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A new study of starch gelatinization under shear stress using dynamic mechanical analysis

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Abstract

A new technique for studying starch gelatinization under shear stress using dynamic mechanical analysis (DMA) with shear sandwich mode is reported. Rice starch was used as the model material in the experimental work. The physical meaning of storage modulus G', loss modulus G'' and tangent of the phase angle $\tan\delta$, measured during starch gelatinization, is discussed. The effects of various factors, such as sample preparation and measurement conditions, on the measured results are discussed. A sharp peak of $\tan\delta$ was detected during heating starch, which well represents the starch gelatinization process under shear stress. Comparison between the results detected by DMA and differential scanning calorimetry was used to interpret the processes and mechanisms of starch gelatinization. Results showed that variations in physical properties occurred both before thermal transition started and after thermal transition was complete. DMA has proved to be a convenient technique to study starch gelatinization under shear stress. One of the important advantages of this technique is it can be used to study starch gelatinization at low moisture contents ($\leqslant$50%) under shear stress.

Keywords: Gelatinization; Shear; Starch; Rice; DMA

1. Introduction

Starch gelatinization has been extensively studied in food science for decades (Hermansson & Svegmark, 1996; Stevens & Elton, 1971; Tester & Morrison, 1992; Zobel, 1984), in particular in applications involving high water contents. Recently, starch has been used as an important raw material in biodegradable plastics, and its gelatinization process has attracted much attention since it represents an important and unique characteristic in the processing of starch-based materials (Biliaderis, Page, Slade, & Sirett, 1985; Lelievre, 1974, 1976; Russel, 1987; Svensson & Eliasson, 1995; Yu & Christies, 2005). Studying the unique microstructures and properties of starch will enhance our fundamental knowledge of polymer science. Various technologies have been developed and used to study gelatinization processes, such as microscopy with hot-stage, viscometry, differential scanning calorimetry (DSC), X-ray diffraction, and nuclear magnetic resonance.

The simplest way to study starch gelatinization is to monitor the process under shearless conditions. The most widely used technique is DSC, which has proven to be an extremely valuable tool in quantifying the gelatinization of starch, and has been widely used since the 1970s to study the thermal behavior of starches (Donovan, 1979; Eliasson, 1980; Liu, Yu, Xie, & Chen, 2006; Lund, 1984; Shogren, 1992; Takahashi, 1982; Tananuwong & Reid, 2004; Tufvesson, Wahlgren, & Eliasson, 2003; Wootton & Bamunuarachchi, 1980; Yu & Christie, 2001). DSC thermograms enable the analysis of transition temperature as well as transition

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enthalpy. The enthalpy (ΔH) of a transition has been interpreted as corresponding to the amount of crystal order (or double-helical structure) in a starch suspension that is disrupted on heating. The gelatinization process can also be recorded by modeling small angle X-ray scattering data from starch slurries of various concentrations. The degree and mode of water absorption and the loss of crystalline order give insight into the gelatinization process, and the results reported here correspond with those of DSC reported elsewhere in the literature (Cameron & Donald, 1993).

However, with the increasing use of starch in processes involving shear conditions, such as extrusion cooking and the production of thermoplastics (Cai & Diosady, 1993; Chiang & Johnson, 1997; Harper, 1989; Yu & Christies, 2005), the study of gelatinization mechanisms under shear stress has both scientific and commercial importance. Freeman and Verr (1972) initially measured gelatinization and paste development by heating starch in a closed bottle submerged in a water bath with a shaking mechanism. At specified times or temperatures, samples were removed and viscosities were determined using a Brookfield Synchro-Lectric viscometer. Samples were also cooled and viscosity again measured to determine setbacks. Zobel (1984) used a Brabender Visco/Amylograph to study the properties of cooled pastes. This instrument records the torque required to balance the viscosity that develops when starch slurry is subjected to a programmed heating and cooling cycle. The recently developed RheoScope can be used to study starch gelatinization under shear stress (Chen, Yu, Kealy, Chen, & Li, 2007; Yu, Kealy, & Chen, 2006), and can simultaneously measure viscosity and observe starch particle variations. However, the above techniques are only suitable for studying starch gelatinization at low starch concentrations (about 0.5–20%). Many extrusion cooking processes and almost all processing of starch-based materials involve much lower water contents ($\leqslant$50%).

Previous research has shown that under shearless conditions, the full gelatinization of starch requires about 70% water content, while under shear conditions less water is required since shear stress enhances the process (Wang, Chiang, Zhao, & Kim, 1989). Processes such as extrusion cooking and the production of starch-based materials are dependent on the proper conversion of starch within the raw materials. In extrusion processing, gelatinization is typically achieved with low water content in high-pressure conditions. By the ''dead-stop'' shutdown and quick opening of the barrel of an extruder, Cai and Diosady (1993) studied gelatinization process under shear stress with lower moisture contents. However, this technique requires a special extruder and higher skills to stop further gelatinization during sample collection.

Dynamic mechanical analysis (DMA) can be simply described as applying an oscillatory force to a sample and analyzing the material's response to that force (Menard, 1999). DMA has been widely used to study the relaxation of polymers, such as glass transition temperature and modulus during heating, and it has also been widely used to investigate the effects of shear rate or frequency on viscosity. In this paper, a technique of studying starch gelatinization under shear stress using DMA is described and discussed. The physical meaning of storage modulus G', loss modulus G'' and tangent of the phase angle $\tan\delta$ measured during gelatinization is discussed. The effects of various factors, such as sample preparation and measurement conditions, on the measured results are also discussed. Rice starch was used as the model material in this work to demonstrate the gelatinization process detected by DMA, in particular at lower water contents ($\leqslant$50%). The results were compared with those from DSC to interpret the physical meaning.

2. Experimental

2.1. Materials

A commercially available rice starch (Bangkok Starch Industry, Thailand) was used in this experimental work. An infra-red heating balance (Model DHS-20) was used to measure the moisture contents of samples during heating to 110 °C for 20 min. The total moisture content of the specimens was taken as the original moisture content of the starch together with the added water.

2.2. Dynamic mechanical analysis

A Perkin-Elmer Pyris Diamond DMA with a shear sandwich measuring system (N5353030) was used in the experimental work. Shear measurements were carried by a sliding plate moving between two samples (see Fig. 1). Materials with various starch/water ratios were well mixed and then molded into 10 (wide) × 10 (long) × (2∼5) mm (thick) blocks (see Fig. 1). The thickness (deep) was further controlled by adjusting the distance between the sliding plate and the side block of the shear sandwich measuring system after mounting the samples since they were flexible. Some moisture was lost during mixing and specimen preparation. The exact water content of each specimen was measured after drying the specimen in a vacuum oven at 130 °C for 30 min. In order to prevent moisture loss in the starch block during measurements, a cup of water was placed in the furnace chamber to increase humidity, and Vaseline was applied to the block surfaces that were exposed to the air.

2.3. Differential scanning calorimetry

A Perkin-Elmer DSC Diamond-I with an internal coolant (Intercooler 1P) and nitrogen purge was used in the experimental work. The melting temperature and enthalpy of indium were used for temperature and heat capacity calibrations. Detailed methods and some critical issues of studying the thermal behavior of starch have been discussed previously (Liu et al., 2006; Yu & Christie, 2001). The gelatinization of starch was carried out at 2 °C/min

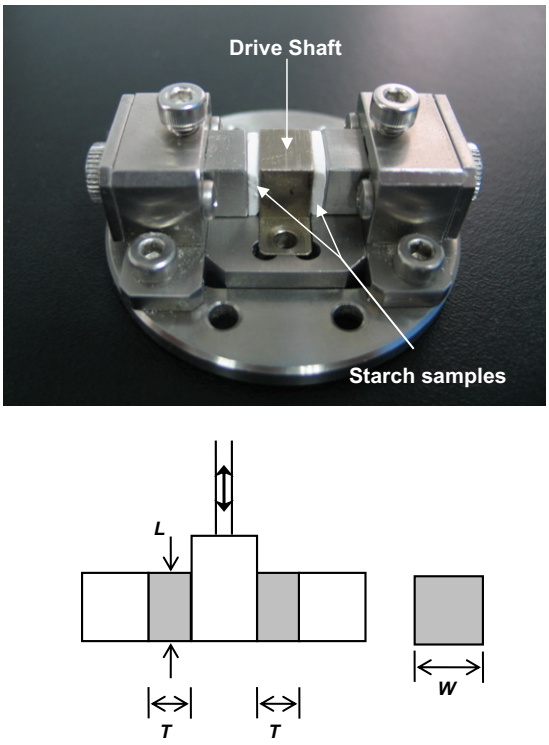

Fig. 1. Example starch samples in the sample holder used in the experimental work.

to correspond with the conditions used in the DMA experiments.

3. Results and discussion

3.1. Typical curves detected by DMA

Fig. 2 shows typical DMA curves for rice starch with 45.5% water content during temperature scanning from 20 to 90 °C at a heating rate of 2 °C/min. It can be seen that, overall, G', G'' and η^* decreased with increasing temperature, but that the decrease rate was not linear, and each displayed a clear "corner" at temperatures between 60 and 70 °C.

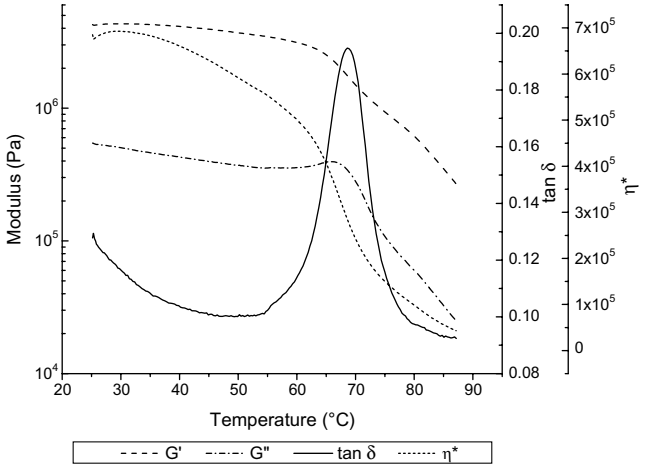

Fig. 2. Typical curves of gelatinization process measured by DMA (water content, 45.5%; sample thickness: 3 mm; heating rate, 2 °C/min; frequency, 1.0 Hz).

As seen in Fig. 2, with increasing temperature, G' initially decreased slightly and then decreased more rapidly from about 65 °C. G'' initially increased slightly with increasing temperature, then remained constant and even increased again slightly for a short temperature range between 60 and 70 °C, before decreasing sharply. The complex viscosity, η^*, decreased gradually with increasing temperature up to between 65 and 75 °C, after which the decrease rate was faster. A sharp peak in $\tan\delta$ was recorded at 61.3 °C (onset) and 74.7 °C (offset), which peaked at about 68.6 °C.

The DMA results of starch during heating are much more complex than those of conventional polymers, since gelatinization involves many physical and chemical reactions, such as water diffusion, particle swelling, melting of native crystalline, dissolving and decomposition (Liu et al., 2006; Sullivan & Johnson, 1964). An order–disorder phase transition occurs when starch granules are heated in the presence of water (French, 1984). When sufficient water is present, this transition – called "gelatinization" – results in near-solubilization of the starch (Donovan, 1979). An important phase transition during gelatinization is the destruction of the crystal structure in the starch granules. When the temperature reaches a critical point, the hydrogen bonds responsible for the structural integrity of the granule weaken, allowing the penetration of water and hydration of the linear segments of the amylopectin. As this occurs, the molecules start to form helices or coils, creating tangential pressure and causing the granules to imbibe water and swell to many times their original volume (Wurzburg, 2000). It is well known that G' is related to the ability of a material to return or store energy in shear. The softening of starch particles during heating could explain the decrease of G'. G'' is related to the ability of a material to lose energy in shear. The slight decrease of G'' observed during initial heating represented the start of gelatinization as water defused into the starch granules.

There are two contradictory factors related to viscosity. Firstly, the viscosity of a sample could increase during gelatinization due to the dissolution of starch. Secondly, as of most other materials, viscosity could also decrease with increasing temperature. Combining these two factors, η^* decreased gradually with increasing temperature. When gelatinization reached the point where most of the rigid starch granules had been destroyed and maximum viscosity was achieved, G' decreased sharply. Meanwhile, G'' remained constant and even increased slightly over a short temperature range, before also decreasing sharply. In the higher temperature range, especially after starch had gelatinized, the dynamic thermal behavior of the materials was similar to other polymeric gels: both G' and η^* decreased with increasing temperature.

Previous studies have suggested that the viscosity of starch varies significantly during and after gelatinization

(Zobel, 1984). The complex viscosity pattern measured by DMA in our study, however, was quite different from that of the traditional steady shear viscosity of Brabender Amylographs (Wurzburg, 2000), where the viscosity of a starch suspension initially rises until it approaches a peak and then drops. This process was achieved in a water-based environment at rather low starch concentration (5.4%). However, in the study reported here, the starch content of the solid starch blocks tested under shear conditions was much higher (54.5%).

Combining the variation of G' and G'', the tangent of the phase angle, $\tan\delta$ (also called "damping"), is one of the most basic parameters measured, as it is an indicator of how efficiently a material loses energy to molecular rearrangements and internal friction. The $\tan\delta$ peak well reflects the disruption of molecular order within the granules and the movement of starch molecules during the gelatinization progress, and, as a result, can be used to describe starch gelatinization behavior during heating under shear stress. The method of determining the gelatinization temperature T_G in DMA can be a contentious issue, similar to the determination of the glass transition temperature T_g (Menard, 1999). There are various methods to consider the four peaks and corners (G', G'', η^*, and $\tan\delta$) detected in DMA. However, values can differ by up to 30 °C between the two methods on the same run. As the onset temperature T_{Go} and peak temperature T_{Gp} of $\tan\delta$ can be calculated more accurately and easily, these will be used to represent the gelatinization temperature for the DMA results in the following discussion.

3.2. Effect of frequency

It can be seen from Fig. 3 that $\tan\delta$ varied with different frequencies, and that viscous or liquid-like behavior predominated in the low-frequency range, as expected (Menard, 1999). As frequency increases, a material will act in a more elastic fashion. As previously explained, lower frequency will result in lower G' and higher η^*. As a result, a higher $\tan\delta$ peak value can be obtained at lower frequency. The lower resolution results in higher sensitivity at the lower frequency. It should be noted that the DMA equipment used only recorded data every four cycles, so the lower frequency (0.1 Hz) could not provide a smooth curve for $\tan\delta$ especially when the heating rate was higher than 2 °C/min. A frequency of 1 Hz was adopted in the following experimental work.

3.3. Effect of sample thickness

Fig. 4 shows the effect of sample thickness on $\tan\delta$. It can be seen that the peak temperature, T_G, and onset temperature, T_{onset}, decreased slightly with increasing thickness, but the offset temperature, T_{offset}, remained constant. It should be noted that there was almost indiscernible differences with thicknesses greater than 3 mm. In this study, the thickness was varied, but the shear area was kept the same. $\tan\delta$ is the ratio of loss modulus to storage modulus and is normally independent of geometry effects (Menard, 1999). As the early stage of starch gelatinization involves particle swelling, thicker samples will display higher resistance forces. The unique process of starch gelatinization caused the variation of T_{onset} and T_G. This resistance force disappears after starch is fully gelatinized, which results in constant T_{offset}. For ease of handling, a specimen thickness of 3 mm was adopted in the following experimental work.

3.4. Effect of heating rate

Fig. 5 shows the effect of heating rate on $\tan\delta$. As expected, $\tan\delta$ peaks occurred at higher temperatures with increasing heating rate, due to the lag time of heat transfer from the outside to the inside of the starch block. The higher heating rates increased sensitivity and resulted in higher peaks, but decreased resolution. On the other hand, the lower heating rates could cause moisture loss during

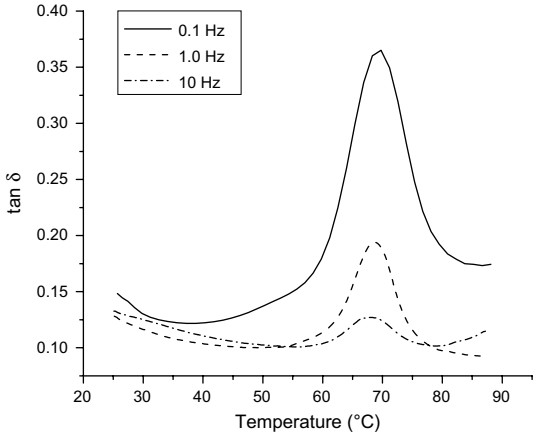

Fig. 3. Effect of frequency on the measured results (water content, 48.8%; sample thickness, 3 mm; heating rate, 2 °C/min).

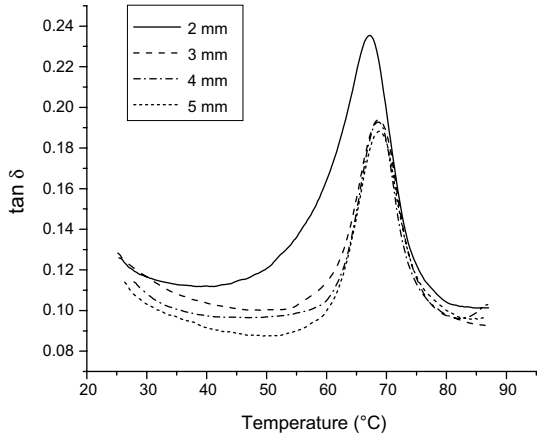

Fig. 4. Effect of sample thickness on the measured results (water content, 48.8% on dry base; frequency, 1.0 Hz; heating rate, 2 °C/min).

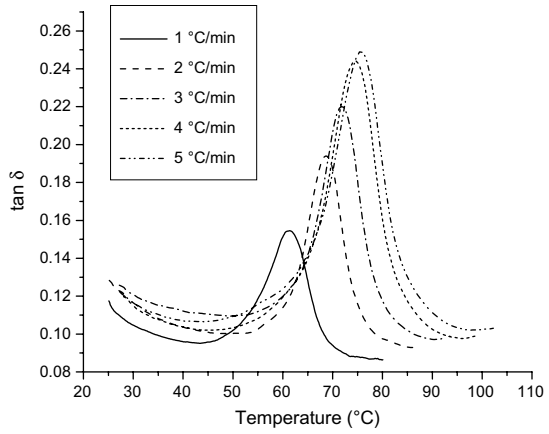

Fig. 5. Effect of heating rate on the measured results (water content, 48.8% on dry base; sample thickness, 3 mm; frequency, 1.0 Hz).

heating. The heating rate 2 °C/min was adopted in the following experimental work.

3.5. DMA results versus DSC results

Direct comparison of the results from different measurement techniques may not have real meaning since the detected physical parameters will be different, however various results can be used to support each other in studying the mechanisms of gelatinization. It is well known that DSC measures thermal behavior, while DMA measures physical properties (viscosity) under certain conditions. Fig. 6 shows the DMA and DSC results for a rice starch with the moisture content of 45.5%. It can be seen that the results from the two different techniques show similar peaks of gelatinization. Table 1 lists the various parameters of gelatinization for the same sample determined by the two different techniques. It is seen that the peak temperature, T_G, detected by both DMA and DSC is almost the same. It is noted that the temperature difference, $T_{offset} -$

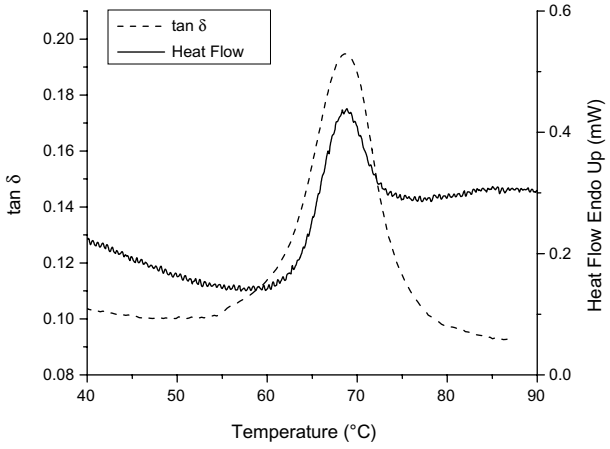

Fig. 6. Gelatinization processing measured by DMA (sample thickness, 3 mm; frequency, 1.0 Hz; heating rate, 2 °C/min) and DSC (heating rate, 2 °C/min) for rice starch with 45.5% water content.

Table 1
Gelatinization parameters detected by DMA and DSC

Method	T_{onset} (°C)	T_G (°C)	T_{offset} (°C)	ΔT ($T_{onset} - T_{offset}$) (°C)
DMA	59.3	68.6	75.0	15.7
DSC	63.3	68.3	72.6	9.3

T_{onset}, detected by DMA is wider than that detected by DSC, which indicates the variation in physical properties occurred both before thermal transition started to increase and after thermal transition was complete. Liu, Lelievre, and Ayoung–Chee (1991) studied starch gelatinization using X-ray and birefringence measurements and found that a decrease in crystallinity occurred both before the birefringence of granules started to disappear and after all birefringence was lost. Comparing the results from DMA and DSC indicates that water defusion and granular swelling started earlier than the disorder of crystalline structure detected by DSC. It also indicates that DMA is more sensitive to the measurement of gelatinization process. Similarly, DMA is more sensitive to the measurement of glass transition than DSC in many cases. The lower T_{onset} detected by DMA indicates that gelatinization starts at lower temperatures than those detected by DMA, which is expected since shear stress enhances the process.

4. Conclusions

In this paper, a technique of studying starch gelatinization using DMA is described and discussed. In our study, frequency (0.1–10 Hz) had no significant effect in determining gelatinization behavior, while sample thickness and heating rate had some effects on the results. A heating rate of 2 °C/min and a sample thickness of 3 mm are recommended as a result of our experimental work. By comparing the results obtained from DMA with those from DSC, it is shown that DMA is quite an efficient and accurate method of studying starch gelatinization, particularly at low water contents (⩽50%). The results from our DMA study will be used to study starch gelatinization behavior in low water content conditions like extrusion processing.

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