Studies on Glass Transition Temperature During Staling of Bread Containing Different Monomeric and Polymeric Additives

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ABSTRACT: Glass transition temperature (T_g) of bread containing different antistaling agents and also of bread superquenched and annealed in a DSC cell and outside, was determined using differential scanning calorimeter (DSC). Increase in T_g during the staling of bread correlated with firming as measured by Instron. Singlet T_g was an indication of miscibility or compatibility of bread components with each other. The lowest increase in T_g was found in bread containing propylene glycol (singlet) followed by glycerol (doublet), maltodextrin (broad), gelatin (singlet), antistaling enzyme (singlet), and polypropylene glycol (doublet) in the order of increase in T_g. Superquenching produced a maximum increase in T_g of bread. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1147–1152, 1999

Key words: glass transition temperature; staling of bread; polymeric additives

INTRODUCTION

Breads contains polymers like gluten and starch, oligomers—namely shortening—and monomers like sucrose and water, and in some cases texture, improves like glycerol, paraffin oil, etc. The extent of miscibility of the above components in bread is the underlying principle of structure–property relation and imparting smooth and soft texture.[1] Miscibility of blends is the mixing of components at a molecular level, and provides structural homogeneity. Miscibility of food polymers (polymer alloying), because of imparting improved texture, has gained much importance in recent years.[2,3] Glass transition temperature (T_g), which is a measure of miscibility or compatibility of food components, can be calculated theoretically and also by experimental means.[4] A completely miscible blend gives a single T_g that is between the T_g values of individual polymers.[5,6] Two polymers are usually immiscible, but can be made miscible by mechanical and chemical means. Oligomers are typically more miscible at a higher temperature, but may phase separate on cooling. Monomers are more likely to be miscible with other polymers, and give a better homogenizing and plasticizing effect.[7]

An increase in T_g is related to staling of bread, which is essentially due to increase in crosslink density due to formation of crystallites.[2] It can, thus, be used to calculate the extent of staling in bread. Fresh-bread T_g at subzero temperature may tend to increase to room temperature (low extent of network formation)—well above room temperature (mature network) is equivalent to T_g gel near 60°C for completely staled bread.[2]

Knowledge of T_g behavior can be used to predict the extent of staling. However, only two references are available in this regard.[8,9] In studies reported in this article, an attempt was made to

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Table I Glass Transition Temperature and Compressibility of Stored Bread Containing Different Antistaling Additives

	Glass Transition Temperature (°C) (T_g)[a]				Compressibility (g)[a]		
	Fresh						
Additive	Exp.	Theoretical	7 days	14 days	Fresh	7 days	14 days
Control	−5 ± 0.18	—	+15 ± 0.35	+22 ± 0.93	195 ± 3.1	1160 ± 7.5	1450 ± 8.5
Glycerol (GL)	−10 ± 0.20	—	+1 ± 0.05	+6 ± 0.11	165 ± 2.8	710 ± 6.3	920 ± 7.1
	−62 ± 0.95	—	−62 ± 0.95	−62 ± 0.95			
Propylene glycol (PG)	−18 ± 0.31	−17.6	−4 ± 0.15	−2 ± 0.07	155 ± 2.0	650 ± 6.1	810 ± 6.9
Polypropylene glycol (PPG)	−6 ± 0.19	—	+14 ± 0.41	−20 ± 0.90	180 ± 2.8	1015 ± 6.9	1400 ± 8.4
	−55 ± 2.15		−55 ± 2.15	−55 ± 2.15			
Maltodextrin (ME)	−32 ± 1.9 to −2 ± 0.15	—	−10 ± 0.19 to +1 ± 0.04	+7 ± 0.54 to +12 ± 0.85	175 ± 2.4	680 ± 6.0	980 ± 7.6
Gelatin (GE)	−10 ± 0.19	−10	+1 ± 0.04	+9 ± 0.085	175 ± 2.6	730 ± 6.8	960 ± 7.5
Antistaling enzyme (NE)	−8 ± 0.18	—	+2 ± 0.06	+10 ± 0.71	175 ± 2.5	740 ± 6.8	980 ± 7.6

[a] Mean ± SD of three determinations of T_g and four determinations of compressibility.

correlate the increase in T_g during staling to firming of bread and the effect of monomer, oligomer, and polymer on T_g of bread and their compatibility or miscibility with bread components. Effect of superquenching and annealing in relation to the structure–property relation of bread was also studied.

MATERIALS AND METHODS

Breads were baked from wheat flour modified with different antistaling additives, as per procedures reported earlier, to yield seven different bread compositions[10] (see Table I).

T_g was measured using a Dupont 910 differential scanning calorimeter; firmness, using an Instron 1123 and moisture content was determined as reported earlier.[10] Superquenching of the bread crumb was done by heating it in a DSC cell as well as outside in an air oven up to 130°C, isothermally holding at that temperature for 30 min, and then immediately superquenching to −130°C using liquid nitrogen. For annealing, the above procedure was also used for heating, but annealed to an ambient temperature at the rate of 2°C per minute and slowly brought −130°C by using liquid nitrogen. The Fungistatic article was prepared in the laboratory by the method described by Ghosh et al.[11]

RESULTS AND DISCUSSION

Effect of Moisture on T_g

The moisture content was same in all the different compositions of bread, i.e., 37.2 ± 0.5%. The moisture content of the stored bread after 20 days showed a decrease to 31.5 ± 0.4%, and thereafter remained almost constant in all the different compositions. It was reported[12] that the moisture of the stored bread for 1 year was 31.5%, which is much above the unfreezable water content (W_g), i.e., 25%. An increase in the moisture level above W_g had no further effect on the T_g of water–polymer system.[9] Therefore, an increase in T_g of the bread is caused mainly by the formation of crosslinks.

Effect of Additives on T_g

The T_g of the different compositions of fresh as well as stored bread is given in Table I, and representative DSC spectra are shown in Figure 1. The T_g is defined as the temperature point in DSC thermogram where abrupt enthalpy change takes place, and also the leading edge of melting of the amorphous portion of food. It can be seen in Figure 1 that control and bread containing PG, GE, and NE showed singlet T_g, thereby indicating miscibility of components with starch/gluten

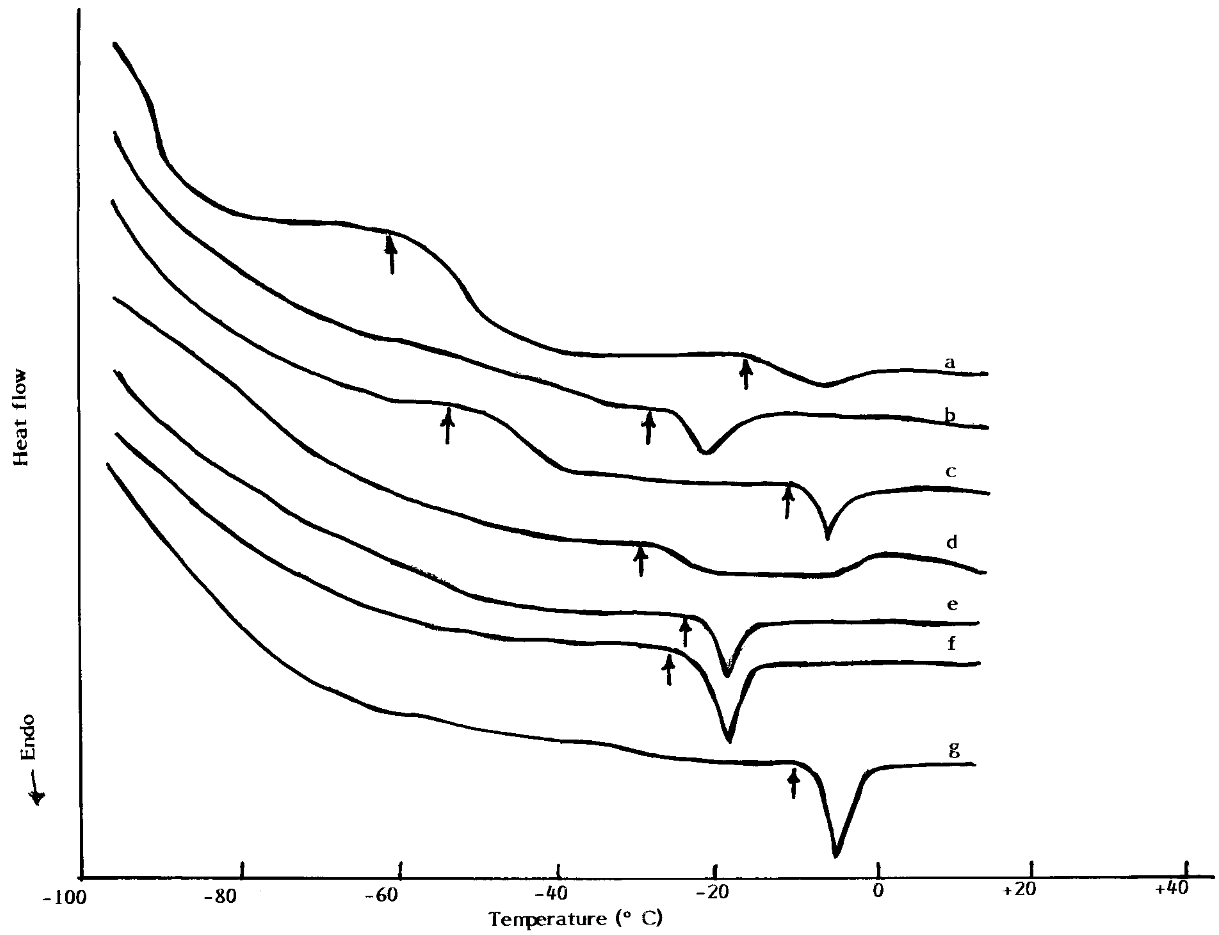

Figure 1 Glass transition temperature (T_g) of a bread crumb containing different antistaling additives: (a) glycerol; (b) propylene glycol; (c) polypropylene glycol; (d) Maltodextrin; (e) gelatin; (f) antistaling enzyme; (g) control.

components of the bread. The T_g calculated theoretically using the Fox equation matched with the experimentally determined value given in Table I. T_g values of antistaling additives have been taken from the food polymer databank.[2] It can be seen from Table I that bread containing PG showed the lowest T_g, followed by GE, NE, and control, in increasing order. Maltodextrin, being a high polymer when mixed with bread, gave a broad transition from −22 to −2°C (Fig. 1). It is reported[13] that high polymer–polymer blend of nitrile rubber–poly(vinyl chloride) gives a broad transition in a DSC thermogram. Bread containing GE and PPG showed doublet T_g, indicating poor miscibility (Table I). All the bread compositions showed smooth and good texture except that containing PPG. This was expected, because bread containing PPG, which is an oligomer and insoluble in water, showed doublet T_g, indicative of phase separation between components or, in other words, poor compatibility. Bread containing GL, a monomer even though showing doublet T_g, imparted smooth and good texture.

Effect of Monomers on T_g

It is interesting to note that both glycerol and propylene glycol are polyols, but the latter exhibited singlet, and the former doublet. Slade and Levine have reported[2] that the anomaly in properties of glycerol and propylene glycol in the food system is due to its difference in T_m/T_g value (PG 1.24 and GL 1.65) and W_g value (PG 56 and GL 43). It was suggested that the underlying basis for these behavioral correlations is that the least viscous and most mobile materials are those with

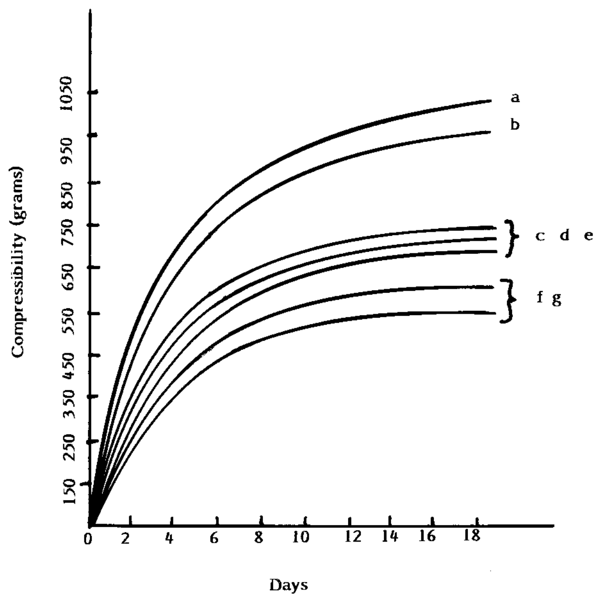

Figure 2 Compressibility in grams of bread crumbs containing different antistaling additives. (a) control; (b) polypropylene glycol; (c) Maltodextrin; (d) gelatin; (e) antistaling enzyme; (f) glycerol; (g) propylene glycol.

the lowest value of T_m/T_g. The very fact that propylene glycol shows single T_g indicates that it must be compatible with a starch/gluten system.

Effect of Staling on T_g

Table I gives the T_g of different compositions of bread stored for 7 and 14 days. A maximum increase in T_g was observed in control, and a minimum in bread containing PG. There was a progressive increase of T_g of the bread crumb towards room temperature. The increase in T_g may be due to increasing formation of crystallites or network formation. The higher the value of T_m/T_g, the higher the tendency of network or coil to helical formation. This may be the reason for a glycerol-containing bread crumb showing a higher T_g compared to that of PG. Bread containing ME, GE, and NE (all biopolymers and soluble in water) gave less of an increase in T_g, probably due to good compatibility with the starch/gluten system. A maximum increase in T_g was observed in bread containing PPG, which also showed poor structural properties (crumbliness). This may also be due to incompatibility between the biopolymer and insoluble oligomer (PPG).

Correlation Between Staling (Firming) and T_g

Table I and Figure 2 show the compressibility (firming) of different compositions of bread. It can be seen from the figure that compressibility increased with time, and became almost constant after 20 days of storage of bread in all the compositions. Bread containing PG showed less compressibility compared to others. Glycerol containing bread had a slightly higher rate of firming compared to that containing propylene glycol. All the bread containing biopolymers such as ME, NE, and GE, showed more or the less same rate of firming during storage. The worst result was shown by the PPG oligomer containing bread, which was almost equal to the rate of firming of the control bread. An increase in T_g during the 15-day storage was correlated with the increase in compressibility for the same period of storage, and the correlation factor found in our study was 0.9653.

Effect of Quenching and Annealing on T_g

Increase in the T_g value due to superquenching (SQ) and annealing (AN) of fresh control bread is given in Figure 3 and Table II. It is reported[2] that superquenching will give maximum structure formation, i.e., crystallite network. Therefore, it was decided to experimentally determine the maximum T_g increase in bread. The annealed bread crumb produced less of an increase in T_g compared to SQ. It is interesting to note that the T_g increase due to SQ and AN inside hermetically sealed in a DSC cell and outside is enormously different. This may be due to the role of moisture in orientation of the molecules. Moisture content of heated and quenched bread in a DSC cell was almost that of fresh bread and, therefore, molecules were able to orient to form a network to the maximum extent and freeze in that state. There-

Table II Glass Transition Temperature (T_g) of Superquenched and Annealed Control Bread

Method	Glass Transition[a] Temperature (T_g) °C	C_p Value (J/g)
Superquenched in a DSC cell	39° ± 1.52	2.88 ± 0.04
Superquenched outside	12° ± 0.51	1.171 ± 0.02
Annealed in a DSC cell	26° ± 1.35	2.029 ± 0.03
Annealed outside	9° ± 0.46	0.932 ± 0.01

[a] Mean ± SD of three determination of T_g.

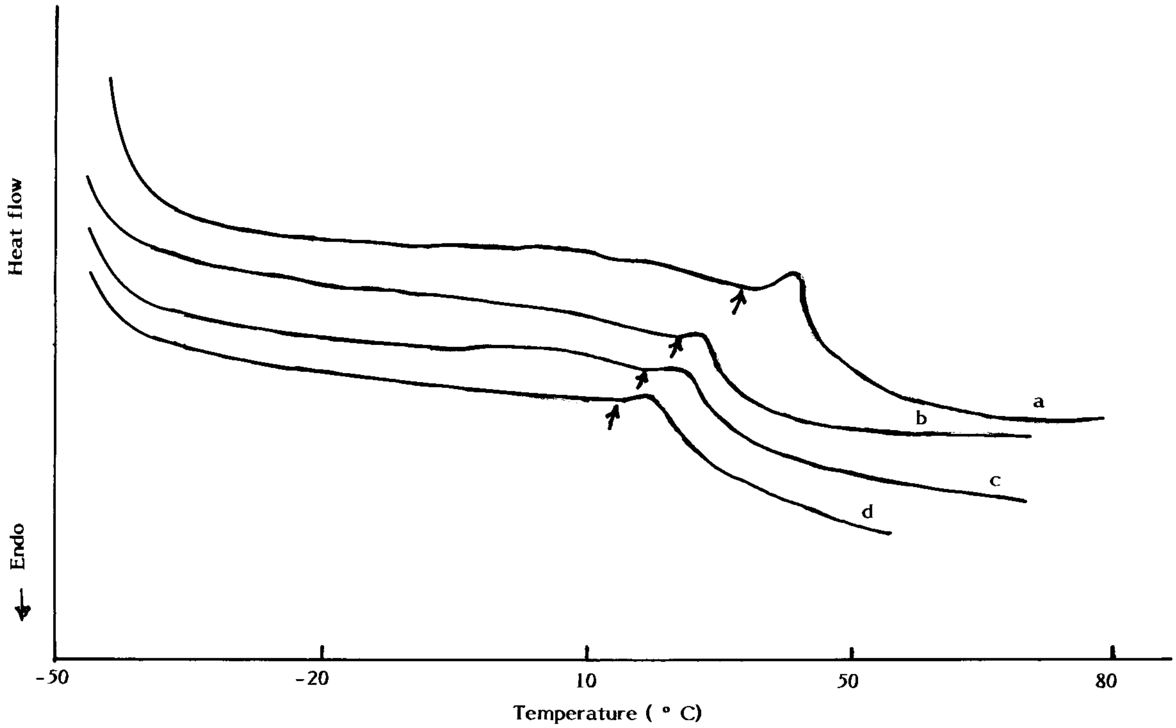

Figure 3 Glass transition temperature of fresh bread exposed to (a) superquenching in a DSC cell; (b) annealing in a DSC cell; (c) superquenching outside; (d) annealing outside.

fore, maximum T_g was expected, whereas the bread crumb heated outside and quenched had little water, and orientation of the molecule was believed to occur to a lesser extent; therefore, the network formation was less and gave less of an increase in T_g. Similar phenomena also occurred during annealing. As expected, the superquenching gave a higher T_g compared to annealing, because the network structure formation was maximum in superquenched materials. Superquenching showed only an increase of T_g at 39°C, contrary to the expected value of 60°C. This may be due to a low extent of network formation in the crumb structure of bread.

CONCLUSION

The measurement of T_g during the storage of bread could be used to quantitatively predict the rate of staling. It depended on miscibility of additives with bread components. An increase in T_g during staling correlated well with the firming of bread. Moisture played an important role in the network formation or crystallites development, as indicated by a more than 50% difference in the T_g value between the bread crumb quenched in the DSC cell and outside. Monomers, like propylene glycol and glycerol, imparted better textural property to bread, but they behaved differently. Bread containing biopolymers like ME, GE, and NE were compatible with the starch/gluten system, as all of these showed singlet T_g. An oligomer, like PPG, was incompatible with the bread component, as revealed by doublet T_g.

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