Journal of Thermal Analysis, Vol. 47 (1996) 195-213

CHARACTERIZATION OF THERMOMECHANICAL PROPERTIES IN STARCH AND CEREAL PRODUCTS

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Abstract

Thermomechanical properties of bread components can be used to characterize various events that have direct rheological impacts. The objective is to observe changes that occur during staling and toughening of a bread or similar products. In this article, characterization of bread polymers, starch and gluten, were examined by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

Keywords: DMA, DSC, rheological impacts, thermomechanical properties

Introduction

Food biopolymers recently have been rediscovered when the polymer science principles started to be increasingly known to other fields, such as agricultural chemistry, cellular biology and biotechnology. In food, the most studied so far has been cereal components (starch and protein so-called gluten) since their properties have many implications in food products and paracrystallinity of starch is a good model (although not the easiest) to study. Value added technologies applied to biopolymers like starch would be most successful when physicochemical properties of starch including its thermomechanical properties are better understood.

The polymer properties of starch and gluten have been of interest among many researchers [1–5]. But yet, data need to be compared and cross investigated from the bulk, microscopic and molecular properties. This area is still yet new and much is needed to be explored. This paper presents some of the current DSC and DMA discoveries in relation to assigning transition of starch, gluten, and cereal products (with respect to staling and toughening). The discussion is by no means exhaustive but only introductory to some of the important considerations needed in studying thermomechanical properties of cereal components.

General considerations

Firstly, it is important to address some basic understanding about thermomechanical measurement and the nature of cereal systems.

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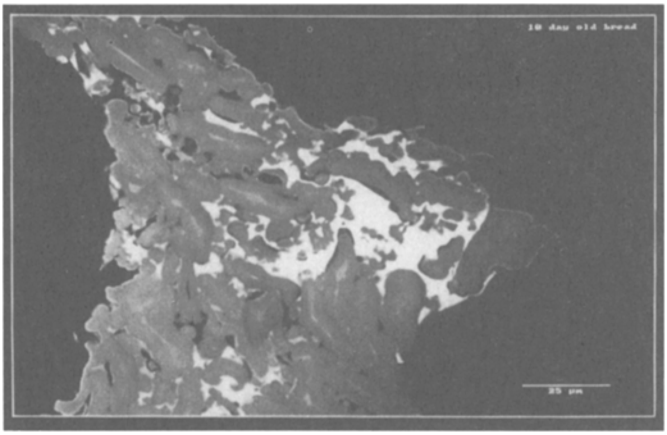

Fig. 1 A confocal laser microscopic image of a standard white bread stored at 25°C for 10 days. The image is 60× magnification. Gluten (white) is continuous matrix inside the cell wall and starch (gray) on the outside. Air cells are shown as black

One of the most important factors to keep in mind is that cereal systems, starch, and gluten, are heterogeneous. Starch or gluten are mixtures of polymers and, thus, their perceived properties must be carefully characterized. Presence of both linear and branched chains in starch often leads to difficulty in differentiating their thermomechanical contributions. Additionally, most literature about cereal systems discuss properties such as glassy-rubbery transition (T_g) as though the material in question is homogeneous and behaves as one. In fact, starch and gluten mixtures, either in nature or after a dough traditional manipulation (kneading and baking), are two separate components and mainly not miscible with one another. Figure 1 shows a microstructural image of a bread with dyes for proteins and starch. It can be seen that cooked starch is located on surfaces of an embedded continuous gluten matrix. Additionally, when starch is recrystallized such as in staled bread, the crystals are in fact a discontinuous phase embedded within a continuous, amorphous matrices of starch and gluten (Fig. 2). Therefore, the mechanical properties of such system must take into account more so of the amorphous components which are not miscible with one another or only embedded crystalline starch. Unfortunately, much of the emphasis has been on the crystalline starch (amylopectin) and not the continuous phase amorphous matrix. Since Levine and Slade [6] introduced the polymer science concept to Food Science, cereal systems have been of most interest. Yet, work done in scientific literature on thermomechanical properties of bread and its components, rarely addresses the heterogeneity and clear distinction between starch and gluten. One of the problems is the fact that starch and gluten show T_g in the same general temperature range at a given moisture content. However, there is no doubt that this lack of miscibility in the systems must be taken into

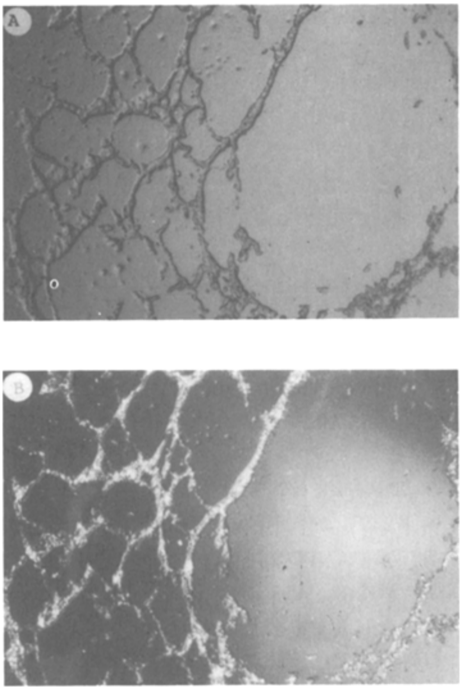

Fig. 2 Lingt microscopic image of a staled bread (40×). A, under a regular light and B a polarized light (taken from 15)

consideration perhaps with complementary study using other methods, such as nuclear magnetic resonance.

Phase separation among components (water, lipids, and crystalline starch) that occurs under some specific time-temperature history has not been adequately studied. Some of the data below will include some of these factors but still far from being conclusive. Distribution of the common plasticizer (water) among various regions maybe one of the key factors and its migration to and from different domains could be one of the factors influencing the thermomechanical properties. Unfortunately, studying such event on a small scale is challenging and yet to be fully explored.

Pitfalls in thermomechanical measurements could include the influence of heating and cooling rates, frequency, levels of strain imposed on to samples, loss of moisture, and changes in geometry and density during the course of a measurement. These are factors that some times avoidable but many times inherent with the sample. Parallel measurement with DSC and other thermal analysis techniques (e.g. DMA) is vital so that interpretation becomes much more meaningful and with a greater degree of confidence.

Interpretation of thermomechanical data and assigning if thermal event on a molecular level takes a considerable amount of speculation unless the system being studied is homogeneous in the thermomechanical and molecular sense. Overlapping events may be mathematically separated but the actual assignment would require other knowledge, such as that from DSC, TMA, and dielectric results. Molecular study may help but it is challenging to do. One of the most obvious misunderstanding is that, similarly to the case of DSC, thermomechanical data is a result from a kinetic event; whether it is a glassy-rubbery or a melting transition, the measured parameters (T_g or T_m) are functions of heating or cooling rate. Additionally, the range of temperature would also shift depending on the time allowing for reorganization of some portions of the polymers.

Microstructural architecture of given sample may influence thermomechanical properties. For instance, a bread when studied may need to be compressed (to avoid extensive moisture loss and to gain a better control in geometry). Thus, the measured modulus represents that of pressed bread and not of the original uncompressed one.

Peleg [7] has raised important concerns about using a single characteristic temperature rather than a range of temperature. In many cases of cereal polymers, the transition(s) has(have) been broad, 50 to 100°C wide. Comparing two broad peaks (100°C wide) using just the peak temperatures of 2–5°C apart, becomes insignificant.

Even though there are many possible concerns, studying biopolymers by mechanical means can yield many interesting phenomena that have direct impact on the rheological changes. Comparing to other means where other properties are being measured, thermomechanical is far more informative and sensitive and most appropriate for rheological interpretation.

Dynamic mechanical analysis

This paper presents the data from DMA or DMTA (dynamic mechanical thermal analysis) which is based upon measured viscoelasticity of a material upon application of a sinusoidal strain (or stress) while it is being heated at a given rate. A DMA instrument applies a controlled strain input (normally very low to assure that the stress-strain level is within the linear region of the stress-strain curve), while the resulting stress is being measured. The sinusoidal strain function can be described as

$$\epsilon(t)=\epsilon_0 e^{i\omega t}$$

where ϵ_0 is the strain amplitude, ω is the radian angular frequency of the sine wave (rad/s) and t is elapsed time. Whenever there is an imposed strain, the material will respond with resulting stress; this stress is also sinusoidal but maybe in-phase or out-of phase (upto 90 degrees) to the imposed strain. The stress response can be described as

$$E^* = E' + iE''$$

where E^* is a complex dynamic mechanical tensile or flexural modulus, E' is the storage modulus (ratio of the in-phase stress to the applied strain), and E'' is the loss modulus (ratio of the out-of phase stress to strain). DMA is popular in that the E' value is related the mechanical energy stored and the E'' to the mechanical energy dissipated. These two terms are complimentary in representing the elastic and viscous components in the material, respectively. The material loss tangent or loss factor (tan δ) is the ratio of energy dissipated to energy stored per cycle of deformation.

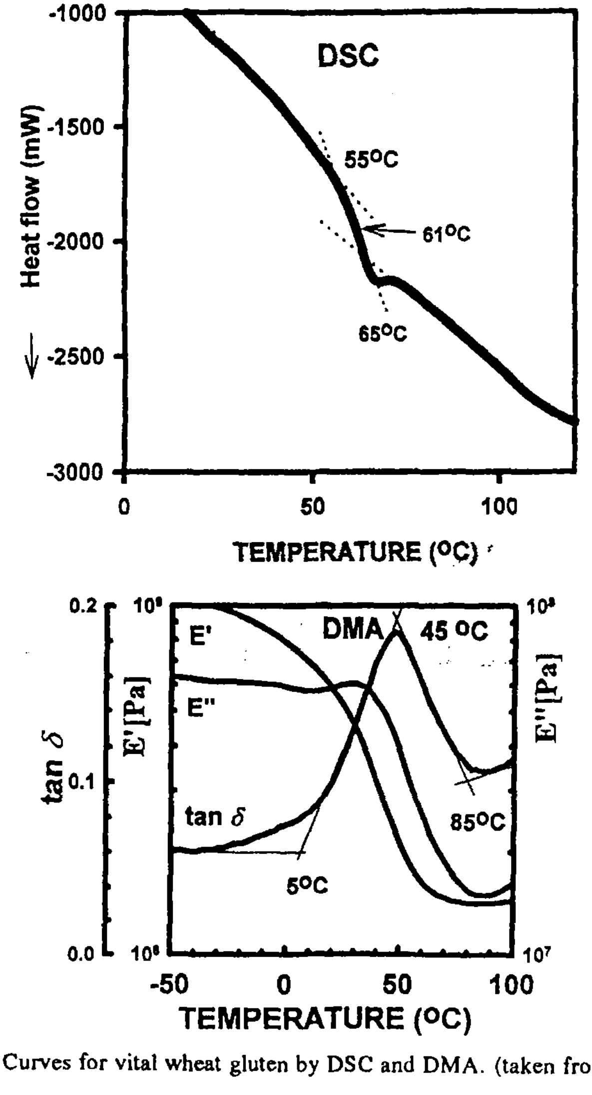

Fig. 3 Curves for vital wheat gluten by DSC and DMA. (taken from 1)

$$\tan\delta = \frac{E''}{E'}$$

A transition (a melt or a glassy-rubbery transition) can be defined as a drop in E' and a corresponding loss dispersion in E'' or tan δ. Figure 3 is a typical DMA curve of wheat gluten using a flexure mode and 1 Hz imposed strain frequency as compared with a DSC curve. The glassy-rubbery transition can be confirmed using a DSC as a baseline shift. The DSC techniques however is considered far less sensitive because it relies on the changing heat capacity to result in a baseline shift; this property changes in a far smaller magnitude comparing the mechanical change under DMA or volumetric change under TMA. It is still not clear what is the molecular contribution for such transition since the proteins are heterogeneous and have varying degree of side chain and backbone mobility that changes with the water present.

Characterization in cereal systems

Starch and gluten are considered hydrophilic in general (although some regions are hydrophobic, such as in gluten) and, thus, they are plasticized by water. The transition temperature, therefore, increases with lowering moisture content as shown in Fig. 4 for the case of gluten (both DSC and DMA results). DMA (1Hz) gave the tan δ peak temperature coincidentally same as the DSC midpoint temperature but DMA gave a much broader transition temperature range than DSC at a given moisture. It should be noted that most T_g reports from DSC measurements are usually the onset temperature. Thus, comparing the onset T_g temperature with the onset temperature from DMA (or midpoint DMA which is usually used to report T_g), one may find a discrepancy of as much as 50°C. Note also that DMA temperature ranges as high as 100°C and thus reporting a single value for such a broad transition is not appropriate. Additionally, DSC temperature ranges shows a relatively low sensitivity to the transition and DMA could detect mechanical changes that occurs over a wider temperature range.

For samples of moisture content well into moisture above 20–25%, when excess water phase separated out (and, thus, when lowered in temperature, it freezes), characterization of DMA curves becomes complicated by the presence of ice. This will be discuss below.

Figure 4 also indicates the transition at room temperature in the gluten is hydrated (i.e., a water sorption isotherm). Solid 25°C lines indicate the onset and final moisture content when a glass-like gluten is plasticized by water at 25°C. Cherian and Chinachoti [1] studied this further to characterize the event using deuterium NMR, water sorption, and freezable water. Diagram in Fig. 5 shows relative relationships among the changing E' (due to plasticization by water), the increase in molecular mobility, water activity, and freezable water. It is interesting to note that the moisture range at which transition occurs covers

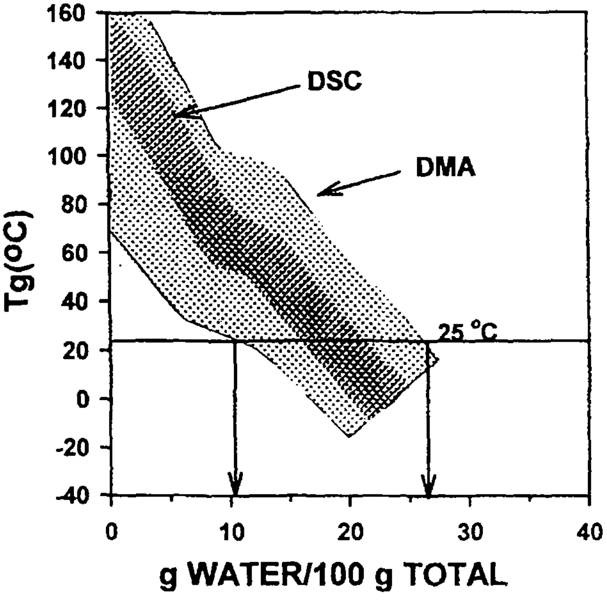

Fig. 4 Glass-rubbery transition temperature range and its change with moisture content from both DSC and DMA. (taken from 1)

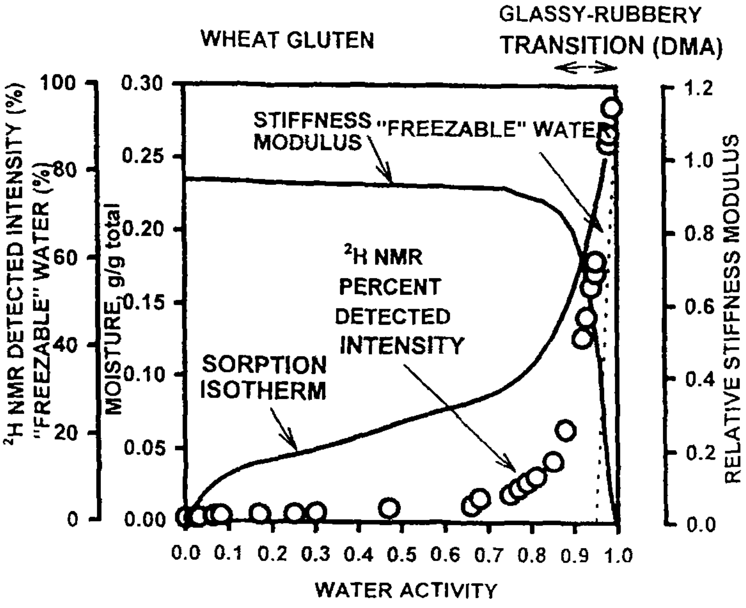

Fig. 5 Isothermal glassy-rubbery transition (observed from relative stiffness modulus), water activity, ^{2}H NMR intensity, and the amount of freezable water. (taken from 1)

approx. 10–20% moisture, above which freezable water (or 'free' or 'capillary' water) starts. Also the monolyer value (BET and GAB calculations) fell in the 5–10% moisture below which the material is brittle.

As mentioned earlier, assigning transitions in the "freezable" moisture range is complicated by the ice melting transition. This can be illustrated using the data from starch. Figure 5 shows the tan δ peaks for starch samples, one with freezable water present (44.4% moisture) and the other without (8.9% moisture). It can be seen that the sample without freezable water gave a symmetrical, broad peak while that with freezable water gave what can be seen as at least two overlapping peaks, an asymmetric and a Gaussian peak. The Gaussian peak is confirmed by DSC to be due to ice melting (its peak amplitude has been found to correlate well with the endothermic energy for ice melting [8]. The asymmetric peak could be due to some possibilities, a lower Tm ice melting endotherm, a glass transition of freeze concentrated starch (T_g'), or others.

It is clear, however, that the main tan δ peak is not likely to be due to a glass transition, since its peak amplitude correlates well with the ice melting enthalpy value from DSC [8].

Because there has been a significant interest around the small transition just below the ice melting transition (T_g'), DSC endothermic peak can be evaluated in a greater detail. Figure 6 shows the curves of a starch sample scanned at

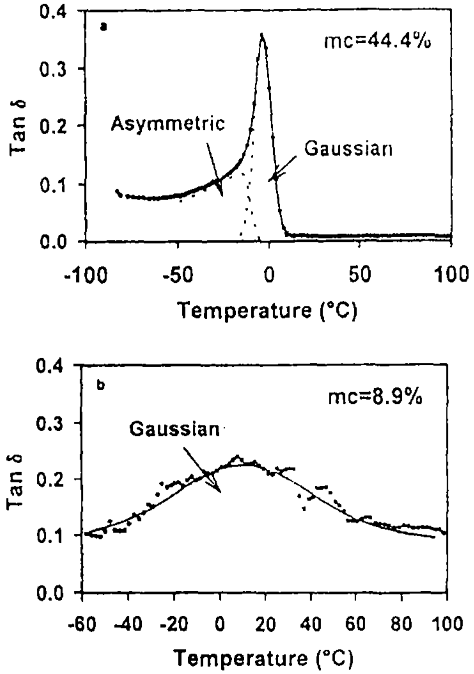

Fig. 6 Tan δ peak characteristics for gelatinized starch at 8.9% and 44.4% moisture content

varying heating rate. It was found that upon increasing of the heating rate, the main peak shows a greater total energy and a higher T_m.

Based on ice recrystallization (annealing) phenomena, ice recrystallization varied among different heating rates (resulting in varying T_m). With a slower heating rate, there is more time allowing further ice crystallization as less perfect crystals continue perfection, indicated by the narrow T_m. Rapid freezing may cause supercooled liquid which, when heated, undergoes a nonequilibrium melting which is referred to as melting under condition of superheating [9]. Additionally, depending on the instrument furnace design, DSC instruments may experience difficulties in controlling and providing heat input and its control under extreme heating rate. Thus, recommended heating rates are varying among instruments. In this particular case, the instrument was known to have a large heat sink and thus at the extreme rate, the actual temperature is lagging behind the programmed temperature.

Note in Fig. 7 that the baseline shift around this transition expected to be due to the magnitude of heat capacity (C_p) change upon melting. However, this too, seems to vary with heating rate. The most extreme case is what was observed in shelf-stable bread, when the baseline shift was found to be so great at some heating rates that integration of the peak is subject to significant error (Figs 8, 10). Figure 9 shows the enthalpy for this peak to increase and then decrease. Coincidently, there is another possible artifact found when this heating rate experiment was repeated under a DMA (three-point bending or flexure mode), the tan δ peak corresponding to ice melting (T_2, Fig. 10) was found to change, after normalizing with the other tan δ peak (T_1 in Fig. 10, thought to be glycerol glassy-rubbery transition), this transition also shows the same trend with changing heating rate (Fig. 9). The transition temperature also increased with increasing heating rate.

Identifying glassy-rubbery transition

Because DSC curves for most biopolymers cannot provide a clearcut identification for glassy-rubbery transition, DMA has been shown to be quite a useful addition in particularly when rheological properties are of interest. Based on examples given above, it can be seen that characterization for DMA and DSC might be possible but resulting information must be carefully interpreted and normally series of analysis should be employed before some conclusion can be reached.

Characterization of melted starch [11] has been done by DMA tan δ analysis (Fig. 11). In the freezable water range ($>30\%$ moisture), the tan δ peak is high in amplitude with skewness to the lower temperature range; this could be subject to a peak-fit analysis (see above). As the moisture content decreases, the curve shape showed a sign of multiple contributions as noticed by broadening

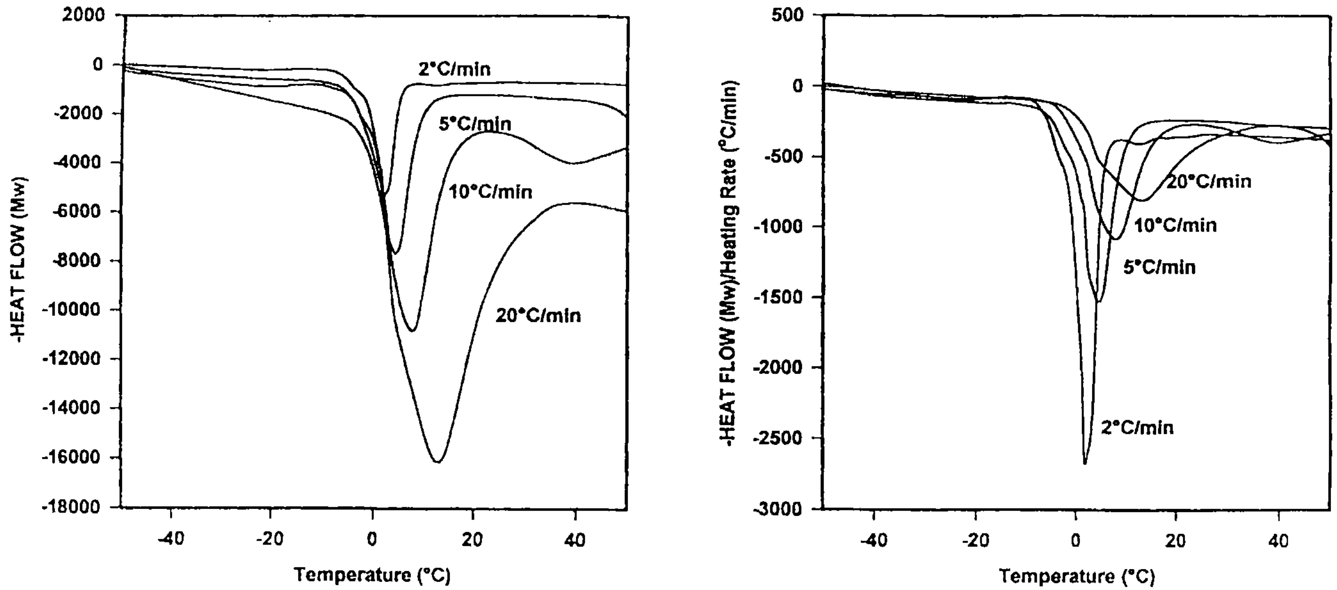

Fig. 7 Ice melting curve (DSC) of gelatinized wheat starch at various heating rate

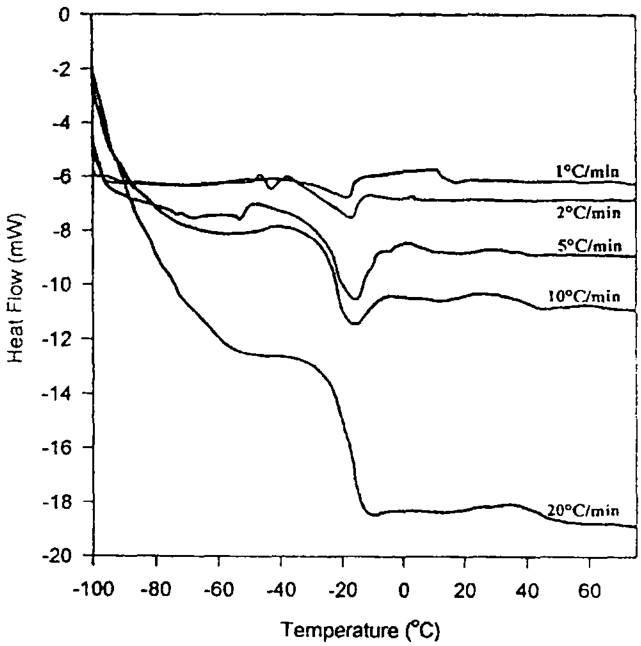

Fig. 8 Ice melting curve (DSC) of military MRE bread at various heating rate

and skewness in the tan δ peak. At moisture below freezable water, the transition(s) moved to a higher temperature range (approx. 80±30°C), leaving a relatively small transition at 0±15°C (Fig. 11, 14% moisture).

In bread [8], however, subjecting a freshly baked bread to drying (Fig. 12, "drying experiment") to similar level of moisture resulted in only a small transition 0±15°C and no broad peak at 80±30°C as found in gelatinized wheat starch subjected to same treatment. At this point, it would be difficult to be more specific on what could be responsible for these two peaks in starch and why it only existed in bread. What can be concluded is that, at 14–16% moisture, dehydrated cooked starch changes somewhat differently than dehydrated cooked bread, exhibiting an additional transition at 80±30°C. The breadth of the transition suggested that the event(s) involved a large distribution of domains than previously thought.

It must be noted on two very important observations, however. Firstly, at moisture around 28–30% (transition point between "freezable" and "unfreezable" water), the samples were slow in 'equilibration' and thus curves were found to evolve with time (data for 28% moisture samples in Fig. 11 were consistent because they were left 'equilibrating' for a constant time period when the curves no longer changing). Thus, it is highly likely that samples of moisture below this point would take longer time and, thus, the broadening in tan δ peak at lower moisture could have been at least partly influenced by this distribution

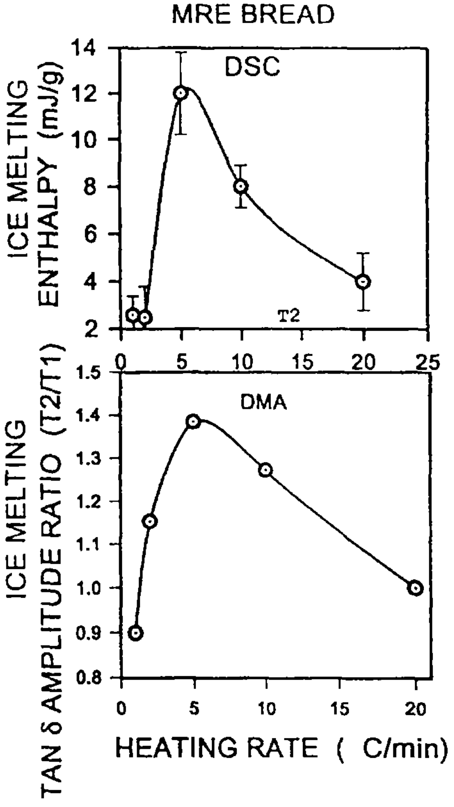

Fig. 9 Effect of heating rate on ice melting enthalpy (DSC) and tan δ amplitude (DMA) for MRE bread

of moisture. Secondly, one must take caution before drawing any further conclusion regarding to transition(s) at and above room temperature in particularly at a higher moisture content when drying is an inherit problem of DMA. Our test on bread showed a significant moisture loss after the sample passed ambient or room temperature in particularly those at higher moisture content. Fortunately, much of the higher temperature transition usually occurs in a lower moisture content. Nevertheless, skewness towards a higher temperature (such as starch at 28% moisture in Fig. 11) could indicate an artifact resulted from dehydration during the experiment, resulting in an increased transition temperature of some components.

Drying *vs.* staling

Staling of standard white bread has been experimented when bread was stored in under a typical condition, i.e., storage in polyethylene bags, and mois-

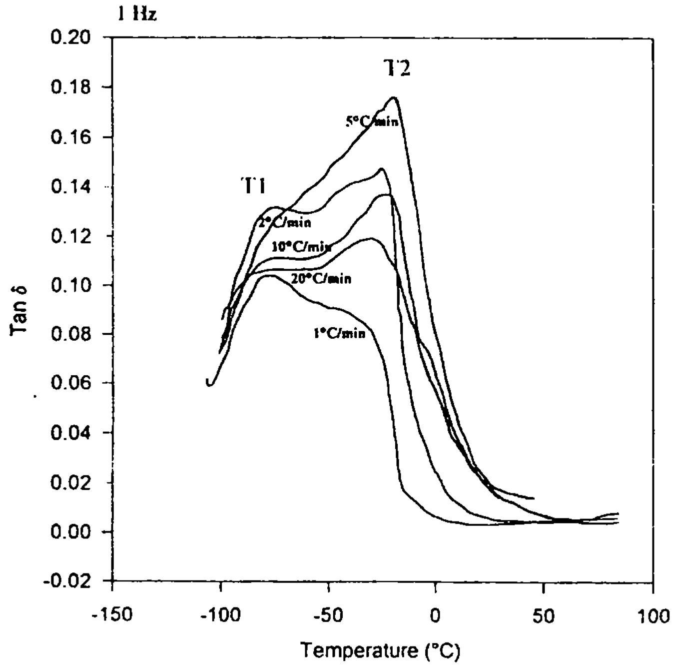

Fig. 10 Tan δ peaks under DMA for MRE bread at various heating rates

ture loss was expected. Over the first two weeks, DMA curves did not show very significant change and, thus, data are not shown here. Very extended storage (preservatives added to this bread) must be reached before a more significant change can be observed. In Fig. 12, the "storage experiment" data showed that 7 months old bread started to exhibit a linebroadening of the main (around 0°C) with skewness to the lower temperature end; a very small transition at 80–90°C was barely noticeable (sometimes not reproducible). Although this experiment is not realistic with respect to bread shelf-life in a normal situation, extended storage has led to an interesting comparison. When the bread lost moisture to below the "freezable" water region, tan δ peak became broad and increased in overall temperature (Fig. 12, "Storage Experiment"). The breadth of the transition was in the order of 100°C or greater. Note that individual data for this sample indicated two overlapping peaks but, after averaging, the mean peak lost such information.

Comparing samples of similar moisture, it was clear that drying and storage experiments were quite different (Fig. 12).

Evidence above showed that changes in the amorphous components during bread staling could play some (if not a major) role resulting in textural deterioration during storage. It has been proposed by Slade and Levine [12] that the

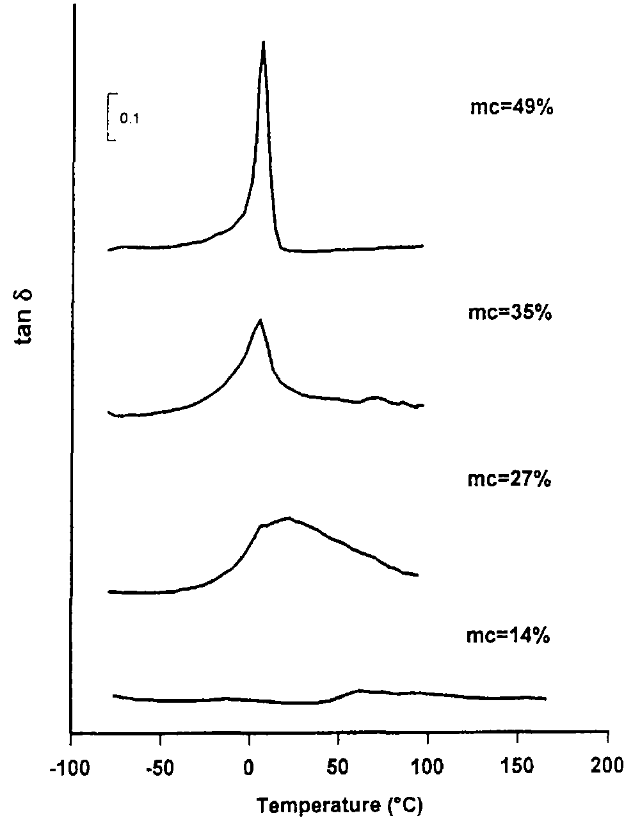

Fig. 11 Tan δ peak for gelatinized starch at various moisture content (from 11)

amorphous polymers in fresh bread might change such that their three dimensional network might become more mature. Thus, the 'effective glass transition temperature' was suggested to increase from –5°C in fresh bread to a value close to 60°C in staled bread. This would have some contribution to firming of bread.

To study this point, thermomechanical properties of two breads have been studied [13], a standard white (SWB) and long-shelf-life (MRE, Meal, Ready-to-Eat) bread. SWB was shown above (Fig. 12) and MRE bread data are shown in Fig. 13. Upto 3 years of storage (in hermetically sealed pouch) at room temperature, the data indicated some but not drastic change in the DMA curves. The only significant change during storage was some small crystallization of lipids (which was high in this bread). No major loss of moisture and "freezable" water remained relatively the same [13]. There seems to be a phenomena that broadening and increasing of transition temperature in staled bread only occurs when subject to a loss of "freezable" water but not when the total moisture remained consistently high.

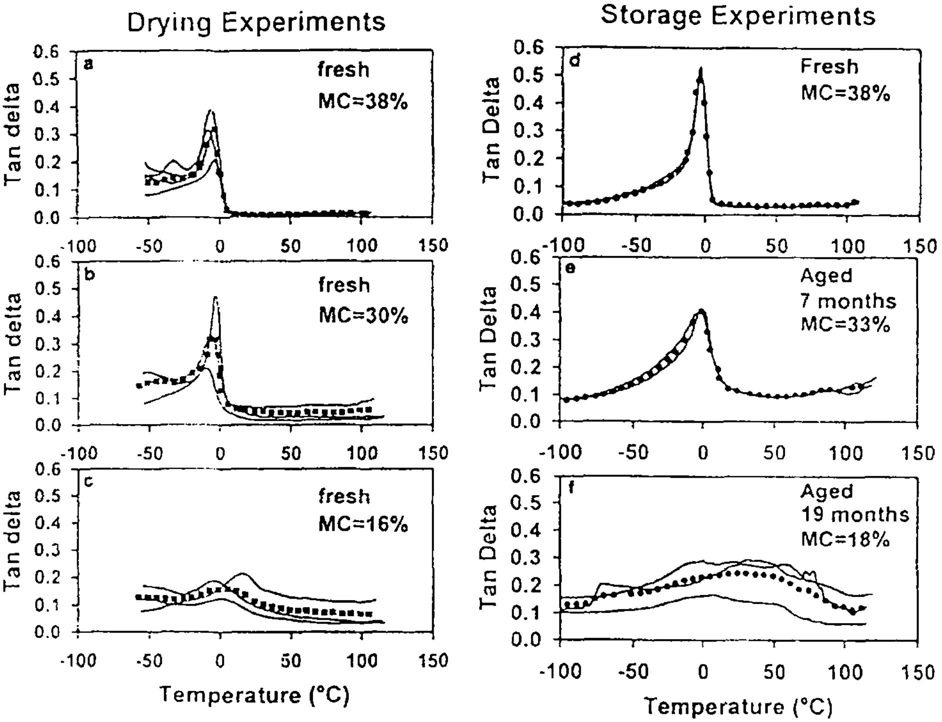

Fig. 12 Effect of drying and aging of bread as determined by DMA tan δ peak. Symbols are averaged values of three replicates (from 8)

Thus, MRE bread did not show any evidence of an increased network maturation as earlier hypothesized. In addition, we observed an increase in amylopectin crystallization over storage of this bread. It was clear that such increase in the starch crystallization did not have a deteriorative effect on texture quality in MRE bread. Added glycerol and prevention of moisture loss by hermetic seal helped keeping the amorphous phase plasticized. It is interesting to note that the T_g (and freezing point) depression effect by glycerol might have caused a slightly higher amylopectin crystallization in MRE bread (as compared to SWB, unpublished results). But, interestingly, this did not lead to firmer texture in MRE bread over same storage period. Thus, it can be concluded that the drying of the amorphous phase during staling of SWB plays a predominating role than amylopectin crystallization and firming was greater during storage of SWB than MRE. More detailed data will be presented in upcoming publications [10].

Microwave toughening of pizza

Vittadini *et al.* [14] studied thermomechanical changes of toughened pizza shells after microwave reheating. The experiment was designed to compare vac-

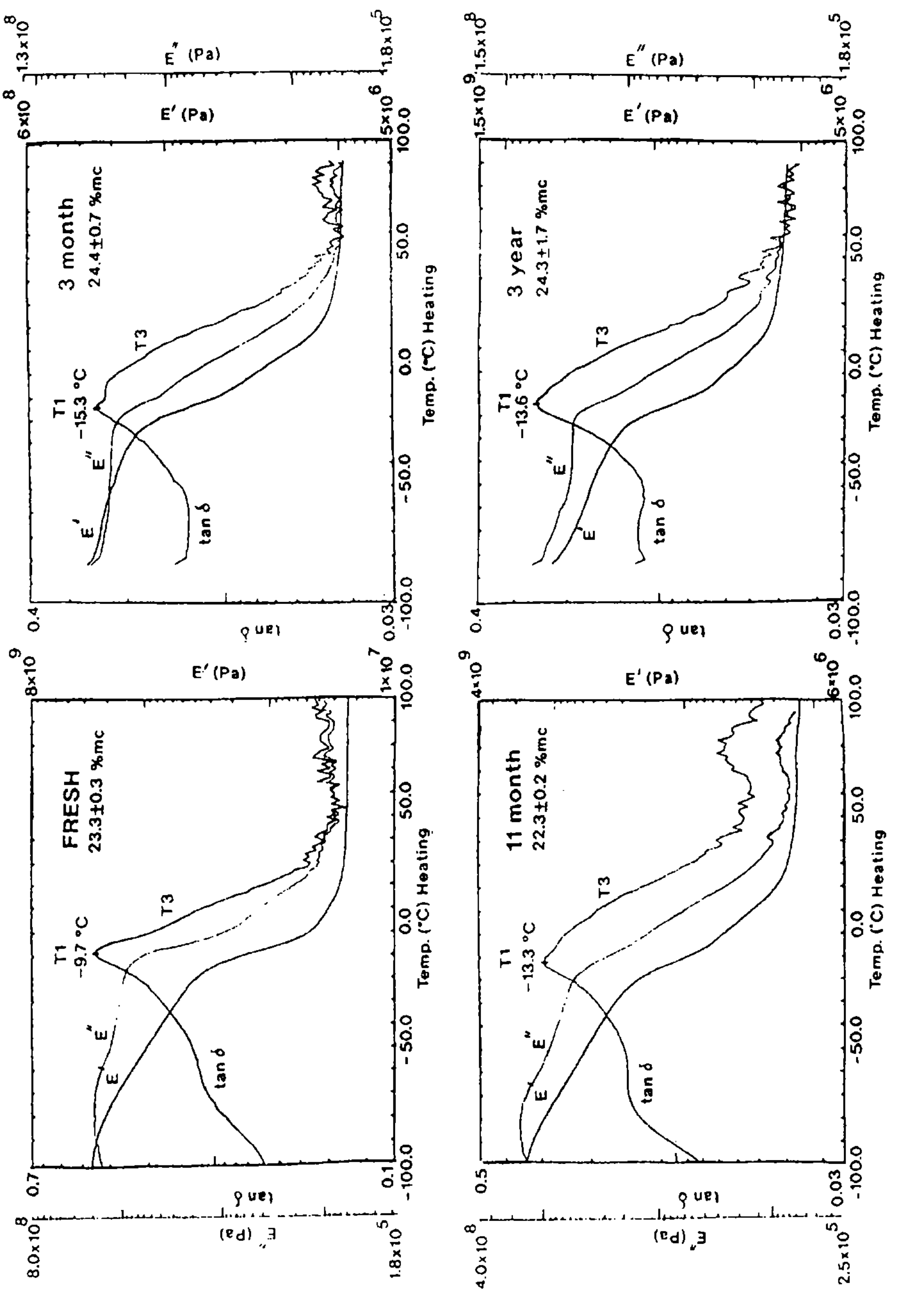

Fig. 13 Tan δ peak in MRE bread over storage (taken from 13)

uum oven drying (no heat), conventional reheating, and microwave reheating of prebaked pizza shells. Specific locations were mapped and regions with maximum texture problem (edge) was studied.

Firstly, after reheating, there was no sign of crystalline starch meaning that all of the starch was amorphous even after cooling back to a room temperature. Thus, toughening of pizza is due to amorphous components.

Secondly, there was a much significant shrinkage in microwaved crust as compared to the conventional means. The pulling force towards the center was developed as the crust shrank upon microwaving while the cake hardening (hard crust formation) and the lack of shrinkage led to much smaller diameter reduction in the pizza.

Comparing samples of same moisture range upon being treated by three different means, it was clear that the changing tan δ upon reheating varied greatly between the conventional reheated samples and the microwaved samples (Fig. 14). In microwaved pizza, as moisture content decreased to below "freezable" water region, there was a clear distinctive emerging of the tan δ peak at approximately 60±50°C while, in conventionally reheated samples of similar moisture, no such peak was observed. In view of the tan δ peak shape analysis

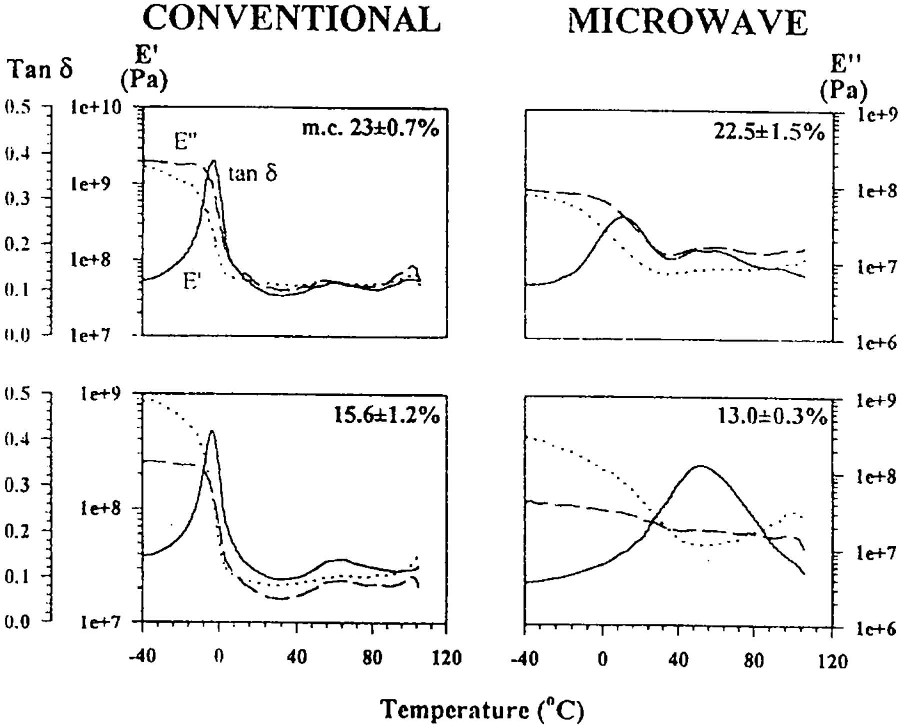

Fig. 14 DMA tan δ changes with vacuum oven drying and microwaving (taken from 14)

of all samples, it was concluded that this peak was present even in unmicrowaved samples but as a very small and relatively insignificant peak (compared to the ice melting tan δ peak). In microwave sample specifically, as the ice melting peak lowered in amplitude (due to increasing loss of "freezable" water), the peak at 50–60°C became more significant. The broad pattern suggests a very wide distribution of transition temperatures. It is almost tempting to draw a conclusion that this is a result of cross-linking in the gluten network, such as disulfide bonding, since it has been suggested earlier by Kokini [5] in pure gluten. However, this pizza dough contains a large amount of starch and it has been shown earlier in this paper that amorphous starch too can give a transition in this range of temperature. It is speculated that the process that leads to shrinkage may be one of the key contributors.

Conclusion

Thermomechanical properties of bread components can be used to characterize various events that have direct rheological impacts. The objective is to observe changes that occur during staling and toughening of a bread or similar products. In this article, characterization of bread polymers, starch and gluten, were examined by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA).

Heterogeneity and phase separations within samples were found to vary with different moisture content. Characterization of tan δ peak in a wide moisture range showed contributions from various events, ice melting and transitions of different domains in glass-like starch and gluten. DMA gave storage modulus (*E'*) drop and tan δ peak broadened in temperature range as wide as 100°C in particularly when the moisture content fell below the "freezable" water range. Transitions (tan δ peak magnitude and *E'* drop) were found small in magnitude and broad in the unfreezable water range; otherwise, they were mostly dominated by ice melting. Less than one order of magnitude in *E'* drop and small or no frequency dependence were observed for all cases. Thus, 'T_g' in cereal systems is neither composed of a single transition, i.e., a truly miscible blend. Bread staling of standard white bread with (moisture loss) led to an increase in tan δ temperature and temperature range only when dehydration was extensive and "freezable" water was depleted. Military MRE bread (shelf-stability enhanced by added glycerol), showing little firming, gave no significant change in tan δ and other overall thermomechanical properties. Both breads however showed extensive amylopectin recrystallization (slightly more in military MRE bread). Thus, amylopectin recrystallization may not contribute to texture staling of bread but rather the amorphous component is more influential. Toughening of microwaved pizza showed an extensive shrinkage and a prominent transition at 50–60°C (not moisture dependent). Data not conclusive about the contributions; possible causes are polymer shrinkage, water redistribution and gluten cross linking.

Work supported by U.S. Army DAAK60-88-C-0054, AASERT DAAL03-97-G-0067, and Massachusetts Agricultural Experiment Station MAS 00623. Conclusions made are based on work performed by G. Cherian, L. M. Hallberg, Y. Vodovotz, X. J. Chen, E. Vittadini, L. Lo, P. Rao, Y. Kuo, A. Nussinovitch and M. Steffens.

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