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Dynamic mechanical thermal analysis of chapati and phulka (Indian unleavened bread)

J.H. Jagannath, K.S. Jayaraman, S.S. Arya*

Defence Food Research Laboratory, Mysore-570 011, India

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Abstract

Glass transition temperature (*Tg*) and relaxation phenomena (α) of bread, chapati, phulka and phulka containing different anti-staling (A/S) additives such as glycerol, propylene glycol, maltodextrin, and anti-staling enzyme were determined using Dynamic Mechanical Thermal Analysis (DMTA). α-Transition which depends upon order of fall in modulus (FE^1), span (σ) and peak amplitude (A_t) of tan δ transition and *Tg* was drastically affected between bread and phulka, by incorporation of A/S agents in phulka and during its ageing (staling). During ageing *Tg* and A_t increased, whereas FE^1 and σ decreased. Phulka containing glycerol, propylene glycol and A/S enzyme gave satisfactory results.

1. Introduction

Phulka, which is fat-free unleavened flat bread prepared from whole wheat flour, is the traditional staple food of the Indian sub continent. Chapati is a variation of phulka which has fat included in the dough. Roughly 70–75% of Indian wheat is consumed in the form of such products (Arya, 1978). Chapati/phulka at present are prepared fresh for main meals. There is a good possibility that commercial production of chapati may start in the near future due to steadily developing urbanization. Under such circumstances, the product must reach the consumer in acceptable form.

It has been shown by Arya et al. (1977) that chapaties can be successfully preserved for more than 6 months by incorporating citric acid and sugar along with sorbic acid. Addition of hydrogenated oil has been found to improve the texture of preserved chapaties (Arya, 1978). This observation is in conformity with X-ray defraction studies in which both gluten and fat were shown to retard the rate of retrogradation of starch and thereby help in checking the staleness of chapati (Parihar and Chatterjee, 1956). Various factors that influence the flavour and aroma of preserved chapaties have been studied in detail by Arya et al. (1976). Chapati/phulka is highly susceptible to staling (Sidhu et al., 1990). This may be due to the compact structure (less free volume) of these products compared to bread (Swyngedau et al., 1991). Staling (firming) of cereal products increases the *Tg* from sub zero to ambient temperature due to development of crystallites forming a net work (Slade and Levine, 1991). α-Transition, which depends on cooperative motions of chains in biopolymers such as starch and gluten is related to *Tg*, which is in turn related to free volume (Slade & Levine, 1991). α-Transition depends on the magnitude of certain parameters, namely *Tg*, A_t FE^1 and σ (Simotos and Peleg, 1994).

One of the most common uses of DMTA is the determination of *Tg* i.e. peak of temperature—Tan δ curve. DMTA enables a full exploitation of the phase-transition present in a viscoelastic material (Vodovolz et al., 1996). Dynamic stiffness (rigidity) depends on FE^1 and σ which are indicative of texture of food and can be determined by DMTA (Simotos & Peleg, 1994). The A_t and tan δ (loss factor) measure the amount of mechanical energy converted to heat energy during the DMTA experiment and depend on free volume present in the material (Annakutty et al., 1994). Free volume and A_t are inversely proportional. DMTA gives a more practical application of materials for any specific use compared to DSC (Hallberg & Chinachoti, 1992).

In the present study, α-transitions of fresh chapati and phulka were determined and compared with that of bread. α-Transition parameters, namely *Tg*, A_t, FE^1 and σ were used to establish A/S properties of additives. α-Transition has been correlated with anti-staling properties of additives.

* Corresponding author.

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2. Materials and methods

The wheat flour used in the present study was obtained commercially with protein and moisture contents of 12.8 and 10.1%, respectively. Glycerol (GL) and propylene glycol (PG) were obtained from sd Fine Chemicals, Murnbai. Maltodextrin (MD, Dextrose equivalent 16) was precured from SA Chemicals, Mumbai. Novamyl 1500 MG anti-staling enzyme (NE) was donated by Bio Chemical Industries, Bangalore. All other chemicals used were of bakery grade. All the A/S additives namely GL, PG,MD and NE are generally regarded as safe (GRAS) (Bralem et al., 1989).

Six different modified flours containing different anti-staling additives were prepared as per the procedure detailed by Jagannath et al. (1997b)), Dough was made using 100 g of flour/modified flour, 60 g of water, 0.1% sodium sorbate, and 0.2% calcium propionate in the case of phulka, 9 g of margarine was added to phulka dough for making chapati. The doughs were prepared in triplicate. Phulka and chapati were prepared by the standard procedure detailed by Haridasa Rao et al. (1986) & Sidhu et al. (1990), respectively. Immediately after baking, each chapati was weighed, allowed to cool for 20 min and packed in paper–aluminium foil–polyethylene laminate (PFP) at room temperature.

A Dupont differential scanning calorimeter fitted with graphic plotter and a thermal analyst 2100 system (TA instruments, USA) were used and the procedure adopted was as reported earlier (Jagannath et al., 1997a).

The procedure for conducting DMTA was detailed by Hallberg et al. (1992). About 4 chapaties were stacked to a thickness of 10 mm and then compressed to 2 mm thickness using a Farinograph press, Toyo-saiki, Japan with 250 kg cm^{-2} pressure. Initially the pressure was slowly increased in steps of 5 kg cm^{-2} for 3 min and released. Finally the pressure was maintained at 25 kg cm^{-2} for about 15 min. This ensured the porous-free slab. The resulting compressed material was cut with a die into 50×12 mm rectangular bars.

The bars were placed in the DMTA sample holder. The clamps were not tightened during freezing by liquid nitrogen. When the sample reached −60°C, the clamps were tightened and the cooling was continued to −90°C. The samples were heated from −80°C to 100°C at a rate of 3°C min^{-1} at 1 Hz. A three-point bending head was used and the stress was applied at 1 Hz.

3. Results and discussion

3.1. Differential scanning calorimeter (DSC)

The *Tg*s of the bread, phulka and chapati were measured using DSC. The representative spectra are shown in Fig. 1. Bread crumb and chapati showed *Tg* of −5, −3 and −1°C, respectively. In the DSC thermogram of phulka and chapati, only onset of *Tg* can be clearly obtained. The *Tg* determined is the leading edge of endothermic melting or change in heat capacity. The DMTA is useful in understanding the phase transition clearly.

3.2. Dynamic mechanical thermal analysis (DMTA)

The DMTA thermograms of bread, phulka and chapati are given in Figs. 2 and 3. Bread showed a broad tan δ transition while that of phulka and chapati was narrow. It can be seen from Table 1, σ value was much more in bread compared to chapati or phulka. Its value was 56°C lesser in chapati, i.e. 12°C but was least in phulka, i.e. 5°C. A similar increase in σ in bread plas-

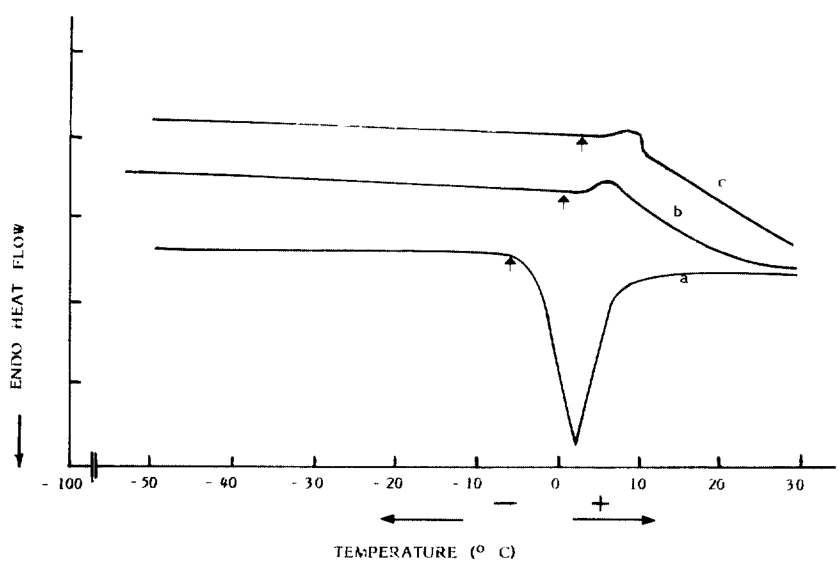

Fig. 1. DSC thermographs of (a) bread crumb, (b) chapati, (c) phulka.

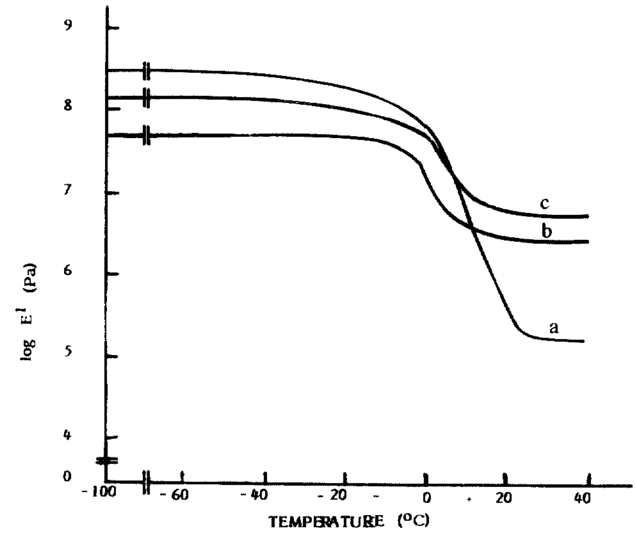

Fig. 2. Modulus (E^1) vs temperature plot for (a) bread, (b) chapati, (c) phulka.

ticized with water was obtained by Hallberg & Chinachoti (1992), Meste et al. (1992) and Vodovolz et al. (1996). Modulas (E^1) values fell with increasing temperature. According to Vodovolz, this abrupt fall in E^1 is an indication of phase transition and also FE^1 provides an insight into mechanical properties such as rigidity of materials and is inversely proportional. The FE^1 values were 3, 2 and 1.5 units in the case of bread, chapati and phulka, respectively. The lower the *Tg* the more flexible the material and the *Tg* of bread, chapati and phulka were −5, −3 and −1°C, respectively (Table 1). As expected, bread shows a low A_t value compared to phulka and chapati. α-Transition which includes *Tg*, A_t, FE^1 and σ in bread is quite different from phulka and chapati. From this it can be inferred that the free volume for molecular mobility is higher in bread compared to phulka and chapati.

The theoretical model derived for flexible polyurethane foam has been applied to explain bread staling and is based on elastic cell walls (Swyngedau et al., 1991). According to this theory, three clearly identifiable regions are found in the stress–strain deformation curve viz., (I) elastic or quasielastic deformation as a result of cell wall bending, (II) collapse as the cell wall buckles and (III) yields or fractures as a result of cell walls crushing together. In DMTA the three stages can be identified as shown in Fig. 3. In the case of chapati and phulka, the stage II almost does not exist, i.e. cell wall buckling and the absence explains the faster staling rate of phulka compared to bread.

Table 1
Mechanical relaxation (α) properties of phulka with different A/S additives

Composition	*Tg* (°C)	A_t	σ (°C)	FE^1
Bread	−5.0 ± 0.1	0.82 ± 0.02	56 ± 1.8	3.0 ± 0.10
Phulka	−1.0 ± 0.0	1.75 ± 0.05	5.0 ± 0.2	1.5 ± 0.08
Chapati	−3.0 ± 0.1	1.62 ± 0.04	12.0 ± 0.5	2.0 ± 0.09
Phulka with propylene glycol	−20.0 ± 1.3	0.66 ± 0.01	80 ± 2.2	3.1 ± 0.11
Phulka with glycerol	−18.0 ± 1.2	0.82 ± 0.01	70 ± 2.1	2.8 ± 0.1
Phulka with A/S enzyme	−8.0 ± 0.5	0.81 ± 0.02	45 ± 1.5	2.2 ± 0.09
Phulka with maltodextrin	−16.0 ± 1.1 to 3.0 ± 0.1	0.72 ± 0.01	80 ± 1.9	2.5 ± 0.11

Reported property values are means of three replicates ± SD.

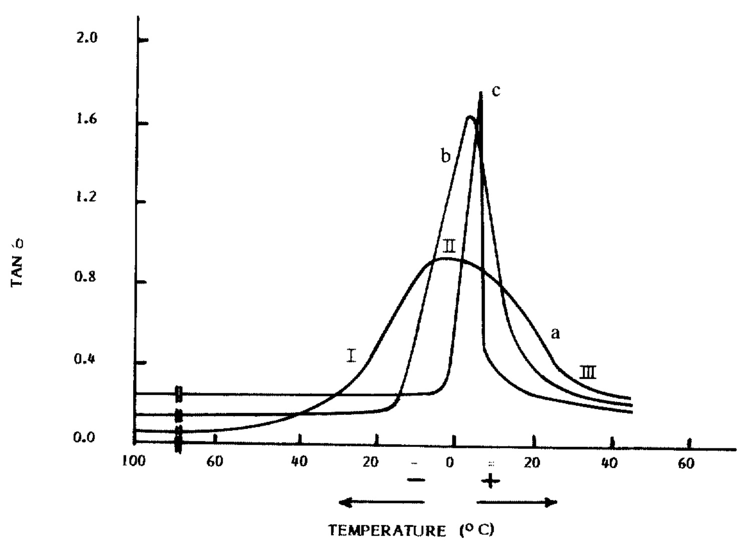

Fig. 3. Tan δ vs temperature plot for (a) bread, (b) chapati, (c) phulka.

Table 2
Mechanical relaxation (α) properties of phulka with different A/S additives stored for 10 days

Pulka with	*Tg* (°C)	A_t	σ (°C)	FE^1
Control	+ 30.5 ± 1.30	3.15 ± 0.06	1.0 ± 0.0	0.7 ± 0.05
Margarine (chapati)	−29.5 ± 1.20	2.87 ± 0.05	2.0 ± 0.0	0.8 ± 0.05
Propylene glycol	−4.0 ± 0.10	1.75 ± 0.01	27 ± 1.8	2.9 ± 0.12
Glycerol	+ 8.0 ± 0.21	1.93 ± 0.03	24 ± 1.5	2.6 ± 0.11
A/S enzyme	+ 12.0 ± 0.26	2.05 ± 0.04	11 ± 0.8	2.2 ± 0.10
Maltodextrin	5.0 ± 0.01 to 12.0 ± 0.25	1.83 ± 0.02	35 ± 1.6	2.3 ± 0.11

Reported property values are means of three replicates ± SD.

3.3. *Effect of anti-staling additives on α-transition*

Table 2 shows *Tg*, A_t, FE^1 and σ for phulka containing different anti-staling additives such as glycerol, propylene glycol, maltodextrin and anti-staling enzyme and the tan δ-temperature curve is shown in Fig. 4. The σ value was more or less the same for most of the modified phulka with anti-staling additives. It was reported by Vodovolz et al. (1996) that plasticizable (non-freezing) water broadens the σ value similarly to A/S additives. Therefore A/S additives more or less act as plasticizers and dampeners which absorb the energy required for nucleation of crystallites. The FE^1 value determines the rigidity of the material and is inversely proportional. All the phulka containing A/S additives show more than one unit FE^1 value (compared to the control). Thus, it can be inferred that the A/S additives make phulka more flexible. The extent of decrease in *Tg* gives the amount of plasticization of additives. Phulka containing propylene glycol shows the lowest *Tg* followed by glycerol and anti-staling enzymes. Maltodextrin, being a polymer, shows broad transition. DMTA measures segmental mobility of polymer chains and polymeric additives such as maltodextrin during transition and signifies an increase in the heterogeneity of segmental mobilities so no single *Tg* can be assigned to such transition. Incorporation of anti-staling agents reduces the A_t value of phulka drastically (Table 1). α-Transition parameters, namely *Tg*, A_t, FE^1 and σ were affected in phulka containing different A/S agents and by this it can be concluded that all A/S agents act as plasticizers and lubricants. However, their effect varies.

3.4. *Effect of ageing on α-transition*

The values of *Tg*, A_t, FE^1 and σ for phulka containing different anti-staling agents stored for 10 days is given in Table 2 and tan δ curves are shown in Fig. 5. The A_t and *Tg* increased and FE^1 and σ values decreased with ageing. The difference is in A/S properties of bread containing PG and GL, have been explained in our earlier report (Jagannath et al., 1997c).

According to Slade & Levine (1991), the increased network formation of crystallites in the amorphous domain, which is responsible for staling, result in increase in *Tg*, i.e. shift in tan δ peak transition. However, Vodovolz et al. (1996) reported that the bread stored for seven months showed a larger σ value but fell in the same general range of temperature. According to these authors, the ageing has resulted in broadening of

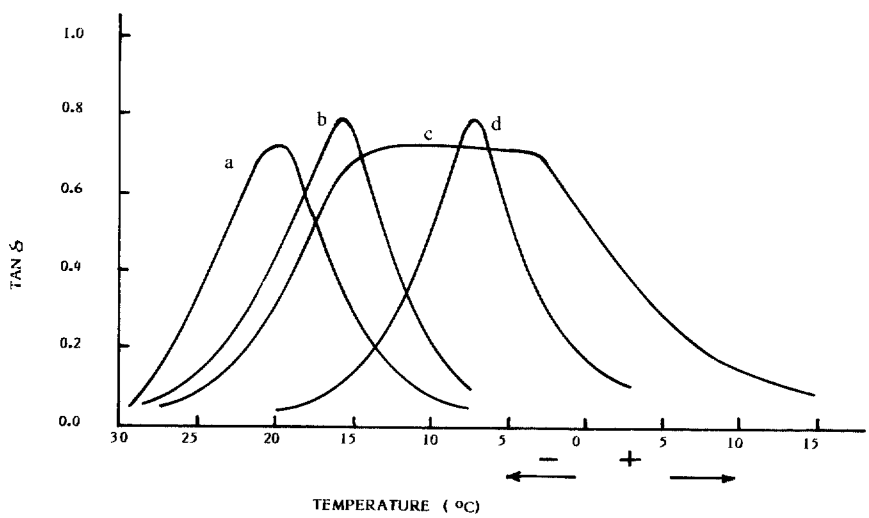

Fig. 4. Tan δ vs temperature plot for fresh phulka with (a) propylene glycol, (b) maltodextrin, (c) anti-staling enzyme.

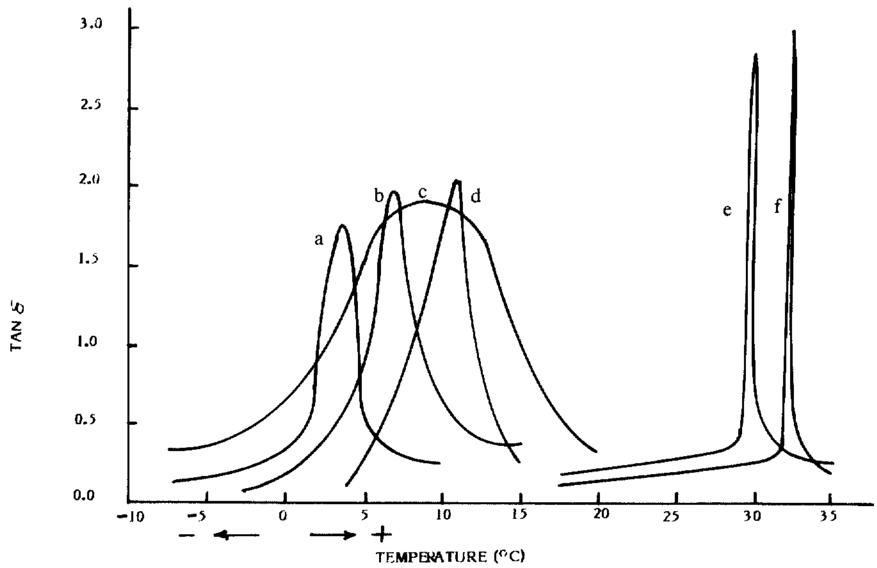

Fig. 5. Tan δ vs temperature plot for stored phulka with (a) propylene glycol, (b) glycerol, (c) maltodextrin, (d) anti-staling enzyme, (e) control, (f) chapati.

the tan δ-transition and increase in *Tg*. Our results conform with the observation of Slade & Levine (1991). The *Tg* of stored phulka containg different A/S agents increased, while σ decreased. The extent of *Tg* increase, however, varied, depending upon A/S additives. *Tg* and A_t values of control and chapati increased enormously during storage. The least increase in A_t and *Tg* was observed in the case of phulka containing propylene glycol. Extents of σ decrease during ageing were more than 100% in most cases (Table 2).

Considering α-transition parameters, namely *Tg*, A_t, FE^1 and σ, phulka containing PG showed the best A/S property (less firming), followed by phulka containing GL, MD and A/S enzyme in the order of decreasing A/S property. Chapati initially showed a broad transition but, on ageing, showed a narrow transition similar to phulka. This shows that the margarine, incorporated in phulka dough to make chapati, did not help in arresting staling.

4. Conclusion

The mechanism of bread staling and relaxation phenomena in bread is well understood, while that of unleavened bread like chapati/phulka is not fully explored. The α-transition parameters namely *Tg*, A_t, FE^1 and σ in bread were quite different from phulka/chapati. All the A/S additives and water play the role of plasticizer, preventing the rigidification of macro molecular starch and gluten chains.The extent of increase in *Tg* and A_t and decrease in FE^1 and σ with ageing of phulka is an indication of increase in cross-links or network formation of chrystallites and correlates with rate of staling (firming). The flexible polyurethane foam structure model used to explain staling of bread cannot be applied to chapati/phulka and a different model has to be evolved.

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References

Annakutty, M., Chakraborthy, B. C., & Deb, P. C. (1994). Studies on interpenetrating polymer networks based on nitrile rubbler—poly (vinly chloride) blends and poly (alkyl methaerylates). *J. Appl. Polymer Sci.*, *53*, 1107–1112.

Arya, S. S. (1978). Studies in some physico-chemical changes during processing and storage of material. PhD thesis. University of Mysore, India.

Arya, S. S., Prernavalli, K. S., & Pariliar, D. B. (1976). Precursors of carbonyl in chapaties. *Int. J. Food. Technology.*, *11*(5), 543–549.

Arya, S. S., Vidyasagar, K., & Parihar, D. B. (1977). Preserved chapaties. *Lebensmittel—Winsensischoff and Technologies*, *10*(4), 208–213.

Bralem, A. L., Devidson, P. M., & Salminer, S. (1989). *Food additives.* 1st edn. Marcel Dekker Inc., New York.

Hallberg, L. M., & Chinachoti, P. (1992). Dynamic mechanical analysis for glass transition of long shelflife bread. *J. Food Sci.*, *57*(5), 1201–1205.

Haridasa Rao, R. P., Leelavathi, L. K., & Shurpalekar, S. K. (1986). Test baking of chapati-development of a method. *Cereal Chem.*, *63*(4), 297–314.

Jagannath, J. H., Jayaraman, K.S., & Arya, S. S. (1997*a*). Effect of wrappers, temperature humidity and modified atmosphere on phase transition during staling of bread. *Int. J. Fd. Sci. and Technology* (in press).

Jagannath, J. H., Jayaraman, K. S., Arya, S. S., & Sornashekar, S. (1997*b*). DSC and WAXS studies of bread staling. *J. Appl. Polymer Sci.* (in press).

Jagannath, L. K., Jayaraman, K. S., & Arya, S. S. (1997*c*). Studies on glass transition temperature during ageing of bread. *J. Appl. Polymer Sci.* (submitted).

Meste, L., Huang, M. V., Panama, J., Akndserson, G., & Lentz, R. (1992). Glass transition of bread. *Cereal Foods World, 37*(3), 264–267.

Parihar, D. B., & Chatterjee, A. K. (1956). X-ray diffraction studies of chapaties. *J. Sci. and Ind. Research, 15c*, 115–120.

Sidhu, S., Wilflled, S., & Dietrich, M. (1990). Gelatinization of starch during Indian unleavened flat breads. *Starch/Starke, 42*(9), 336–339.

Simotos, B. G., & Peleg, J. (1994). Basic aspect of glass transition. In *Food Preservation by Moisture Control Fundamental of Application*. ed. G. V. Barbosa-Canovas and J. W. Chanes, Technomic publications, Lancastes. pp. 3–31.

Slade, L., & Levine, H. (1991). Beyond water activity: recent advances based on an alternative approach to the assessment of food quality and safety critical reviews. *Food Sci. and Nutrition, 30*(2–3), 155–360.

Swyngedau, S., Nussinovitch, A., Roy, L., Peleg, M., & Huang, V. (1991). Comparision of four models for the compressibility of breads and plastic foams. *J. Food. Sci., 56*, 756–759.

Vodovolz, V., Hallberg, L., & Chinachoti, P. (1996). Effect of ageing and drying on the thermomechanical properties of white bread as characterised by DMA and DSC. *Cereal Chem., 73*(2), 264–270.