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Chapter 25

Effect of Aging Temperature on Retrogradation of Concentrated Cassava Starch Gel

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ABSTRACT

The retrogradation behaviour of a cassava starch gel was monitored using X-ray diffraction (XRD), differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR) and mechanical test. The cassava starch gel containing 40% solid was produced under the heating temperature of 100°C for 30 minutes. The starch gel was aged at the temperatures of -20, 5, 25 and 45°C for 4 weeks. The crystallinity of the freeze-dried gelatinized starch was quantified using XRD and DSC. Greater crystallinity or retrogradation occurred at -20 and 5°C. At 45°C, the least extent of retrogradation appeared. The retrogradation tendency at -20°C was slightly greater than that at 5°C on XRD and FTIR, whereas the opposite result was observed on compression test. The enthalpy of the retrograded cassava starch endotherms as measured by DSC was 0.31-2.18 J/g. When increasing temperature from -20 to 25°C, the peak temperature of the retrograded starch increased from 56.8 to 60.4°C.

Key words: retrogradation, cassava starch, temperature, aging

INTRODUCTION

Starch retrogradation has been described as phase transition of starch molecules following gelatinization. It has been considered to be basically a crystallization process due to association of starch chains as double helices, and variably ordered semi-crystalline array of these helices, which has been extensively studied by DSC and XRD. FTIR spectroscopy coupling with attenuated total reflectance (ATR) was recently used for the investigation of starch retrogradation, based on conformational changes, which could be monitored by analysis of the observed band-narrowing process and intensity changes of conformational sensitive bands in the 1200-900 cm^{-1} region [1]. Mechanical or textural changes were also used to observe starch retrogradation on macroscopic level [2]. The rate and extent of retrogradation was dependent on starch structure, botanical sources, starch concentration, storage temperature and storage time. With respect to the storage temperature, the retrogradation rate of potato amylose decreased as the incubation temperature increased from 5°C to 45°C [3]. In wheat starch containing 25-80% moisture and aging in the temperature range 4-32°C, the enthalpy values of the retrogradation endotherm, which are often referred to as the degree of retrogradation, were higher at a lower storage temperature [4]. From the viewpoint of the temperature effect on crystallization, it has been known that crystallization of partially crystalline polymers, in most cases, occurred at a temperature region between glass transition temperature (T_g) and melting temperature (T_m) [5]. From the study on crystallization behaviour of amorphous corn starch, it is known that the extent of crystallization is dependent on storage temperature and T- T_g condition [6]. The relationship between the extent of crystallization and T- T_g was apparently parabolic. Therefore, the starch crystallization behaviour appeared to be related to T_g, similar to synthetic semicrystalline polymer theory.

Most works on starch retrogradation were conducted on potato, wheat, and corn starches. Limited reports on cassava starch retrogradation behaviour have been published. The objective of this study was to investigate the effect of aging temperature on the behaviour of concentrated cassava starch gel retrogradation using different techniques.

MATERIALS AND METHODS

Methods

Sample preparation: Cassava starch (Sanguan Wongse Industries Co., Ltd., Nakornratchasima) and deionised water were weighed in cans with 40% solid (w/w). The starch suspension was equilibrated over night at ambient temperature to ensure fully hydrated starch granules. The starch suspension was heated in a shaking water bath with the temperature of 50°C for 15 min, 60°C for 15 min, 70°C for 15 min and 80°C for15 min. Then, it was subjected to thermal treatment in a retort at 100°C for 60 min. Completely gelatinized starch was observed using polarized light microscopy. The cassava gel samples were stored at -20, 5, 25 and 45°C for 30 days. On sampling day, the sample was freeze-dried using a freeze-dryer (Heto, model FD8, Denmark) after rapid freezing with liquid nitrogen. The freeze-dried sample was ground under the temperature of 10°C using a mortar grinder. The powder sample was sieved to obtain the particle size range of 75-100 μm. The powder sample was used for XRD and DSC. The starch gel sample was tested on FTIR and compression test.

X-ray diffractometry: X-ray diffractograms were recorded using a powder diffractometer (D5005, Bruker GmbH, Germany), which generated Cu $K_{\alpha 1}$ radiation. The powder sample was exposed to X-ray beam at an operating condition of 40 kV, 40mA with a divergence slit 1°, antiscattering slit 1°, and a tray rotation speed of 30 rpm. The diffraction angles (2θ) were from 4-30° (step size 0.02°, time per step 2.5 sec). The Diffract Plus #1 software was used to obtain peak area and quantify relative crystallinity. The ratio of sample peak area to native starch peak area was calculated as percentage of relative crystallinity [7].

FTIR spectroscopy: All FTIR spectra were recorded on a Spectrum GX spectroscopy (Perkin Elmer Ltd., Buckinghamshire, UK) equipped with the attenuated total reflectance (ATR) accessory with a ZnSe crystal (Perkin Elmer Ltd., Buckinghamshire, UK). Starch gel was placed on the surface of a ZnSe crystal. The spectra, in the region of 4000-600 cm^{-1}, were average of 32 scans with the resolution of 4 cm^{-1}. All spectra were baseline corrected and deconvoluted with a deconvolution factor of 2.4 using a Spectrum GX software. According to Van Soest et al. [1], the absorbance ratio was measured in the region of 1053-1035 cm^{-1}.

Differential scanning calorimetry: DSC measurements were performed using a Pyris Diamond DSC (Perkin Elmer, Connecticut, USA). The 10 mg powder samples were placed in an 50 µl aluminium DSC pan (Perkin Elmer, Connecticut, USA). Deionised water was added to obtain a sample to water ratio of 1:3 and then the pans were sealed. The DSC pans were equilibrated over night before heating from 5°C to 95°C at scanning rate of 10°C/min. Empty pan was used as a reference.

Compression test: A compression force of the gel was measured using Texture Analyzer (TA-XT2i Texture analyzer, Godalming, UK) equipped with 10 mm diameter cylinder aluminium probe. The test speed was 1 mm/s with a distance of 10 mm.

RESULTS AND DISCUSSION

The relative crystallinity of retrograded cassava starch gel aging at -20, 5, 25, 45°C determined using XRD was shown in Fig. 1. Although there was variability in the percentage of crystallinity during the storage period, the trend of aging temperature was apparently obvious. Aging concentrated starch gel at -20°C and 5°C accelerated starch reorganization to become an ordered structure, showing a greater percentage of crystallinity than that of 25°C and 45°C. FTIR results, which monitored starch retrogradation in the gel structure, also indicated a similar effect of temperature (Fig.2). In the compression test shown in Fig. 3, the mechanical or textural change of the gel was monitored to observe starch retrogradation on a macroscopic level, in which the texture of the gel was stiffer as a progression of the retrogradation.

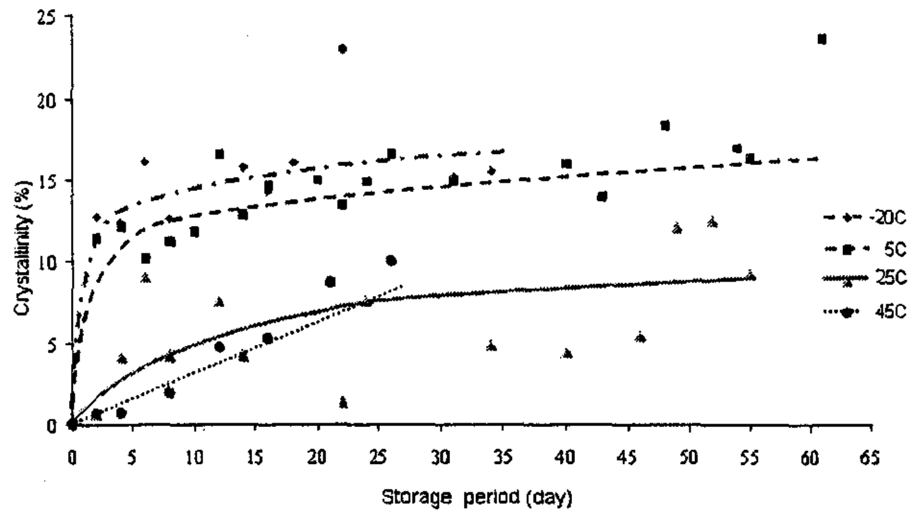

Figure 1. XRD crystallinity of retrograded cassava starch aged at -20, 5, 25 and 45 °C.

As the extent of retrogradation at low temperature was compared to that of high temperature in compression force, the effect of aging temperature was identical to XRD and FTIR. The compression force of the gel was substantial at -20°C and 5°C. In general, the effect of temperature on starch retrogradation was comparable to other reports [4].

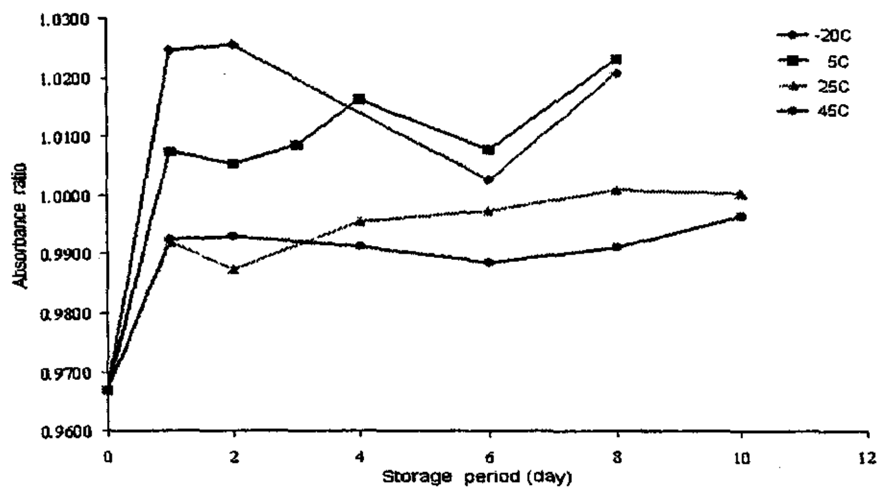

Figure 2. FTIR absorbance ratio (1042/1037) of cassava starch gel aged at -20, 5, 25 and 45 °C.

Gel storage at the temperature of -20°C was another viewpoint necessary to be considered due to some parameter changes involved. Aging the gel at -20°C brought about phase change of water into ice formation. The higher concentration of starch solid was a consequence of this phenomenon.

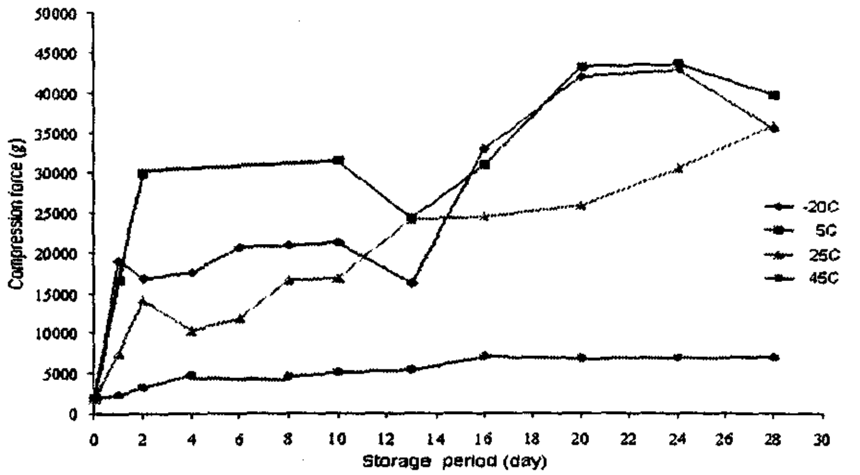

Figure 3. Compression test of cassava starch gel aged at at -20, 5, 25 and 45 °C.

According to Jouppila and Roos [6], onset temperature of glass transition temperature (T'_g) within maximally freeze-concentrated solution of gelatinized corn starch was -11°C and the concentration of solid in the maximally freeze-concentrated unfrozen material (C'_g) was estimated to be 73% (w/w). Slade and Levine [8] reported T'_g for gelatinized wheat starch to be -5°C, but the same C'_g value. Therefore, the cassava starch gel in 40% solid should be more concentrated than the original one aging at -20°C and it might contain a solid concentration in the region of 73%. The result of aging starch gel at low temperature showed that the extent of retrogradation at -20°C appeared slightly above that at 5°C in XRD and FTIR. As mentioned previously, aging the gel at -20°C was likely to be below T'_g of freeze-concentrated starch gel. Theoretically, storage at this temperature should allow the starch gel to crystallize to the least extent. However, the result showed a great extent. Two possible explanations could be remarked. First, since this freezing method was slow freezing, it took approximately five hours for 40% solid starch gel to attain the temperature of -20°C.

During cooling down to -20°C, it might promote starch retrogradation. As noticed in Fig. 1, the extent of the retrogradation seemed to be relatively constant at the beginning of the sampling day. Second, starch crystallization might proceed during thawing stage, from -20°C to ambient temperature before measurement. This step would facilitate crystal growth as some crystals were formed in nucleation step during cooling down to -20°C.

In the compression test, the extent of retrogradation at -20°C was less than that at 5°C, which was contrary to that obtained by XRD and FTIR. Ice formation in retrograded starch gel may cause damage of gel structure. When the frozen gel was thawed and the mechanical strength of the gel was measured, a damaged structure caused a reduction in the strength of gel, resulting in a lower compression force for -20°C gel than for that of 5°C. Therefore, the mechanical test was unsuitable for studying starch retrogradation under slow freezing. However, the extent of crystallinity formed at -20°C was extensively larger than that of 25°C, consequently the stiffness of damaged gel was still higher than that of gel at 25°C. This result confirmed the speculation of the retrogradation progress at -20°C. The effect of aging temperature on the melting temperature of the retrograded starch gel is shown in Fig. 4. It was clear that the higher the storage temperature, the higher the melting temperature of the crystals formed. This observation was in agreement with other publications [4, 7]. It was suggested that more perfect crystalline regions were formed at a higher aging temperature.

The XRD pattern of the native cassava starch was apparently A-type crystallinity (Fig. 5). The A-type pattern is commonly observed in cassava starch. However, no ordered structure was noticed after cassava starch was gelatinized. Therefore, amorphous starch was sometimes described instead of gelatinized starch. As the cassava starch gel retrograded for 26 days, the XRD pattern was dissimilar to A-type crystallinity and it was likely to be B-type crystallinity. Although no distinct peak was developed in the region of 4-6 degree of diffraction angle, double peaks in 20-25 degree of diffraction angle, which were a characteristic of the B-type crystallinity, became visible. Furthermore, some works also mentioned that retrograded amylose showed a B-type XRD pattern [9].

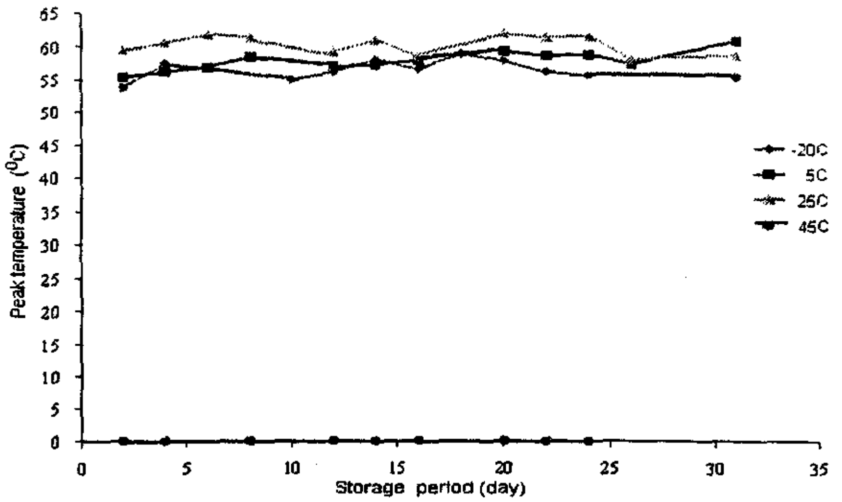

Figure 4. DSC peak temperature of retrograded cassava starch aged at -20, 5, 25 and 45 °C.

The enthalpy of melting endotherm determined in the retrograded cassava starch gels was 0.31-2.18 J/g during aging at -20, 5, 25, 45°C for 2-30 days.

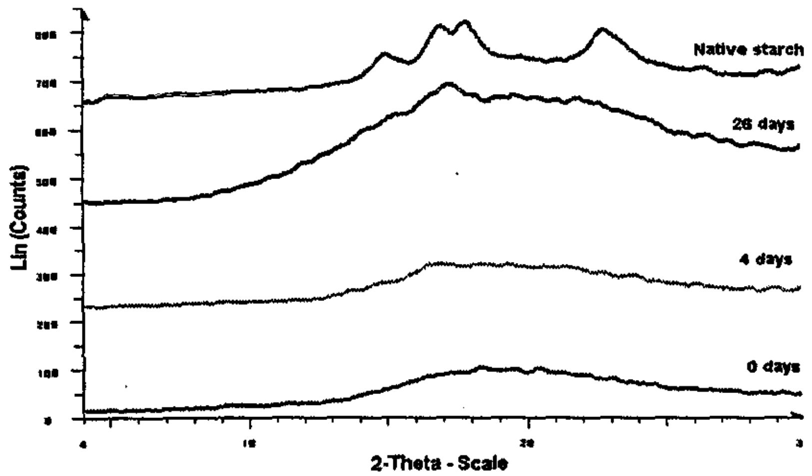

Figure 5. XRD pattern of native starch and retrograded starch aged at 5 °C for 0, 4, 26 days.

This enthalpy value was relatively low compared to other starch sources, i.e. corn starch, wheat starch. Jouppila and Roos [6] found that the enthalpy of retrograded corn starch prepared in 60% solid and stored at 10-60°C was 4-5 J/g after their leveling-off, where the storage time was 7-30 days. Silverio et al. [10] also presented the enthalpies of several starches (from wheat, rye, barley, potato, and pea), after retrogradation at 6°C for 2 days. Their retrogradation enthalpies were 7.3-13.6 J/g.

CONCLUSIONS

1. In 40% solid cassava starch gel aging above 0°C, the maximum extent of retrogradation occurred at the lowest temperature, 5°C. The higher aging temperature, the less progress of retrogradation, because the aging temperature was closed to the crystal melting temperature.
2. Slow freezing and storage of the starch gel at -20°C inducing high concentrated solid caused a great extent of retrogradation similar to that at 5°C.
3. Increased aging temperature, resulted in higher melting temperature of the retrograded starch.
4. The extent of the cassava starch retrogradation was relatively low.

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