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# The effect of partial gelatinization of corn starch on its retrogradation

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ABSTRACT

The objective of this work was to investigate the effect of partial gelatinization of starch on its retrogradation using differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques. The Avrami equation was used to predict the evolution of starch retrogradation kinetics. The degree of retrogradation in starch samples partially gelatinized 64 °C (*S64*), 68 °C (*S68*) and 70 °C (*S70*) and control (*S25*) increased with storage time. The retrogradation enthalpies of *S68* and *S70* were almost four times as high as that of *S64*. The *S25* and *S64* had dominant A-type crystalline pattern while *S68* and *S70* showed dominant B-type crystalline pattern. The growth of remainder crystals was faster in *S25* and *S64*, while both the nucleation and growth rates of new crystals were faster in *S68* and *S70*. The Avrami model was found to represent the retrogradation kinetics data of these partially gelatinized starch samples quite satisfactorily ($R^2 > 0.95$).



## 1. Introduction

Starch is one of the most common storage polysaccharides in plants and it is the major carbohydrate source in human diets. Partial gelatinization of starch commonly occurs in production processes such as high hydrostatic pressure, parboiling of rice, and drying of moist cereals because of exposure to heat, high humidity and mechanical stress. The partial gelatinization of starch is of great interest in some special cases such as formulation of sustained release tablets due to its cold water-swelling capacity and gel barrier formation (Sánchez, Torrado, & Lastres, 1995).

Retrogradation is the term that describes the changes that occur in gelatinized starch from an initially rubbery or disordered state to a more ordered or crystalline state. Starch retrogradation occurs readily during the storage of heat-processed starch-rich foods, as a spontaneous process endeavoring to reach a thermodynamically low energy stable (crystalline) state from a thermodynamically high energy metastable state. In foods, the retrogradation of starch during processing or storage greatly affects the product texture, stability, quality, digestibility and functionality (Mutungi, Passauer, Onyango, Jaros, & Rohm, 2012). Hence, better understanding of the retrogradation process of starch is essential for product development and quality and process control.

The rate of retrogradation is affected by a number of factors, such as the amylose to amylopectin ratio (Fredriksson, Silverio, Andersson, Eliasson, & Åman, 1998), temperature (Silverio, Fredriksson, Andersson, Eliasson, & Åman, 2000), water content (Zhou, Wang, Yoo, & Lim, 2011), lipids (Peterson, Eller, Fanta, Felker, & Shogren, 2007), hydrocolloids (Charoenrein, Tatirat, Rengsutthi, & Thongngam, 2011), sugars (Cairns, Miles, & Morris, 1991) and botanical source of the starch (Inaba, Hatanaka, Adachi, Matsumura, & Mori, 1994). Variation in molecular structure of starch induced either through genetic manipulation (to alter the pathway of starch biosynthesis) alters the retrogradation behavior of starch. In addition, chemical or physical modification of starch can also result in altered retrogradation behavior (Liu, & Thompson, 1998). However, most of the studies dealing with the retrogradation of starch are confined with the fully gelatinized starch and there are only very limited publications dealing with the implication of partial gelatinization of starch on its retrogradation (Adebowale, & Lawal, 2003; Kohyama, Matsuki, Yasui, & Sasaki, 2004; Lawal, 2004). Fisher and Thompson (1997) and Liu, Yu, Chen, & Li (2007) studied the effects of thermal treatment at different temperature on the retrogradation of corn starch. It was shown that the residual starch crystalline structure (double helices of amylopectin chains) profoundly affected the retrogradation of starch. Although these studies have quantified the variation in retrogradation enthalpy even after several days of storage; however, the development of recrystallization process and proportion of different crystalline patterns in partially gelatinized starch were not investigated.

The evolution of starch retrogradation kinetics can be predicted by using Avrami equation type mathematical models, which are

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originally derived to describe the crystallization kinetics of polymer melts (Jouppila, Kansikas, & Roos, 1998; Kibar, Gönenç, & Us, 2011). According to the Avrami theory, the nucleation and growth of the crystals continue until the degree of crystallization levels off to a constant value. The Avrami equation has two parameters: the rate constant and the Avrami exponent. The former depends on the crystals growth and crystals nucleation constants. The Avrami exponent depends on the nature of crystal nucleation and the crystal dimension in which the growth takes place (Aguirre, Osella, Carrara, Sánchez, & Buera, 2011; Del Nobile, Martoriello, Mocci, & La Notte, 2003). When the Avrami equation is applied to characterize the starch retrogradation, the presence of starch crystals at the beginning of retrogradation process is generally neglected (Farhat, Blanshard, & Mitchell, 2000).

In these contexts, the objective of this present work was to study the effect of partial gelatinization of starch on its retrogradation using differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques. A mathematical model based on the Avrami equation was proposed to predict the time course of starch retrogradation during storage. We also explored the aspects of formation and growth of different crystalline patterns of partially gelatinized starch during the retrogradation process.

## 2. Materials and methods

### 2.1. Materials

Partially gelatinized starch *S64*, *S68* and *S70* were prepared as previously reported (Fu, Wang, Li, & Adhikari, 2012). Corn starch dispersions at a solid concentration of 10.0% (w/w) were prepared by adding 20.0 g of pre-dried corn starch into deionized water at 24 ± 1 °C. Each batch of dispersion was thoroughly stirred at 300 rpm (in beakers) for 15 min using a thermostated water bath at 64, 68 and 70 °C. The partially gelatinized starch dispersions were spray dried using a bench-top spray drier (GPW120-II, Shandong Tianli Drying Equipment Inc., China). The inlet temperature, exhaust aspiration level, flow rate of the air and feed rate used in the spray drying process were set at 200 °C, 95%, 0.375 $m^3$/h and 7.2 ml/min, respectively. Partially gelatinized starch *S25* as a control was prepared by stirring corn starch slurry for 15 min at room temperature followed by spray drying.

The degree of gelatinization of *S25*, *S64*, *S68* and *S70* samples was determined in previous study (Fu et al., 2012). Distilled water (7.5 μL) was added with a microsyringe into starch (2.5 mg) in an aluminum pan. This mixture of starch and water was then immediately sealed with an aluminum lid and hermetically sealed. Each sealed sample was equilibrated for 3 h at ambient temperature before thermally scanning in the differential scanning calorimeter (DSC-Q10, TA Instruments, New Castle, USA). The samples were then heated from 20 to 120 °C at 10 °C/min. The gelatinization enthalpy ($\Delta H_{gel}$) was quantified. The degree of gelatinization (GD) was calculated using equation as follows (Błaszczak et al., 2007):

$$GD = \{(\Delta H_{ns} - \Delta H_{ts})\Delta H_{ns}^{-1}\} \times 100\%$$

where $\Delta H_{ns}$ and $\Delta H_{ts}$ are the melting enthalpies of native and modified starches, respectively. The degree of gelatinization of *S25*, *S64*, *S68* and *S70* samples was calculated and was 32.30%, 47.75%, 69.40% and 96.78%, respectively.

### 2.2. Samples preparation and conditioning

Starch slurries at a solid concentration of 20.0% (w/w) were prepared by adding 20.0 g of *S25*, *S64*, *S68* and *S70* into deionized water at room temperature. Then the starch samples were stored at 4 °C for 30 days. The stored samples were taken out at set time intervals (0, 1, 3, 7, 14, 21 and 30 days of storage), a section of samples were taken out for DSC and X-ray diffraction analysis.

### 2.3. The DSC analysis

DSC measurements were performed using a differential scanning calorimeter (DSC-Q10, TA Instruments, New Castle, USA) equipped with a thermal analysis data station. 10 mg samples were transferred into an aluminum pan and were immediately sealed with an aluminum lid. Each sealed sample was equilibrated for 3 h at ambient temperature before carrying out the thermal scanning. The thermal scanning involved heating of the samples from 20 to 120 °C at 5 °C/min. The enthalpy associated with retrogradation ($\Delta H$) was also recorded.

### 2.4. X-ray diffraction (XRD) analysis

The XRD patterns of samples were obtained using a XD-2 X-ray diffractometer (Beijing Purkinje General Instrument Co., Ltd., China) performed at 36 KV and 20 mA with nickel-filtered CuKα (wavelength 0.15406 nm) radiation. The XRD patterns were recorded within a diffraction angle range of 10°–40° ($2\theta$) with a scanning rate of 0.5° per minute and sampling interval of 0.02°. Samples were dried at 35 °C in a convection forced air oven for over 7 h before carrying out these tests. The effects of annealing can be avoided by drying at this (35 °C) temperature (Osella, Sánchez, Carrara, de la Torre, & Buera, 2005).

The XRD patterns were analyzed with the software associated with the XRD instrument to calculate the crystallinity ($\Phi(t)$). The crystallinity was calculated as the ratio of area under the crystalline peaks to the entire area of under the diffractogram as given by Eq. (1):

$$\Phi(t) = \frac{A(t)}{A(t) + B} \quad (1)$$

where, $A(t)$ is the area of crystalline region and $B$ is the area of amorphous region. By subtracting $A(t)$ from the area under the diffractogram the non-crystalline fraction was calculated.

In fact, the retrogradation of partially gelatinized starch was in part due to the growth of remainder crystals ($\Phi_1$) in starch granules and in part due to nucleation and growth of new crystals ($\Phi_2$) (Del Nobile et al., 2003). Therefore, the starch crystals volume fraction at a given storage time can be expressed as follows:

$$\Phi(t) = \Phi_1(t) + \Phi_2(t) \quad (2)$$

Using the Avrami equation to describe both $\Phi_1(t)$ and $\Phi_2(t)$, $\Phi(t)$ can be expressed as follows (Del Nobile et al., 2003):

$$\Phi(t) = \{\Phi_1^{\max}[1 - \exp(-k_1 t)] + \Phi^{in}\exp(-k_1 t)\} + \{k_2 t^2\} \quad (3)$$

The starch crystallinity level can be normalized as given by Eq. (4):

$$\Gamma(t) = \frac{\Phi(t) - \Phi^{in}}{\Phi^{last} - \Phi^{in}} \quad (4)$$

Substituting Eq. (3) in Eq. (4) and rearranging the normalized starch crystallinity value was obtained.

$$\Gamma(t) = \frac{1 - \exp(-k_1 t) + k_2 t^2/(\Phi_1^{\max} - \Phi^{in})}{\Phi^{last} - \Phi^{in}/\Phi^{\max} - \Phi^{in}} \quad (5)$$

$\Gamma(t)$ is the normalized starch crystallinity level at time $t$ (%), $k_1$ is the growth rate constant of the remainder crystals in starch granules ($day^{-1}$), $k_2$ is the growth rate constant of newly formed crystals ($day^{-1}$), $\Phi(t)$ is the volume fraction of the starch crystals at time $t$, $\Phi^{in}$ is the initial value of $\Phi(t)$ at storage time $t = 0$, $\Phi^{last}$ is the finally measured value of $\Phi(t)$ and $\Phi^{max}$ is the value of $\Phi(t)$ at very long storage time ($t = \infty$).

### 2.5. Statistical analyses

All experiments were carried out at least in triplicate and results are reported as the mean and standard derivation of these measurements excluding the X-ray diffractogram data. Duncan's multiple comparison tests were carried out to determine the significant effect of heating processes on the properties of starch samples at 95% ($p < 0.05$) confidence level using the SPSS statistical package (LEAD Technologies, US).

## 3. Results and discussion

### 3.1. Differential scanning calorimeter (DSC) analysis

Fig. 1 shows the typical thermograms for starch samples *S25*, *S64*, *S68* and *S70* which were stored at 4 °C for a different length of time (0–30 days). As can be seen from this figure, there is an endothermic peak in all the starch samples (*S25*, *S64*, *S68* and *S70*) with 0 days of storage. This endothermic peak is due to starch gelatinization of the intact granules and partially gelatinized starch granules after the preheat treatment and spray drying. The gelatinization enthalpy of starch samples has not significantly ($p > 0.05$) changed with the increase in the storage time (Table 1). The gelatinization peak moves to higher temperature for *S68* and *S70* due to the less stable crystallites have been gelatinized in the process of preheat treatment and spray drying (Fig. 1). As can be seen from Fig. 1, an endothermic peak of retrogradation is also observed below 60 °C in all the starch samples except in the case of *S25*. The retrogradation endotherm is observed in a broad temperature range (44 °C to 69 °C) and the area under this endothermic peak increased with increase in the storage time. The peak retrogradation temperature was lower than the gelatinization temperature which means that the formation of less perfect crystallites occurs in the retrograded starch samples (Iturriaga, Lopez de Mishima, & Añon, 2010).

The retrogradation enthalpies of starch samples are presented in Table 2. The enthalpy of S25 could not be detected. As can be seen from this table, the enthalpy of *S64* increased significantly from 0 to $1.15 \pm 0.08$ J/g as the storage time increased from 0 to 30 days. Similarly, the retrogradation enthalpy of *S68* when stored for 30 days is $4.48 \pm 0.08$ J/g which is almost four times as high as that of *S64* at the same storage period. The maximum enthalpy of *S70* at the end of 30 days long storage period is $4.99 \pm 0.11$ J/g which is in accordance with the enthalpy value reported by Sandhu and Singh (2007). However, there is no significant difference in the enthalpy of *S70* after 7 days of storage. The difference in the retrogradation enthalpies in these starch samples suggests to the differences in their tendency toward retrograde.

It has been reported that starch retrogradation involves two kinetically distinct processes. In the first process, rapid gelation of amylose occurs through formation of double helical chain segments which is followed by helix-helix aggregation. In the second process slow recrystallization of the amylopectin chains occurs (Clark, Gidley, Richardson, & Ross-Murphy, 1989; Orford, Ring, Carroll, Miles, & Morris, 1987). We have reported in our previous study that the intermolecular interactions do not occur in *S70* because of which this starch loses the ordered structure (Fu et al., 2012). Therefore, the molecular chains of *S70* move freely during the retrogradation process and follow the two kinetically distinct processes. It has been pointed out that the retrogradation enthalpy reflects the loss of double helical order or crystallite melting (Koo, Park, Jo, Kim, & Baik, 2005). Because of this reason, the retrogradation enthalpy of *S70* increased rapidly in the first seven days and remained almost constant thereafter. However, the degree of gelatinization of *S64* and *S68* is lower than that of *S70* which means that *S64* and *S68* have higher proportion of ordered or denser structure. The higher proportion of initially ordered structure in partially gelatinized starch decreases the macromolecular mobility of starch molecules and slows down the formation of double helices during the retrogradation process. Because of this reason, the retrogradation enthalpies of *S64* and *S68* increased slower than that of *S70*. It can be observed from Table 2 that the final (30 days) retrogradation enthalpy of *S68* is very close to that of *S70* even though *S68* contains more ordered structure. It can also be observed from Table 2 that the final retrogradation enthalpy of S70 is four times as high as that of *S64*, which means that the degree of gelatinization has a significant impact on the retrogradation rate of starch (Farhat et al., 2001).

### 3.2. X-ray diffraction (XRD) analysis

The XRD patterns for starch samples during storage at 4 °C for 30 days are shown in Fig. 2. The four strong peaks at $2\theta = 15°$, 17°, 18° and 23° suggested that the crystalline structure of *S25* and *S64* follows A-type pattern (Fig. 2A and B). After storing these starch samples at 4 °C for 30 days, the peak at $2\theta = 17°$ showed only a minor increase. The X-ray diffractograms of freshly prepared *S68* and *S70* samples (stored for 0 days) show that the peaks became weak or disappeared at $2\theta = 15°$, 17°, 18° and 23°. This observation suggests to a substantial loss of A-type crystallinity in these two starch samples (Aguirre et al., 2011). When these two starch samples were stored at 4 °C for 30 days, the two peaks appeared at $2\theta = 17°$ and 22° indicating to the fact that the characteristic B-type crystallinity appeared and increased very rapidly with the increase in storage time.

When non-crystalline starch gels are cooled and stored, the amylopectine and amylose molecules re-associated to form a new crystalline order. It has been reported that the starch samples having more than 43% moisture content develop B-type crystalline patterns while samples with less than 29% moisture content develop A-type crystalline patterns (Karim, Norziah, & Seow, 2000). The fact that *S68* and *S70* exhibited XRD patterns typical of B-type structure (characteristic peaks at $2\theta = 17°$ and 22°) agrees well with this reference. However, a new peak has appeared in *S68* and *S70* during storage but not in *S25* and *S64* during the same length of storage. This observation suggests that the formation of new crystalline patterns due to recrystallization or retrogradation depends not only on the moisture content of the starch samples but also the degree or completeness of gelatinization. The numerous initial ordered structures presented in *S25* and *S64* limit the mobility of amylose and amylopectin chains. As a result, the formation of nuclei and the growth of crystals both get greatly retarded.

### 3.3. Crystallinity

Fig. 3 presents the total crystallinity of starch samples during storage at 4 °C for 30 days. As can be seen from this figure, the crystallinity has increased quite remarkably on the very first day of storage. The crystallinity has kept on increasing up to 7 days for *S64*, *S68* and *S70*. The *S25* showed higher crystallinity than other starch samples during the whole storage period. However, the crystallinity of *S25* increased very slowly from the first to the 30th days of storage. As the storage time increased to 30 days, the crystallinity of *S64* and *S68* increased to $20.86 \pm 0.71\%$ and $18.67 \pm 0.53\%$, respectively. The crystallinity of *S70* increased from $3.13 \pm 0.22\%$ to $14.30 \pm 0.62\%$ which was still far lower than that of *S25*.

Starch retrogradation depends on both the amylopectine and amylose contents of starch. Indeed, crystallization consists of (1) nucleation, (2) crystal growth, and (3) maturation stages (Vandeputte, Vermeylen, Geeroms, & Delcour, 2003). It has been reported that the retrogradation of starch occurs less than a day

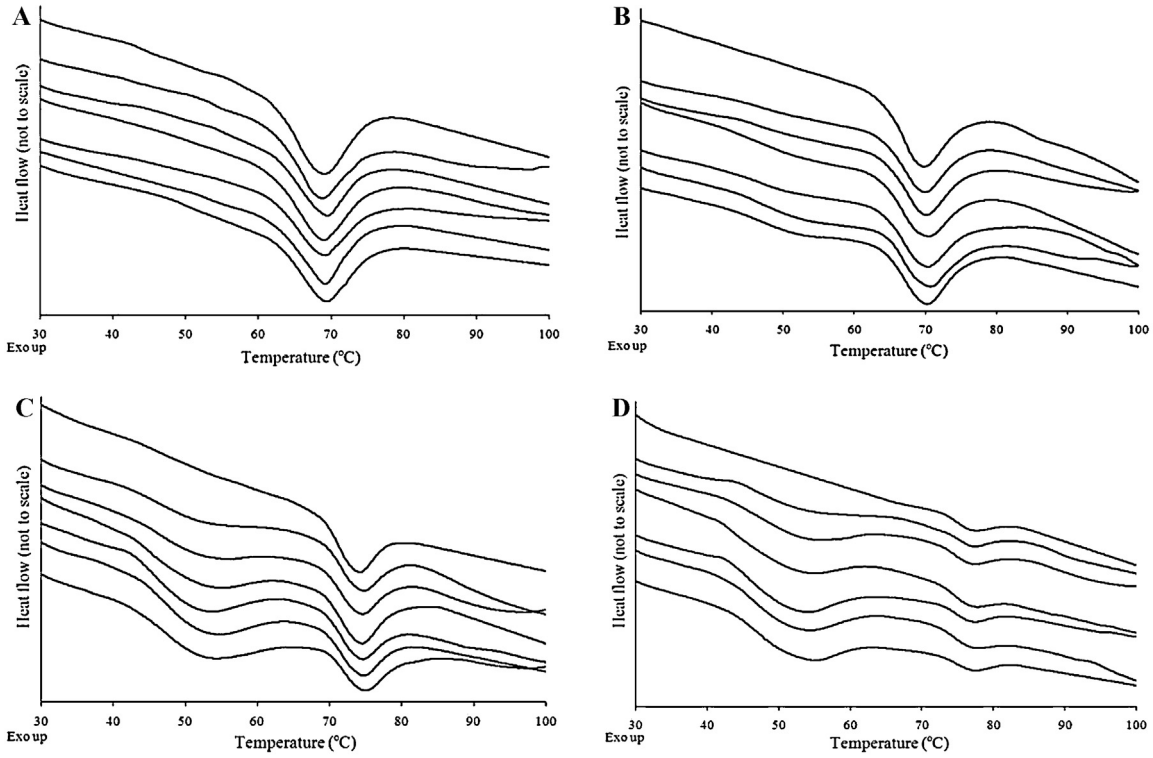


**Fig. 1.** DSC thermograms of partially gelatinized starch stored at 4 °C for 30 days: (A) *S25*; (B) *S64*; (C) *S68*; (D) *S70*. (0d, 1d, 3d, 7d, 14d, 21d and 30d from top to bottom for all the samples).

**Table 1**
The gelatinization enthalpies of partially gelatinized starch stored at 4 °C for 30 days.

| Starch | 0d | 1d | 3d | 7d | 14d | 21d | 30d |
|---|---|---|---|---|---|---|---|
| *S25* | 8.78 ± 0.43[a] | 8.92 ± 0.34[a] | 8.66 ± 0.26[a] | 9.04 ± 0.24[a] | 8.75 ± 0.17[a] | 8.56 ± 0.09[a] | 8.77 ± 0.61[a] |
| *S64* | 6.77 ± 0.33[a] | 6.53 ± 0.20[a] | 6.57 ± 0.29[a] | 6.63 ± 0.20[a] | 6.85 ± 0.19[a] | 6.57 ± 0.14[a] | 6.71 ± 0.14[a] |
| *S68* | 3.96 ± 0.15[a] | 4.15 ± 0.28[a] | 3.94 ± 0.14[a] | 3.84 ± 0.21[a] | 4.02 ± 0.15[a] | 4.10 ± 0.28[a] | 3.82 ± 0.06[a] |
| *S70* | 0.42 ± 0.03[a] | 0.46 ± 0.04[a] | 0.46 ± 0.02[a] | 0.44 ± 0.04[a] | 0.41 ± 0.01[a] | 0.40 ± 0.02[a] | 0.44 ± 0.04[a] |

Values are mean ± standard deviation ($n = 3$). Values in the same line followed by different letters differ significantly ($p < 0.05$).

**Table 2**
The retrogradation enthalpies of partially gelatinized starch stored at 4 °C for 30 days.

| Starch | 0d | 1d | 3d | 7d | 14d | 21d | 30d |
|---|---|---|---|---|---|---|---|
| *S64* | 0.00[a] | 0.23 ± 0.01[b] | 0.38 ± 0.06[c] | 0.93 ± 0.07[d] | 1.07 ± 0.08[e] | 1.23 ± 0.02[f] | 1.15 ± 0.08[ef] |
| *S68* | 0.00[a] | 2.35 ± 0.17[b] | 2.48 ± 0.15[b] | 3.52 ± 0.11[c] | 3.83 ± 0.20[c] | 4.33 ± 0.31[d] | 4.48 ± 0.08[d] |
| *S70* | 0.00[a] | 2.69 ± 0.17[b] | 3.63 ± 0.34[c] | 4.82 ± 0.29[d] | 4.89 ± 0.40[d] | 4.72 ± 0.36[d] | 4.99 ± 0.11[d] |

Values are mean ± standard deviation ($n = 3$). Values in the same line followed by different letters differ significantly ($p < 0.05$).

and the retrograded amylose provides the ground for the formation of starch nuclei and their further growth into crystals (Yu, Ma, & Sun, 2009). The degree of gelatinization of *S64*, *S68* and *S70* is higher than that of *S25*. This suggests there are high numbers of mobile amylose molecules in *S64*, *S68* and *S70* which are available to form crystal nuclei than in *S25* creating a favorable environment for the formation of crystals in these starch samples. However, *S64*, *S68* and *S70* were not fully gelatinized and they contained large number of crystals in their granules which were not gelatinized. These crystals seemingly impeded the formation of more crystals because of which the final crystallinity values of *S64*, *S68* and *S70* were lower than that of *S25* after 30 days of storage.

### 3.4. Retrogradation kinetics

Fig. 4 Presents the rate of crystallization $\Gamma(t)$ calculated using Eq. (4) and plotted as a function of storage time for each starch samples. In this same figure the lines representing the best fit of Eq. (5) to the experimental data are also presented. The Avrami equation parameters ($\Phi^{max}$, $k_1$ and $k_2$) obtained by fitting Eq. (5) to the experimental data are presented in Table 3. As can be seen from the best fit line presented by Fig. 4 and the $R^2$ values listed in Table 3 that the Avrami model fits the experimental data satisfactorily. Starch retrogradation is in part due to the growth of starch

**Table 3**
The Avrami equation parameters obtained by fitting the experimental data with Eq. (5).

| Starch | $\Phi_{max}$ | $k_1$ (day$^{-1}$) | $k_2$ ($\times 10^{-5}$ day$^{-1}$) | $R^2$ |
|---|---|---|---|---|
| *S25* | 0.219 | 0.323 | 0.492 | 0.846 |
| *S64* | 0.205 | 0.263 | 0.234 | 0.965 |
| *S68* | 0.164 | 0.668 | 2.843 | 0.963 |
| *S70* | 0.132 | 0.604 | 1.123 | 0.951 |

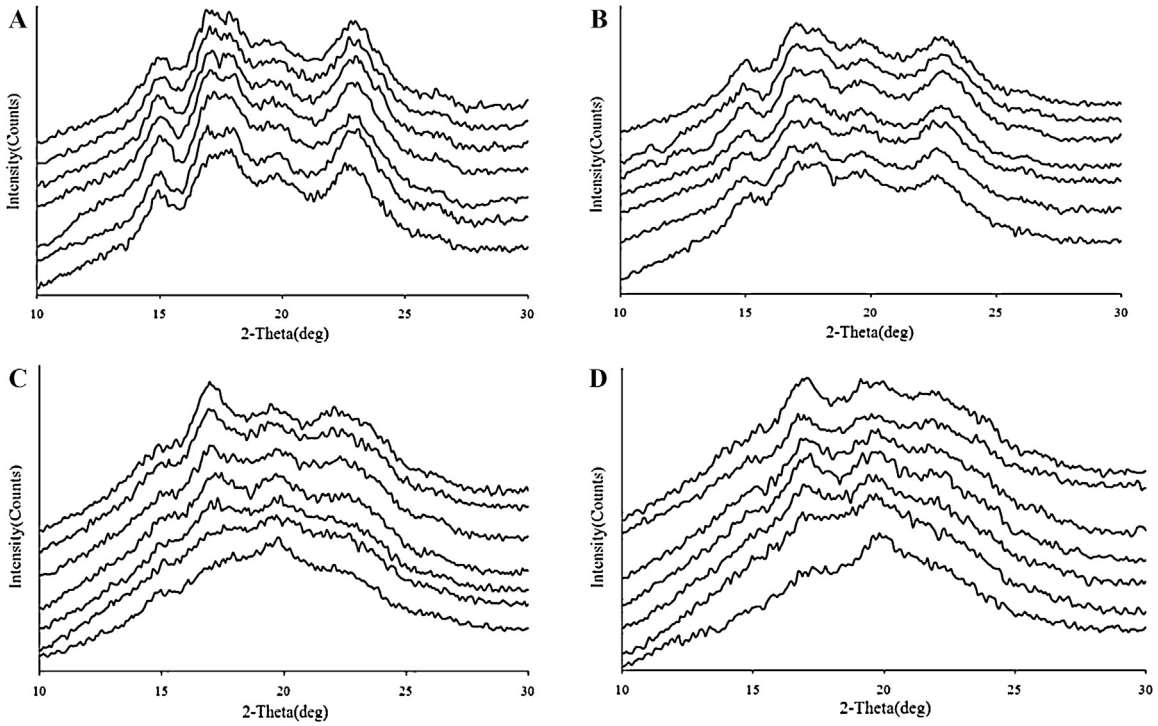


**Fig. 2.** X-ray diffraction patterns of partially gelatinized starch stored at 4 °C for 30 days: (A) *S25*; (B) *S64*; (C) *S68*; (D) *S70*. (0d, 1d, 3d, 7d, 14d, 21d and 30d from bottom to top for all the samples).

crystals already present in partially gelatinized starch granules and in part due to nucleation and growth of new crystals.

According to the Avrami theory, $k_1$ depends only on the mobility of the crystallizing macromolecules and it is related to the growth of the remainder crystals in starch granules. This means that the higher $k_1$ values indicate to the slower growth of the crystal. On the other hand, $k_2$ depends on both the growth and nucleation rates of new formed crystals. This means that if the $k_2$ values are high, the magnitude of crystallinity will also be higher. $\Phi^{max}$, in turn, depends on the final crystallinity. The higher the $\Phi^{max}$ values, the higher will be the final crystallinity values (Aguirre et al., 2011; Del Nobile et al., 2003). As reported in Table 3, the $k_1$ values of *S25* and *S64* are lower than those of *S68* and *S70*. This suggests that the growth of remainder crystals is faster in *S25* and *S64* due to their higher initial crystallinity. The $k_2$ values of *S68* and *S70* are higher than those of *S25* and *S64* indicating that both growth and nucleation rates of new formed crystals are higher in *S68* and *S70*.

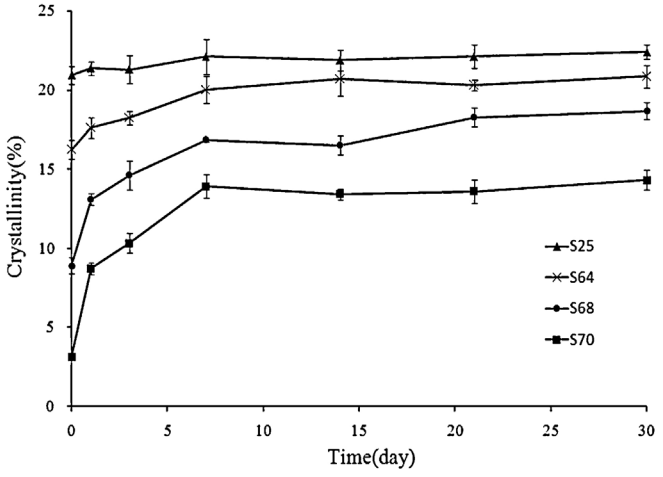


**Fig. 3.** Evolution of total crystallinity of partially gelatinized starch stored at 4 °C for 30 days.

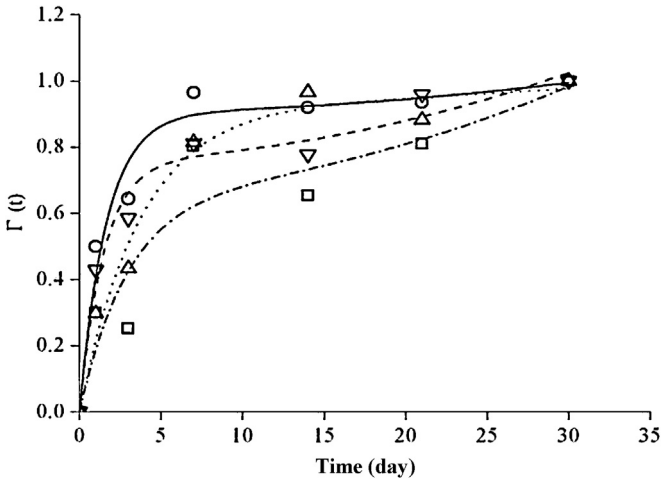


**Fig. 4.** $\Gamma(t)$ plotted as a function of storage time for partially gelatinized starch conditioned at 4 °C. (□) *S25*; (△) *S64*; (▽) *S68*; (○) *S70*; (----) best fit of Eq. (5) to the experimental data of *S25*; (—) best fit of Eq. (5) to the experimental data of *S64*; (---------) best fit of Eq. (5) to the experimental data of *S68*; (——) best fit of Eq. (5) to the experimental data of *S70*.

## 4. Conclusions

The gelatinization enthalpies of *S25*, *S64*, *S68* and *S70* did not change significantly ($p > 0.05$) within storage time of 30 days. However, the retrogradation enthalpies of *S68* and *S70* were about four times higher than that of *S64* when stored for 30 days. The retrogradation enthalpy was found to be closely related to the initial degree of gelatinization of starch samples.

The degree of crystallinity of all starch samples increased when stored for 30 days. The *S25* and *S64* starch samples had A-type crystalline pattern, while *S68* and *S70* starch samples had B-type crystalline pattern having two peaks at $2\theta = 17^\circ$ and $22^\circ$. This B-type crystalline pattern appeared and developed very fast as the storage time increased. The recrystallization kinetics showed that the growth of the remainder crystals in starch granules was faster in *S25* and *S64* than that in *S68* and *S70*, while the formation of new crystals was faster in *S68* and *S70* than that in *S25* and *S64*. The Avrami model was found to represent the retrogradation kinetics data of this partially gelatinized starch samples quite satisfactorily ($R^2 > 0.95$).

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## References

Adebowale, K. O., & Lawal, O. S. (2003). Microstructure, physicochemical properties and retrogradation behavior of Mucuna bean (*Mucuna pruriens*) starch on heat moisture treatments. *Food Hydrocolloids*, *17*(3), 265–272.

Aguirre, J. F., Osella, C. A., Carrara, C. R., Sánchez, H. D., & Buera, M. P. (2011). Effect of storage temperature on starch retrogradation of bread staling. *Starch/Stärke*, *63*(9), 587–593.

Błaszczak, W., Fornal, J., Kiseleva, V. I., Yuryev, V. P., Sergeev, A. I., & Sadowska, J. (2007). Effect of high pressure on thermal, structural and osmotic properties of waxy maize and Hylon VII starch blends. *Carbohydrate Polymers*, *68*, 387–396.

Cairns, P., Miles, M. J., & Morris, V. J. (1991). Studies of the effect of the sugars ribose, xylose and fructose on the retrogradation of wheat starch gels by x-ray diffraction. *Carbohydrate Polymers*, *16*(4), 355–365.

Charoenrein, S., Tatirat, O., Rengsutthi, K., & Thongngam, M. (2011). Effect of konjac glucomannan on syneresis, textural properties and the microstructure of frozen rice starch gels. *Carbohydrate Polymers*, *83*(1), 291–296.

Clark, A. H., Gidley, M. J., Richardson, R. K., & Ross-Murphy, S. B. (1989). Rheological studies of aqueous amylose gels: The effects of chain length and concentration on gel modulus. *Macromolecules*, *22*(1), 346–351.

Del Nobile, M. A., Martoriello, T., Mocci, G., & La Notte, E. (2003). Modeling the starch retrogradation kinetic of durum wheat bread. *Journal of Food Engineering*, *59*(2-3), 123–128.

Farhat, I. A., Blanshard, J. M. V., & Mitchell, J. R. (2000). The Retrogradation of waxy maize starch extrudates: Effects of storage temperature and water content. *Biopolymers*, *53*(5), 411–422.

Farhat, I. A., Protzmann, J., Becker, A., Vallès-Pàmies, B., Neale, R., & Hill, E. S. (2001). Effect of the extent of conversion and retrogradation on the digestibility of potato starch. *Starch/Stärke*, *53*(9), 431–436.

Fisher, D. K., & Thompson, D. B. (1997). Retrogradation of maize starch after thermal treatment within and above the gelatinization temperature range. *Cereal Chemistry*, *74*, 344–351.

Fredriksson, H., Silverio, J., Andersson, R., Eliasson, A. -C., & Åman, P. (1998). The influence of amylose and amylopectin characteristics on gelatinization and retrogradation properties of different starches. *Carbohydrate Polymers*, *35*(3–4), 119–134.

Fu, Z.-Q., Wang, L.-J., Li, D., & Adhikari, B. (2012). Effects of partial gelatinization on structure and thermal properties of corn starch after spray drying. *Carbohydrate Polymers*, *88*(4), 1319–1325.

Inaba, H., Hatanaka, Y., Adachi, T., Matsumura, Y., & Mori, T. (1994). Changes with retrogradation of mechanical and textural properties of gels from various starches. *Carbohydrate Polymers*, *24*(1), 31–40.

Iturriaga, L. B., Lopez de Mishima, B., & Añon, M. C. (2010). A study of the retrogradation process in five argentine rice starches. *LWT – Food Science and Technology*, *43*(4), 670–674.

Jouppila, K., Kansikas, J., & Roos, Y. H. (1998). Factors affecting crystallization and crystallization kinetics in amorphous corn starch. *Carbohydrate Polymers*, *36*(2-3), 143–149.

Karim, A. A., Norziah, M. H., & Seow, C. C. (2000). Methods for the study of starch retrogradation. *Food Chemistry*, *71*(1), 9–36.

Kibar, E. A. A., Gönenç, İ., & Us, F. (2011). Modeling of retrogradation of waxy and normal corn starch. *International Journal of Food Properties*, *14*(5), 954–967.

Kohyama, K., Matsuki, J., Yasui, T., & Sasaki, T. (2004). A differential thermal analysis of the gelatinization and retrogradation of wheat starches with different amylopectin chain lengths. *Carbohydrate Polymers*, *58*(1), 71–77.

Koo, H. J., Park, S. H., Jo, J., Kim, B. Y., & Baik, M. Y. (2005). Gelatinization and retrogradation of 6-year-old Korean ginseng starches studied by DSC. *LWT – Food Science and Technology*, *38*(1), 59–65.

Lawal, O. S. (2004). Composition, physicochemical properties and retrogradation characteristics of native, oxidised, acetylated and acid-thinned new cocoyam (*Xanthosoma sagittifolium*) starch. *Food Chemistry*, *87*(2), 205–218.

Liu, Q., & Thompson, D. B. (1998). Effects of moisture content and different gelatinization heating temperatures on retrogradation of waxy-type maize starches. *Carbohydrate Research*, *314*(3-4), 221–235.

Liu, H., Yu, L., Chen, L., & Li, L. (2007). Retrogradation of corn starch after thermal treatment at different temperatures. *Carbohydrate Polymers*, *69*(4), 756–762.

Mutungi, C., Passauer, L., Onyango, C., Jaros, D., & Rohm, H. (2012). Debranched cassava starch crystallinity determination by Raman spectroscopy: Correlation of features in Raman spectra with X-ray diffraction and $^{13}C$ CP/MAS NMR spectroscopy. *Carbohydrate Polymers*, *87*(1), 598–606.

Orford, P. D., Ring, S. G., Carroll, V., Miles, M. J., & Morris, V. J. (1987). The effect of concentration and botanical source on the gelation and retrogradation of starch. *Journal of the Science of Food and Agriculture*, *39*(2), 169–177.

Osella, C. A., Sánchez, H. D., Carrara, C. R., de la Torre, M. A., & Buera, M. P. (2005). Water redistribution and structural changes of starch during storage of gluten-free bread. *Starch/Stärke*, *57*(5), 208–216.

Peterson, S. C., Eller, F. J., Fanta, G. F., Felker, F. C., & Shogren, R. L. (2007). Effects of critical fluid lipid extraction on the gelatinization and retrogradation of normal dent cornstarch. *Carbohydrate Polymers*, *67*(3), 390–397.

Sánchez, L., Torrado, S., & Lastres, J. L. (1995). Gelatinized/freeze-dried starch as excipient in sustained release tablets. *International Journal of Pharmaceutics*, *115*(2), 201–208.

Sandhu, K. S., & Singh, N. (2007). Some properties of corn starches II: Physicochemical, gelatinization, retrogradation, pasting and gel textural properties. *Food Chemistry*, *101*(4), 1499–1507.

Silverio, J., Fredriksson, H., Andersson, R., Eliasson, A. -C., & Åman, P. (2000). The effect of temperature cycling on the amylopectin retrogradation of starches with different amylopectin unit-chain length distribution. *Carbohydrate Polymers*, *42*(2), 175–184.

Vandeputte, G. E., Vermeylen, R., Geeroms, J., & Delcour, J. A. (2003). Rice starches. III. Structural aspects provide insight in amylopectin retrogradation properties and gel texture. *Journal of Cereal Science*, *38*(1), 61–68.

Yu, S., Ma, Y., & Sun, D. W. (2009). Impact of amylose content on starch retrogradation and texture of cooked milled rice during storage. *Journal of Cereal Science*, *50*(2), 139–144.

Zhou, X., Wang, R., Yoo, S.-H., & Lim, S.-T. (2011). Water effect on the interaction between amylose and amylopectin during retrogradation. *Carbohydrate Polymers*, *86*(4), 1671–1674.