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Relationship between enthalpy relaxation and water sorption of ball-milled potato starch

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ABSTRACT

This study reports on the enthalpy relaxation and water sorption behaviors of ball-milled potato starch. Ball milling converts the semi-crystalline state of starch to an amorphous state, and a prolonged procedure promotes enthalpy relaxation. It has been reported that prolonged treatment leads to a decrease in starch water sorption. In the present study, ball milling of potato starch was carried out for up to 90 h. The relaxed enthalpies and water sorption isotherms were measured by differential scanning calorimetry and equilibrium sorption of water vapor. Enthalpy was found to increase and water sorption to decrease with milling time. The time-dependant increase in enthalpy was found to follow the Kohlrausch–Williams–Watts (KWW) equation. The sorption isotherms were analyzed with a dual-mode sorption model and the concentration, C'_H, of Langmuir type sorption sites was found to decrease with time. This decrease was also found to follow the KWW equation. Moreover, a linear relationship was found between the decrease in C'_H and the increase in enthalpy.

1. Introduction

Many studies have reported on the enthalpy relaxation of natural and synthetic polymers (Struik, 1978; Roos, 1995; Yoshida, 1995; Drozdov, 2000; Kim et al., 2003; Kawai et al., 2005). It is known that certain macroscopic properties, such as density, mechanical strength, and vapor permeability, are accompanied by a time-dependent relaxation in amorphous glassy polymeric materials, including foods. Roos (1995) summarized that the relaxation can be related to changes in various physical states of the glassy structure of foods.

Kawai et al. (2005) studied the activation energy of the relaxation related stability of sugars (trehalose, sucrose, maltose, and glucose) and found that the energy for glassy trehalose was the highest among the four sugars. They concluded that trehalose glass was the most stable sugar below the T_g.

Shogren (1992), Livings et al. (1997), Thiewes and Steenken (1997), and Bizot et al. (1997) have reported a phenomenon known as enthalpy relaxation in molten starch systems. Kim et al. (2003) pointed out that the water vapor permeability of glassy starch films decreases with increasing aging time, at a temperature below the T_g, as a result of the relaxation. When aging below the T_g, the state of an amorphous starch quickly relaxes to a stable energy state. However, the relationship of relaxation to other physical properties of starch has not been studied in detail. It is also expected that for starches in various amorphous states, studying the glass transition phenomena may provide a better understanding of the detailed structural alterations. In the fields of polymer science and metallurgy, mechanical operation of ball milling is known to lead to glass formation of materials (Elliott, 1990). Ball milling has also been applied to starch for conversion of its physico-chemical properties (Morrison and Tester, 1994; Morrison et al., 1994; Tester et al., 1994; Yamada et al., 1997; Tamaki et al., 1997). With ball milling of semi-crystalline native starch, the crystalline region is destroyed, leading to slight depolymerization and an increase in the amorphous structure. This occurs even when milling is performed under ambient temperature in a dry state.

Kim et al. (2001a,b) reported that prolonged ball milling, extending to the period after potato starch is converted to an amorphous state, still promotes starch relaxation. This means that ball milling can modify the amorphous state as a result of the relaxation. Moreover, we have reported preliminarily that prolonged treatment results in a decrease in water sorption ability (Kim et al., 2001a,b; Suzuki et al., 2002). However, until now the relationship between enthalpy relaxation and water sorption behavior has not been discussed in detail. The present study reports some physico-chemical changes in potato starch as a result of ball milling for 0–90 h at room temperature. The crystallinity was evaluated using X-ray diffractometry. Relaxed enthalpy, ΔH, was evaluated using differential scanning calorimetry. In addition, the water sorption isotherms of the ball-milled starches were measured by a conventional desiccator method, and analysed with a dual-mode sorption model (Kim et al., 2001a,b; Suzuki et al., 2002).

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2. Materials and methods

2.1. Materials

Potato starch supplied by Wako Pure Chemicals Industries, Ltd. (Osaka, Japan) was used as received. The initial moisture content before milling was 16.0 w/w%.

2.2. Ball milling procedure

Ball milling was carried out by using a rolling-type ball mill (Irie Shokai V-1, Kanagawa, Japan). Stainless steel balls (384 g) 1 cm in diameter were added to 15 g of starch in a stainless steel cylindrical container 9 cm in diameter. The container was tumbled at 90 rpm for 0–90 h at room temperature.

2.3. Wide angle X-ray diffraction measurement

The measurement was performed using a benchtop X-ray diffractometer (MiniFlexII, Rigaku, Tokyo, Japan). The measurement was carried out at 30 kV and 15 mA with Cu Ka radiation of wavelength $\lambda = 1.54$ Å of Cu at a scanning rate of 2° (2θ)/min with a 4–40° scanning range of the diffraction angle at 0.1° intervals.

2.4. Differential scanning calorimetry (DSC)

The measurement was performed on a DSC (DSC-50, Shimadzu, Kyoto, Japan). The equipment was calibrated for temperature and enthalpy using indium and pure water as standards. Approximately 25 mg of the starch powder was placed in an aluminum pressure pan and sealed to prevent water loss due to evaporation. α-Alumina powder was used as the reference material. The samples were scanned from −10 to 180 °C at a heating rate of 5 °C/min.The area of the endothermic peak (ΔH) was determined using following equation:

$$\Delta H = \int Cp_{\text{milling}}(T)dT - \int Cp_{\text{non-milling}}(T)dT \qquad (1)$$

where Cp_{milling} and $Cp_{\text{non-milling}}$ are the specific heat of milling starch and non-milling starch (native starch), respectively. These thermal analyses were performed using the analysis software TA-60WS (Shimadzu Kyoto, Japan).

2.5. Water sorption measurement

Water sorption isotherms were determined for ball-milled samples over a range of milling times. Approximately 0.3 g of the samples were left for 7–8 days to attain the sorption equilibrium at 25 °C in a humidity controlled semi-micro desiccator using various saturated salt solutions as follows; NaOH, LiCl, CH_3COOK, $MgCl_2{\cdot}6H_2O$, Mg $(NO_3){\cdot}6H_2O$, NaCl, KCl, KNO_3, of which water activity (a_w) at 25 °C was 0.070, 0.110, 0.224, 0.330, 0.528, 0.752, 0.842, 0.924, respectively (Greenspan, 1977). The initial water content under ambient conditions was precisely measured and referred to as the dry state. The starch content of the equilibrated samples was determined by the dry-oven method at 105 °C.

3. Results and discussion

3.1. Crystallinity

X-ray diffraction measurements have been widely used to study the structure of semi-crystalline carbohydrate polymers. Wide angle X-ray diffraction provides information on the inter-atomic length scale; in the case of starch, it has been used to identify the crystalline polymorphs of the amylopectin helices (Imberty et al., 1991).

The results of the X-ray diffraction measurements are shown in Fig. 1. The sharp peaks around 2θ = 17° represent the diffraction by the crystalline parts (B-type crystalline) of native and ball-milled potato starches (Kim et al., 2001a,b). However, the diffraction patterns of ball-milled potato starches exhibit increasing broad blunt peaks with increased ball-milling time. It is found that every potato starch's parts are almost fully amorphous at 17 h of ball milling. Kim et al. (2001a,b) reported that starches ball-milled for either 17 or 140 h exhibited no sharp peak, but rather a broad peak was observed. The present results also suggest that the internal structure of the starch milled for at least 17 h is entirely amorphous at 30 °C, which is in line with previous studies (Morrison et al., 1994; Tamaki et al., 1997).

Morrison and Tester (1994) found that the amylose content of wheat starch does not change with prolonged ball-milling time, while the low molecular weight amylopectin content is increased accompanying a decline in the crystallinity. Hoseney (1998) reported that ball milling of wheat starch at room temperature eventually completely destroys both the birefringence and the XRD pattern. The semi-crystalline granules of the starch largely preserve its glassy state; the milled starch absorbs a relatively small amount of water (Matveev et al., 2000).

The crystallinity of each starch was calculated from the patterns shown in Fig. 1. The diffraction intensity of 4a was assumed to be an index of the peak that originated in the crystal portion of each starch. The crystallinities of native potato starch and 17 h ball-milled starch were assumed to be 25% (Zobel and Senti, 1960) and 0% (completely amorphous state), respectively, on which the crystallinities of each ball-milled starch were calculated. The calculated values are shown against ball-milling time in Fig. 1. As shown in this figure, the crystallinity decreases in the initial 4 h of ball milling, after which it decreases moderately during prolonged milling. It is known that parts of the straight chains in the non-reducing termini of the amylopectin side chains form double helices (Kainuma and French, 1972). These helices are arranged in parallel composition with hydrogen bonding between adjoining glucose residues (Stein and Rundle, 1948). This is the basis of crystal formation in starch. The complete destruction of the crystals by prolonged ball milling suggests that hydrogen bonds are broken, disintegrating the crystalline arrangements of the helices. This ef-

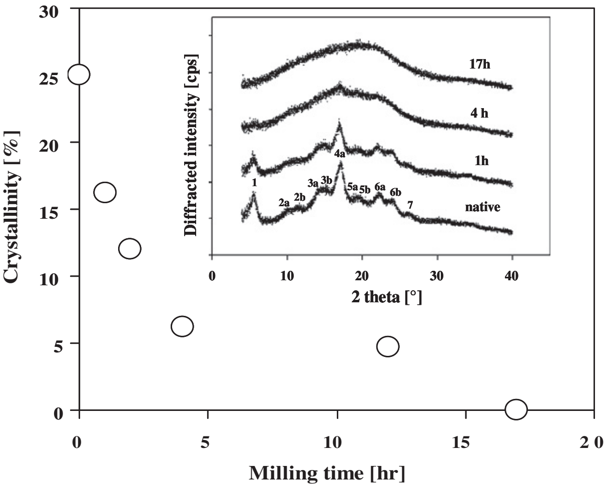

Fig. 1. X-ray diffraction patterns of native and ball-milled potato starches and change in the crystallinity of potato starch with ball-milling time. The diffraction intensity of 4a was assumed to be an index of the peak that originated in the crystal portion of each starch.

fect may result in the increased exposure of hydroxyl groups in the amylopectin chains (Devi et al., 2009). As shown in Fig. 1, ball milling changes the crystal into a substantially amorphous state in 4 h. It is thought that the physical impact that starch receives from ball milling enables the collapse of the basic crystalline structure of the starch with newly forming hydrogen bonding. Such a reforming process may also take place in the amorphous state of the starch (Kiburn et al., 2005).

3.2. Enthalpy relaxation

DSC curves of the native (0 h ball-milled) and the 90 h ball-milled starches are shown as typical results in Fig. 2. The DSC curve of the native starch sample showed an endothermic peak approximately at 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 (Kim et al., 2001a,b). Thiewes and Steenken (1997) reported a DSC endothermic peak at approximately 60 °C for 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.

For the ball-milled starch, the endothermic peak overlapped with the glass transition. Although not shown for all milling times in Fig. 2, this endothermic peak developed with increasing milling time. Apparently, the milling process promotes enthalpy relaxation. Two possible interpretations for this have been presented (Kim et al., 2001a,b). One is that the impact of ball milling may provide activation energy for the endothermic phenomenon of rearranging the molecular arrangement of chains toward equilibrium; the ball milling process accelerates enthalpy relaxation, which is similar to that which occurs during the so-called aging process with heating, or annealing process. The second is that depolymerization may promote this effect. Although we did not check the molecular weight change of the ball-milled starch in the present study, some researchers (Yamada et al., 1997; Tamaki et al., 1997; Alder et al., 1994) have suggested that mechanical processing of starch, including ball milling, causes depolymerization of starch. If this is the case, the enthalpy relaxation of the sample is thought to increase with milling because depolymerized smaller molecules have higher enthalpy relaxation (Kim et al., 2001a,b). However, Morrison et al. (1994) have definitely shown that depolymerization of starch molecules by ball milling hardly takes place. It is likely that the former interpretation is inadequate for the relaxation mechanism of the starch by ball milling.

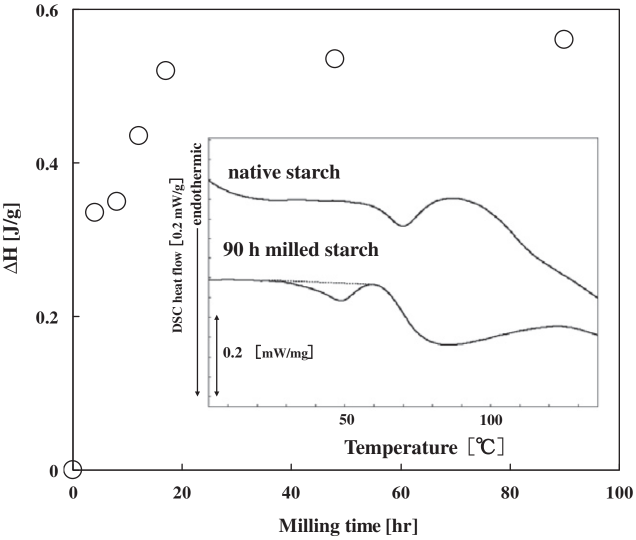

Fig. 2. DSC curves of native and 90 h milled starches and dependence of ΔH on ball-milling time. ΔH was determined using Eq. (1).

ΔH values for potato starch as a function of ball-milling time from 0 to 90 h are shown in Fig. 2, and indicate an increasing trend with increasing milling time up to ca. 20 h, leveling off thereafter.

Using this data, we verified the applicability of the Kohlrausch–Williams–Watts (KWW) equation for describing quantitatively the enthalpy relaxation process of potato starch (Williams and Watts, 1970)

$$\phi(t) = \exp[-(t/\tau)^{\beta}] \tag{2}$$

where, τ is the mean relaxation time constant and β is the relaxation time distribution parameter. Typically, the enthalpy relaxation in amorphous polymeric substances is non-exponential, for β takes a value between 0 and 1.

In this study, τ was calculated by fitting ΔH_t values in the form of Eq. (3)

$$\frac{\Delta H_t - \Delta H_\infty}{\Delta H_0 - \Delta H_\infty} = \exp\left[-(t/\tau)^{\beta}\right] \tag{3}$$

where, ΔH_0 is the value of enthalpy relaxation at $t = 0$. For the ball-milled starch, the increase in enthalpy relaxation showed non-linear dependence on t, as shown in Fig. 2. For such a case, the KWW equation has been rewritten to a linear relationship of double logarithm of $(\Delta H_t – \Delta H_\infty)/(\Delta H_0 – \Delta H_\infty)$ (Shamblin and Zografi, 1998; Liu et al., 2007):

$$\ln\left[-\ln\left(\frac{\Delta H_t - \Delta H_\infty}{\Delta H_0 - \Delta H_\infty}\right)\right] = \beta \cdot \ln t - \beta \cdot \ln \tau \tag{4}$$

τ and β were calculated using Eq. (4) by assuming an appropriate ΔH_∞ to linearize the plot of the left hand side of Eq. (4) against ln t. The best-fit linear regression with $\tau = 0.53$ h and $\beta = 0.55$ is shown in Fig. 3. This τ value is substantially shorter as compared with the τ, 100 h, of the physical aging of the starch (Hancock et al., 1995). However, under ball milling, which exerts various stresses to the material, the time constant should be far shorter than that under physical aging. As it is, ball milling accelerates the relaxation to a considerable degree.

3.3. Water sorption

Water sorption isotherms of the starches ball-milled for different times are shown in Fig. 4. These were remeasured in the present study to confirm the small changes in the sorption of ball-milled starches. It is apparent that water sorption ability by the ball-milled starch decreases with milling time. The contrary has

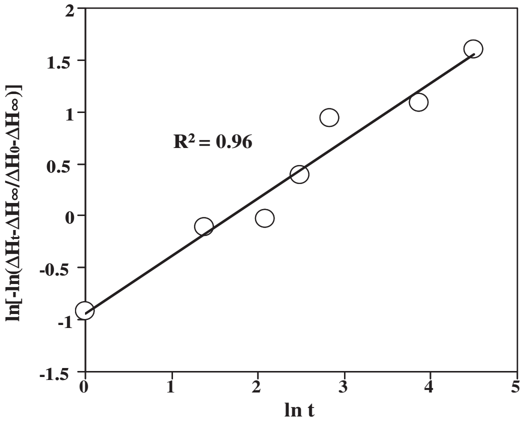

Fig. 3. The best-fit linear regression of Eq. (4), ΔH_∞ was assumed to be 0.56.

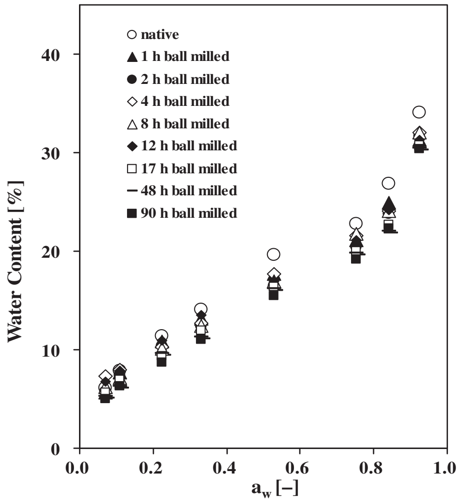

Fig. 4. Water sorption isotherms (25 °C) for potato starches ball-milled for different times.

been thought, that the ball-milled starch becomes more water absorbent due to the destruction of the crystalline portion (Yamada et al., 1997; Tamaki et al., 1997). Later, Yamada et al. (1997) reported that the water holding ability of milled starch increases with milling time. The increase of the water sorption which they reported means that the swelling property of starch increases under excess water condition. Therefore, it is different from the water sorption properties in the monomolecular sorption region that we described in the present study. Thus, it can be said that it is adequate result that the water sorption ability of milled starch decreased in the present study.

It has been reported that physical aging of some synthetic polymers (Nagai and Nakagawa, 1995; MaCaig and Paul, 1999, 2000) results in a decrease in water vapor permeability with the increase in aging time. Especially for potato starch, the mechanism of such a permeability reduction was explained in terms of reduction of the "free volume", which is defined as a vacant space not occupied by the local structure of the polymer molecule (Kim et al., 2001a,b; Suzuki et al., 2002).

For a more detailed quantitative analysis of the present isotherms, we applied a dual-mode sorption model (Odani, 1995) to the isotherms, Eq. (5), combining the Henry's and Langmuir mode sorption equations. Eq. (5) is successfully applied to the analysis of the sorption of many penetrants by glassy polymers, including starch (Kim et al., 2001a,b; Suzuki et al., 2002; Ubbink et al., 2007)

$$C = k_d a_w + \frac{C'_H b a_w}{1 + b a_w} \tag{5}$$

where, C and a_w are the total amount of sorption and relative vapor pressure of penetrant, respectively; k_d, Henry's constant; b, the affinity constant to the Langumuir type sorption site; and C'_H is the capacity constant of the Langumuir site. In the present study, a_w was used in place of p (Kim et al., 2001a,b; Suzuki et al., 2002).

Eq. (5) is rearranged to Eq. (6) between $1/(C–k_d{\cdot}a_w)$ vs. $1/a_w$ (Komiyama and Ijima, 1974)

$$\frac{1}{(C - k_d a_w)} = \frac{1}{C'_H b}\left[\frac{1}{a_w}\right] + \frac{1}{C'_H} \tag{6}$$

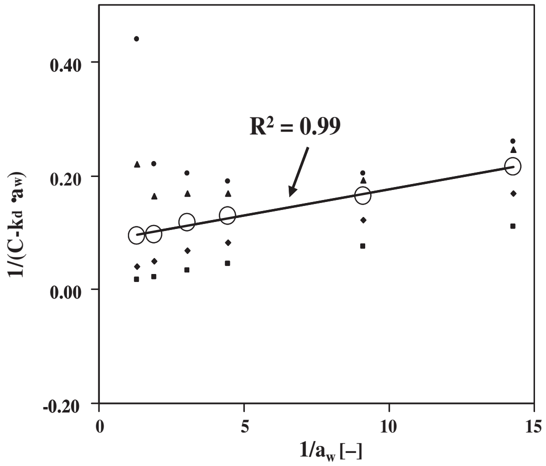

Fig. 5. An example of linearizing plot of Eq. (6) for ball-milled potato starch.

Table 1
Change of parameters in the dual-mode sorption model equation, Eq. (6), representing the change for water sorption ability of potato starch during ball-milling.

Milling time (h)	C'_H (%)	b (atm^{-1})	k_d (cm^3 g^{-1})
0	16.4	6.7	10.5
1	15.2	6.8	10.0
2	14.0	8.0	9.0
4	13.9	11.6	8.0
8	13.7	9.3	9.0
12	12.9	11.6	10.5
17	12.2	9.1	10.0
48	12.0	7.9	10.5
90	11.0	8.5	10.5

By assuming an appropriate k_d, C'_H and b were obtained from the slope and the intercept of the linear relations. An example of such plots by Eq. (6) for the ball-milled potato starches is shown in Fig. 5. Values of C'_H, b and k_d are shown in Table 1. In the table, C'_H values show a reasonable decreasing trend with the ball-milling time, while k_d values are seen to be reasonably constant. The scattered values of b may be a result of the uncertainty in the curvature of the isotherms in an a_w range of less than ca. 0.15.

Change the C'_H value is shown in Table 1, which indicates that C'_H decreases monotonically with the milling time. This result shows definitely that the milling process reduces the water sorption ability of potato starch through the reduction in C'_H. For water vapor permeability experiments, it has been reported for several starches (Kim et al., 2003) and synthetic polymers (MaCaig and Paul, 1999, 2000) that water permeability tends to decrease with increasing aging time. Although the reduction in water permeability by milling has been discussed in terms of the decrease in free volume with the proceeding of relaxation, the present results, that C'_H of the starch decreases with ball milling, may give a more detailed insight into the decrease in the free volume; the decrease in Langmuir type sorption sites is the origin of the decrease in the apparent diffusion coefficient.

The other two parameters, b and k_d, of the Langmuir sorption are also shown in Table 1. Although b values show a scatter between 6.7 and 11.6, as discussed above, k_d values, representing the strength of partition type sorption, show almost no change with milling time.

A possible interpretation of the decrease in C'_H with milling time may be that the decrease in the concentration of Langmuir type sorption sites is accompanied by a decrease in the relatively strong interaction with water molecules due to decreased –OH group accessibility (Kiburn et al., 2005). Further study may advance the interpretation of the detailed molecular scheme of water sorption of ball-milled potato starch.To further advance the decreasing phenomena of C'_H, we rewrote the KWW equation in terms of $C'_{H,}$ as:

$$\ln\left[-\ln\left(\frac{C'_H - C'_{H,\infty}}{C'_{H,0} - C'_{H,\infty}}\right)\right] = \beta \cdot \ln t - \beta \cdot \ln \tau \tag{7}$$

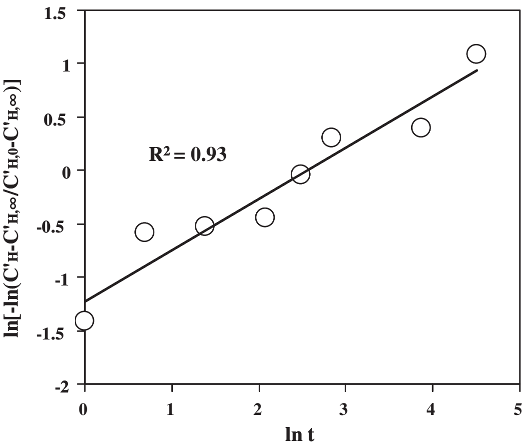

Fig. 6. The best-fit linear regression of Eq. (7), $C'_{\mathrm{H},}$ was assumed to be 10.8.

where, $C'_{\mathrm{H},}$ and $C'_{\mathrm{H},0}$ are the final and initial values of C'_{H}, respectively. For the starch, a non-linear dependence of C'_{H} on t is shown in Fig. 4. By taking the double logarithm of Eq. (7) on assumed $C'_{\mathrm{H},}$, the linear relationship shown in Fig. 6 was obtained. The result shows that the decreasing behavior of C'_{H} with ball-milling time also conforms to the KWW type equation. The parameters, τ and β for the best-fit were found to be 0.94 h and 0.48, respectively. These values are comparable to those, 0.53 h and 0.55, found for the plot of ΔH vs. t. This fair agreement seems to support the interpretation that the increase of the endotherm with milling and the decrease of Langmuir sorption sites are concomitant. In other words, the structural change of the starch toward a more endothermic state accompanies lessening of the water sorption sites with certain interactions.

3.4. Relationship between enthalpy relaxation and water sorption

A plot between C'_{H} and ΔH is shown in Fig. 7, where a linear reciprocal relationship between them is the definite trend. This correlation again implies that on milling, an enthalpy increase accompanies a decrease in the concentration of Langmuir type adsorption sites. In the fields of starch and synthetic polymers, this type of reciprocal relationship between the two properties has been previously reported. In fact, with amorphous copoly (vinylidene chloride–vinyl acetate), Hachisuka et al. (1988) showed that the increase in the enthalpy relaxation during aging accompanies the decrease in the C'_{H} determined from the CO_2 sorption. They concluded that the sorption ability of the penetrant into the amorphous polymer decreases as the free volume, accompanied by the relaxation, increase. Thus, for quite different polymeric systems, the increase in the endothermic process gives rise to the same decreasing effect on the change in C'_{H}; C'_{H} decreases both for the aged synthetic polymer as well as for the ball-milled starch. Such an agreement seems to suggest that the molecular processes of aging and milling are similar.

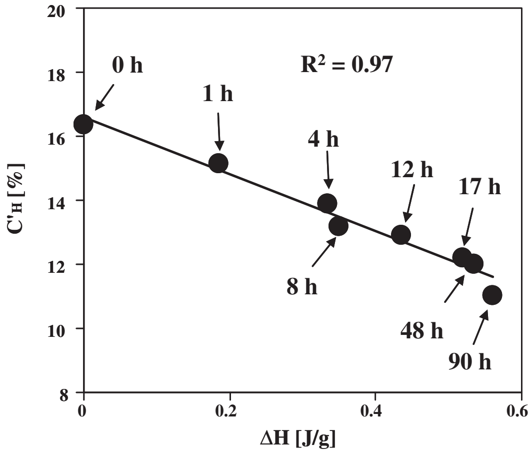

Fig. 7. C'_{H} vs. ΔH plot for starches subjected to different milling times.

4. Conclusion

Consistent with our previous study, ΔH of amorphous starch was confirmed to increase with increasing ball-milling time. The water sorption decreased with increased milling time. The KWW equation applied to the changes in ΔH and C'_{H} with ball milling revealed that τ and β values for the changes are in fair agreement. A linear reciprocal relationship was found between ΔH and C'_{H}. Although the physical meaning of this relationship is not yet clear, in terms of the mechanical rearrangement of the macromolecules comprising starch, this correlation suggests that the decrease in the C'_{H} concentration of potato starch may be a result of structural alteration upon milling, which leads to enthalpic relaxation upon heating.

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