

Enthalpy relaxation and glass to rubber transition of amorphous potato starch formed by ball-milling

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Abstract

Ball-milling is known to convert native potato starch into an amorphous state. Using differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD), we demonstrated that the ball-milled amorphous starch exhibits a glass to rubber transition accompanied by a recovery from enthalpy relaxation. Such transition behavior differs from that of the glassy starch formed by heating and subsequent quenching. We further found that the ball-milling process for potato starch enhances the enthalpy and volume relaxation with breaking the crystalline inner native potato starch. In addition, our results suggest that WAXD examination may capture the volume relaxation phenomena of amorphous materials such as starch. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The physical state of starch has become better understood by examining its glass transition. Slade (1984) first reported evidence that a glass to rubber transition of the amorphous region in a native starch precedes the melting of the crystalline region during heating. In other words, gelatinization of starch cannot commence unless the characteristic glass transition temperature (T_g) of the amorphous region is exceeded. Subsequent studies have provided evidence that this is relevant to the starch gelatinization mechanism (Biliaderis, Page, Murice, & Juliano, 1986; Biliaderis, 1991, 1992; Chungcharoen & Lund, 1987; Waniska & Gomez, 1992). Based on these studies, understanding the glass transition behavior of amorphous starch appears to be essential in the prediction and control of the physical state of the starch-based system. Shogren (1992), Livings, Breach, Donald, & Smith (1997), Bizot et al. (1997), and Thiewes and Steenekken (1997) have also reported a phenomenon known as “enthalpy relaxation” in molten starch systems. This phenomenon is related to changes in the physical properties of the glassy state of starch, including the specific volume and heat, during storage. These characteristics can change, even momentarily over time during storage, indicating that aging may influence the physical state of starch. However, few studies have examined enthalpy relaxation in glassy

starch. To better understand the glass transition, we must better understand the conditions that influence and induce enthalpy relaxation in the glassy state of starch.

In the field of polymer science and metallurgy, mechanical operations such as ball-milling are known to progressively destroy the crystalline order, leading to the formation of a glass (Elliott, 1990). Ball-milling has also been applied to starch for conversion of its physico-chemical properties. During ball-milling of the semi-crystalline native starch, the crystalline region is destroyed, leading to slight depolymerization and formation of an amorphous structure. This occurs even when performed under ambient temperature in a dry state. (Morrison, Tester, & Gidley, 1994; Morrison & Tester, 1994; Tester, Morrison, Gidley, Kirkland, & Karkalas, 1994; Adler, Baldwin, & Melia, 1994; Yamada, Tamaki, Hisamatsu, & Teranishi, 1997). In these studies, mechanical operations such as ball-milling reportedly had a strong effect on the various physico-chemical properties, including molecular distribution. However, none of these studies showed a “glass–rubber transition” in ball-milled starch. A glassy solid is by definition, an amorphous solid that exhibits a glass transition (Elliott, 1990). Even if the ball-milled starch exhibits a glass transition, it is not clear whether the above physico-chemical changes in the starch granule interior affect the glass transition temperature. Moreover, the possible role of thermo-mechanical processes such as enthalpy relaxation has not been determined with respect to ball-milled amorphous

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starch. The present study investigates the glass–rubber transition behavior, including enthalpy relaxation, in ball-milled amorphous starch using differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD).

2. Experiments and methods

First, we describe the experiments generally. The detail of DSC and X-ray diffraction methodology will be explained later.

We examined potato starch (Wako Chemical Ind. Ltd., Osaka Japan) which had a moisture content of 16% as determined by oven drying.

Ball-mill treatment was carried out using an Irie Shokai V-I Co., Ltd. Japan. For the study, balls, 1 cm in diameter (total weight, 297 g), were added to 10 g of potato starch in a cylindrical container with a diameter of 9 cm and a height of 9 cm. The cylindrical container was tumbled for 1, 2, 4, 17, 45, 70, and 140 h at 90 rpm to obtain various degrees of grinding. Tumbling was carried out at room temperature and immediately after milling, a portion of each milled sample underwent DSC measurement. The remaining portion of each sample was stored in a hermetically sealed vessel at room temperature until measurement 10 days and 1 month later.

A repeat DSC measurement was also carried out on native starch and the sample stored for 10 days after milling for 100 h, to determine whether the thermal events detected by DSC are reversible. In addition, X-ray diffraction analysis was carried out at 30°C on samples stored for a month after milling for 17 and 140 h, as well as native starch as a reference, in order to determine the degree of crystallinity in each sample. In the case of the sample milled for 140 h, changes in the X-ray diffraction patterns were examined for every 10°C increase while heating from 30 to 80°C. This experiment provided complementary information to DSC on the structural changes associated with heating the sample.

2.1. Differential scanning calorimetry measurement

Calorimetric studies were conducted using a Shimadzu DSC-50 differential scanning calorimeter. The equipment was calibrated for temperature and enthalpy measurement using indium and pure water as standards. Approximately 20 mg of sample was placed in an aluminum pressure pan and hermetically sealed to prevent water loss due to evaporation. α -Alumina powder was used as the reference material. The samples were scanned from 10 to 100°C at a heating rate of 5°C/min. In the repeat scanning experiment, samples were heated once to 200°C at a rate of 5°C/min, cooled from 200 to 10°C at a rate of 20°C/min, and then reheated from 10 to 100°C at 5°C/min.

2.2. X-ray diffraction measurement

X-ray diffraction measurement was carried out using a PW 3050/10, X'Pert-MPD, Philips Co. (40 kV, 55 mA,

and wavelength, $\lambda = 1.5406 \text{ \AA}$ of Cu) X-ray diffractometer. The scanning region of the diffraction angle, 2θ , was 4.05–69.95°, at an angular interval of 0.1°. An accessory heating unit controlled the sample temperature. Before and after ball-milling, the difference in the moisture was within 2%.

3. Results and discussion

Fig. 1 shows the DSC thermograms of the potato starch at the various milling times from 0 to 70 h, which were measured immediately after ball-mill treatment without any storage time. The DSC curve of the non-milled starch sample (0 h sample) showed an endothermic peak around 60°C. This endothermic peak is not likely to be due to gelatinization of the starch because gelatinization of starch with 16% water content generally occurs at higher temperatures. Thiewes and Steenekens (1997) described a DSC endothermic peak at about 60°C as a “sub- T_g endotherm” in their study of native starch with the same water content as that in the present study. They suggested that this endothermic peak was related to the recovery of enthalpy relaxation or structure in the amorphous portion of the native starch, which had occurred during starch isolation and/or storage. The same phenomenon of enthalpy relaxation may have occurred in the present study. This endothermic peak disappeared after milling for 1 h. However, a new endothermic-like peak of unknown origin reappeared as ball-milling continued. Looking at only the characteristics of the DSC curves obtained for samples milled for longer than 2 h, two mechanisms can be proposed. First, the baseline may shift in

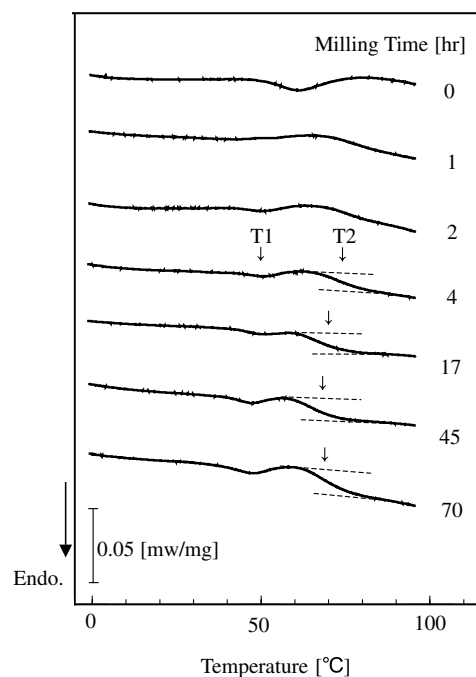


Fig. 1. DSC curves of potato starches after ball-milling for different times. All samples were measured immediately without storage.

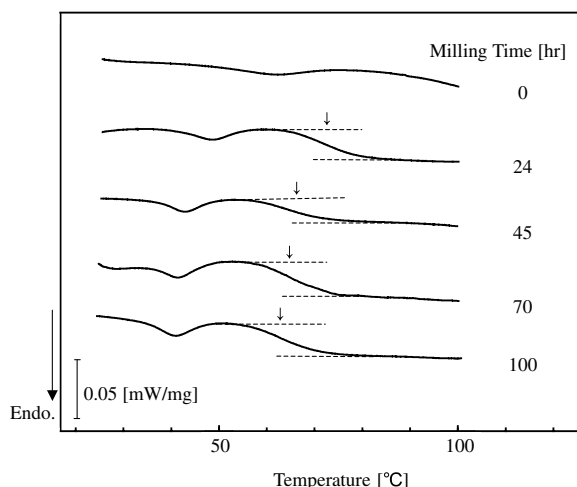


Fig. 2. DSC curves of potato starches stored for 10 days after ball-milling for different times.

the endothermic direction, as denoted by arrows (T_2) in Fig. 1, following the endothermic peak around 50°C (T_1). Alternatively, the DSC curves of these samples may have one broad exothermic peak between 50 and 70°C.

Subsequent analysis using the samples stored for 10 days and a month after milling may provide better insight into these theories (Figs. 2 and 3). Looking at these results, the endothermic peak-like thermal events, not clearly distinguishable in Fig. 1, increased in size and could be clearly observed as a clear peak with increasing storage time. Given these results, it appears more likely that there is a shift in the baseline following the endothermic peak at 50°C. Furthermore, the baseline shift and change in peak height can be

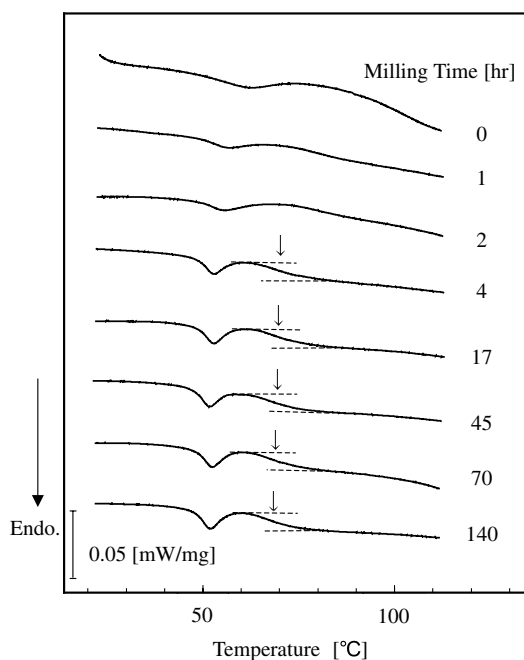


Fig. 3. DSC curves of potato starches stored for a month after ball-milling for different times.

observed in the early stages of milling and increases with milling time, regardless of the storage period. In addition, a downward shift in temperature can be observed for milling times greater than 17 h for both the unstored and 10-day storage conditions. However, this trend is not noted in the 1-month storage condition. Fig. 4 show the first and second scans of the DSC heating curves for native starch (A) and starch that was ball-milled for 100 h (B). While the first scan curves of both samples showed the characteristic peak and/or shift as that noted in Figs. 1–3, the second scan curves demonstrated a simple baseline shift to endothermic with no accompanying peak as indicated by the arrows. This shift seen in the second scan is a typical DSC pattern observed in the glass to rubber transition of amorphous materials. Furthermore, the endothermic shift in the first scan for the ball-milled sample (B) closely resembles the shift in the second scan with respect to the increment in heat capacity and transition temperature region. Based on these results, we assumed that the shift transition denoted by a' in the first scan for milled starch represents the ‘glass to rubber transition’. However, DSC analysis alone provides no direct evidence for the cause of the endothermic peak observed for milled starch.

Fig. 5 shows the X-ray diffraction patterns of the native and ball-milled samples stored for one month. The measurement temperature, 30°C, was below that at which the endothermic peak and baseline shift were observed in the DSC heating experiment. The native starch showed peaks at approximately 17 and 24° (2θ) in the X-ray diffraction pattern, which represents the B-type crystallite. In contrast, starch ball-milled for either 17 or 140 h exhibited no sharp peak, rather a broad shallow peak was observed (Fig. 5). This result strongly suggests that the interior structure of starch milled for at least 17 h, is entirely amorphous at 30°C, in line with other reports (Morrison et al., 1994). Thus, the endothermic peaks observed in Figs. 1–4 do not represent a melting peak. Moreover, the endothermic peak appears to be due to recovery of enthalpy relaxation, as described above for native starch, and the subsequent baseline shift can be attributed to the glass to rubber transition.

We should note the difference in the DSC curves between the second scan of the native starch and the first scan of the milled starch, despite both samples being in the glassy state (Fig. 4). This suggests that the second scan of the native starch showed a simple glass to rubber transition, and thus the starch was in the glassy state just before the reheating. On the other hand, although X-ray diffraction confirmed that the 17 h milled starch was in an amorphous state, the DSC first scan showed a glass to rubber transition accompanied by an endothermic peak attributed to enthalpy relaxation. This characteristic within the DSC curve appears to be common within starches milled more than 17 h.

These results suggest that parameters such as enthalpy and volume of glassy starch formed by milling, which represents the thermodynamic state, are not necessarily consistent with those obtained by the melt and quenching method.

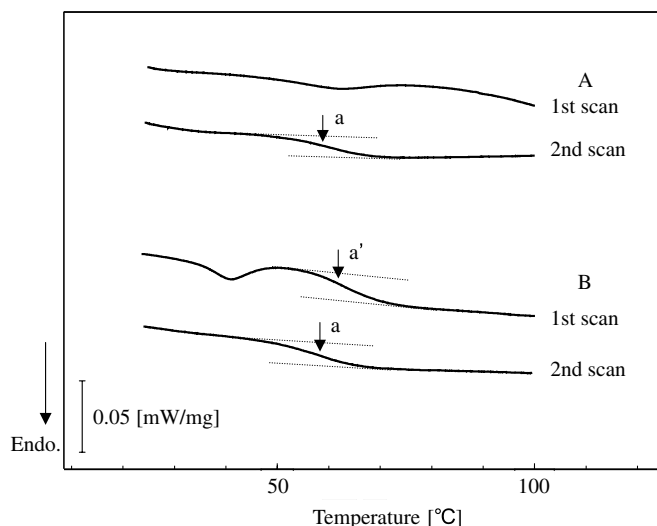


Fig. 4. Comparison of repeated DSC thermograms for (A) native starch and (B) 100 h ball-milled starch. Sample (B) was measured at 10 days after milling. Arrows denoted by (a) and (a'), indicate glass transitions.

Furthermore, as seen from Figs. 1–3, the endothermic peak indicating the degree of enthalpy relaxation increases with milling time, as well as with storage time. Moreover, even the unstored sample after milling exhibits this endothermic peak (Fig. 1), and this peak increases with milling time. Apparently, the ball-milling process seems to accelerate enthalpy relaxation. There are two possible interpretations for this, one is that the impact by ball-milling would act as activation energy to rearrange the molecular arrangement toward equilibrium, in a way similar to heating for aging or annealing. Another is that depolymerization may cause such acceleration. We did not check the molecular weight, however, many researchers (Morrison et al., 1994; Morrison & Tester, 1994; Tester et al., 1994; Adler et al., 1994; Yamada et al., 1997) have suggested that mechanical processing of starch, including ball milling,

causes depolymerization of starch molecules. In this case the enthalpy relaxation of the sample is thought to increase because depolymerized smaller molecules have higher relaxation rates. However, since depolymerization of starch molecules by ball-milling is reported to be slight (Morrison & Tester, 1994), the former explanation is thought to be the most likely. Furthermore, the T_g of the milled starch tended to decrease with milling time during the early stage. In the case of synthetic polymers, T_g is known to increase with increasing degree of crystallinity (Jin, Ellis, & Karasz, 1984). The reversible reduction of the crystalline inner native starch by ball-milling is thought to cause the drop in T_g . On the other hand, the small molecules generated by depolymerization might act as a plasticizers, and thus depress the T_g . At the same time, depolymerization would cause a decrease in molecular weight of large molecules that have high T_g , resulting in decreased T_g . Whatever the mechanism, the milling process for starch appears to lead to a depression in T_g .

X-ray diffraction analysis at 10° intervals, while heating in parallel with the DSC heating experiment, of starch milled for 140 h from 30 to 80°C revealed structural changes (Fig. 6). At all temperatures, the diffraction signals showed a halo peak, which represents an amorphous structure. However, there was a slight shift of the peak positions to smaller angles with increasing temperature. In general, the X-ray diffraction angle 2θ is related to spatial parameters such as lattice distance by following Bragg's equation

$$d = \lambda / 2 \sin(\theta) \quad (1)$$

where d is the lattice distance and λ is the X-ray wavelength. Though this equation satisfies ordered material systems such as crystals, it does not appear to be applicable to amorphous materials. In an amorphous system, a radial distribution function, which can be calculated from X-ray

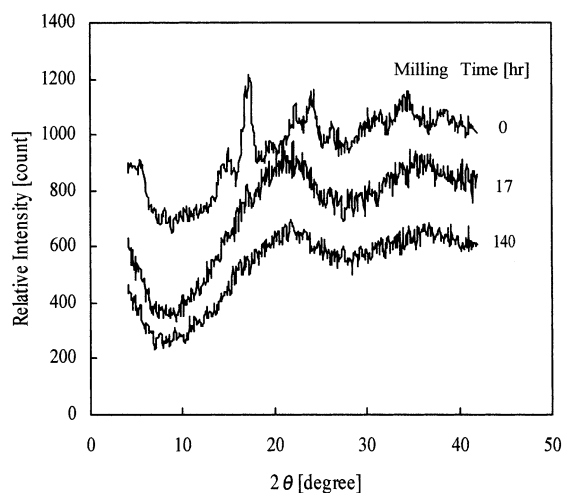


Fig. 5. X-ray diffraction patterns for (a) native starch; (b) 17 h ball-milled starch; and (c) 140 h ball-milled starch.

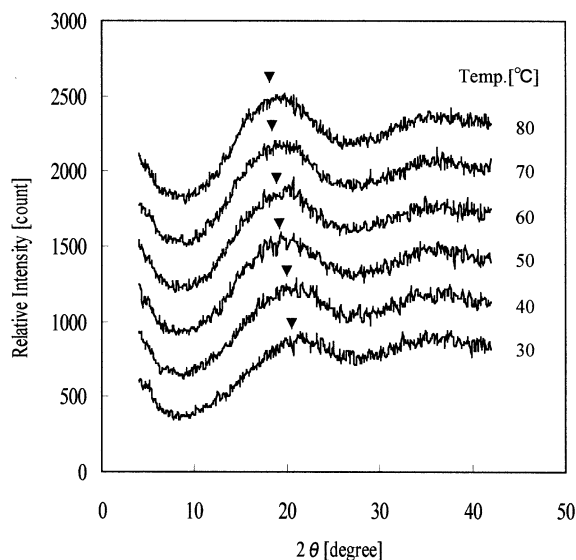


Fig. 6. Change in the X-ray diffraction patterns of 140 h milled starch during heating.

diffraction, should be used for detailed analysis. However, in the case of a heterogeneous system in atomic composition such as starch, the calculation of the radial distribution becomes complicated because the X-ray diffraction information from the multi-atomic system should be considered in the characteristic scattering factor of each atom (Zarzycki, 1991). In the present study, we assumed that d calculated in Eq. (1) is an apparent spatial parameter, reflects the degree of molecular packing. The higher the molecular packing density, the smaller the 'd' values. If the composition of materials is constant, then the above assumption is not far-fetched. Thus, we plotted the d value calculated from the diffraction angle associated with the peak against temperature (Fig. 7). This graph showed a tendency for d to increase with increasing temperature. This relationship seems to indicate the occurrence of thermal expansion. For comparison, the DSC curve of the same sample with that used in the X-ray diffraction experiment was interposed in Fig. 7. This showed that the d value increases remarkably at temperature ranges related to the recovery of enthalpy relaxation and the glass to rubber transition in the DSC curves. In general, the glass transition and the recovery phenomena of the relaxed physical state can be characterized by the temperature dependence in the specific heat and/or thermal expansion coefficient.

We did not measure the moisture change during heating in the X-ray experiment. The apparent Bragg spacing d detected in this X-ray experiment would reflect almost the position of carbohydrates because the scattering from water is considerable smaller than that from carbohydrates. Therefore, even if a loss of water occurred, it would have little effect on the X-ray detected density, since the initial water content was small, i.e. 16%. In addition, if water was lost with heating, the sample density would increase because of shrinkage. However our experimental result showed a

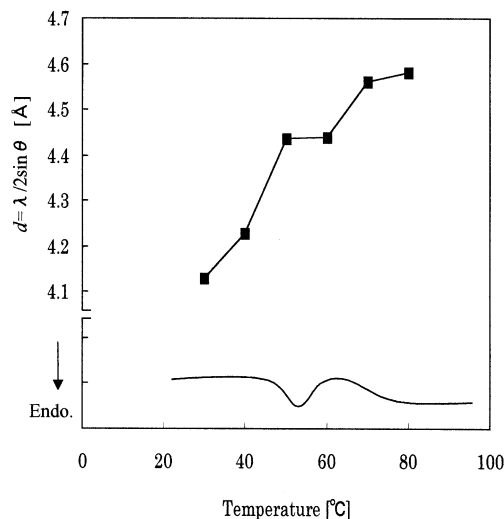


Fig. 7. Change of apparent lattice distance, d , of 140 h milled starch during heating. The d values were calculated using Bragg's equation from peak top angles shown in Fig. 6. For comparison, DSC curves of same samples are superimposed.

reversible decrease in density. In particular, the rate of decrease was high in the transition temperature range. Therefore we believe that the effect of a water loss is negligible. However, due to the degree of uncertainty in the X-ray diffraction data, we cannot derive solid conclusions concerning the behavior of d . If more precise X-ray experiments could be applied to this study, we may gain a better insight into the physical state of amorphous starch.

We then plotted the thermal dynamic state of the ball-milled starch (Fig. 8). In general, when material in a molten liquid state (e) is cooled down very quickly, the state of the material leaches to a glassy state (a) through a glass

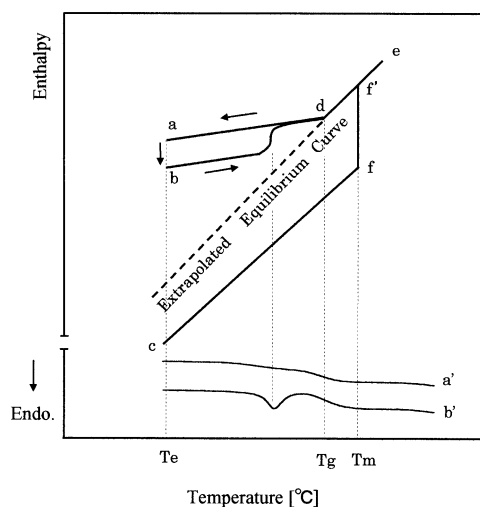


Fig. 8. Schematic representation of the change in enthalpy of starch on heating, cooling and ball-milling. As reference, corresponding DSC thermograms of 17 h ball-milled starch were superimposed. Each curves of a' and b' shows the second and first heating processes, respectively.

transition point (d). This is thought to be the process by which glass can be formed. When starch is heated and quenched, glassy starch is formed through the same process. When freshly formed glassy materials (a) are stored, they often undergo alteration in physical properties such as changes in enthalpy of glass as a function of time, even at temperature below T_g . The enthalpy then drops toward point (b). This is because the properties of the glassy material in the non-equilibrium state continue to undergo relative slow relaxation toward equilibrium, even below the glass transition temperature (Struik, 1978). However, in the case of the ball-milling process, native starch (c) does not pass through the route (c–f–f'–e–d–a), which is the route of the heat and quench method. After milling for a relatively long period, the starch reaches point (b) where enthalpy relaxation occurs. We superimposed the DSC thermograms, (a') and (b'), which are obtained when the material is in state (a) and (b), as references (Fig. 8). Although the precise route taken in ball-milling remains unclear, the present results indicate that the process taken for the native starch to arrive at point (b) is as follows: by ball-milling of early stage, native starch (c) yields an almost completely amorphous material which subsequently leaches near point (a) of high enthalpy. This process corresponds with that observed in the present study in starch that has undergone ball-milling for at least 17 h. Ball-milling beyond this time tends to lower enthalpy, from near (a) to (b). The reason for this remains unclear. Repeated weak impacts during ball-milling may give the necessary activation energy for diffusion of molecules in the solid state to rearrange to a more energetically favorable conformation. The result of this effect would be acceleration of enthalpy relaxation.

4. Conclusions

The present results demonstrate that ball-milling under ambient temperature converts native starch to the relaxed glassy state, which exhibits a glass to rubber transition, accompanied by recovery of enthalpy on heating. The ball-milling process accelerates enthalpy relaxation, which is similar to that which occurs during the so-called “aging process” near T_g . These results suggest that the ball milling process provide an alternative way to make glassy starches of different states. Furthermore, our results suggest that X-ray diffraction technique may be applicable in the detection of the glass–rubber transition and structural changes in the glassy state, although further study is required. Thus, mechanical processes such as ball milling may provide not only a chemical function, but also a physical function in starch by controlling its enthalpy and/or molecular density.

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