

Water Sorption for Amorphous Starch and Structural Relaxation by Ball Milling

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Recently, we reported that the ball milling for starch, converts the semi-crystal state to an amorphous state, and the prolonged procedure promotes the enthalpy relaxation, substantially accompanied with the structural relaxation such as a decrease of free volume [1]. From such a result, it is predictable that the prolong ball milling might cause a decrease of water sorption ability by decreasing the free volume. In this study, to confirm the above presumption, the change of water sorption properties by milling for amorphous starch was investigated. Ball milling for potato starch was carried out at room temperature for 1hr, 2hr, 4hr, 17hr, 45hr, and 140hr. The water sorption isotherms for each milled samples were measured by a conventional desiccators method, and analyzed by a dual mode sorption model to obtain a so called sorption capacity parameter that relates to the free volume in an amorphous polymer. The result surely showed a decrease of the water sorption capacity with milling time, which supported our presumption. Further analysis, as for the rate process, elucidates that a decreasing rate process on water sorption ability of starch during milling obeys the so-called KWW equation that has been applied for relaxation processes of amorphous polymers. From these results, it was suggested that long ball milling for starch would cause the structural relaxation, and result in the decrease of water sorption ability.

Key words: starch, amorphous, enthalpy relaxation, water sorption, ball mill

1. Introduction

Change in the amorphous state of food material below the glass transition temperature, that is structural and enthalpy relaxation, affects the stability during storage, leading to macroscopic properties such as density, elastics, and sorption properties. Understanding their behavior was a large topic even at the recent conference, "Amorphous State – a Critical Review", held in May 2001 in the UK [2]. As for starch, the relaxation phenomenon of enthalpy has been reported by several researchers [3,4,5,6]. Due to aging near the glass transition temperature, the state of an amorphous starch relaxes to stabilize the energy state. That is, a fresh amorphous starch should be distinguished in the state from the older ones. We have also reported that the prolong ball milling procedure after the starch converted to the amorphous, did promote the enthalpy relaxation [1]. Thus, ball milling can easily make an enthalpic relaxed amorphous starch. As so, the enthalpy relaxation phenomenon for starch has been

well recognized, however, even nowadays there is limited information as to the correlation between enthalpic relaxation of starch and their physical properties.

Water sorption ability among the physical properties of starch, is a well-investigated issue in relation to the inner structure. Some reports elucidated that the water sorption ability of starch increases as the crystalline decreases [7,8], since the crystalline in starch has less ability in water sorption than that of amorphous portion. This result is also supported by the general view from a semi crystalline synthetic polymer, that sorption of solvent to the polymer is proportional to the portion of amorphous [9]. On the other hand, it is well known that a mechanical operation such as milling of starch causes breaking of inner crystalline structures of starch and/or molecular chains, and converts into damaged starch or amorphous starch [10]. When we consider the water sorption of starch in relation to such structural changes, milled starch should show higher water sorption ability than native semi-crystalline starch. Yamada et al. [11] reported that water holding ability of milled starch increases with milling time.

However, according to our previous study [1] on

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enthalpy relaxation by ball milling, conversely it is predictable that prolong ball milling might cause a decrease of water sorption with enthalpy relaxation. That is why the enthalpy relaxation of amorphous materials is substantially accompanied with the structural relaxation such as a decrease in the free volume which is acceptable for the space of water molecules. In this study, in order to confirm the above presumption, the change of water sorption properties by prolonged ball milling of starch was investigated, and discussed in relationship with the free volume using a dual-mode sorption model which has been used for analysis of penetrant sorption into an amorphous polymer [9]. Furthermore, the decreasing process rate on water sorption ability of starch during milling was discussed considering the analogy with the relaxation process of amorphous polymers.

2. Materials and Methods

2.1 Ball Milling procedure

Potato starch (Wako Chemical) was used without any treatment. The initial moisture before milling was constant (ca.16%). Ball-milling was carried out using an Irie Shokai V – I. The stainless balls, 1cm in diameter (total weight, 297 g), were added to 10 g of potato starch in a stainless cylindrical container with a diameter of 9 cm and a height of 9 cm. The cylindrical container was tumbled at room temperature for 1hr, 2hr, 17hr, 22hr, 45hr, and 100hr at 90rpm. This milling condition was the same as that in the previous experiment [1] for enthalpy relaxation. During tumbling, the increase in the sample temperature was confirmed to be within 5°C

2.2 Water sorption

Each milled sample during a given hour underwent the measurement of water sorption isotherm. About one gram of the samples was left in humidity controlled desiccators using various saturated following salt solutions as follows; NaOH, LiCl, CH₃COOK, MgCl₂·6H₂O, Mg(NO₃)₂·6H₂O, NaCl, KCl, KNO₃, of which water activity *A_w* at 25°C were 0.070, 0.110, 0.224, 0.330, 0.528, 0.752, 0.842, 0.924, respectively [12]. The initial water content was not controlled, however, it was in the range of 14% to 16% (dry base). The solid content of the sample was determined by the dry-oven method at 110°C. The sample weight which was left in the desiccators was measured at intervals of about 4 to 12 hours. When the decrease of the sample weight showed less than 0.005g/1g after 12 hours, it was considered that the equilibrium in the water content was

attained. In most of the cases, it took about 2-3 days to attain the equilibrium.

3. Results and Discussion

All water sorption isotherms of the potato starch milled for a given hour were typical sigmoidal BET type curves as shown in Fig. 1. It can be seen that the sorption isotherms shows a trend to shift down with increasing milling time. Particularly, there seemed to be a significant difference between native starch, (i.e.0 hr milling) and a 100 hrs milled sample. In our previous report [6], it was confirmed that milling of native potato starch, which was done under the same conditions in this research, converts perfectly to an amorphous state within a few hours, and also subsequent 100 hrs milling gives a considerable enthalpic relaxation progress as shown in Fig. 2. Indeed, the obtained result substantially supports our presumption that enthalpy relaxed amorphous starch might show a lower ability on water sorption.

For a more detailed quantitative analysis, we attempted using a dual-mode sorption model [9] combined of the Henry's Law and the Langmuir sorption equation, instead of the BET analysis. The dual mode model is often used for analysis on sorption of penetrant to a glassy polymer, which is expressed by Eq.1,

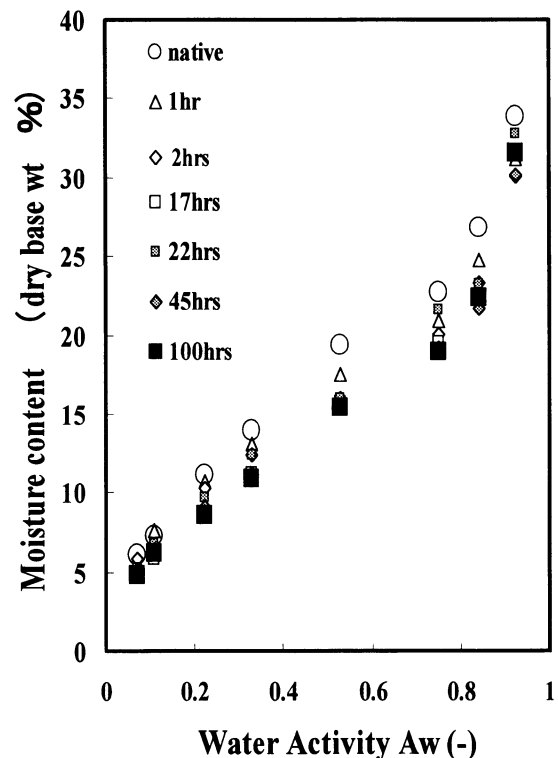


Fig. 1 Water sorption isotherms at 25°C for potato starches after various mill times.

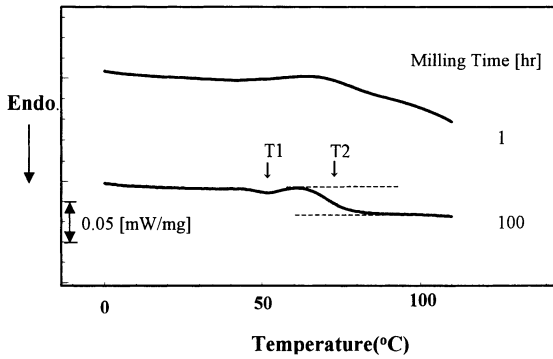


Fig. 2 DSC warming curves of dry potato starch milled during different times, 1hr and 100 hrs (reproduced from ref [1]). The curve of 1hr milled sample shows no evidences of glass transition and enthalpic relaxation, whereas that of 100hrs sample indicates a recovery endothermic peak T1 of relaxed enthalpy and subsequently a glass-rubber transition T2.

$$C = k_d p + \frac{C'_H b p}{1 + b p} \quad (1)$$

where C and p are sorption amount and relative vapor pressure of penetrant, respectively, and k_d Henry constant, b affinity constant. C'_H is a parameter, called a capacity constant in the Langmuir equation, which has been considered to relate with the amount of free volume in a glassy polymer. In this study, water is used as penetrant, so that the sorption amount C and the relative pressure p are replaceable to equilibrium moisture content and water activity A_w , respectively. We attempted to fit Eq.1 to the sorption data below $A_w = 0.8$. Fig. 3 shows the fitting curve by Eq.1 to the experimental result after 22hrs of milling as an example. Eq.1 could express fairly well the water sorption equi-

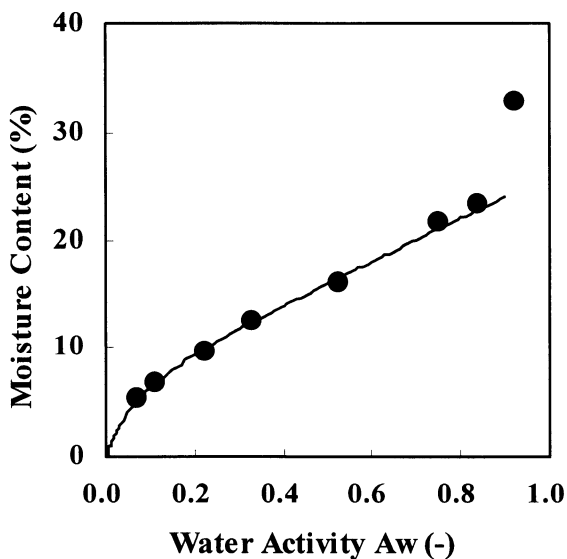


Fig. 3 Water sorption isotherm of potato starch after 22hrs milling and the curve calculated by a dual mode model equation, Eq. (1), represented by a solid line.

librium up to 0.8 in A_w , so that C'_H could be determined.

As for the C'_H parameter, there is an opinion that the C'_H is not suitable to consider the direct correlation with free volume in amorphous materials, because the physical feature of the Langmuir model is far from a physical image of a free volume [9]. However, even today an alternative adequate theory has not been developed for connecting the structural relaxation and sorption properties. We considered that the C'_H parameter might have correlations with a microstructure in amorphous material, i.e. space for water molecules sorption, even though it is ambiguous in the physical figure. Therefore, the analysis for the decreasing phenomena of the C'_H is thought to give some insight into the interpretation of our result.

From the plot of C'_H value against milling time, it was confirmed that the capacity constant C'_H decreases monotonically with milling time as shown in Fig. 4. In the early period of milling the decreasing was quick, subsequently the C'_H attained apparently constant after 20 hours. Other calculated parameters, b and k_d , are also listed with C'_H in Table 1. The change of b values to milling time showed a converse trend with C'_H , whereas the k_d value had almost no change during milling. These changes, except for C'_H , are not discussed here because the focus of this research is on the relationship of the structure and the sorption ability, even if they may be significant.

Hachisuka et al. [13] showed that the enthalpy relaxation amount for amorphous vinylidene during aging has a linear relation to the C'_H determined from the CO_2 sorption experiment and they concluded that the sorption ability of penetrant into amorphous polymers decreases as the free volume accompanied with enthalpy relaxation decreases. Since we did not calculate the enthalpic relaxation amount from DSC data, the relationship between C'_H and enthalpy relaxation amount could not be discussed directly. However, the characteristics in the decreasing curve of C'_H were closely similar to the result by Hachisuka et al. [13], which cannot be expressed by a simple exponential decreasing function as shown in Fig. 4.

Furthermore, to understand the rate process of C'_H

Table 1 Change of parameters in a dual model sorption model equation Eq.1, representing the change for water sorptionability of potato starch during ball milling.

Milling time(hr)	C_H (%)	b ($^{\circ}$)	k_d ($^{\circ}$)
0	11.4	8.7	17.5
1	9.94	11	16.5
2	9.3	11.8	15.5
17	8.03	8.6	16.8
22	7.5	14	18.8
45	7.75	12.6	16.2
100	6.9	13.3	16.8

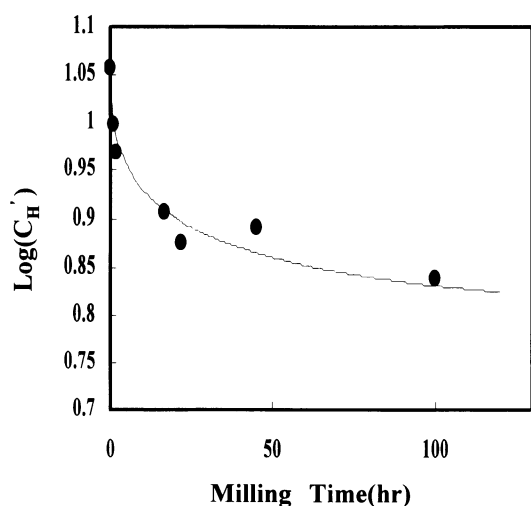


Fig. 4 Milling time dependence of capacity parameter C'_H , defined by a dual mode theory Eq.(1), corresponding the water sorption ability to potato starch. The solid line represents the fitting result by using KWW equation Eq.(2) which is able to express a relaxation process of many polymers.

decreasing phenomena, we attempted to utilize the so-called KWW equation for our data of C'_H vs. milling time t . The KWW equation written by Eq.2, which was developed by Kohlrausch, Williams and Watts, is known today to be a very reliable equation that can express the relaxation process for many kinds of amorphous materials [14,15,16].

$$\frac{C'_H - C_H^\infty}{C_H^0 - C_H^\infty} = e^{-(t/\tau)^\beta} \quad (2)$$

Where, C_H^∞ and C_H^0 are an initial and final value of C'_H , respectively. And τ and β are mean relaxation time constant and relaxation time distribution parameter, respectively. The best fitted result of the above equation, Eq.2, to plots of C'_H vs. time, by adjusting β , τ , and C_H^∞ , is shown as a solid line in Fig. 4. From this result, it was found that the decreasing process of C'_H value during ball milling, obeys the KWW equation. Then, β and τ were 0.4 and 19hr, respectively. It is interesting that the β value was reasonable since it is comparable to literature value, 0.4 ~ 0.6, for other polymers [16]. According to KWW theory, β is thought to represent size distribution of domain that gives a cooperative mobility in amorphous material, and is one of the characteristics of amorphous material. When $\beta = 1.0$, the domain size is unity. So, $\beta = 0.4$ obtained in this study suggests that the domain size in amorphous starch may have a relatively wide distribution, whereas τ is relatively smaller than any known values[14]. This is thought to be a characteristic appearance of the ball milling effect. The difference on the effects between aging temperature and

impact by the ball milling to the relaxation process of starch, might be able to be understood on the basis of KWW equation in future research.

However, regarding the decrease of water sorption within an initial period of milling, it should be considered that during such periods the crystalline portion of native potato starch would gradually break, even though the enthalpic relaxation of the amorphous portion progresses. If so, the water sorption ability should increase during the initial milling period, however, such effect could not be observed. On the other hand, in the case of potato starch, it is well known that the ratio of amorphous portion inner native potato starch is more than 70%, i.e. less crystalline. So, water sorption into potato starch may not be affected negligibly by decrease in the ratio of the crystalline due to milling. Now, an experiment to confirm the effect is being planned.

The result in this study, despite that it is phenomenological, would give a useful way for prediction of water sorption properties on enthalpy relaxation processes. It should be noted that the relaxation of starch always occurs when the starch material is stored for long periods such as a few months to a year. This means that water sorption ability does decrease gradually.

In conclusion, it is found that the water sorption ability of the starch decreases by ball milling. This phenomenon cannot be explained by decreasing of crystalline portion in starch granule but is thought to relate to the relaxation on enthalpy and the structure of amorphous starch molecules. Furthermore, the decreasing rate of water sorption ability could be expressed by KWW equation, suggesting some relation with the relaxation time of starch molecules in an amorphous state.

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*** 和文要約 ***

ボールミル操作によるスターチの水分収着能変化と構造緩和

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スターチは長時間ボールミルすることにより室温でも非晶質のアモルファススターチに転換されると同時に Fig. 2 のようにエンタルピー緩和を伴うことが示されてきた[1]. アモルファス物質のエンタルピー緩和は自由体積の減少といった体積緩和を伴い、アモルファス物質の様々な物性に影響を与える。一般的にボールミルしたスターチは結晶質部分割合が低下するため、高い水分収着性をもつと考えられてきたが、先のボールミルによるエンタルピー緩和を考慮すると自由体積減少によって水分収着能の減少が予測される。本研究では、この予想を確認するためボールミル処理時間の違いによるスターチの水分収着能の変化を調べた。

試料にはポテトスターチを用い、室温で種々の時間(1 から 100 時間) ボールミル処理を行った。それぞれ処理時間の異なる試料を、飽和塩類を用いて相対水蒸気圧をコントロールしたデシケータに 25 °C で放置し、試料の重量変化を測定することで水分収着平衡を調べた。ポテトスターチの水分収着平衡量は Fig. 1 に示したようにミル時間の増加とともに、ほとんどの相対水蒸気圧において、全体的に低下した。この結果は、エンタルピー緩和したアモルファスデンプンは水分収着能が低下するであろうという我々の推測を支持するものであった。さらに詳細な分析のため、ヘンリー型とラングミュア型吸着を合わせた次式のように表される二元収着モデルを用いて検討を行った。二元収着モデルは、ガラス状高分子へのペネトラントの収着に対する解析にしばしば用いられる。

$$C = k_d p + \frac{C_H b p}{1 + b p}$$

ここで C , p はそれぞれ収着量割合およびペネトラントの相対蒸気圧であり、 k_d はヘンリー一定数である。そして、 C_H , b はそれぞれラングミュア容量定数および親和力定数であり、前者 C_H はガラス状高分子内の自由体積と関係するとされる。Fig. 3 には、例として 22 時間ミルした試料の水分収着平衡と上式による曲線を示した。

その結果、二元収着モデルは $Aw = 0.8$ までの範囲で水分収着平衡をよく表せ、ラングミュア容量定数 C_H' を決定することができた。さらに、この C_H' とミル時間をプロットしたところ (Fig. 4), C_H' はミルの進行とともに徐々に減少することが示された。ただし、Fig. 4 では、縦軸を対数表示しているにもかかわらず直線関係が得られないことから、単純な一次反応的な減少ではないことが明らかになった。ここで、アモルファス合成高分子の緩和過程をよく表現できるとされる次の KWW 式を用いて、水分収着能の時間依存性を検討した。

$$\frac{C_H - C_H^\infty}{C_H^0 - C_H^\infty} = e^{-(t/\tau)^\beta}$$

ここで C_H^0 , C_H^∞ は C_H' の初期値および、最終値であり、 τ , β は緩和時間とその分布を表すパラメーターである。後者 3 つのパラメーターは fitting によって決定されるものである。

結果として、Fig. 4 の実線で示すように KWW 式は、 $\tau = 19\text{hr}$, $\beta = 0.4$ のとき、水分収着能の指標である C_H' のミル時間による減少過程を非常によく表せた。このような一致は、水分吸収能減少の現象および KWW 式が本来適用される構造緩和と直接的な対応を有することを保証するものではないが、ボールミルによるスターチの水分収着能の減少は、スターチのアモルファス構造の緩和に起因することを示唆するものと考えられる。

以上、ボールミル処理によってポテトスターチの水分収着能が低下することがわかった。また、この現象はスターチ内の結晶質の減少としては説明できず、ボールミル処理によりアモルファススターチ分子の構造緩和が引き起こされた結果、水分子の収着し得る自由体積が減少したと考えることによって理解される。スターチの構造緩和、あるいはエンタルピー緩和は、ボールミル処理だけでなく、通常の保存時でも起こりうる現象である。したがって、スターチを用いる食品、フィルム等への水分収着能を考えるうえで貯蔵中の構造緩和の影響を留意する必要性が示唆される。