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Glass transition temperature of starch studied by a high-speed DSC

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ABSTRACT

The glass transition temperature (T_g) of corn starch was measured using a high-speed DSC with heating rate up to 250 °C/min. The high heating rate allows the weak T_g of starch to be visible since the high rate increases the sensitivity of thermal events. For example, the T_g of gelatinized corn starch containing about 13% moisture is too weak to be detected when the heating rate is lower than 50 °C/min, but is clearly visible when the heating rate is higher than 100 °C/min. Specifically, the technique was used to study the T_g of corn starch film with different moisture contents. The true T_g was calculated by the linear regression equation through plotting the results from different heating rates.

1. Introduction

The glass transition temperature (T_g) of starch is one of the critical thermal properties for starch-based products. However, measurement of T_g by DSC is difficult since the change of heat capacity or the signal on heat flow is usually weaker than that of conventional polymers. For example, the heat of fusion for polypropylene is about 80 kcal/g (Miller, 1989), whereas the measured energy for starch gelatinization is only about 0.95 cal/g (Liu, Yu, Xie, & Chen, 2006; Lund, 1984). Furthermore, the multiple phase transitions that starch undergoes during heating and the instability (such as evaporation) of water contained in starch make it more difficult to study the thermal behaviour of starch materials using DSC (Zeleznak & Hoseney, 1987). The instability of water contained in starch is also the reason why dynamic mechanical analysis (DMA) is not suitable for studying the T_g of starch since the moisture evaporates during heating.

Many attempts have been made previously using DSC to study the T_g of starch and its products. There are significant differences in the results. For example, Zeleznak and Hoseney (Yu & Christie, 2001) reported T_g values of 30–90 °C for wheat starches with 13–18.9% moisture content, and postulated that the T_g would be below room temperature if the water content was above 20%. Stepto and Tomka (1987) reported that extruded potato starch containing 15–20% moisture had a T_g of about 25 °C. Van Soest, Benes, and De Wit (1996) reported the T_g of extruded potato starch with 14% moisture at 5 °C and that the T_g for moisture content above 14% could not be measured. Shogren (1992) reported that no T_g was observed for the corn starch on the first scan and suggested that most of the polysaccharide was highly ordered. The glass transition temperature of corn starch containing 25–50% moisture was detected in the temperature range 20–60 °C on the second scan. Lourdin, Coignard, Bizot, and Colonna (1997) reported a T_g at about 90–100 °C with 13–15% moisture content for potato starch. Rindlava, Hulleman, and Gatenholma (1997) reported a T_g of 75–95 °C with 13–15% moisture content for potato starch, and the T_g decreased linearly as the moisture content increased. Some researchers (Biliaderis, 1992; Chinachoti, 1996; Maurice, Slade, Sirett, & Page, 1985) considered that DSC may not be suitable to study the T_g of starch because the heat capacity of the transition is too weak and frequently is masked by the gelatinization endotherm.

Theoretically, an increase of heating rate could increase the sensitivity of thermal events measured by DSC. The DSC output is a function of heat flow (mW) or energy per unit time (J/s). As the heating rate is increased, there is a greater input of energy per unit time and hence the same heat flow occurs over a shorter time frame. The result of an increase in the overall sensitivity allows the measurement of transitions that may be below the limit of detection possible by conventional DSC (Gramaglia, Conway, Kett, Malcolm, & Batchelor, 2005; Katayama et al., 2008; McGregor, Saunders, Buckton, & Saklatvala, 2004). Recently a high-speed differential scanning calorimetry (Hyper-DSC), has attracted much attention for observing glass transitions using its extremely high controlled heating rate, up to 500 °C/min (McGregor & Bines, 2008; Saunders, Podluii, Shergill, Buckton, & Royall, 2004).

On the other hand, although a high heating rate can increase sensitivity, it also causes a lag in the thermal events, which delays the characteristic temperature (T). In order to eliminate the lag ef-

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fect and obtain an accurate T, some adjustable methods are developed. One of them is the calibration method, in which a calibration should be done using a standard sample under the corresponding heating rate before the measurement of the experimental sample (Oladiran & Batchelor, 2007; Silva, Nunes, Eusebio, Pais, & Sousa, 2006). In this work, another adjustable method, the extrapolation method, was used. Theoretically, the heating rate can only change the kinetics of a thermal event when all other heating conditions are constant, so the relationship between T and the heating rate should be linear. Through the linear regression equation, the extrapolated T can be obtained, which represents the theoretical T under an extremely slow heating rate (approaching 0 °C/min).

In this work, the T_g of starch was studied by a Hyper-DSC with heating rate up to 250 °C/min. The high heating rate increases the temperature of the thermal event, which allows the weak T_g of starch to be visible. Corn starch was used as a model material. The true T_g of samples with different moisture content is calculated using the equation of linear regression through plotting the results from different heating rates.

2. Experimental

2.1. Materials and sample preparation

A natural corn starch (Huanglong Food Industry Co. Ltd. China), with moisture content of 13.5% was used in this work. Starch film was prepared by casting. A 3% starch suspension was first stirred and then heated to 98 °C, and kept for 2 h to fully gelatinize the starch (Chen, Yu, Kealy, Chen, & Li, 2007), then cast on a glass sheet and dried by air flow at 50 °C for 24 h. The thickness of the film is about 0.12 mm. The film was stored in different relative humidity environments for 48 h to equilibrate the moisture content. The actual moisture contents of the film samples were measured by drying samples in a vacuum at 130 °C for 24 h and measuring weight loss.

2.2. Hyper-DSC

A Perkin-Elmer DSC Diamond-1 with an internal coolant (Intercooler 1P) and nitrogen purge gas was used in the experimental work to confirm thermal behaviour. The instrument was calibrated for temperature and heat flow using indium and zinc as the standards under 10 °C/min. A baseline for an empty pan was established for each corresponding heating rate. Specimen with about 2 mg was sealed in an aluminium pan (PE No. 0219-0041). T_g was taken at the half variation in heat capacity occurring at the transition. All results were the average of triplicate parallel experiments.

All of the measured results, such as sample temperature, time, T_g, and heating rate, were imported into Excel software to obtain the linear regression equation and linear dependent coefficient (R^2). The R^2 was used to evaluate the linearity of variable X vs. Y, with the value of R^2 decreasing from 1 as the linear fit decreases.

3. Results and discussions

3.1. The linearity of sample temperature variation vs. time

In order to study the thermal behaviours at high-speed, it is important to confirm the linearity of temperature variation vs. time under different heating rates. The linearity of temperature variation vs. time can be evaluated by Eq. (1):

$$C_p = \frac{dQ}{dT}\cdot\frac{1}{m} = \frac{d}{dT}\cdot\frac{H}{m} \quad (1)$$

in which C_p is the thermal capacity of sample; m is the mass of sample; Q is the input energy when heating or cooling; T is sample temperature; H is heat flow, $H = dQ/dt$; t is time. It can be seen that only when dT/dt is a constant, then C_p is directly proportional to H. In other words, only when the curve of temperature vs. time is a straight line, can the change of H directly represent that of C_p.

Fig. 1 shows the plots of temperature vs. time for a starch sample (11.6% moisture content) measured by Hyper-DSC. It can be seen that except for the temperature lag at the very beginning, the linearity of the sample temperature vs. time is very high. It means that the variation of H in heat flow curve can perfectly reflect that of C_p.

On the other hand, because of the lag in heat conduction and sample relaxation, the characteristic temperature (T) of thermal properties is delayed due to the high heating rate. Theoretically, if all experimental conditions are constant, such as the heat conduction of the pan and sample thickness, the heating rate can only change the kinetics of the thermal behaviour. In that case, the relationship between T and heating rate should be linear. Fig. 2 shows the DSC thermogram of indium under different heating rates. Fig. 3 shows plots of the onset temperature of melting vs. heating rates based on the data from Fig. 2. It can be seen that as the heating rate increased, the size of the melting peak of indium also increased, and the onset temperature T_o increased linearly. The linearity between the T_o of indium and the heating rate is very high (R^2 is about 0.9981) in the heating rate range of 20 and 300 °C/min. It indicates that the relationship between T_o and heating rate is linear. Furthermore, from the linear regression equation, the extrapolated T_p can be calculated. The result is 156.88 °C that is very close to the data from handbook (156.60 °C).

3.2. Glass transition temperature measured by Hyper-DSC

Figs. 4–6 show the DSC thermograms of gelatinized corn starch containing different moisture levels under different heating rates. It can be seen that there is no clear step change being detected when the heating rate is lower than 50 °C/min. The size of the step change increased with increasing heating rate for all samples. The medial point of the step change (T_g) increased with increasing heating rate for all samples. Due to moisture evaporation, there is an upward excursion on each curve when the temperature exceeds 95 °C. Fig. 7 shows the plots of measured T_g vs. heating rate. It is observed that the T_g increases linearly with increasing heating rate (with $R^2 > 0.95$).

The slope and extrapolated T_g calculated from the regression equation are listed in Table 1. It is observed that the extrapolated T_g increased with decreasing moisture content, which is expected.

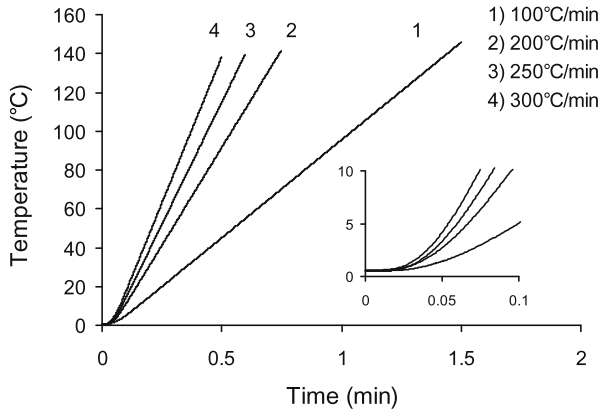

Fig. 1. The linearity of sample temperature vs. time under different heating rates.

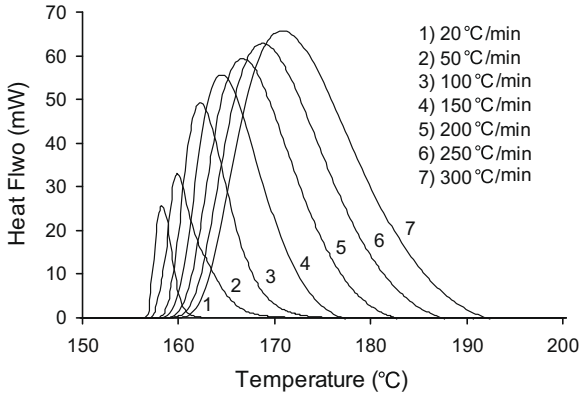

Fig. 2. DSC thermograms of indium under different heating rates.

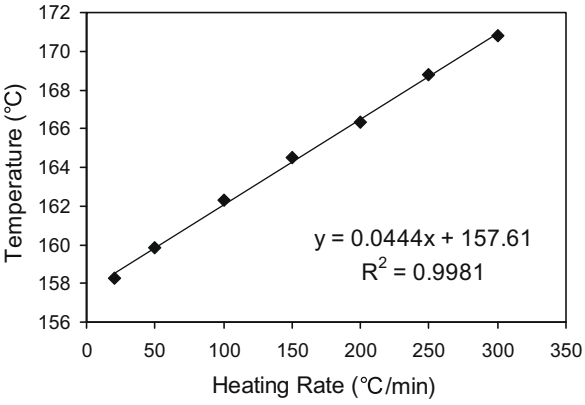

Fig. 3. Linearity of T_o of indium vs. heating rate.

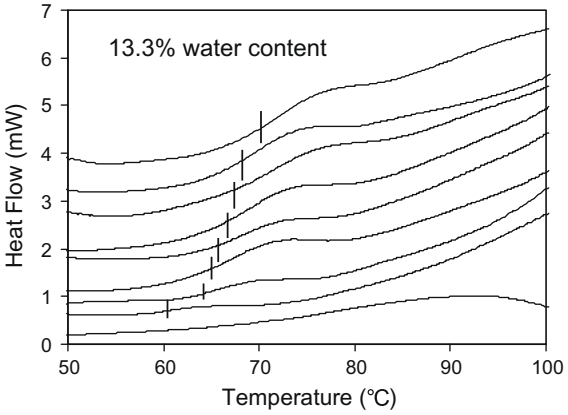

Fig. 4. DSC thermogram of corn starch film containing 13.3% moisture under different heating rates: 20, 50, 100, 120, 140, 160, 180, 200, and 250 °C/min (from bottom to top).

It is also noticed that the slope increased with decreasing moisture content, which indicates that the influence of the heating rate on the sample is different, and could be explained by different thermal conductivity.

4. Conclusions

The glass transition temperature, T_g, of corn starch films with different moisture content was measured by high-speed DSC. Since the high heating rate increased the sensitivity of thermal event, the glass transition of corn starch film, which was a very weak signal on conventional DSC, was enlarged and observable. The T_g of gelatinized corn starch containing about 8.7–13.3% moisture is too weak to be detected when the heating rate is lower than 50 °C/min, but is clearly visible when the heating rate is higher than 100 °C/min.

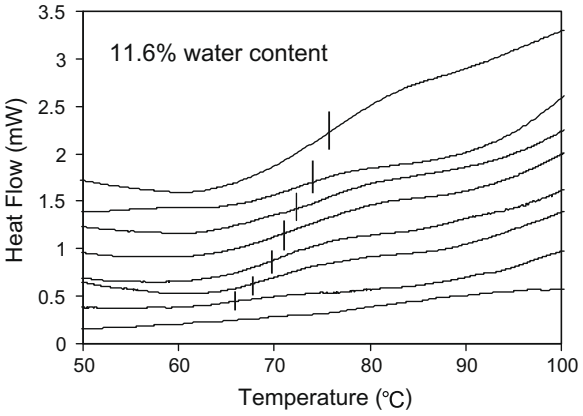

Fig. 5. DSC thermogram of corn starch film containing 11.6% moisture under different heating rates: 50, 100, 120, 140, 160, 180, 200, and 250 °C/min (from bottom to top).

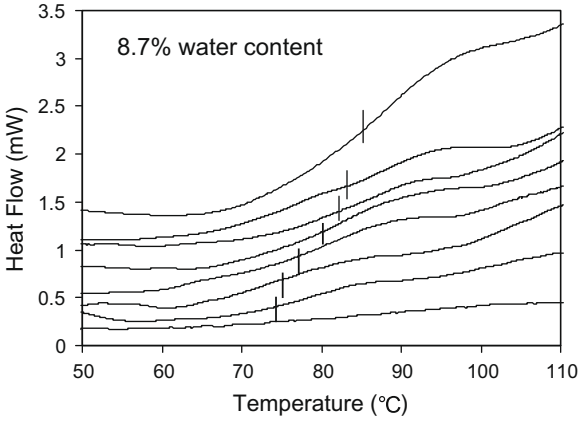

Fig. 6. DSC thermogram of corn starch film containing 8.7 % moisture under different heating rates: 50, 80, 100, 120, 140, 160, 180, 200, and 250 °C/min (from bottom to top).

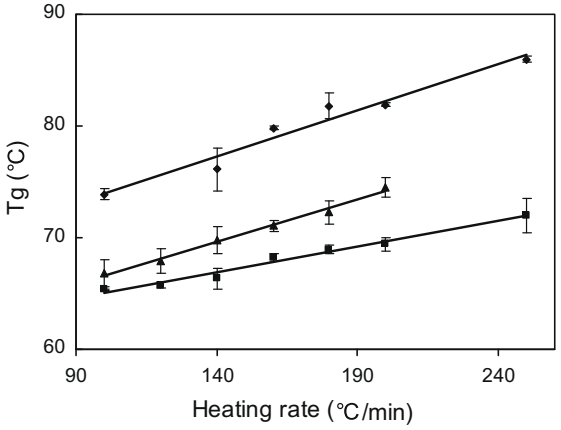

Fig. 7. Plots of T_g vs. heating rate of corn starch film with different moisture content (♦ 8.7%, ● 11.6% and ▲ 13.3%).

Table 1
T_g of corn starch with different moisture contents.

Moisture content	Regression equation	Slope	Ex T_g
13.3%	$y = 0.0499x + 59.221$	0.0499	59.22 °C
11.6%	$y = 0.0594x + 61.363$	0.0594	61.36 °C
8.7%	$y = 0.0749x + 67.328$	0.0749	67.34 °C

The linearity between temperature and time was confirmed by plotting dT/dt under different heating rates. The linearity between characteristic temperature (T) and heating rate was evaluated by plotting the melting onset temperature of indium vs. heating rates. Both linearities are very high with $R^2 > 0.99$. The extrapolated T_g, which represents T_g when the heating rate is extremely slow and approaching 0 °C/min, was calculated by regression equation. The extrapolated T_g of corn starch film with 13.3%, 11.6% and 8.7% moisture content is 59.2, 61.4, and 67.3 °C, respectively.

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