the best at the heating rate of 20 K/min. Although the baseline step was larger at the heating rate of 40 K/min, the baseline was not smooth; also, the higher value of T_g was observed because of superheating. On the other hand, from Figure 3 it can
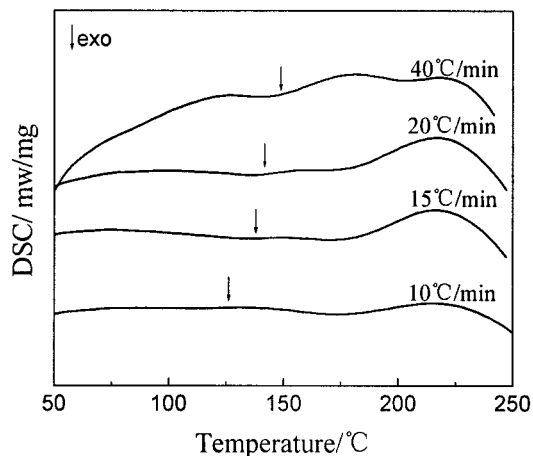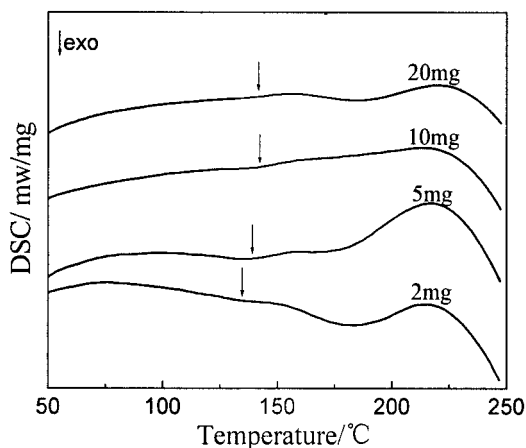
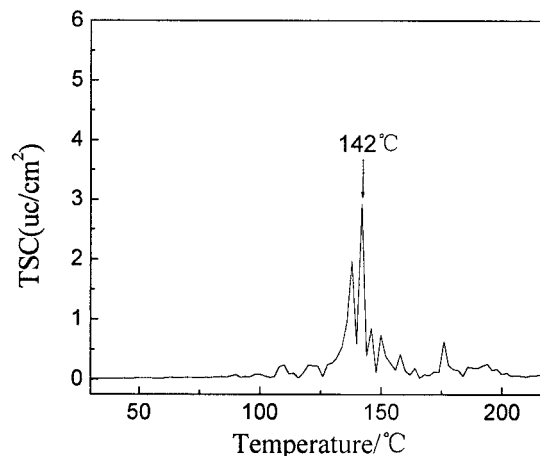**Figure 2** DSC traces of chitosan films at different heating rates.

be observed that 5–10 mg was the suitable weight of sample. Therefore, 20 K/min and 5–10mg was the most optimizing condition.

TSC measurement

Thermally stimulated current spectroscopy (TSC) or thermally stimulated discharge current spectroscopy (TSD), which measures the thermally stimulated release of the polarization that was frozen in during previous electric field polarizing at an elevated temperature with continued polarization during cooling down to the "freezing temperature," have inherently a high resolution on a low noise level. The sensitivity of the TSC has been shown to be quite good in the case of weak relaxations. Therefore, TSC has been used for polymeric investigations.[10–14] In this paper, TSC was used to study the molecular motion of chitosan. Figure 4 shows that there are a series of current peaks cen-
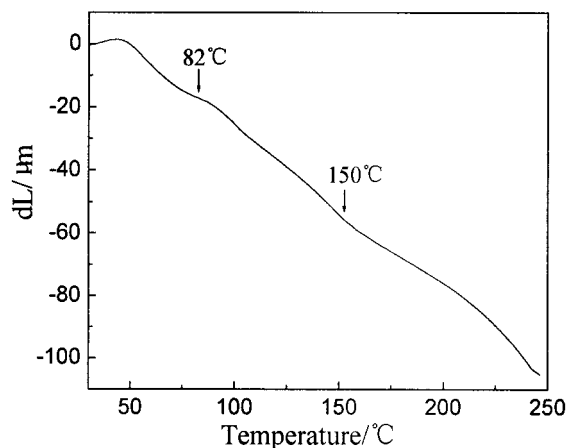

Figure 4 TSC curve of chitosan film.

tered at 142°C, which relates to the glass transition. The value agrees with the T_g measured by DSC.

DIL measurement

Dilatometry is one of the intimate methods for measuring T_g. Different from general dilatometry results of the polymers, in our dilatometry experiment, the chitosan film continuously contracted as the temperature increased because of the pressure of the ejector rod in our apparatus. The sudden motion of segments at glass–rubber transition will cause a step of baseline. In Figure 5, the inclination of DIL curve existing at 150°C corresponded to the T_g, which is basically in accord with that measured by DSC. There is an additional inclination of DIL curve appearing at about 82°C, which can be explained by the water-induced relaxation.

DMTA measurement

DMTA is one of the most sensitive techniques to study all kinds of relaxation. It has been widely applied to

Figure 3 DSC traces of chitosan films with different weights of sample.

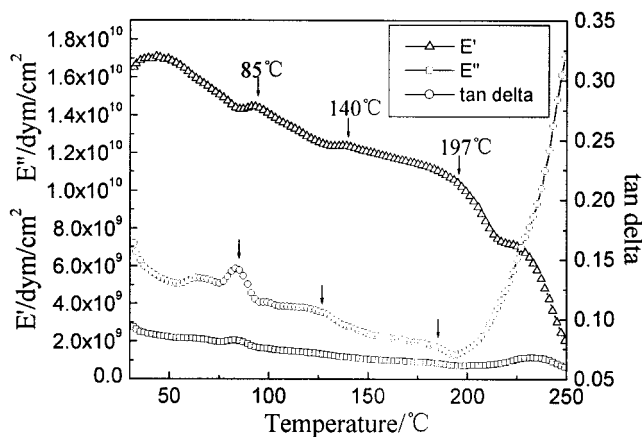
Figure 5 DIL curve of chitosan film.

Figure 6 DMTA curves of chitosan film

measure the glass transition of polysaccharides, such as cellophane, amylose, dextran,[15] and chitin/chitosan.[3-8]

Figure 6 shows the temperature dependence of the dynamic mechanical spectra on storage modulus (E′), loss modulus (E″), and damping (tan δ) of chitosan, obtained from the DMTA measurement. Three abrupt changes of E′ and peaks of tan δ at ∼ 85°C, ∼ 140°C, and ∼ 197°C before the decomposition temperature of ∼ 220°C correspond to water-induced relaxation, T_g, and α transition unknown respectively. Some authors have reported that the T_g of chitosan was ∼ 200°C, which was very close to decomposition temperature, based on the results of DMA (or DMTA). However, if the change at ∼ 200°C is attributed to the T_g and the change at 140–150°C is attributed to the β relaxation, it is difficult to explain that there were no primary relaxations observed in DSC, TSC, and DIL measurements, while obvious secondary relaxation appeared in these measurements. Normally the changes of α relaxation are much larger than the β relaxation. So we
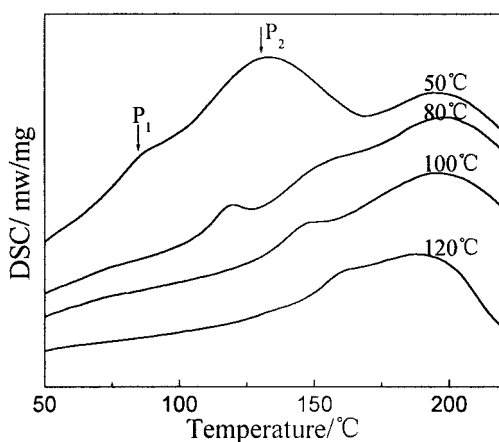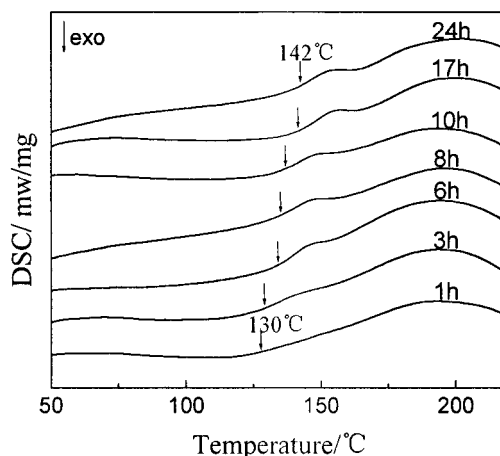
prefer to believe that the T_g is 140–150°C. The change at ∼ 200°C indeed corresponds to some transition. The transition may be the liquid–liquid transition ($T_{l,l}$), which was first found in PVC and PS in 1950. In 1976, Boyer[16] suggested that the liquid–liquid transition corresponds to the motion of very long segments or even the whole chain from imaginary liquid[17] to the real liquid above T_g. So the liquid–liquid transition ($T_{l,l}$) may be the reasonable interpretation for the change at ∼ 200°C.

Physical aging

As mentioned previously, the baseline step is small in DSC trace of chitosan. To improve the sensitivity of the T_g measurement of chitosan, a physical aging method was developed.

Physical aging is a phenomenon that has been regarded with great importance, considering the state of molecular chains during the storage of a glassy polymer, which is not in a thermal equilibrium, relaxes toward an equilibrium under a kinetic control. It is commonly referred to as enthalpy relaxation or sub-T_g annealing.[18-24] Aging affects a number of physical properties including modulus, density, enthalpy, and volume, the changes of which are often measured by using DSC. The DSC determines the enthalpy changes induced by both structural rearrangement and cohesional entanglement in glassy polymer. It has been well known that the glass transition behaviors of polymers are closely related to their thermal and mechanical histories. Therefore, their glass transition behaviors will also change during physical aging.

After sub-T_g heat treatment, two heat flow transitions can be seen (Fig. 7). The lower heat flow transition P_1 moved to the higher heat flow transition P_2 with the increase of annealing temperature. At the annealing temperature of 100°C, these two heat flow

Figure 8 DSC traces of chitosan films after physical aging at 100°C for different times.

Figure 7 DSC traces of chitosan films after physical aging at different temperatures for 8 h.
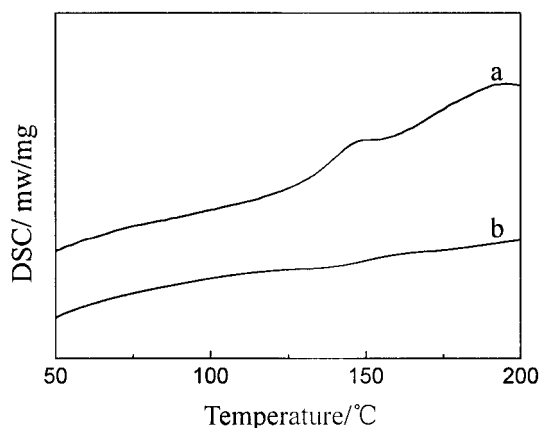
Figure 9 DSC traces of chitosan films (a)without aging; (b) after aging at 100°C for 8 h.

transitions merged into one. When the annealing temperature was higher (e.g., 120°C), there was still only one heat flow transition, but it shifted to slightly higher temperature. The sub-T$_g$ heat flow transition P$_1$ could be attributed to the molecular motion of internal stress-relaxed chain.[25] Many authors have reported that in other polymers the sub-T$_g$ heat flow transition shifts to higher temperature, and the magnitude of endotherms increase as the time of annealing is longer or the temperature is higher.[25–30] Our observations were similar to those of the literature, resulting in the higher heat flow transition P$_2$ corresponding to the T$_g$.

At the fixed aging temperature, the T$_g$ gradually increased with the increase of aging time, and became constant after a rather long time (Fig. 8). Therefore we found the T$_g$ of the chitosan film, which has been aged at 100°C for 8h, was the same as that of the sample without aging. Nevertheless, the heat capacity increment of the former is much larger than that of the latter (see Fig. 9). It implies that physical aging in

suitable conditions is able to improve the sensitivity of the T$_g$ measurement.

Influence of degree of deacetylation

In general, chitosan is partly deacetylated chitin. In this paper, the degree of deacetylation (D.D.) was estimated by FTIR method.[31] If the transition at 140–150°C belongs to the β relaxation, the D.D., which relates to the amount of side group (i.e., acetamino group or amino group), would affect this transition. If the transition at 140–150°C belongs to the α relaxation, there will be no influence of D.D. on T$_g$, because the α relaxation only attributes to the motion of segments in the main chain.

To confirm these effects, we prepared chitosan films with different D.D. according to the method of literature.[32,33] These chitosan films were used to perform DSC measurements both without physical aging and after aging. From Figure 10, no obvious change of T$_g$ can be noted. A very large heat capacity increment was observed for the chitosan with D.D. = 100% after aging. On the other hand, huge endotherms were observed for the chitosan with smaller D.D., which avoided the measurement of the T$_g$. This may be caused by larger molecular motion of internal stress-relaxed chain because of the more random structure. According to the results of Figure 10, there were no influences of D.D. on T$_g$. The T$_g$ is ~ 140°C for chitosan with different D.D, measured by DSC.

Summary of conclusions

The T$_g$ of chitosan was determined by means of four techniques, that is, DSC, DMTA, TSC, and DIL. The results agree with each other. T$_g$ value was 140–150°C. After a physical aging of samples, this transition became much more distinct. The effects of aging temper-
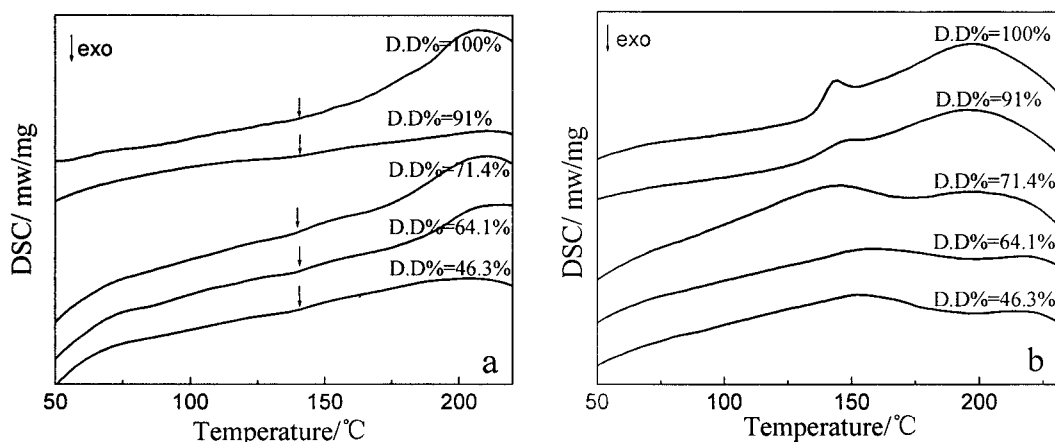
Figure 10 DSC traces of chitosan films with different D.D. (a) without physical aging; (b) after physical aging at 100°C for 8 h.

ature and aging time on this transition were discussed. The T_g of chitosan did not depend on the degree of deacetylation, as measured by DSC. Another transition found at ~ 200°C by DMTA may be attributed to the liquid–liquid transition. The physical aging treatment is regarded to be a good method to overcome the difficulties for DSC to detect the weak α relaxation of polysaccharides.

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