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# Crystallization kinetics of precooked potato starch under different drying conditions (methods)

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**Abstract**

Isothermal Differential Scanning Calorimeter investigations of potato starch, dried using sun, cabinet, fluidised bed, high temperature-short-time or freeze-drying methods were carried out to elucidate on the crystallisation kinetics, i.e. *Avrami* exponent, half time, degree of crystallisation and glass transition temperature. Moisture content, resistant starch, rehydration percent and volume were also determined and correlated with kinetics of crystallisation. The freeze-dried and high-temperature short-time-dried potatoes showed high rehydration percentages and volumes. The Avrami exponent reached values of 1.04–1.05, depending on drying conditions, indicating that the mechanism of crystallisation was the same in all the cases. The bulk density, rehydration percent and volume significantly correlated with glass transition temperature and half time of crystallisation. 

*Keywords:* Starch; Dehydration techniques; Crystallites; DSC; Avrami plots

## 1. Introduction

Starch normally constitutes the greater part of potatoes (about 80% in dry matter) and is present in a semicrystalline form. However, precooked starch is completely gelatinised or in an amorphous form. The phase transition (retrogradation) from amorphous to crystallites is modified by factors affecting the drying methods (Roos, Karel, & Kikini, 1996). There is a continuous transformation of amorphous form to crystallites in precooked starch-based food products (Jagannath, Jayaraman, & Arya, 1998b). The formation of crystallites in the amorphous domain hardens the tuber and makes it firmer in texture (Slade & Levine, 1991).

In general, crystallisation consists of three steps: (1) nucleation, i.e. formation of critical nuclei; (2) propagation, i.e. growth of crystal; and (3) maturation, i.e. crystal perfection. Kinetics of crystallinity can occur only at a temperature between glass transition temperature ($T_g$) and crystalline melting temperature ($T_c$) (Slade & Levine, 1991). Generally, it is true that the same aspects of chemical structure in a biopolymer tend to modify $T_g$ and $T_c$ in a similar manner (Crompton, 1993; Sperling, 1992).

Starch crystallinity is commonly observed in the form of a ''B'' structure and double helices. Thus for ''B'' starch double helices are depicted as enclosing a column of water located in the unit cell centre. To the extent that this hydrate water is not readily removed, it can be regarded as trapped inside the structure. It is speculated that water may give the exothermic effect during isothermal DSC (Sievert, Czuchajowsra, & Pumeranz, 1991). Dehydrated food, in which water is a small amount (trapped), is a nucleating agent in the process of crystallization and this is a rate-determining step in crystallisation kinetics. A theory of phase-change kinetics developed by Avrami has been used by several investigators to describe retrogradation in starches (Moo-Yeol, Kwang-Joong, Ko-Cheol, Yeon-Chul, & Wang-Soo, 1997). The rates of retrogradation were found to conform to the Avrmi equation, provided $n$ is close to unity.

$$\theta = e^{-kt^n}$$

In the above equation, $n$ is the Avrami exponent, $k$ represents crystal growth and $\theta$ indicates non-crystalline

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material present after time $t$. $n$ Equal to unity implies that (1) the nucleation process is instantaneous and (2) the crystal growth is rod like.

Drying of vegetables is a complex process because of the difficulties in mathematical description of the phenomena (Majumdar, 1995). Case-hardening in dehydrated vegetables is not well understood (Nicholas, 1991). However, it is an important parameter as it reduces the rehydration characteristics, as well as the storage life (Roos et al., 1996). The extent of case-hardening, like kinetics of crystallisation depends on temperature and time (ageing) and can affect texture and morphology of dehydrated materials (Nicholas, 1991). This is an important consequence, since the rehydration properties differ for crystalline and amorphous states. The case-hardening in dried vegetables is directly proportional to degree of crystallisation. Case-hardening is an inhibitive factor in the rehydration process and determines the type of moisture adsorption isotherm curve. Starches that are not digestible in the human small intestine are known as RS and are less soluble (Mangala, Ramesh, Udaya Sankar, & Taranathan, 1999). Potato starch contains more amylose (non-waxy) than other starches, namely rice, or wheat. Both amylose and amylopectin are involved in crystallisation of starch. It is reported that the amylose portion of starch is responsible for development of RS. Amylopectin is responsible for retragradation of amorphous starch, but may not contribute to RS. Further work needs to be done in this direction.

The purpose of this study was to investigate the effect of drying methods on rehydration parameters, namely rehydration percent (RP) and volume (RV; case-hardening) and resistant starch (RS) and correlate these with crystallisation kinetics and $T_g$. The isothermal DSC curves are evaluated in the ''classical'' manner, that is, according to Avrami plots to determine degree of crystallinity (DC) with respect to time.

## 2. Materials and methods

Commercially-available potato was procured from the local market. About 20 kgs of potatoes were washed, brushed, peeled and cut into cubes (about $1\,cm^3$). All those with dark spots were rejected. Potato cubes selected for different types of dehydration were stored in sulphite-containing water as detailed in the process of DeWeltigen (1964). Thereafter, potatoes were blanched in boiling water for 15 min. This also ensures that the starch is completely gelatinised.

The diced and blanched potato samples were divided into five lots and dried by different treatments, namely freeze-dried (FD), high-temperature-short-time (HTST) dried, fluidised (FD), cabinet (CD)-or sun-dried (SD). The procedure adopted for hot-air-cabinet and direct sun-drying is as described by Nicholas (1991) and that for fluidised bed and HTST is as given by Jayaraman, Gopinathan, Pitchmuthu, and Vijayaraghavan (1982). Freeze-drying was carried out in a pilot scale freeze-drier (Hull Corporation, USA) equipped with rapid freezing and drying facilities. The products were frozen by placing in a blast freezer at $-30^{\circ}C$ for 2–3 h. Drying was carried out by maintaining chamber pressure at 100–300 microns and the product temperature was allowed to increase from $-30$ to $+50^{\circ}C$.

### 2.1. DSC measurement

A Dupont differential scanning calorimeter (DSC), model DSC-910 fitted with graphic plotter and with a thermal analyst 2100 system (TA instrument USA), was used for determination of $T_g$ and isothermal crystallisation. The procedure for determining $T_g$ by DSC is as described by Jagannath, Jayaraman, and Arya (1998a).

The procedure for isothermal crystallisation experiments was as given by Krause, Kalilnka, Aver, and Hinvichsen (1994). Preliminary investigations proved 10 mg of material as optimum mass. All experiments were carried out with a sealed empty pan as the reference and with $N_2$ as a flushing agent over the head. The hermetically sealed sample pan was held at an initial temperature (low enough to ensure no crystallisation) for 1 min. The sample was then ramped up to a maximum rate ($320^{\circ}C$/min) to the final isothermal holding temperature where it was held for 20 min, during which time crystallisation was observed. The crystallisation curves were then recorded with respect to time. Triplicate measurements were made at each chosen temperature. In order to make the Avrami, constant and exponent isothermal, the DSC curves were integrated step-by-step to give the Avrami plots, $\log\{\ln[1-\theta]\}$ vs. $\log t$.

Moisture content, rehydration percentage and volume and bulk density were determined as by the procedure of Jayaraman, Das Gupta, and Babu Rao (1990). Resistant starch (RS) was determined by an enzymatic-gravimetric procedure using Sigma kit TDF - 100.

## 3. Results and discussion

### 3.1. Effect of moisture

The moisture contents of potatoes dehydrated by different methods are given in Table 1. Moisture content in freeze-dried sample is lowest, followed by HTST, FBD, CD and SD potatoes in order of increasing moisture content. The effect of small amounts of moisture in dehydrated products are not well understood. It is reported (Roos et al., 1996) that decreased water removal during drying and increased moisture retention reduce the product quality and rehydration ability. This

also leads to agglomeration and renders the product hard and non-porous. This may be the reason that the SD, and to some extent CD, potatoes take a long time to dry and retain more moisture. These were harder and non-porous compared with other dehydrated potatoes. This fact is reflected in the bulk density data given in Table 1. Freeze- and HTST-dried samples are very soft and prous because of their low bulk density values.

### 3.2. Rehydration characteristics

The RP and RV for potatoes dried under different conditions are given in Table 1. The FD- and HTST-dried samples show higher RP and RV than other dehydrated potatoes. These two parameters depend on the soft and porous nature of the material. The bulk density of dehydrated material is related to the texture and is directly proportional to case-hardening (CH) and is inverssely proportional to RP and RV; in other words, CH is greatest in sun-dried and least in freeze-dried potatoes. CH is one of the major problems in the drying of vegetables and residual moisture plays an important role as it reduces the rehydration capabilities as well as the storage life of dehydrated products. The CH phenomenon is not well understood and depends on temperature, moisture content and duration of dehydration and is related to molecular mobility (free volume) and thus depends on $T_g$.

### 3.3. Effect of RS

The parameter, RS, depends on the amount of crystallinity in the starch material. The enzymes used in the RS determination are capable of hydrolysing the amorphous portion of starch but not crystallites. As the network of crystallite increases in the amorphous domain, or in other words percent crystallinity increases, the RS also increases. The RS is less in FD potatoes than other dehydrated potato samples (Table 2).

### 3.4. Effect of $T_g$

$T_g$ depends on free volume (molecular mobility) and is inversely proportional to it. FD- and HTST-dried samples are porous and soft (similar to flexible polyurethane foam) and hence they possess more free volume. These samples show lower values of $T_g$ and therefore contain lesser amounts of crystallites than other dehydrated samples. The $T_g$ can be used as an indicator of crystal growth. Salekigerhardt and Zografu (1994) have observed the profound effect of small amounts of moisture on the crystallization of amorphous sugars. The small amount of water retained in dehydrated products may have more nucleating effect on crystallization of amorphous starch and thus increase $T_g$. Increase in $T_g$ is due to increased formation of crystallites in the amorphous domain. It is reported (Jagannath et al., 1999a, b) that increase in $T_g$ is proportional to rate of retrogradation or, in other words, rate of crystallite formation. It can be seen in Table 2 that SD potatoes show higher-$T_g$ values than other dehydrated potatoes. The $T_g$ is lowest in the FD sample, indicating the least amount of crystallites.

### 3.5. Isothermal crystallisation

According to Slade and Levine (1991), optimum crystallisation rate would occur somewhere between $T_g$ and $T_c$. To determine $T_c$ for dehydrated starches is difficult, by DSC, because the sample may decompose at higher temperature. Coster, Biliaderis, Page, Maurice, and Bienvenide (1986) considered the melting point ($T_c$) of the heated potato starch–water mixture as the melting point of the most perfect crystallites and determined the value, by extrapolation of the $T_c$ (melting of dry starch powder), using the Flory–Higgins equation, to be 471K. In recent studies, Slade and Levine (1991) have reported that starch gelatinisation is nonequilibrium in character and the $T_c$ reported by them was 485K. The reported value of $T_c$ for 3% water–potato starch mixture was 465k and this value was taken for our studies.

Fig. 1 shows typical DSC curves of isothermal crystallisation at a given temperature (403K) of potatoes dehydrated by different methods. The induction times, for each dehydrated method studied, are the same, i.e. 15 s. The induction time was taken to be the point at which the trace left the base line, taking the end of the induction period as time zero. The crystallisation curve

Table 1
The physical and dehydration parameters of potatoes dried by different methods

| Methods of drying | Bulk density ($g/cm^3$) | Moisture content (%) | Rehydration percentage (%) | Rehydration volume ($cm^3$) |
|---|---|---|---|---|
| Sun | 0.4575 | 7.5 | 36.1 | 35.9 |
| Cabinet | 0.3804 | 6.8 | 43.5 | 42.3 |
| Fluidized bed | 0.3066 | 6.4 | 68.3 | 51.8 |
| HTST | 0.1473 | 5.6 | 73.2 | 59.8 |
| Freeze | 0.0981 | 3.3 | 88.9 | 68.3 |

Table 2
Kinetics of crystallisation parameters and resistant starch of potatoes dried by different methods

| Method of drying | TgK | Avrami constant | | | Resistant starch (g/100 g) |
|---|---|---|---|---|---|
| | | $t_{1/2}$ (s) | $n$ | log $k$ | |
| Sun-dried | 348 ± 4 | 45 | 1.05 | −2.06 | 3.161 |
| Cabinet-dried | 342 ± 4 | 75 | 1.05 | −2.31 | 2.932 |
| Fluidized bed | 340 ± 4 | 90 | 1.04 | −2.38 | 2.593 |
| HTST | 336 ± 3 | 105 | 1.04 | −2.46 | 2.135 |
| Freeze-dried | 331 ± 3 | 115 | 1.04 | −2.51 | 1.653 |

for sun-dried is positioned at one end, whereas that of freeze-dried is at the other end and others falls in between. The slower crystallization of freeze-dried samples may be due to lesser amounts of moisture and less nucleating effect. On the other hand, the fast crystallisation of the sun-dried potatoes proves that the nucleating effect of the water is dominant.

Each peak in Fig. 1 was integrated with respect to time to obtain the degree of crystallinity and plots are shown in Fig. 2. Fig. 2 proves that, in the case of all investigated drying methods, the freeze-dried shows the least degree of crystallinity, followed by HTST, FBD, CD and SD in order of increasing degree of crystallisation.

### 3.6. Kinetics of crystallisation

The isothermal crystallisation results were analysed using the Avrami equation

$$X(t) = 1 - e^{k^n} \quad (1)$$

where $k$ is a constant, depending on nucleate rate and growth velocity and $n$ is an exponent describing the growth order. $X(t)$ is the degree of crystallisation at time $t$.

Rearrangement of Eq. (1) gives

$$\log_{10}k + n\log_{10}t = \log_{10}\{-\ln\{1 - X(t)\} \quad (2)$$

$\log_{10}\{-1n\{1-X(t)\}$ was plotted against $\log_{10} t$ (Fig. 3) and $k$ and $n$ values extracted from the linear portion relating to relative crystallinity value. The Avrami exponent $n$, which has an effect on dimentionality of growth of crystal, affects the shape of the integrated curves and varies with the mode of nucleation and with the geometry (dimention) of growing entity.

Table 2 gives the effect of Avrami exponent on potatoes dehydrated under different methods. Reported (Moo-Yeol et al., 1997) values for Avrami exponents ($n$) for different rice starches were close to 1.0. This indicates that crystallisation of potato starch at a single temperature has instantaneous nucleation, followed by rod-like growth of crystals. This quantity appears to be independent of dehydration methods having values from $n = 1.4$ to 1.5 (Table 2). This indicates that the crystallization growth is two-dimensional. The value of the time constant ($k$) was found to be lowest for the FD sample (Table 2). This is an agreement with the degree of crystallinity. To calculate $t_{1/2}$ of crystallisation Eq. (1) can be arranged as follows :-

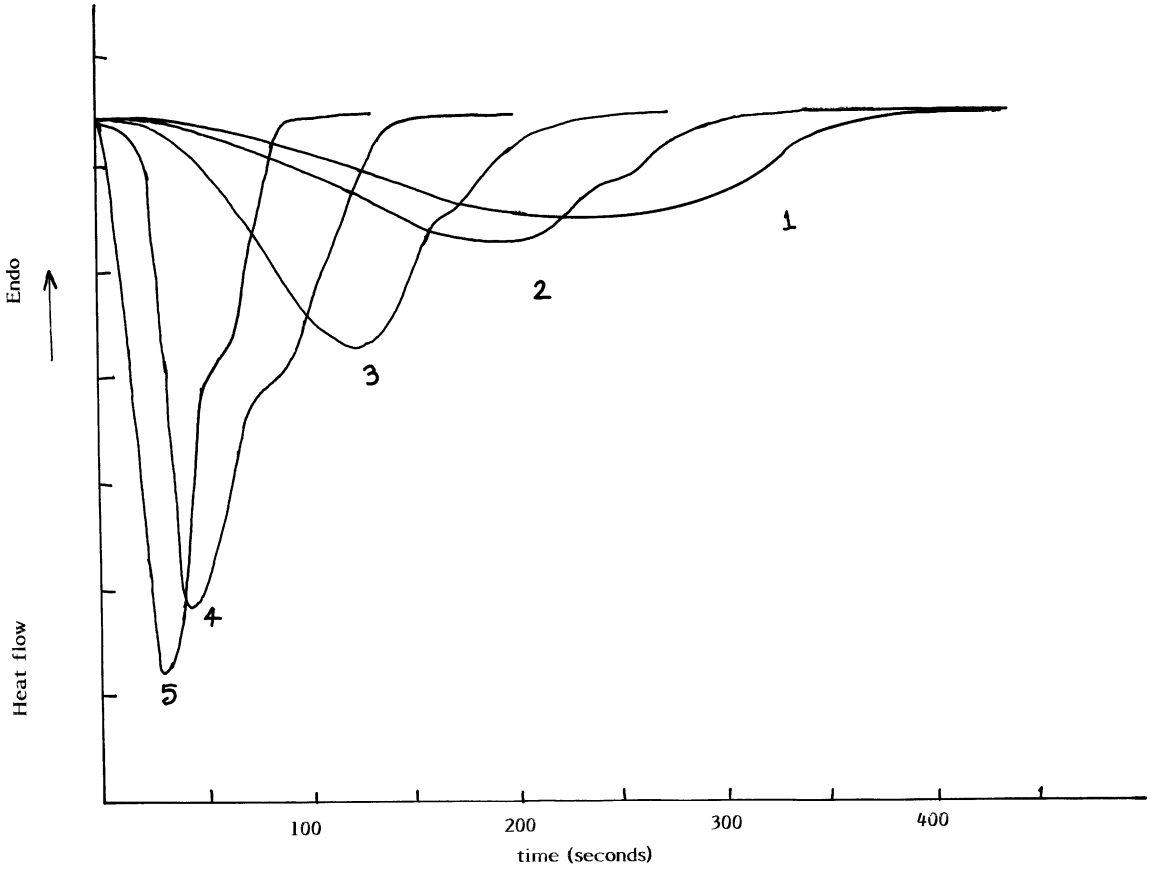


Fig. 1. Isothermal DSC curves for potatoes dehydrated under (1) FD (2) HTST (3) FBD (4) CD (5) SD.

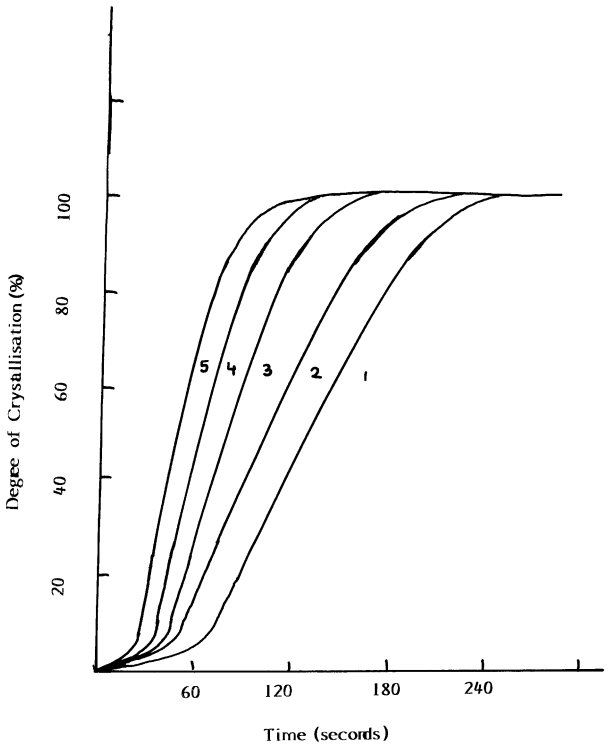


Fig. 2. Degree of crystallisation for potatoes dehydrated under (1) FD (2) HTST (3) FBD (4) CD (5) SD.

$$\log t_{1/2} = \frac{\log 1n2 - \log k}{n}$$

Unlike the Avrami exponent, half-time of crystallization depends on temperature and time (ageing). In other words, $t_{1/2}$ depends on dehydration methods. The value of $t_{1/2}$ was least in freeze-dried material followed by HTST, FB, CD and SD in order of increasing $t_{1/2}$.

All the isothermal traces (Fig. 1) show double peaks and this is more prominent in sun- and cabinet-dried samples. This implies that starch recrystallisation takes place by two kinetically distinct processes: (1), rapid time-independent recrystallisation of amylose and (2) slow time-dependent recrystallisation (retrogradation) of the short amylopectin chains.

### 3.7. Correlation coefficient

The parameters, namely $t_{1/2}$, $T_g$, RP and RV were significantly correlated with bulk density. The bulk density of dehydrated potatoes determines the kinetics of crystallisation, as well as conventional rehydration properties. Parameters such as $T_g$ and $t_{1/2}$ depend on free volume or molecular mobility, which are significantly correlated with bulk density. Similarly, rehydration parameters, namely RP and RV, depend on

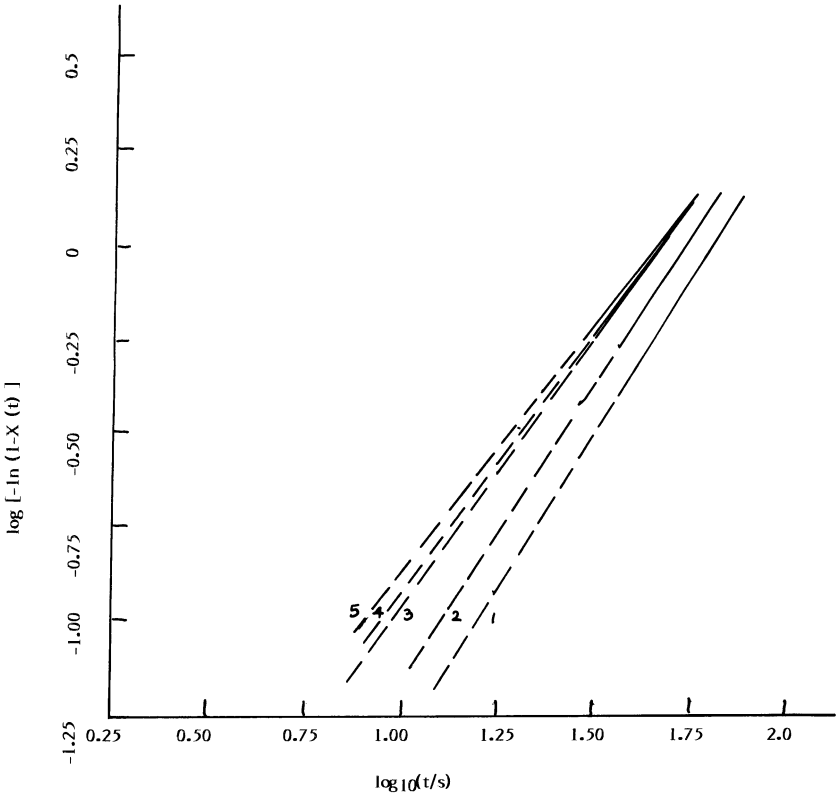


Fig. 3. Avrami plot for potatoes dehydrated under (1) FD (2) HTST (3) FBD (4) CD (5) SD.

Table 3
Correlation coefficient of bulk density, $t_{1/2}$, Tg, RP and PV

| | Bulk density | $t_{1/2}$ | Tg | RP | RV |
|---|---|---|---|---|---|
| Bulk density | – | – | – | – | – |
| $t_{1/2}$ | 0.8998 | – | – | – | – |
| Tg | 0.9491 | 0.9658 | – | – | – |
| RP | 0.9028 | 0.9528 | 0.9291 | – | – |
| RV | 0.9472 | 0.9684 | 0.9777 | 0.9863 | – |

water uptake by sample and are significantly correlated with bulk density. The correlation coefficients given in Table 3 indicate that bulk density of dehydrated material determines the kinetics of crystallisation and classical rehydration parameters.

## 4. Conclusion

By studying crystallisation kinetics, it is possible to determine the suitability of the method for dehydration of potato. By obtaining shapes of isothermal traces, it is possible to predict the optimum method for dehydration and degree of crystallisation. The slower the rate of crystallisation (crystallisation peak) the better is the product quality and shelflife. $T_g$ and $t_{1/2}$ indicate the extent of retrogradation/case hardening in the potato starch and can be used as quallity parameters. Kinetics of crystallisation parameters, namely $T_g$ and $t_{1/2}$ significantly correlate with conventional rehydration parameters, namely RP and RV. Further work on DSC/DMTA time-temperature superposition would be useful to generate master curves for potato starches so that shelf life of the product could be predicted.

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