

# Glassy–Rubbery Transition and Recrystallization during Aging of Wheat Starch Gels

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Dynamic mechanical analysis (DMA) data indicated an increase in final glass transition temperature with storage time, with no increase in initial temperature. After deconvolution, the  $\tan \delta(T)$  curve for ice melting was identified as the main peak, whereas glassy–rubbery transition peak(s) occurred at lower temperatures. Accompanying increase in “unfreezable” water and degree of amylopectin recrystallization showed that increase in the glassy–rubbery transition involved more than just moisture loss, and it may be possible that some amorphous network may have progressed extensively.

**Keywords:** Starch aging; DMA; glassy–rubbery transition

## INTRODUCTION

The changes (most notably firming) occurring in starch and starch-containing products during storage have been attributed to several factors including recrystallization of amylopectin, water redistribution, and the state of the amorphous phase. More recently, suggestions have been made that the latter could have a significant impact on staling (Laine and Roos, 1991; Hallberg and Chinachoti, 1992; Slade and Levine, 1991). Characterizing the glassy (brittle) to the rubbery (or vice versa) transition ( $T_g$ ) has been identified as an important step in determining the physical state of a system (Zeleznaek and Hosenev, 1987; Slade and Levine, 1991; Hallberg and Chinachoti, 1992; LeMeste et al., 1992). Much controversy exists as to the location of  $T_g$  and its impact on product quality. In particular, the glass transition of starch (whether native, gelatinized, or retrograded) has been difficult to identify and to characterize (Biliaderis, 1991; Gidley et al., 1993).

In high-moisture systems, excess water freezes upon cooling. When freezing is slow and enough time is provided for the maximum ice crystal formation to occur at a normal experimental time and temperature, the maximally freeze-concentrated phase exhibits a  $T_g$  called  $T_g'$ ,  $\approx -5$  °C for the case of starch (Slade and Levine, 1991). Upon aging or annealing of starch or bread, the  $T_g$  has been proposed to increase as the amylopectin recrystallizes, and such maturation of the amorphous starch polymer could lead to the increased firmness. During retrogradation some water has been suggested to become incorporated into the crystal lattice (Whittam et al., 1990; Sarko and Wu, 1978; Imberty et al., 1991), a process that some researchers believe to be one of the causes of a significant decrease in “freezable” water normally observed upon aging of starch (Ablett et al., 1993; Leung et al., 1983).

However, starch crystals in bread are in the discontinuous phase (Rao et al., 1992; Zeleznaek and Hosenev,

1987), and therefore their contribution to firming of bread can be viewed as far less significant than that caused by the continuous amorphous phase. Hallberg (1996) reported that a bread plasticized by glycerol could maintain a relatively soft texture over 3 months–1 year, even though the amylopectin crystallization reached a maximum (asymptotic) level. Wynne-Jones and Blanshard (1986) calculated the percent freezable water lost to the starch crystals upon aging to be only 1–2%, which was less than the decrease of the total freezable water. Additionally, Kim-Shin et al. (1991) reported that the amount of water that decreased in mobility was far in excess of the estimated number of moles of water in the crystalline lattice of starch and, thus, additional mechanisms were involved. Because the redistribution of water during staling occurs in the amorphous phase (Kim-Shin et al., 1991), an antiplasticizing effect is likely, and this could be one of the key factors controlling the increased firmness and crumbliness in staled breads.

Dynamic mechanical analysis (DMA) has been introduced to study thermomechanical changes in food (Roulet et al., 1988; MacInnes and Roulet, 1988; Kalichevsky et al., 1992; Vodovotz et al., 1996; Vodovotz and Chinachoti, 1996). This technique applies a sinusoidal stress as the sample temperature is increased at a given heating rate. In the case of viscoelastic material, the resulting strain is out of phase by an angle  $\delta$ . The  $\tan \delta(T)$  curve is defined as the ratio of the loss modulus ( $E''$ ) to the storage modulus ( $E'$ ), and a peak in  $\tan \delta(T)$  often corresponds to a phase change (e.g. glass or melting transition) at that temperature range. A simultaneous drop in the storage modulus during this transition reflects a decrease in the elastic component as the sample loses its ability to restore the mechanical energy (Murayama, 1978; Roulet et al., 1988).

The thermal transition region in bread (Vodovotz et al., 1996) and starch (Vodovotz and Chinachoti, 1996) represented by the  $\tan \delta(T)$  curve was found to increase in temperature range with drying from 50 °C to >100 °C wide, and this broadening was attributed to a great degree of segmental heterogeneity in the amorphous phase resulting in a greater distribution of transition temperatures. The shape of the  $\tan \delta(T)$  curves was found to be asymmetrical, skewing toward the lower

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temperature end. Deconvolution of the  $\tan \delta(T)$  (Charlesworth, 1993; Rotter and Ishida, 1992) yielded a symmetric Gaussian (typical of most phase transitions; Rotter and Ishida, 1992) and an asymmetric double-sigmoidal curve (mathematically most fitted function). While the spread of these peaks suggests multiple transitions, it is important that the general origins of these transitions be further identified. It is hypothesized that the Gaussian curve is attributed to ice melting (i.e. freezable water), whereas the asymmetric curve may be due either to ice melting of low  $T_m$  (melting temperature) water fractions or to a glassy-to-rubbery transition of the freeze-concentrated amorphous phase (Vodovotz et al., 1996; Vodovotz and Chinachoti, 1996).

DMA has been proven to be a powerful tool for distinguishing between the effects of drying and aging on the thermomechanical properties of bread (Hallberg and Chinachoti, 1992; Chinachoti, 1994; Vodovotz et al., 1996). It has been shown that the  $\tan \delta(T)$  curves for aged and fresh bread of similar moisture contents are very different in the transition temperature range; that is, the curve for aged bread was found to be broader (Vodovotz et al., 1996).

In the present work, gelatinized starches of different concentrations were analyzed by DMA and DSC techniques to characterize the glass transition and melting of ice (which reflects the amount of freezable/unfreezable water). Changes occurring during aging were studied with special emphasis on distribution of water and amorphous network ( $T_g$ ) in these systems.

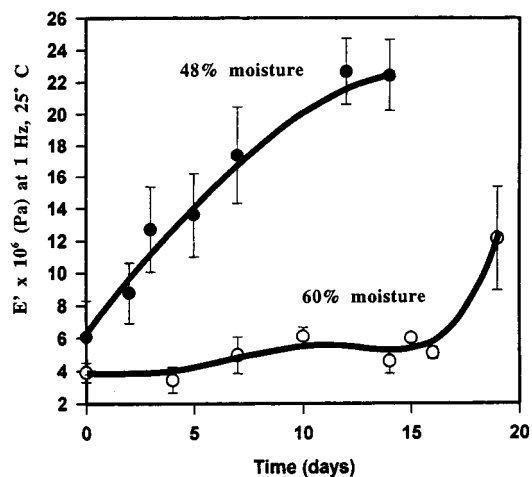
## MATERIALS AND METHODS

Wheat starch (Gemstar 100, kindly provided by Manildra Milling Corp., Minneapolis, MN) was mixed with water to obtain two mixtures with 48% and 60% water. Fifteen grams of a mixture with 48% moisture (paste) was placed between two sheets of aluminum foil and pressed for 5 min to 1.5 mm thickness with a Carver press (F. S. Carver, Inc., Summit, NJ) preheated to 85–90 °C. It was then cut into 50 mm  $\times$  25 mm  $\times$  1.5 mm slabs. In this process, samples reached 80 °C and the starch was completely gelatinized. The gelatinized starch sample was cooled at –4 °C for 5 min before the aluminum foil was peeled off. Moisture contents of the samples were 48  $\pm$  2% and 60  $\pm$  3%. In the case of 60% moisture (liquid), the sample could easily run off and the mixture had to be poured into a metal mold (50 mm  $\times$  25 mm  $\times$  2 mm) before pressing under above conditions. The final geometry of the sample bars was measured precisely, and these dimensions were entered into the DMA instrument for final calculations.

**Dynamic Mechanical Analysis (DMA).** Rectangular bars were placed in hermetically sealed glass cylinders. Samples were stored at 4 °C for up to 19 days. A cut bar was placed in the sample holder inside the furnace of a DMA (DMA 110, Seiko Instruments, Torrance, CA) and clamped (Hallberg and Chinachoti, 1992). The test was performed in a three-point bending mode at a strain level of 0.1% of the thickness. After cooling with liquid nitrogen, the sample was heated from –80 to 180 °C at 2 °C/min and sinusoidal strain was applied at 1 Hz. Storage modulus ( $E'$ ), loss modulus ( $E''$ ), and  $\tan \delta$  ( $E''/E'$ ) were recorded. More detailed analysis can be found elsewhere (Hallberg and Chinachoti, 1992; Vodovotz et al., 1996; Vodovotz and Chinachoti, 1996). Samples were run in four to six replicates.

**Characterization of DMA Transitions.** Multiple transitions were deconvoluted using PeakFit (Jandel Scientific, San Rafael, CA). The peak height, width at half-height, and area were measured.

**Differential Scanning Calorimetry (DSC).** The DSC was used to detect the degree of crystallization of water and



**Figure 1.** Storage modulus ( $E'$ ) values (stiffness) obtained by DMA at 1 Hz and 25 °C for 48% and 60% moisture starch gels during storage at 4 °C.

amylopectin retrogradation. About 10 mg of sample was placed in a stainless steel hermetic sample pan (Perkin-Elmer, Somerset, NJ). The instrument was calibrated using indium, and an empty pan was used as the reference. A Seiko Instrument DSC system (DSC 100, Seiko Instruments) was used at a heating rate of 2 °C/min (from –80 to 200 °C). The presence of crystalline amylopectin was measured from an endothermic melting peak at ~60 °C. The amount of freezable water (% FW) was obtained from the enthalpy associated with an endothermic peak at ~0 °C using the following equation:

$$\% \text{ FW (g/100 g of sample)} = \frac{\text{enthalpy (mJ/mg of sample)}}{\text{heat of fusion of water (335 mJ/mg of water)}} \times 100$$

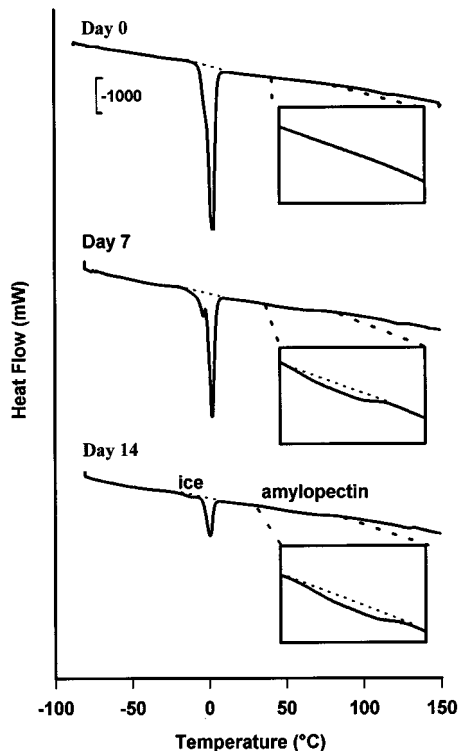
Analysis were done in three to four replicates. Standard deviation was between 1% and 3%.

**Moisture Content Determination.** Moisture content was determined in duplicate by the vacuum oven drying method (60 °C and 686 mmHg vacuum) for 24 h (AOAC method). The final weight of each sample was then determined, and the moisture content was calculated from weight loss. The percent error was  $\approx$ 2%.

## RESULTS AND DISCUSSION

**Storage Modulus ( $E'$ ).** The changes in  $E'$  during storage at 4 °C were determined by DMA. As shown in Figure 1 for the data obtained at 1 Hz and 25 °C, the  $E'$  values (stiffness) at 25 °C increased with storage time, depending on moisture content. For the case of 48% moisture, the stiffness increased significantly from 6  $\times$  10<sup>6</sup> to 24  $\times$  10<sup>6</sup> Pa over 12 days and then increased much less significantly or not at all thereafter. In contrast, the 60% moisture starch showed little change in stiffness in the first 16 days of storage and then increased significantly. The variable rate of increase in  $E'$  values at the two starch concentrations did not agree with the rate of amylopectin recrystallization rate (see below), and this shows that these discrepancies warrant further characterization.

**Amylopectin Recrystallization.** It has been well established that amylose is mainly responsible for the network structure formed in the initial stage of aging within 24 h after gelatinization and cooling (Leloup et al., 1991; Miles et al., 1985a,b). This effect was attributed to amylose leaching out from starch granules during gelatinization and subsequently forming crystals upon cooling and storage. Amylose then forms a gel

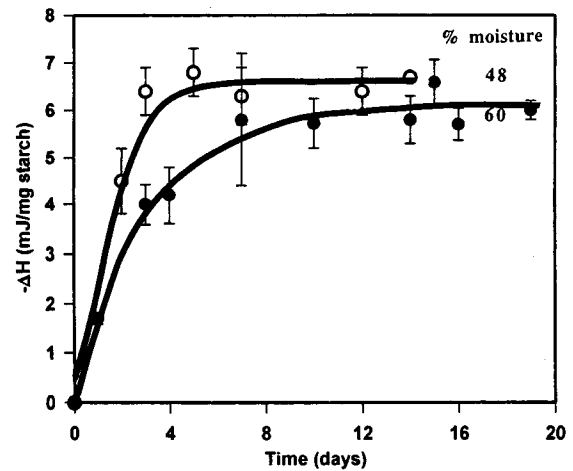


**Figure 2.** Typical DSC results of starch gels (48% moisture) stored at 4 °C for up to 14 days. Endotherms used to calculate percent freezable water (ice) and amylopectin recrystallization are indicated. Inset expands the temperature range at which amylopectin recrystallization occurred.

network with amylopectin embedded within (Biliaderis and Juliano, 1993; Miles et al., 1985a). In this work, we are interested in changes that take place during long-term storage (days) when amylose shows very little change (Biliaderis and Zawistowski, 1990; Miles et al., 1985a,b). Therefore, amylopectin has been suggested to play a more significant role in the staling process [e.g. Czuchajowska and Pomeranz (1989), Krog et al. (1989), and Wilson et al. (1991)]. Additionally, gel network development appears to originate from crystallization of the short chains of amylopectin molecules (Biliaderis and Zawistowski, 1990).

To assess the effect of amylopectin recrystallization on firming, the DSC endothermic transition at ~60 °C was followed during storage (Figure 2). The thermograms showed that over storage time, there was a decrease in ice melting enthalpy and an increase in amylopectin melting enthalpy (Figure 2). The enthalpy of ice melting was further analyzed and calculated to obtain the amount of freezable and unfreezable water, which will be discussed later (Figures 5 and 10). The amylopectin melting endotherm was found to be broad, and the enthalpy developed over time is plotted in Figure 3. The recrystallization of amylopectin agreed closely with those reported by Longton and LeGrys (1981) and Roulet et al. (1988). The sharp increase of the enthalpy at the early storage times occurred in the first 3 days of the 48% moisture samples and in the first 7 days (60% moisture samples), with final enthalpies of ~6.5 and ~5.7 mJ/mg of starch, respectively.

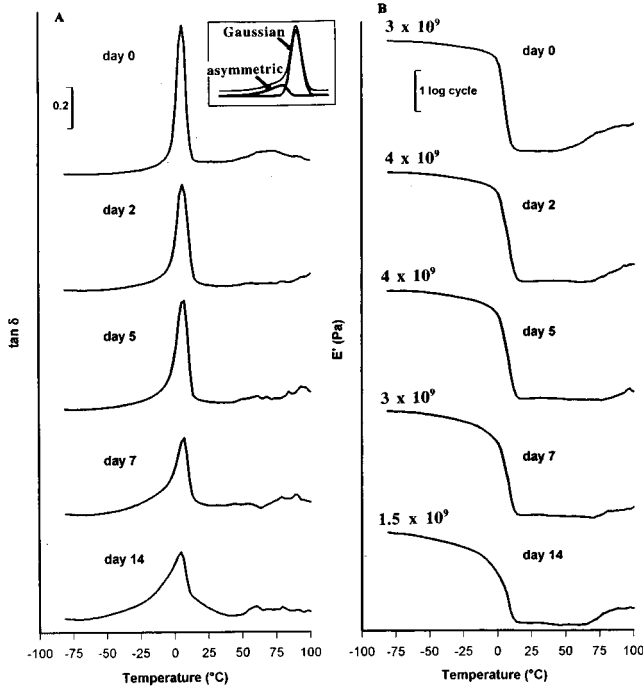
However, it can be seen that the relative increase in stiffness ( $E'$ , Figure 1) did not agree with that of the amylopectin crystallization (Figure 3). At 48% moisture,  $E'$  continued to increase and appeared to increase at a much slower rate at ~5 days of storage (Figure 1),



**Figure 3.** Enthalpy of amylopectin recrystallization (obtained from DSC) as a function of time for starch gels at 48% and 60% moisture contents.

whereas amylopectin crystallization showed a similar decrease at 3 days (Figure 3). Likewise, samples with 60% moisture showed a significant increase in amylopectin recrystallization during the first 4 days (Figure 3) but no increase in  $E'$  was observed (Figure 1). A similar lack of correlation has been observed in bread. Rogers et al. (1988) found no correlation between the rate of amylopectin crystallization and that of bread firming. Similarly, Hallberg (1996) observed only a slight increase of Meal, Ready-to-Eat (long shelf life, military) bread firming during long-term storage but a very significant increase in amylopectin crystallization.

Molecular network formation is highly dependent on a number of factors such as crystallization, the degrees of freedom (entanglement), which are a function of moisture–temperature, history, molecular weight, degree of branching (amylose/amylopectin ratio), and starch granule integrity at various stages of gelatinization. From a comparison of our data with others, it is clear that our discrepancies between  $E'$  and amylopectin crystallization appear to be different from previously published data [e.g. Ring et al. (1987), Roulet et al. (1988), and Miles et al. (1985a)]. The data reported by Ring et al. (1987) were not comparable as these researchers used waxy maize starch at different concentrations (20% starch) as compared to ours (wheat starch at 40% and 50% starch). Roulet et al. (1988) reported wheat starch gels at similar concentrations showing that modulus increased over time similarly to amylopectin recrystallization. However, their samples were extensively gelatinized (100 °C for 110 min) and most starch granules were likely to be ruptured, releasing polymers interspersed with water. In this paper, the gelatinization was relatively less extensive. It is possible that the starch, although containing none of its original crystallinity, maintained some of the granular structure and/or “memory” to recrystallize. Because amylopectin and amylose in starch are phase separated (Leloup et al., 1991), the contribution to the net rheological properties is dependent not only on how much recrystallization occurred but also on how well amylopectin is interspersed in the amylose network. This might have contributed to the difference in findings in this paper and that of Roulet et al. (1988). In our case, the amylopectin is likely to remain in some form of granular structure and thus the developed crystallites may be more concentrated in locations of the granules

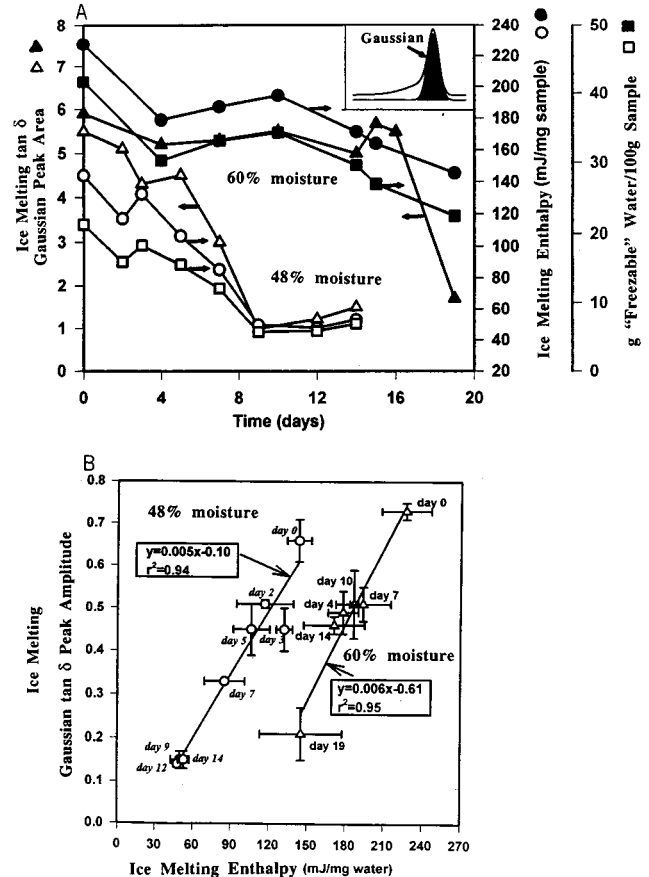


**Figure 4.** DMA results for starch gels of 48% moisture stored at 4 °C for up to 14 days: (A)  $\tan \delta(T)$  curves; (B)  $E'(T)$  curves. (Inset) Deconvolution of  $\tan \delta(T)$  curve into asymmetric double-sigmoidal and Gaussian curves.

(as a discontinuous phase). Thus, the amylopectin impact on the storage modulus is much less significant, particularly in the less concentrated sample (60% moisture). It is possible that other factors may have a more significant contribution to the observed firming during storage. These changes were likely to be in the amorphous domains.

**DMA Results.** To identify the origin of these changes, transition temperatures were followed with DMA. Parts A and B of Figure 4 show the  $\tan \delta(T)$  and  $E'(T)$ , respectively, for 48% moisture samples during 14 days of storage at 4 °C. A transition region at  $\sim 0$  °C for both cases of 48% and 60% moisture starch gel samples was observed as a sharp drop in  $E'(T)$  and a peak in  $\tan \delta(T)$ . The  $\tan \delta(T)$  peak height for 48% moisture starch gel samples decreased from  $\sim 0.7$  to 0.4 in 14 days (Figure 4A); the same decrease was observed for the 60% starch gels in 19 days (data not shown). Similarly, the  $E'(T)$  drop decreased during storage from  $\sim 3$  orders of magnitude at day 0 (Figure 4B) to  $\sim 2$  orders of magnitude at day 14 (Figure 4B) for 48% moisture samples. For 48% moisture gels, the transition occurred between  $-45$  and  $10$  °C for the freshly gelatinized sample (day 0, Figure 4A) and between  $-50$  and  $40$  °C for the aged starch gel (14 days, Figure 4A). Similarly, the 60% moisture starch samples resulted in a transition range of  $-45$  to  $15$  °C, increasing to  $-50$  to  $35$  °C after aging for 19 days.

The peak temperature of the  $\tan \delta(T)$  curve (averaging for both starch concentrations),  $4 \pm 2$  °C, remained unchanged during storage, although the shape of the curve was significantly altered (Figure 4A). The  $\tan \delta(T)$  curve was more skewed and the drop in  $E'(T)$  became less steep with storage time (parts A and B of Figure 4, respectively). Therefore, to better characterize the transition region, deconvolution of the  $\tan \delta(T)$  curve was carried out as was done previously for bread (Vodovotz et al., 1996).

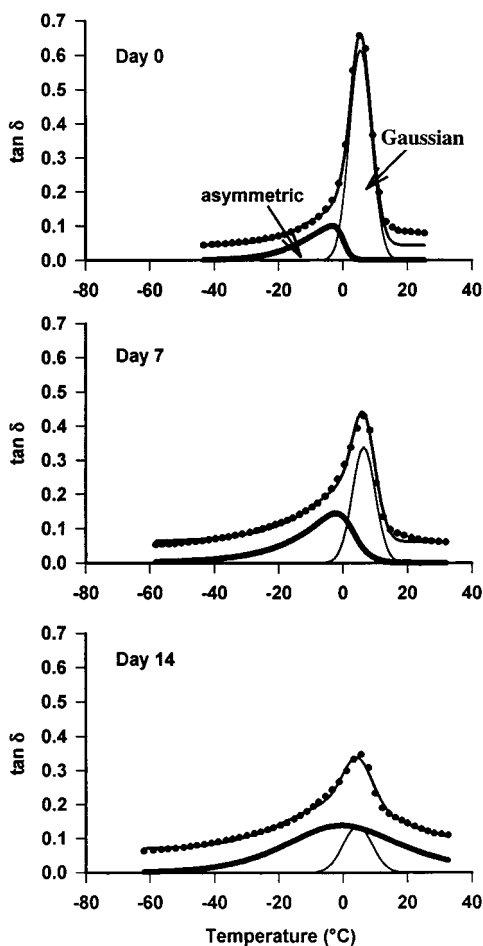


**Figure 5.** (A) Comparison of the DMA  $\tan \delta(T)$  deconvoluted Gaussian curve area (triangles) to ice melting enthalpy (circles) and percent freezable water (squares) of 48% moisture (open symbols) and 60% moisture (solid symbols) during aging. (B) Relationship between the Gaussian curve peak amplitude and ice melting enthalpy. Regression results are shown in boxes.

The deconvolution of the  $\tan \delta(T)$  curve resulted in a main Gaussian peak (most typical for thermal transitions; Rotter and Ishida, 1992) and an asymmetric double-sigmoidal curve (inset in Figure 4A). The origin of these deconvoluted curves is discussed below.

**Gaussian Curve.** Various parameters of the deconvoluted Gaussian curve were analyzed. The peak center temperature and width at half-height remained unchanged for both concentrations during the storage period. For both moisture concentrations, the peak area decreased with time (Figure 5A); however, the decrease was most drastic during the first 8 days for 48% moisture, whereas for 60% moisture the decrease was not significant until day 16. The same trends were seen for the Gaussian peak amplitude or peak height (data not shown).

Concurrently, the enthalpy of ice melting and percent freezable water (obtained by DSC) decreased in a parallel fashion with increased storage time. The ice melting peaks for DSC data are shown in Figure 2 as the major endothermic transition at  $\sim 0$  °C. This peak decreased in magnitude during storage for both 48% and 60% moisture contents. The change in enthalpy of this DSC endotherm was used to calculate the percent freezable water in the different starch samples during storage. The percent freezable water (total basis) for 60% moisture gels decreased from  $\sim 42\%$  to  $23\%$  in 19 days of storage, and, for 48% moisture, from  $23\%$  to  $7\%$  in 14 days of storage (Figure 5A).



**Figure 6.** DMA  $\tan \delta(T)$  deconvolution results of starch gels (48% moisture) stored at 4 °C for up to 14 days: symbols, actual data points; bold line, asymmetric double-sigmoidal curve; faint line, Gaussian curve; line, fitted results.

A plot of the Gaussian curve height (DMA results) against the enthalpy of ice melting (DSC results) for both starch concentrations (Figure 5B) yielded a straight line relationship with very good correlation coefficients (0.94 and 0.95 for 48% and 60% moisture, respectively). Similar results have been reported earlier in the same systems with different moisture contents (Vodovotz and Chinachoti, 1996). This indicates that the Gaussian curve was due to freezable water. Therefore, the main contribution to the transition region observed in DMA of these starch gels is due to ice melting.

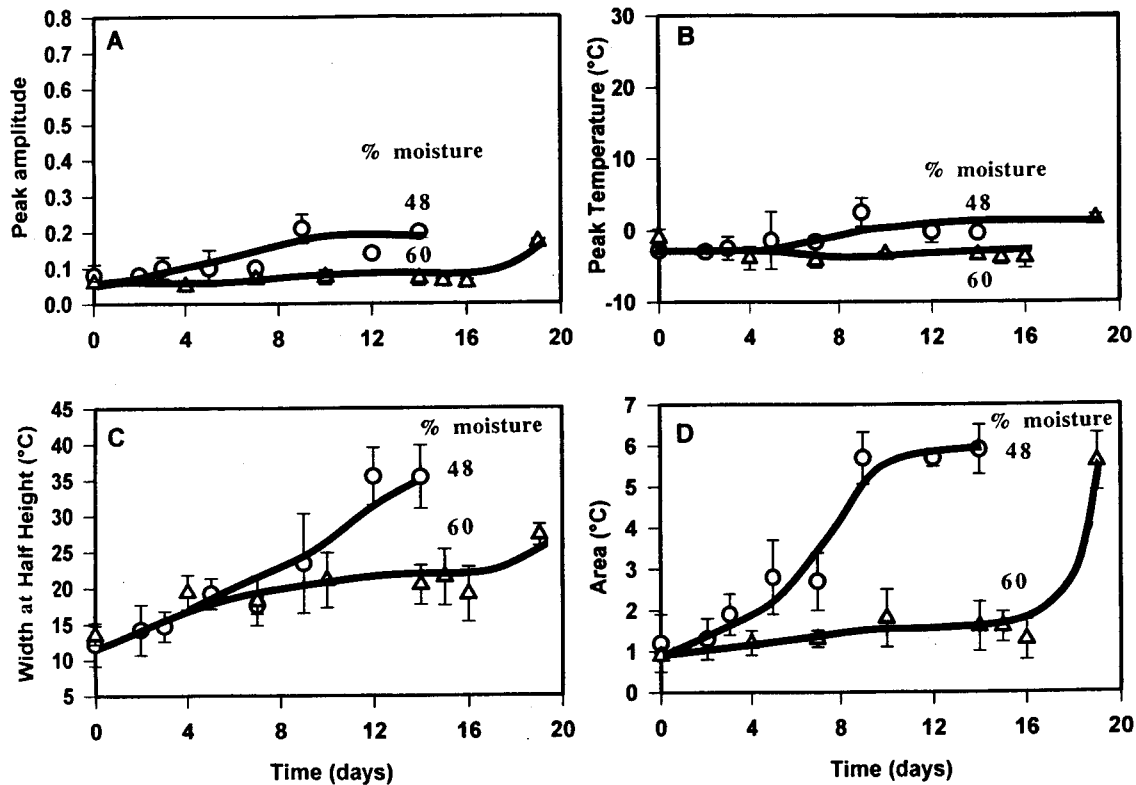
**Asymmetric Curve.** The  $\tan \delta(T)$  asymmetric curves (48% moisture gels) thus represent transition(s) in the freeze-concentrated phase. The curve became broader and more symmetrical with increasing storage time (Figure 6). The changes in peak amplitudes, peak temperatures, widths, and areas at different storage times for both starch concentrations are shown in Figure 7. No significant change was observed in either peak amplitude or peak temperature for both starch concentrations over the storage period studied (Figures 7A,B, respectively). The peak width (at half-height) increased significantly over time at 48% moisture and only slightly at 60% moisture (Figure 7C). The most significant change was found in the peak area, which increased significantly after lag periods of 7 and 16 days for 48% and 60% moisture, respectively (Figure 7D). All of these changes occurred while the initial temperature remained relatively constant ( $\sim -40$  °C), and the final

temperature was the one that increased from 0 to 10 °C to over 50 °C (Figure 8). Note that this agreed with relative changes in the asymmetric peak area (Figure 8) and changes in  $E'$  (Figure 1). Therefore, it may be concluded that stiffness of starch gel upon aging was dominated by changes associated with and increase in transition temperature(s) within the asymmetric peak.

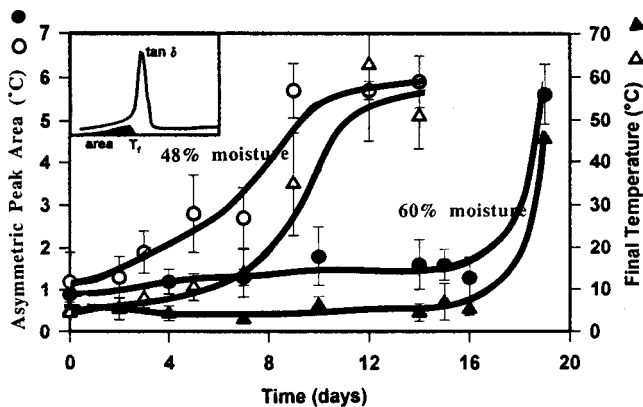
Assuming that the asymmetric curve represented the glass–rubber transition, the observed widening of the transition region and consequent larger area may be attributed to an increase in cross-linking (Brinke et al., 1983; Zeleznak and Hosney, 1987) and a greater degree of heterogeneity (Nielsen, 1962). These changes in the starch gel system could be represented by the “fringed micelle” model in which crystalline regions act as junction zones between flexible coil chain segments in the amorphous matrix, resulting in a three-dimensional network (Slade and Levine, 1991). Figure 9A shows a schematic representation (top) of the polymer network during aging of gelatinized starch that is being suggested to help explain the observed DMA data (Figure 9B). In such systems, an increase in the number of cross-links upon aging would lead to the formation of a more closely packed starch network with decreased mobility. The extent of packing of the starch segments in the network most likely was nonuniform. Increasing the heterogeneity of the system (Figure 9A) leads to a broader glass transition temperature range [seen as a higher final temperature of the transition in the deconvoluted  $\tan \delta(T)$  asymmetric curve (Figures 8 and 9B)]. Changes in  $E'$  did not follow the same trends as amylopectin crystallization, indicating a lack of its direct impact on rheological properties (concluded from the lack of agreement between data in Figures 1 and 3). Alternatively,  $E'$  increase during aging could have been more influenced indirectly by the amorphous network on a structural level.

Other factors must also be considered as possibly leading to the observed broadening of the asymmetric curve. One of them is moisture loss, which was detected (for example, a decrease from 48% to 43% moisture content in 14 days), which may have contributed to firming of the starch gel and increased the temperature range of the transition region. However, the magnitude of change was far more extensive than that due to moisture loss alone. In fact, a moisture loss of 5% in this high-moisture range should not have significantly affected the glass transition temperature range since at this very high-moisture level  $T_g$  should be at values near  $T_g'$  ( $-5$  °C) (Slade and Levine, 1988; Roos and Karel, 1993; Simatos et al., 1993; Ablett et al., 1993).

It is interesting to note that the increasing changes in the asymmetric curve area were accompanied by the increasing amount of unfreezable water in the system. Figure 10 compares these two factors of aging starch gels containing 48% moisture. The increase in the amount of unfreezable water was more rapid initially and then leveled off after 9 days (Figure 10). As stated earlier, moisture loss might have contributed to this change. However, on the basis of our previous study on the moisture effect (Vodovotz and Chinachoti, 1996), such a small amount of moisture should have resulted in an increase in peak area to a value of  $\sim 2$ , but our observed increase was 6 (Figure 7D). This suggests additional contribution(s) possibly from the amorphous network (leading to an increased  $T_g$  range) of the starch gel during aging, which may be contingent on the amount



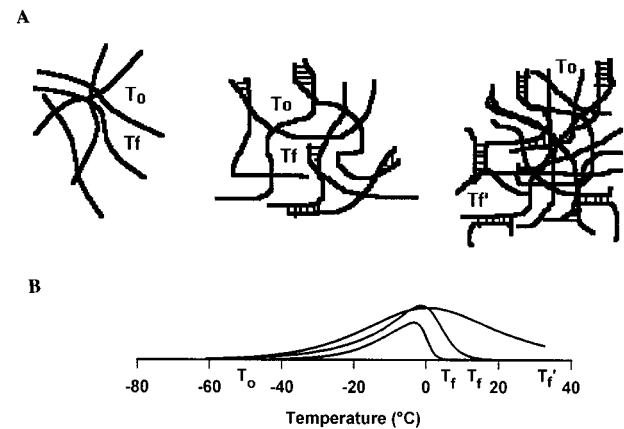
**Figure 7.** Parameters obtained from the  $\tan \delta(T)$  deconvoluted asymmetric double-sigmoidal curve of starch with 48% moisture (circles) and starch with 60% moisture (triangles); both were aged at 4 °C.



**Figure 8.** Comparison of the area (circles) and final temperature (triangles) of  $\tan \delta(T)$  deconvoluted asymmetric curve of 48% moisture (open symbols) and 60% moisture (solid symbols) starch gels stored for different lengths of time at 4 °C. (Inset) Area and final temperature ( $T_f$ ) of the asymmetric curve (shaded area) derived from the  $\tan \delta(T)$  curve.

of unfreezable water or vice versa. As a tighter network is formed, increasing amounts of water are trapped in three-dimensional network matrices and becomes unfreezable. Note that the increase in the asymmetric peak area and temperature (Figure 7) did not seem to be closely related to the amylopectin crystallization (Figure 3), at least in the 50% starch sample.

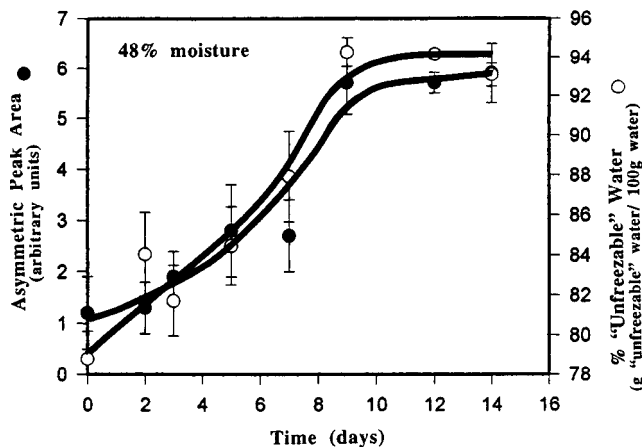
Additional evidence of a development of a more rigid starch chain during storage at 4 °C has been studied by this group (Vodovotz, 1996).  $^{13}\text{C}$  CP-MAS NMR experiments of aged gelatinized starch showed a gradual increase in rigidity of the polymer chain upon aging at 4 °C for up to 10 days (Vodovotz, 1996). Additionally, a cross-relaxation proton NMR experiment (60% moisture) resulted in an increase of rigid solid proton transition (Vodovotz, 1996). However, such molecular



**Figure 9.** (A) Suggested schematic representation of the proposed network formation upon aging of starch gels.  $T_0$  represents initial temperature and  $T_f$  and  $T_f'$  represent the final temperatures of the glass-rubber transition. Crystalline domains are also shown. (B) Changes in DMA  $\tan \delta(T)$  asymmetric deconvoluted curve representing network formation.  $T_0$ ,  $T_f$ , and  $T_f'$  are indicated.

transitions might reflect the development of the microcrystalline starch due to retrogradation.

**Conclusion.** Thermal transitions as monitored by DSC and DMA have been shown to go through some changes upon aging. The main  $\tan \delta(T)$  peak investigated was confirmed to be due to ice melting, decreasing with increased storage time. Changes in amylopectin were investigated since amylose is mainly responsible for network structure in the initial stages of storage. Amylopectin recrystallization (DSC) increased over time as expected but at a rate different from that of the rheological change ( $E$ ). The asymmetric curve (obtained after deconvolution) seems to represent the  $T_g$  range of the amorphous domain. The increase in final



**Figure 10.** Comparison of the deconvoluted  $\tan \delta(T)$  asymmetric curve (solid symbols) and percent unfreezable water (open symbols) for gelatinized starch (48% moisture) stored at 4 °C.

temperature and  $\tan \delta(T)$  peak area of this curve during storage time accounted for more than just moisture loss alone, and it was possible that the glassy-to-rubbery transition may have increased upon aging. This transition was found to be closely related to the amount of unfreezable water but not amylopectin crystallization. The transition regions depicted by the asymmetric curve can have a wide span of 50–>100 °C in temperature range. Considering the complexity of starch, it is clear that a wide distribution of  $T_g$  values exists, and the network formation, if it occurs, would be represented by an increase in some  $T_g$  values, leading to an increase in final temperature of the transition. More about this subject is discussed in detail elsewhere (Vodovotz et al., 1996; Vodovotz and Chinachoti, 1996). During storage, the segmental mobility in certain regions may be increasingly restricted due to the additional cross-links (fringes caused by the microcrystalline phase).

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