Moisture Redistribution and Phase Transitions During Bread Staling

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ABSTRACT

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Standard white breads were stored with or without crust at 25°C in hermetic pouches. During two weeks of storage, the crumb moisture content and water activity (a_w) decreased significantly when stored with crust. When stored without crust, moisture content and a_w remained relatively unchanged. The causes of the initial firming of both breads over zero to seven days were not conclusive. But when stored beyond seven days, bread stored with crust was significantly firmer in texture and higher in amylopectin recrystallization than bread stored without crust. Moisture redistribution from crumb to crust played a significant role. This was accompanied by a decrease in freezable water in the bread crumb stored with crust. This loss in freezable water coincided with changes in the thermomechanical profile only in the case of sample stored with crust intact (and with a significant total and freezable water loss). Bread crumb stored without crust did not change in total and freezable water and showed less change in thermomechanical transitions. The transition occurring at ≈60°C (T_2) correlated with amylopectin recrystallization but it could also have been caused by moisture loss during the analysis. Moisture migration from crumb to crust greatly reduced the total and freezable water in the crumb region, resulting in a significant reduction in the magnitude of the mechanical transition at ≈0°C (T_1) as well as an increase in the storage modulus.

Bread is a food that has shorter shelf life than most other processed foods. Bread rapidly loses freshness (texture and flavor) and is subject to mold spoilage. The limited shelf life of bread has an economical impact of millions of dollars in the United States and perhaps of billions of dollars for the world per year (Berkowitz and Oleksyk 1991).

Bread staling has been mostly related to the retrogradation of starch (Schoch and French 1947). Recent reports have shown that starch retrogradation is not the only major factor (Zobel and Senti 1959, Dragsdorf and Varriano-Marston 1980, Ghiasi et al 1984, Rogers et al 1988, Martin and Hoseney 1991, Martin et al 1991). Other mechanisms involved may be cross-linking between partially solubilized starch and gluten (Martin and Hoseney 1991, Martin et al 1991), partial drying (He and Hoseney 1990), and glassy-rubbery transition (Levine and Slade 1988).

Water plays a critical role in bread staling (Leung et al 1983, Wynne-Jones and Blanshard 1986, He and Hoseney 1990, Piazza and Masi 1995, Vodovotz et al 1996). Softening of the crust and hardening of the crumb are related to moisture redistribution (crumb-to-crust migration) during storage (He and Hoseney 1990, Piazza and Masi 1995). Thus, slowing down the dehydration of the internal crumb might be a better countermeasure than increasing the initial moisture content in the bread (Piazza and Masi 1995). However, the higher the moisture, the slower the firming rate (He and Hoseney 1990). Additionally, separation of crumb from crust (thus eliminating water migration) might maintain the original crumb moisture during storage but might not prevent firming of the crumb (although firming rate would be lower) (He and Hoseney 1990). Vodovotz et al (1996) reported the difference in thermomechanical properties resulting from drying and aging bread using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Aging led to a broadening of the main multiple thermomechanical transition (T_1) that could be deconvoluted into at least two tan δ peaks, while drying of fresh bread resulted in only one peak (T_1).

The glass transition temperature (T_g) of bread has been investigated by various thermal analytical methods such as DSC, DMA, and thermomechanical analysis (TMA) (Levine and Slade 1988, Hallberg and Chinachoti 1992, Le Meste et al 1992, Vodovotz and Chinachoti 1996, Vodovotz et al 1996). One of the problems with those analyses is that there are a number of overlapping contributors to thermomechanical behavior such as gluten, starch, and water (Chinachoti 1996). For bread at >35% moisture content, T_g may overlap with the ice-melting transition and deconvolution may be necessary. DMA is more sensitive than DSC, but sample preparation methods may alter the physical characteristics of the sample (by pressing into a bar shape, etc.), and lack of moisture control during the heating cycle may lead to a significant moisture loss and a subsequent false positive for a transition derived from hardening due to a drying artifact.

The objective of this work was to study the role of moisture in the aging of bread. Firmness, thermal characteristics, and thermomechanical properties of white bread stored with or without crust were investigated during storage.

MATERIALS AND METHODS

Bread

Wheat flour (unbleached, all-purpose; 10% protein; 73.3% carbohydrate starch containing ≈71% amylopectin; and 16.7% water), shortening, sugar, nonfat dry milk, active dry yeast, and salt were purchased at the local grocery store. Potassium sorbate was purchased from Sigma Chemical Co. (St. Louis, MO) and calcium propionate from Pfizer Inc. (New York, NY).

Standard white bread was made using an automatic breadmaking machine (bread bakery model SD-BT51P, Panasonic, Secaucus, NJ) and a general baking method. The mixing time was 20 min, the resting time was 5 min, and the kneading period was 5 min. The dough was allowed to rise for 160 min, and then it was baked at 160°C for 50 min. The formulation of the standard white bread is shown in Table I. After baking, two storage methods were used: 1) each loaf of bread was packed with the crust intact, or 2) the crust was removed by cutting a loaf into shapes (height × width × length) of 15 × 25 × 25 mm for firmness testing and 13 × 13 × 60 mm for DMA testing. Before or after cutting, each sample was hermetically sealed in a trilaminated pouch and stored at 25°C. At

TABLE I
Formulation of White Bread

Component	Weight (g)
Wheat flour	200.00
Water	120.00
Shortening	10.00
Sugar	9.40
Nonfat dry milk	6.00
Active dry yeast	5.40
Salt	4.50
Calcium propionate	0.96
Potassium sorbate	0.48

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least three replicates from three different loaves were used for each experiment.

Moisture

Moisture content was determined using a vacuum-oven drying method at 70°C and 30 mmHg overnight (Method 925.09, AOAC 1973), and calculated from the weight change. Water activity (a_w) of the bread crumb was determined using a modified isopiestic method (McCune et al 1981).

Texture

A modification of Approved Method 74-10 (AACC 2000) was used to measure the firmness of bread crumb using a universal testing machine (model 5540, Instron Corp., Canton, MA). The bread crumb (15 × 25 × 25 mm) was uniaxially compressed from 15 to 11.25 mm in height to measure force at 25% deformation. The diameter of the cylindrical plunger was 50 mm and the cross-head speed was 10 mm/min.

DSC Analysis

Samples (≈15 mg each) were placed in a stainless steel sample pan (Perkin Elmer, Somerset, NJ) and hermetically sealed. Using an empty pan as reference, a sample was put into the DSC instrument (DSC100, Seiko Instruments, Torrance, CA), cooled to –40°C using liquid nitrogen, then heated to 140°C at 5°C/min to obtain a thermogram. Ice and amylopectin melting enthalpies were calculated from the DSC thermogram. The DSC instrument was regularly calibrated with indium.

DMA Analysis

Each loaf center was cut to a shape 13 × 13 × 60 mm and then compressed using a Carver press at room temperature to obtain ≈2.0 mm thickness. The sample was analyzed using a three-point bending mode in a DMA instrument (DMA110, Seiko Instruments, Torrance, CA) as described by Hallberg and Chinachoti (1992). The sample was heated from –100 to 120°C at 2°C/min. During the heating process, a sinusoidal force was applied to the bar over a range of preselected frequencies (1, 2, 5, 10, 20, 50, and 100 Hz). The results were recorded as the storage modulus (E'), the loss modulus (E''), and the tan δ (E''/E'). At least three replicates from different loaves were determined for each sample in all measurements. To characterize the phase transition, the tan δ curve was deconvoluted using PeakFit software as previously described (Vodovotz et al 1996).

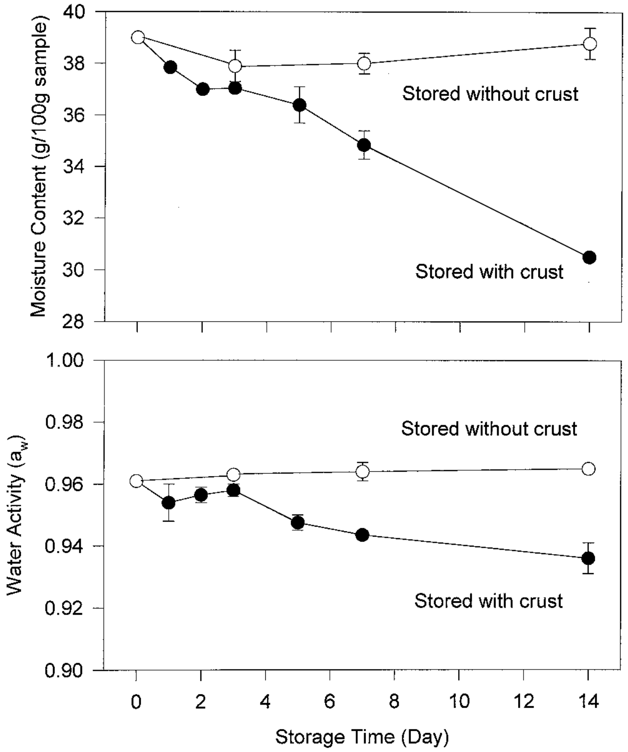

Fig. 1. Changes in moisture content and water activity of bread crumb during storage at 25°C.

RESULTS

Moisture Content and Water Activity (a_w)

Figure 1 shows the changes in moisture content and a_w of bread crumb during storage at 25°C. Both moisture content and a_w of the bread crumb stored with crust decreased significantly during storage; those of bread crumb stored without crust did not change over time. After baking, there was a moisture gradient between crust and crumb that tended to equilibrate during storage. In a closed system, water would equilibrate between the crumb and crust during storage

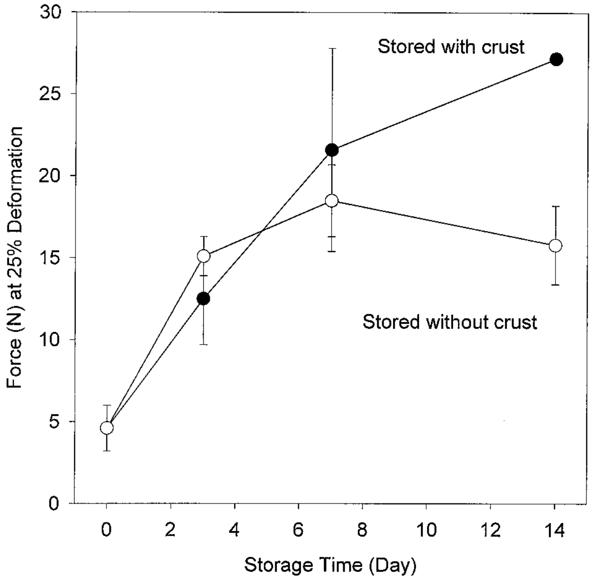

Fig. 2. Changes in bread crumb firmness during storage at 25°C.

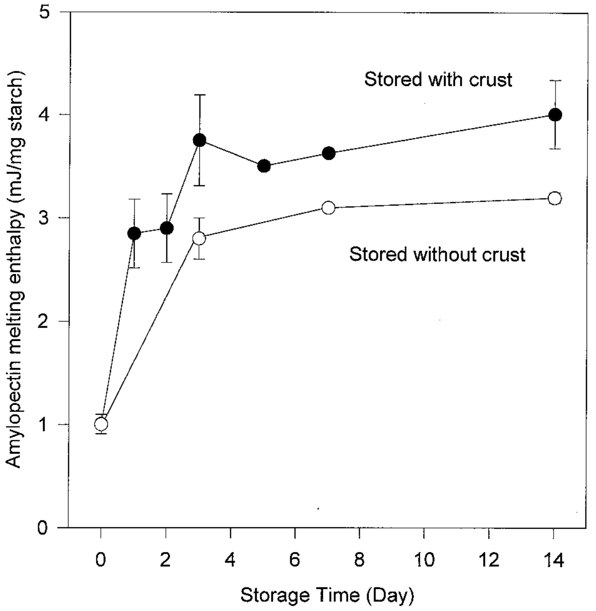

Fig. 3. Changes in amylopectin crystallinity of bread crumb during storage at 25°C.

driven by the moisture gradient. This moisture redistribution could affect the localized a_w and the localized amylopectin recrystallization kinetics (Czuchajowska and Pomeranz 1989). Thus, moisture content of the crust increased, while that of center crumb gradually decreased during storage, as reported earlier (Piazza and Masi 1995).

The bread crumb samples stored with crust maintained original a_w = 0.954–0.961 during the first three days and then decreased after three days to reach a_w = 0.936 by day 14.

Firmness

Bread crumb firmness increased initially with storage time for samples stored with and without crust (Fig. 2). After the first week of storage, the bread crumb stored without crust started to level off in firming, while that with crust continued to increase in firmness (Fig. 2). In the latter case, this was accompanied by a significant moisture loss (from 39.0% at day 0 to 30.5% at day 14). Thus, the additional firming beyond the first week of storage with crust was due at least in part to drying of the crumb. This work confirmed, however, that keeping the crumb moisture constant by storing without crust did not prevent staling of the bread, firming still occurred.

DSC Analysis

Enthalpy associated with amylopectin recrystallization increased with storage time, reaching an asymptotic level after three to seven days of storage for both cases (Fig. 3). However, the sample stored with crust showed a significantly larger endotherm than that stored without crust. Rogers et al (1988) reported that the increase in the size of DSC transition over time might not correlate exactly with bread firming. Figures 2 and 3 indicate that while both firmness and enthalpy increased over time, they did not increase in an exactly parallel fashion. Bread firming in some cases might not be related simply to starch crystallization, although both are known to develop simultaneously (Martin et al 1991). The results reported here demonstrate additional roles of other factors such as local and bulk water migration in addition to amylopectin recrystallization.

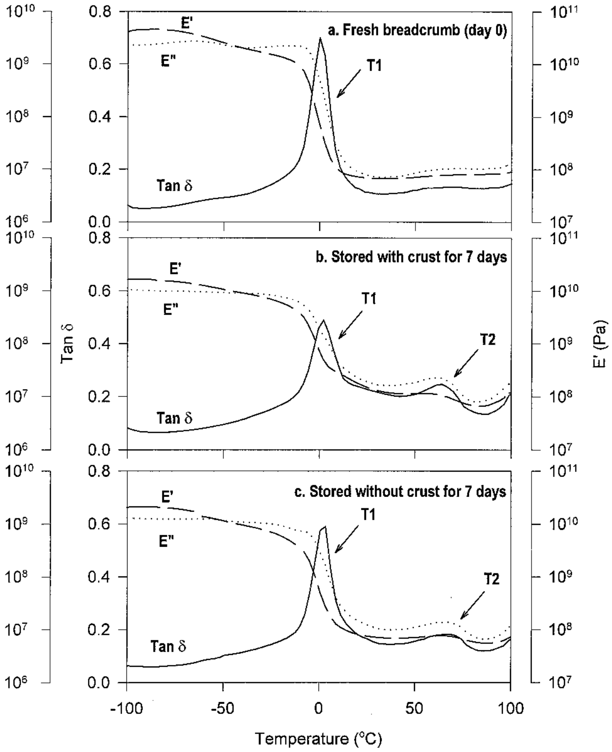

Fig. 4. Dynamic mechanical analysis (DMA) thermograms for bread crumb during storage at 25°C. E' = storage modulus, E'' = loss modulus, tan δ = E''/E'.

The initial firming (zero and three days of storage) showed no significant difference between bread stored with crust and without crust (Fig. 2). Within experimental error (25%), samples at three days stored without crust appeared to be less firm ($P < 0.05$) as compared with those stored with crust (Fig. 2). This was in spite of significantly less amylopectin crystallization (day 3, Fig. 3) and relatively higher moisture content (day 3, Fig. 1). Other changes in the amorphous regions might be responsible. For example, amylopectin crystallization in the sample stored with crust could lead to exclusion of water in the neighboring amorphous region as a part of increased physical cross-linking (fringe in the starch micelle). This is supported by the change in DMA transition: T_1 decreased in tan δ with the broader base moving to a higher temperature (Fig. 4b) (Vodovotz and Chinachoti 1996). The expelled water might become absorbed by neighboring amorphous components such as gluten weakening and soften the bread structure. There may be other possible mechanisms responsible. This remains to be investigated.

The ice-melting enthalpy measured by DSC was used to approximate the amount of freezable water under experimental conditions. Stored with crust intact, the bread crumb decreased gradually in freezable water up to seven days of storage and decreased dramatically thereafter (Fig. 5). When stored without crust, freezable water decreased slightly from zero to three days and remained constant thereafter. These data were in agreement with the moisture loss data (Fig. 1), suggesting that most of the loss in crumb moisture occurred during transfer of bulk-free water (more readily freezable fraction) from the crumb to the crust.

DMA Analysis

Figure 4 shows DMA thermograms expressed in terms of E', E'', and tan δ as functions of temperature. The thermograms follow a similar pattern as reported earlier for bread and starch systems (Hallberg and Chinachoti 1992, Vittadini et al 1996, Vodovotz and Chinachoti 1996, Vodovotz et al 1996). Fresh bread crumb has only one transition (T_1) (Hallberg and Chinachoti 1992, Vodovotz and Chinachoti 1996) (Fig. 4a) at ≈0°C, mostly due to ice melting. In this work, bread crumb samples stored with or without crust showed, over time, a decrease in T_1 tan δ peak and a simultaneous increase in another transition (T_2) at a higher temperature (Fig. 4b and c).

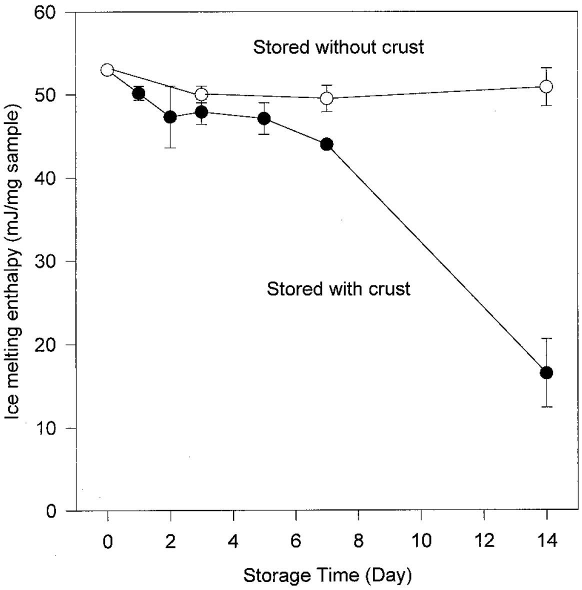

Fig. 5. Changes in ice-melting enthalpy of bread crumb during storage at 25°C.

Figure 6 shows the changes in DMA tan δ peak height for both T_1 and T_2 during storage of both breads. The T_1 tan δ peak intensity decreased with storage time. The sample stored with crust decreased in peak height more significantly after seven days of storage. This was strikingly similar to the moisture loss, firming, and freezable water data (Figs. 1, 2, and 5, respectively). The T_2 tan δ peak height, on the other hand, increased slightly with storage time, and bread crumb stored without crust showed a lower intensity than that stored with crust. Unlike T_1, the T_2 transition seemingly corresponded to the amylopectin crystal melting enthalpy (Fig. 3), in contradiction to Vittadini et al (1996), who found T_2 in microwaved pizza but no starch crystallinity. The results of our experiment showed a good correlation ($r^2 = 0.92$) between T_2 tan δ peak height and amylopectin melting enthalpy (Fig. 7).

The T_2 transition might have also been a result of moisture loss during the DMA analysis. Approximately 20% of total moisture was lost after heating to 60°C in both fresh and aged breads. This could lead to a change in the material viscoelastic properties of these samples causing a T_2 tan δ peak at ≈60°C. It is not clear how significant this factor is. Strong T_2 correlation with amylopectin recrystallization indicates a possible relationship between amorphous domains drying upon amylopectin recrystallization.

DISCUSSION

Vittadini et al (1996) reported a similar thermomechanical transformation from their study of the effect of microwave heating on pizza. Pizza shells reheated by conventional or microwave oven methods showed similar changes in the T_1 and T_2 transitions, that is, a gradual decrease in the T_1 tan δ peak and an increase in the T_2 tan δ peak with microwave heating time. They suggested that T_2 was related to polymer networking but not to starch retrogradation. The reason for the difference between our results and theirs could be due to differences in the systems, experimental methods, and the corresponding inherent physicochemical changes. For instance, in their microwave experiment, the sample was a prebaked and stored pizza shell which was then reheated by microwave, so the physicochemical changes should not be compared directly with those of stored (annealed) bread with no microwave reheating. We suggest, therefore, that the T_2 transitions in the two cases were caused by different phenomena.

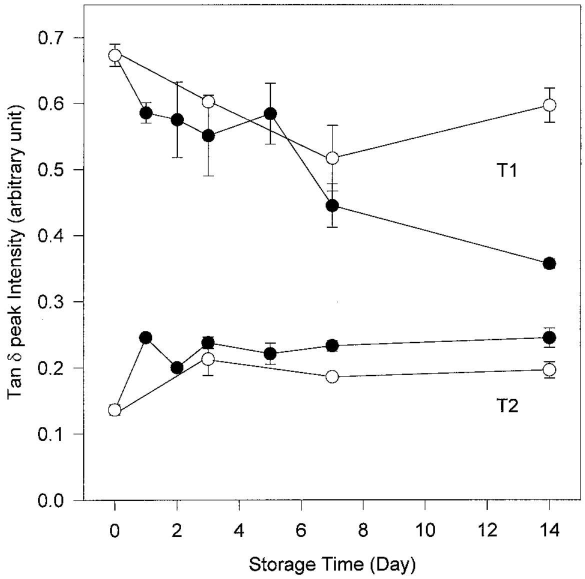

Fig. 6. Dynamic mechanical analysis (DMA) tan δ peak intensity changes in bread crumb during storage at 25°C. Bread crumb stored with crust (●), bread crumb stored without crust (○).

It has been reported that water in bread becomes more bound or immobilized (as observed by nuclear magnetic resonance) during staling (Leung et al 1983, Wynne-Jones and Blanshard 1986, Kim-Shin et al 1991). The physicochemical changes suggested to be responsible for such a change include the increase in water of starch recrystallization (Leung et al 1983, Wynne-Jones and Blanshard 1986) and a transition of water within the amorphous domains, some of which undergo aging or networking, changing hydration behavior (Kim-Shin et al 1991). The data reported in this work indicated that the loss of the bulk or freezable water during storage only occurred when the sample was stored with crust, and this led to a more significant decrease in T_1 and an increase in T_2 tan δ peak amplitudes. The resulting firming in this case was probably related to the thermomechanical changes caused by drying.

The fact that T_2 peak height and starch melting enthalpy correlated well does not necessarily mean that the T_2 transition represents the starch melting transition. Rather, it implies that T_2 and the amylopectin melting enthalpy both increased with storage time in a similar fashion. Whether they are the same transition process or not is not yet proven and needs to be further investigated. The fact that T_2 has been observed in other systems, even when DSC analysis showed no starch melting transition (Hallberg and Chinachoti 1992, Vittadini et al 1996), suggests that T_2 may not be a starch melting transition. However, T_2 might be a transition (such as networking of polymers in various amorphous domains) that is promoted by localized moisture loss (within a sample or drying out of a sample during DMA analysis), which in some cases involves or is triggered by starch recrystallization. It has been proposed that recrystallization of starch or starch crystallinity affects the rigidity of the domains of amorphous network, leading to a glass transition at a higher temperature (Zeleznak and Hoseney 1987, Levine and Slade 1988, Biliaderis 1992, Baik et al 1997). The data reported here might support such an argument.

CONCLUSIONS

Initial (zero to seven days) firming of bread during storage was caused by multiple factors and the results could not be explained based on moisture loss or amylopectin crystallization alone. Other complicated mechanisms involving moisture gain and loss among

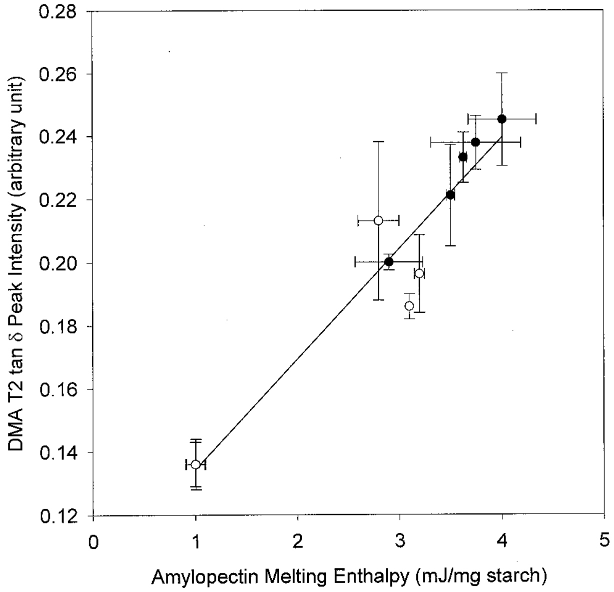

Fig. 7. Correlation between amylopectin melting enthalpy and T_2 tan δ peak intensity in bread crumbs. Bread crumb stored with crust (●), bread crumb stored without crust (○). Solid line shows linear regression results ($r^2 = 0.92$).

some amorphous domains have been suggested. Extended storage beyond seven days led to an adverse staling or firming in bread with crust intact, possibly due to moisture loss from crumb to crust, resulting in a decrease in freezable water. Amylopectin recrystallization did not show a direct strong correlation with firming; however, it seemed to influence the thermomechanical properties by increasing the T_2 transition. Significant firming at constant moisture was related to amylopectin recrystallization and the T_2 transition.

The correlation between the T_2 amplitude and the starch melting enthalpy also suggested that the recrystallization of amylopectin occurred in a parallel fashion. How much this affected firmness was not clear. However, bread crumb stored without crust and with very little moisture loss, showed significant firming and significant amylopectin recrystallization. In this case, firming was more influenced by the starch recrystallization process.

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