

Effect of Crystallinity on the Glass Transition Temperature of Starch

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The glass transition temperature (T_g) of potato and wheat starches, stored for several periods after gelatinization, was measured by differential scanning calorimetry (DSC), and the relative crystallinity of the starches was measured by X-ray diffractometry. T_g of stored starches was higher than that of starches without storage, and the T_g increment of starches gelatinized at 120 °C was higher than that of starches gelatinized at 60 °C. The water content at which the glass transition of a starch occurs at 25 °C was estimated from DSC data, and it increased linearly with relative crystallinity in two groups that differed in the gelatinization method. These results also showed the quantitative relationship between T_g and retrogradation. In addition, these results suggested that the glass transition of starch could be interpreted in the same way as the glass transition of cross-linked synthetic polymers.

Keywords: Glass transition; starch; crystallinity; retrogradation

INTRODUCTION

Starch is a major component of cereal-based dry foods, which are produced by several processes, such as baking, extrusion, gelling, and drying. In these processes, starch granules in the product are gelatinized or retrograded, and gelatinization and retrogradation of starch have a great effect on the quality, especially the texture, of cereal-based dry foods. Therefore, it is not surprising that considerable attention has been paid to studies of starch gelatinization and retrogradation by various means, such as thermal analysis (Wada et al., 1979; Shiotsubo and Takahashi, 1984; Nakazawa et al., 1985; Slade and Levine, 1987), X-ray diffraction (Zobel et al., 1988; l'Anson et al., 1988), and NMR (Chinachoti et al., 1991; German et al., 1992).

Recently, these phenomena have been studied by methods used in polymer science (Donovan, 1979; Biliaderis et al., 1980; Slade and Levine, 1987). Starch has been considered as a semicrystalline polymer, which is composed of highly branched amylopectin molecules, which are partially crystalline, and nearly linear amylose molecules, which are apparently amorphous. On the basis of this approach, the glass transition temperature (T_g) of starch has been measured (Zeleznek and Hosney, 1987; Slade and Levine, 1988; Liu and Lelievre, 1991; Kalichevsky et al., 1992). In addition, the textural changes of starch-containing foods are considered to be attributable to the glass transition of the food system (Slade and Levine, 1987), and T_g of a bread has been measured (LeMeste et al., 1992; Hallberg and Chinachoti, 1992). The textural changes of dry starch-containing foods, due to water migration during storage, are also considered to be related to the glass transition of the food (Levine and Slade, 1993); thus, T_g of dry starch-containing foods must be an indicator for predicting the stability of such foods during storage (Levine

and Slade, 1993). Therefore, it is important, for optimizing the quality of dry cereal foods, to understand the mechanism of the glass transition of starch.

However, there have been few studies about the relationship between the state of starch and its glass transition, and our knowledge about the mechanism of the glass transition of starch is incomplete. One way to evaluate the state of starch is to determine the relative crystallinity, which may change with the extent of gelatinization, by an X-ray diffraction method (Nara et al., 1978). This method has the advantage of providing direct information about starch molecules, but there are no quantitative X-ray data on the relationship between the glass transition and starch crystallinity.

Therefore, the objective of this work was to study the effect of crystallinity on the T_g of starch. First, we measured T_g of starch by using two different methods: one a thermal method, differential scanning calorimetry (DSC), and the other a mechanical method, dynamic mechanical analysis (DMA). By comparing T_g data measured by DSC and DMA, we determined the adequacy of our data. Next, we measured T_g of potato and wheat starches, stored for several periods after gelatinization, by DSC and their relative crystallinities by X-ray diffractometry. Finally, the relationship between the change in T_g and crystallinity of starch was investigated.

MATERIALS AND METHODS

Sample Preparation. We purchased potato starch and wheat starch from Wako Chemicals Industries (Tokyo) and used them without further purification. First, a 20% (w/w) starch/water suspension was heated for 10 min at 120 °C in an autoclave or for 60 min at 60 °C. Under the former condition, the starch in the suspension is expected to be almost completely gelatinized. A portion of both heated suspensions was lyophilized after rapid freezing in liquid nitrogen. The remainder of each suspension was lyophilized after storage

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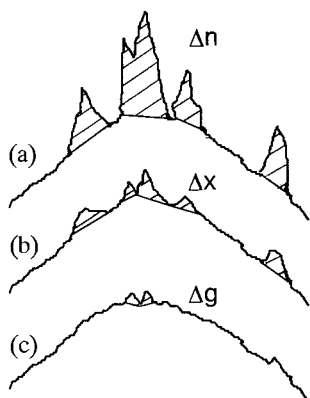


Figure 1. Schematic diagram of the method for determination of starch crystallinity by X-ray diffractometry: (a) native starch; (b) retrograded starch; (c) gelatinized starch.

at 5 °C for 3, 10, or 21 days. The dried starch samples were used for calorimetric, mechanical, and X-ray diffraction measurements according to the methods described below. Before each measurement, we adjusted the water content of dry samples by blowing supersaturated water vapor over them for appropriate times and equilibrating them in a hermetic vessel for >24 h at ambient temperature. The water content (w/w, wet basis) of each sample was determined by heating at 105 °C for 18 h; the maximum water content attained by using this method was ≈25%.

Determination of Glass Transition Temperature by DSC. Calorimetric measurements were carried out using a DSC120 (Seiko Instruments) that was calibrated with In, Sn, and Ga. Each starch sample, prepared with a range of water contents from ≈3 to 25%, was placed in a silver pan (70 μL), and the pan was hermetically sealed and the sample accurately weighed (≈25–45 mg). An empty silver pan was used as the reference. The standard heating rate used was 10 °C/min, and occasionally, heating rates of 5 and 20 °C/min were also used. The temperature range of the scan was from –20 to 200 °C. From the DSC scan, specific heat (C_p) of the sample and the derivative of C_p were traced. In this study, we defined T_g as the peak in the derivative of the C_p accompanying the shift in C_p , which is considered by us to provide the most unequivocal T_g value.

DMA Measurements. A sample, the water content of which was previously adjusted, was shaped into a disk by a pressing treatment before the DMA measurement. Samples of 10 mm thickness were placed in a cylindrical mold (20 mm in diameter) and pressed at about 20 MPa. Consequently, disk samples (~1.5 mm thick) were prepared for the DMA measurements. DMA measurements were performed using a Stresstech Rheometer (Stresstech) with a plate (20 mm in diameter) that applied a shear stress to the disk sample in the oscillation strain control mode at 0.1, 0.5, 1, or 5 Hz, and the strain at which the stress was measured was 0.1%. The samples were heated from 0 to 120 °C at a rate of 2 °C/min. We measured the storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \delta = G''/G'$) accompanying the heating of the samples.

Determination of Starch Crystallinity by X-ray Diffractometry. We measured the relative crystallinity of starch samples with an X-ray diffractometer (PW1700, Philips Co.) that generated copper K α radiation, using Nara's method (Nara et al., 1978). Powder samples, the water contents of which were adjusted to 19–23% (w/w), were exposed to the X-ray beam (40 kV, 30 mA). The scanning region of the diffraction angle, 2θ , was 5–30°, and the scanning rate was 0.05°/s. The quantitative determination of relative crystallinity was done as described below.

In Figure 1, we show a schematic diagram of X-ray diffractograms of starch samples. As shown in each diffractogram, each separated point of minimum intensity was joined by a straight line, and the area of the upper region above the line

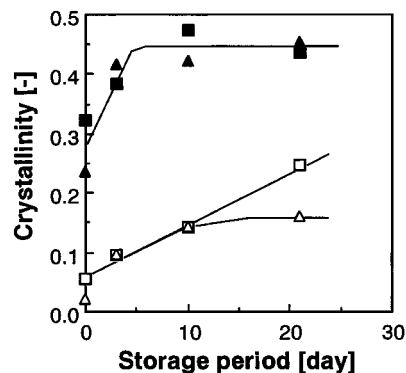


Figure 2. Changes in relative crystallinity of starch samples during storage at 5 °C: (Δ) wheat gelatinized at 120 °C; (□) potato gelatinized at 120 °C; (▲) wheat gelatinized at 60 °C; (■) potato gelatinized at 60 °C.

(shaded part) was calculated. We indicate the areas for native (Figure 1a) and gelatinized starch (Figure 1c) by Δn and Δg , respectively. In this study, we defined the relative crystallinity (X) of a starch sample by the equation

$$X = (\Delta x - \Delta g) / (\Delta n - \Delta g) \quad (1)$$

where Δx indicates the area of the sample. According to this method, the crystallinities of native and gelatinized starch can be regarded as ≈1 and ≈0, respectively.

RESULTS AND DISCUSSION

Changes in Crystallinity of Starch Samples during Storage. In Figure 2, we show the changes in crystallinity of starch samples during storage at 5 °C. In all samples, crystallinity gradually increased with storage time, which is considered to be caused by the recrystallization of gelatinized starch (Miles et al., 1985), and reached maximum values. We can see that starch samples gelatinized at 60 °C reached maximum values in shorter times than did samples gelatinized at 120 °C. Hizukuri et al. (1972) observed, by enzymic analysis, that retrogradation in sufficiently gelatinized starch was inhibited. The finding that starch gelatinized at 120 °C took longer to attain maximum crystallinity is considered to agree with the observation from enzymic analysis.

The crystallinity of samples, following gelatinization at 120 °C but prior to storage, was ≈0, which indicated the almost complete gelatinization of these samples. Therefore, the crystallinity of starch samples gelatinized at 120 °C is considered to indicate the degree of retrogradation of the starches after storage.

Determination of T_g of Starch Samples. In Figure 3, we show plots of G' and $\tan \delta$ against temperature, measured by DMA, for potato starches. The samples were prepared by gelatinizing at 60 °C for 1 h, lyophilizing immediately after the gelatinization, and then adjusting the water content to ≈23.2%. We see that, at all frequencies (ν), each G' curve decreases remarkably, while $\tan \delta$ gradually increases through a peak or shoulder (which is indicated by an arrow in the figure) with increasing temperature. In addition, both the onset temperature of the decrease in G' and the temperature of the maximum in $\tan \delta$ increased with increasing frequency. This means that the decrease in G' and the peak (shoulder) in $\tan \delta$ were caused by a time-dependent transition. We can estimate the apparent activation energy (E_{ac}) of the transition from an Arrhenius plot of $\log \nu$ against the reciprocal of the

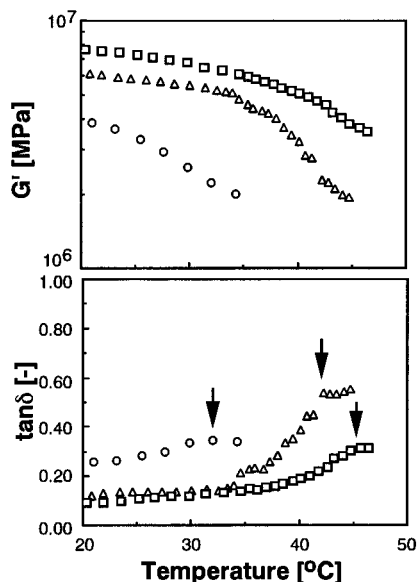


Figure 3. Plots of storage modulus, G' , and loss tangent, $\tan \delta$, against temperature for potato starch samples (23.2% w/w water): (○) 0.1 Hz; (△) 0.5 Hz; (□) 1 Hz.

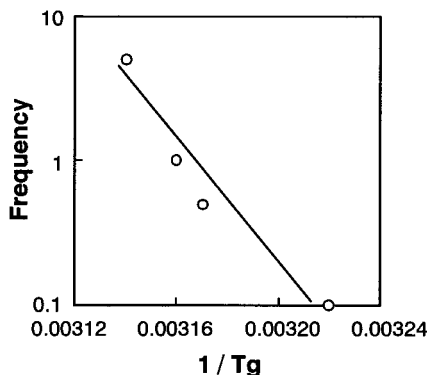


Figure 4. Arrhenius plot of the DMA data for potato starch samples (23.2% w/w water).

transition temperature (Kalichevsky et al., 1993), according to the Arrhenius equation

$$\nu = A \exp(E_{\text{act}}/RT) \quad (2)$$

where R is the gas constant, T is the transition temperature, A is a constant, and ν is the frequency of the DMA measurement. We defined the transition temperature as the temperature maximum of $\tan \delta$, and Figure 4 shows the Arrhenius plot of the DMA data for the potato starch samples.

The E_{act} value obtained from the slope of the plot is 383 kJ/mol. This value agrees with the apparent activation energy of a glass transition in biopolymers, which is generally said to be in the range of 200–400 kJ/mol (Kalichevsky et al., 1993). Therefore, the decrease in G' observed for the starch samples (Figure 3) is taken to be caused by a glass transition. It is well-known that a significant decrease in modulus (typically ~ 3 orders of magnitude) is usually observed for the glass transition of an amorphous synthetic polymer (Kalichevsky et al., 1993). However, the decrease in modulus for starch samples (Figure 3) was much smaller than that generally seen for synthetic polymers; this may have been caused by the presence of partial crystallinity or cross-linking, mainly due to hydrogen bonding in starch.

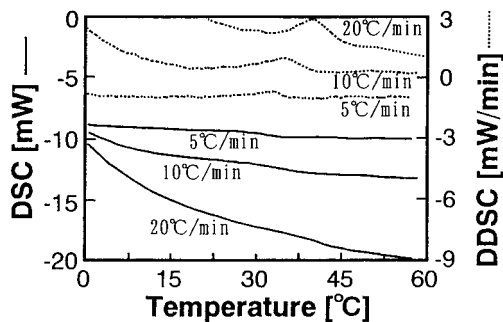


Figure 5. DSC data for potato starch sample containing 23.2% water.

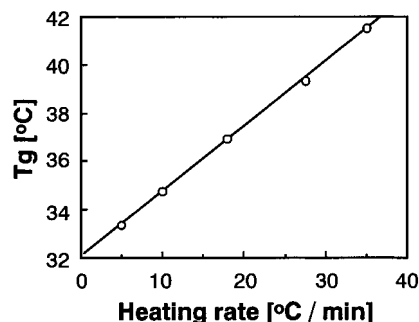


Figure 6. T_g of potato starch, measured by DSC as a function of heating rate.

In Figure 5, the DSC data for the same potato starch sample (water content = 23.2%) as measured by DMA are shown. The heat flow (DSC) curve and the derivative of the heat flow (DDSC) curve are described for each heating rate. For each heating rate, a clear shift in specific heat and a peak in the derivative of heat flow were observed. Biliaderis et al. (1986) and Slade and Levine (1987, 1988) suggested that the glass transition in native granular starch with excess water occurred immediately prior to gelatinization and that the increased heat capacity observed after gelatinization on heating was due to the glass transition. As shown in Figure 5, an endothermic peak representing gelatinization could not be observed in our experiment, because the sample had already been gelatinized. The temperature range of the shift in specific heat agreed approximately with other data for starch at low water contents <25% (Zeleznaek and Hosney, 1987). Therefore, the shift in specific heat, shown in Figure 5, was considered to be due to a glass transition. The transition temperature obtained from the peak of the DDSC curve increased with increasing heating rate, confirming that this transition was time-dependent (Slade and Levine, 1987).

In Figure 6, the dependence of the transition temperature on heating rate is shown. By extrapolating the data to zero heating rate ($T_{g\text{DSC}}$), we can estimate a transition temperature of $\approx 32^\circ\text{C}$. For synthetic polymers, the $T_{g\text{DSC}}$ is generally said to correspond to the temperature maximum of $\tan \delta$, from DMA measurements at ≈ 0.001 Hz (Kalichevsky et al., 1993). Following this approach, we estimated the equivalent frequency, at which the $T_{g\text{DSC}}$ could be obtained from DMA measurements from the Arrhenius plot in Figure 4. The estimated value was ≈ 0.005 Hz. This value agreed roughly with that for synthetic polymers; this agreement suggests that the T_g values obtained from DSC and DMA are fairly reasonable. On the basis of this confirmation of the validity of such T_g values, we subsequently measured T_g of starch samples by DSC.

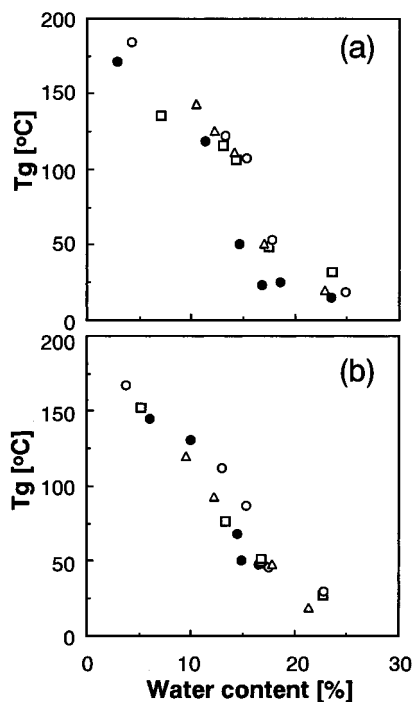


Figure 7. Dependence of T_g on water content, for potato (a) and wheat (b) starch samples that were gelatinized at 120 °C. The samples were stored for different periods: (●) 0 days; (○) 3 days; (△) 10 days; (□) 3 weeks.

Relationship between T_g and Crystallinity of Starch Samples. In Figure 7a, the dependence of T_g on water content of potato starch samples is shown. The samples were prepared by gelatinization at 120 °C followed by storage at 5 °C for the periods indicated in the figure legend. The values of T_g decreased with increasing water content, confirming that water acted as a plasticizer of the starch samples (Slade and Levine, 1987). The solid symbols are data for samples prior to storage, which is taken to be the condition producing an essentially completely gelatinized starch, i.e. essentially zero crystallinity. Although there were a few exceptions, we generally see that the T_g values of completely gelatinized samples are lower than those for the other samples, indicated by open symbols, in the range of measured water contents. In Figure 7b, the data for wheat starch samples, prepared according to the same method as for potato starch in Figure 7a, are shown. The plasticizing effect of water on the wheat starch samples was also observed. However, the difference in T_g between samples that were stored for different periods was less than the corresponding difference between potato starch samples.

The dependence of T_g on water content, for starch gelatinized at 60 °C, is shown in Figure 8. As shown in Figure 8a, the T_g of potato starch samples increased slightly with increasing storage period, as it did for samples gelatinized at 120 °C. However, the extent of the increase in T_g was less than that for samples gelatinized at 120 °C (Figure 7a). Especially in the case of wheat starch gelatinized at 60 °C (Figure 8b), there was very little difference in T_g values between samples that were stored for different periods, suggesting that the T_g of wheat starch gelatinized at 60 °C was little affected by the storage period prior to lyophilization.

Since many foods are generally stored at constant temperature, textural changes (e.g. softening or hardening) may be caused by changes in water content rather

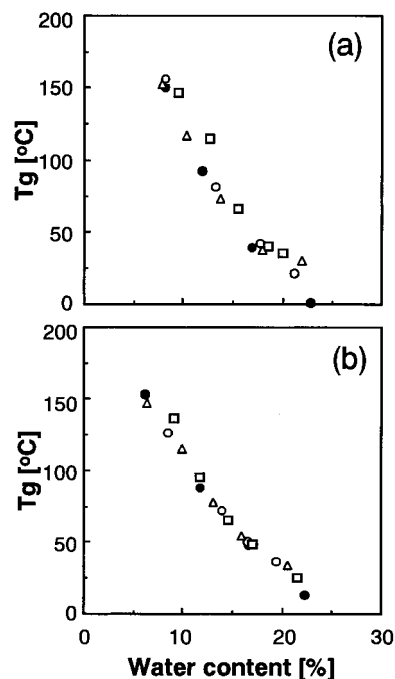


Figure 8. Dependence of T_g on water content, for potato (a) and wheat (b) starch samples that were gelatinized at 60 °C. The samples were stored for different periods: (●) 0 days; (○) 3 days; (△) 10 days; (□) 3 weeks.

than temperature. Therefore, to prevent or retard textural changes in starch-containing foods, arising from water migration during storage at ambient temperature, we must determine the water content at which the glass transition of a food occurs at ambient temperature; this water content can be a good indicator of textural stability (Slade and Levine, 1987; Levine and Slade, 1993). Moreover, the glass transition of such foods appears to be dominated by the glass transition of starch, which is a main component of them. From this practical point of view, we estimated, from the measured T_g , the water content (W_{g25}) at which the glass transition of the starch samples would occur at 25 °C, according to the method described below.

First, the dependence of T_g on the water content of each sample was represented by the first-order equation

$$T = a + bW \quad (3)$$

where T is the measured T_g , W is the water content corresponding to the T_g , and a and b are constants. The correlation coefficients of the resulting regression equations were >0.94 . From the equations obtained, we could calculate W_{g25} . High W_{g25} signifies that the glass transition of the starch sample occurs at ambient temperature only at a high water content, suggesting a large resistance to textural softening caused by water migration.

In Figure 9a, the change in W_{g25} of starch samples, during storage at 5 °C after gelatinization at 120 °C, is shown. The W_{g25} increased with storage time, and the increment for potato was greater than that for wheat. On the other hand, as shown in Figure 9b, the increment in W_{g25} for starch gelatinized at 60 °C was smaller and reached a maximum value in a shorter period than for starch gelatinized at 120 °C. As shown earlier in Figure 2, the crystallinity of starch samples gelatinized at 60 °C reached maximum values in shorter periods than that for samples gelatinized at 120 °C. Therefore,

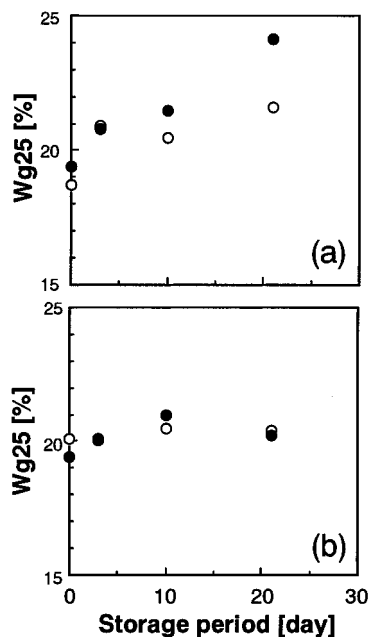


Figure 9. Change in W_{g25} of starch samples, gelatinized at 120 (a) and 60 °C (b), during storage at 5 °C: (○) wheat; (●) potato.

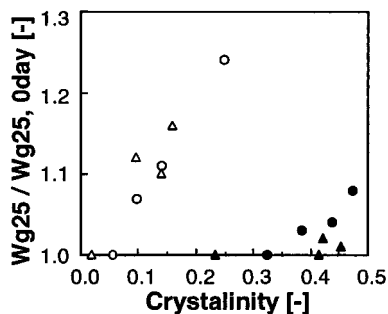


Figure 10. Relationship between the increment of W_{g25} and starch sample crystallinity: (○) potato gelatinized at 120 °C; (△) wheat gelatinized at 120 °C; (●) potato gelatinized at 60 °C; (▲) wheat gelatinized at 60 °C.

crystallinity in starch may be correlated with the extent of increase in W_{g25} . To clarify the correlation, the relationship between the increment of W_{g25} (i.e. the ratio of W_{g25} for each sample to the W_{g25} for the sample prior to storage, $W_{g25,0day}$), and sample crystallinity is shown in Figure 10. The open symbols are data for samples gelatinized at 120 °C, and the solid ones are for those gelatinized at 60 °C. For each group of samples that were different in the method of gelatinization, there appears to be a correlation between the increment in W_{g25} and crystallinity on the whole. That is to say, in each group of samples that were gelatinized in the same way, the higher the crystallinity of the starch sample, the higher W_{g25} of the sample became, regardless of the type of starch. This is worthy of note, as a result showing a quantitative relationship between T_g and the crystalline structure of starch. In addition, since the crystallinity of starch gelatinized at 120 °C signifies, in practice, the degree of retrogradation, the data for starch gelatinized at 120 °C demonstrate the effect of retrogradation on T_g of the starch. Zeleznak and Hosney (1987) investigated the effect of gelatinization on T_g of wheat starch, by comparing T_g data for native granular and pregelatinized starches. In our study, we

were able to determine the effect of retrogradation on T_g , as well as the quantitative relationship between T_g and crystallinity that was measured directly by X-ray diffraction.

To date, many studies of retrogradation of starch have been done, and several ideas about the mechanism of retrogradation have been suggested (Matsukura et al., 1983; Nakazawa et al., 1985). In one study (Miles et al., 1985), it was suggested that the retrogradation of starch consisted of two separate processes, one involving the amylose solubilized during gelatinization and the other involving amylopectin within the gelatinized granule. The former was considered to be caused mainly by gelation of amylose, and the process was found to occur over a short time period (within ~24 h). On the other hand, the process involving amylopectin was relatively slow (several weeks), and during the process, intra- and intermolecular associations of amylopectin chains, which were related to the development of crystallinity, were believed to occur. In our study, the retrogradation process involving associations of amylopectin chains appeared to have occurred, since gelatinized starch samples were stored for a sufficient period. Starch is a semicrystalline polymer, and crystalline regions, which are developed through the associations of amylopectin chains, are probably interspersed throughout the amorphous regions (Slade and Levine, 1987). In effect, the crystalline regions appear to act as physical cross-links that restrict the mobility of the polymer chains in the amorphous regions and, thus, elevate T_g (Slade and Levine, 1987). The relationship between crystallinity and T_g , experimentally determined in our study, appears to result from the T_g -elevating mechanism described above. Brinke et al. (1983) showed that T_g of styrene was elevated due to cross-linking by divinylbenzene, which joined the polymer chains by covalent bonds. This effect of cross-linking on T_g of synthetic polymers appears to be similar to the effect in starch, despite the difference in the types of cross-linking. This cross-linking in starch is believed to be caused mainly by hydrogen bonding. In future work, the effect of different types of cross-linking on the T_g of starch should be studied in detail.

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