Effect of Selected Hydrocolloids on Bread Staling as Evaluated by DSC and XRD

Hassan Ahmadi Gavilighi, Mohammad Hossein Azizi, Mohsen Barzegar and Majid Arab Ameri Department of Food Science and Technology, Tarbiat Modarres University, P.O. Box: 14115-336, Tehran, Iran

Abstract: The influence of the selected hydrocolloids (Guar gum, Locust bean, Xanthan and Carboxy Methyl Cellulose (CMC) with ratio of 1% flour basis on the quality of Lavash bread was tested by using two different techniques X-Ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC)). The samples after baking were stored in polyethylene bag for 1, 5 and 7 days and then this method were used for evaluation. The greatest enthalpy of retrogradation (Δ H) after 1, 5 and 7 days was observed for breads containing locust bean and control sample, respectively. The lowest Δ H was observed for breads containing guar gum. Generally the control sample had the greatest differences and highest staling in all days. The Guar gum, Xanthan, CMC and locust bean treated samples had the least staling rate as against the control, respectively. The results show that breads containing hydrocolloids had better quality than control sample.

Key words: DSC, XRD, staling, lavash bread

INTRODUCTION

Staling is the general term that describes the textural and flavor changes in bread. Bread staling is due to rearagement in the starch fractions. These starch transformations include gelation and crystallizing is called retrogradation^[1]. The formation of crystallizes is considered to be the interchain association of the amylase and amylopectin fraction^[2]. However, other studies describe the gluten-gluten and gluten-starch as the main causes of bread firming^[3].

Hydrocolloids are used as anti-staling agent in bread making. In the bakery foods, hydrocolloids were used for adjustment of dough and bread. Davidou et al.[4] found that, among locust bean gum, alginate (presumably sodium alginate) and xanthan, only locust bean gum reduced the rate of dehydration. However, any increased on moisture content of breads, if the moisture is available to the starch molecules, increases the rate of retrogradation^[5]. Schiraldi et al.^[6] studied the effects of added hydrocolloids (pentosans, modified pentosans, galactomannans, whey protein) on bread and reported that guar and locust bean gums retarded starch retrogradation, but did not have any clear antistaling activity. They also found that all the hydrocolloids they used generally improved quality and those with higher water-holding capacity increased crumb firmness. In contrast, Davidou et al.[4] reported that both degrees of crumb firmness and the rate of staling during storage were reduced by addition of locust bean gum, alginate

(presumably sodium alginate) and xanthan. They proposed that the gums modified the organization of the amorphous part of the crumb, perhaps by inhibiting gluten-starch interactions, in the same manner as proposed for dextrin's^[3]. They also reported that only locust bean gum affected water retention. Carboxy Methyl Cellulose (CMC) and hydroxpropylmethylcellulose (HPMC, 0.3%) also decreased initial firmness^[7].

Thermal analysis has been used extensively to study starch retrogradation as well as bread staling[8-13]. Differential scanning calorimetry has proven to be the most useful in providing basic information on starch retrogradation^[14]. When aged bread samples are heated in a DSC pan, an endotherm is observed as reordered amylopectin reaches its glass transition melting temperature and the enthalpy change associated with this transition can be measured. Because the time scales for endotherm development and for the increase in crumb firmness are broadly similar in magnitude, DSC can be used to measure the rate of bread staling quantitatively^[15]. However, there are overlapping transitions over a wide temperature range because of the variety of components and range of structures present, difficulty in analysis^[16]. crystallography has been used to examine bread staling[17] specifically the crystalline nature of the starch in the system, which can be related to the firmness of the product^[11]. Starch in freshly baked bread is mostly amorphous, but slowly reorders during storage. The re crystallization is reflected in X-Ray Diffraction (XRD) patterns^[14]. Therefore, X-Ray crystallography can be used

to determine the molecular organization of starch in bread^[18]. X-Ray crystallography has been compared with DSC for determining the increase in crystallinity during storage of Arabic bread^[19] and used in conjunction with DSC in the analysis of the effect of various antistaling additives on wheat bread^[20].

The objective of the present study was to evaluate the effect of hydrocolloids on the quality of bread using two powerful techniques DSC and XRD.

MATERIALS AND METHODS

Wheat flour was used for preparation Lavash bread obtained from local market. The wheat flour had moisture, ash and protein content of 13.42, 1.10 and 11.57%, respectively. The Zeleny number was 19 mL. Xanthan (XG2 71478, France), guar gum and locust bean were obtained from RADO Company (France). Carboxy Methyl Cellulose (CMC) was obtained from Dow chemical Company (K4M, USA). Dried baker's yeast was obtained from Fariman yeast Company (IRAN).

Procedure for bread making: Hydrocolloids were incorporated at 1% level (flour weight basis) to the flour befor the mixing. The lavash dough consisted of 590 g of premixed wheat flour, water (up to optimum consistency of 500 Brabender units) and, 5 g of baker's yeast and 5 g of table salt. The mixed ingredients were left at 30°C for a time of 1 hr. Doughs were mixed and further incubated for 10 min at 30°C. Control lavash dough was prepared in the same manner without hydrocolloid. Loaves of 32 g each were baked on a rotary baking machine for 2 min and air-cooled for another 1 min. Breads were packed in polypropylene bags and evaluated after 1, 5 and 7 days. Water absorption of hydrocolloids applied dough was presented in Table 1.

Differential Scanning Calorimetry (DSC): DSC studies were carried out on a DSC-7 (Perkin-Elmer). About 30-40 mg of stored bread was weighted directly into DSC stainless steel pan. After sealing, stored bread (1, 5 and 7 days) was heated at rate of 10° C/min from 25-200°C. The equipment was calibrated with indium and an empty pan was used as reference. The parameters measured were the onset temperature (To), the peak temperature (Tp) and the conclusion temperature (Tc). Straight lines were drawn between To and Tc and enthalpy associated with starch retrogradation (Δ H) was calculated as the area enclosed by the and straight line and the endotherm curve. It was expressed in J/g of dry sample. Three replicates were run for each sample.

Table 1: Water absorption of hydrocolloids applied dough

Sample	Water absorption (%)		
Control	50.4		
CMC	63.4		
Locust bean	61.8		
Guar	60.6		
Xanthan	64.8		

X-Ray Diffraction analysis (XRD): A Siemens D 5005 X-Ray diffractometer was used (Cu K α radiation λ = 1.540). Operating parameters were 45 kV and 40 mA. Aliquots of 0.5 g of ground sample that for stored 1, 5 and 7 days were pressed to a thickness of 1 mm in the XRD holder. Samples were scanned from 5 to 60 2- θ (0.1, 2 sec). Three replicates were run for each sample.

RESULTS AND DISSCUSION

Effect of hydrocolloids on the DSC parameters: Investigations on starch retrogradation complemented by DSC measurements. Retrogradation of amylopectin can easily be followed and quantified by DSC, whereas retrogradation of amylose is difficult to follow by DSC^[14]. Influence of 1% hydrocolloids on the retrogradation of amylopectin on aged bread was presented on Table 2. During aging, melting enthalpy (ΔH) of retrograded amylopectin increased continuously as a function of aging time in control sample and in bread with hydrocolloids. The greatest enthalpy retrogradation after 1, 5 and 7 days were observed in bread containing control sample. The lowest ΔH in all days was observed in Guar gum. The effects of hydrocolloids on the enthalpy (ΔH) and Tp (Peak temperature) were shown in (Table 2). The Tp of all modified breads (by adding hydrocolloid) has a decreasing trend. The increment of the bread storage time altered the amylopectin retrogradation peak whose area was also increased, in agreement with other authors^[14,15]. The results in the retrogradation rate of amylopectin revealed that the hydrocolloids has the ability to delay the bread staling and that might be due the major water content of the bread containing hydrocolloids. Similarly, Davidou et al[4] suggested that the hydrocolloids affect the retrogradation level by limiting both the diffusion and the loss of water from bread crumb. In addition, other possible mechanism for explaining the antistaling effect is that the stabilizing effects of the hydrocolloids on starch retrogradation result from the interactions of them cooperatively with water as well as with starch chains in the mixture^[21], therefore the water content and its mobility have strong participation in this process^[22,23].

Table 2: Thermal properties of 1, 5 and 7 days stored Lavash bread as affected by hydrocolloids

Sample	Tp (C)			ΔH (j/g)		
	1 day	5 day	7day	1 day	5 day	7day
Guar	54a	45a	50a	4 cd	бъс	9d
Xanthan	56b	50b	44b	5ab	6.7b	12c
CMC	64d	62cd	56 d	7c	9.2b	12.5bc
Locust bean	61c	55c	50c	6.5ab	10.5a	12b
Control	65 d e	61e	58 d	8a	9.5a	14a
SEM ±	1.5	2.4	2.3	0.05	0.23	0.24

Tp: peak temperature, ΔH: Retrogradation enthalpy. Different letters within a column mean significant differences (p<0.05)

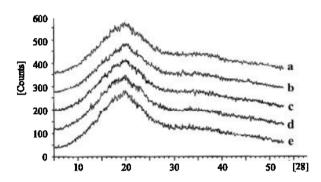


Fig. 1: Diffractograms of 5 days stored lavash bread. (a) control, (b) CMC, (c) locast bean, (d) xanthan, (e) guar

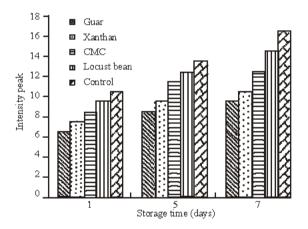


Fig. 2: Relative intensity of 1, 5 and 7 days stored lavash bread as affected by hydrocolloids

Effect of hydrocolloids on the XRD parameters: XRD has been used to study various existing starch crystal types^[24], the extent of starch melting and gelatinization^[25] and the extent of retrogradation^[26,15]. Different crystal types give their own specific diffractogram and peak intensities are amount of crystalline material. It has been demonstrated that fresh baked bread apparently shows only the V-type structure, indicative of amylose complexation with fatty acids to form helical clusters. With aging, the B-type structure increases, while the V-type structure remains virtually unchanged^[27]. Diffractogram of aged bread for 5 day with and without

hydrocolloids addition and relative intensity of 1, 5 and 7 days stored Lavash bread as affected by (1%) hydrocolloids are presented in Fig. 1 and 2. Diffractograms of all samples in first day were similar. However, diffractograms of control sample in 7 days represented the highest. The least difference in diffractograms in 7 days was in bread containing Guar gum.

Generally, the control sample showed the greatest differences and highest staling in all days. A descending order in staling, Guar gum > Xanthan > CMC > locust bean was observed for retarding the staling rate of different breads. These differences between treatments were because of properties of hydrocolloids. These materials compete with starch for water and caused to reduction water adsorption.

CONCLUSION

One of the proper ways for improve the quality of bread is to use hydrocolloids in formulations. These materials responsible for retention of moisture in bread crumb. The results from XRD and DSC indicate that control samples had the greatest staling and among studied hydrocolloids Guar gum showed the best characteristic for being an antistaling agent.

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REFERENCES

- Miles, M.J., V. Morris, P.D. Orford and S.G. Ring, 1985. The roles of amylose and amylopectin in the gelation and retrogradation of starch. Carbohydrate Res., 135: 271-281.
- Slade, L. and H. Levine, 1991. Beyond water activity: Recent advances based on an alternative approach to the assessment of food quality and safety. Crit. Rev. Food Sci. Nut., 330: 115-360.
- Martin, M.L. and R.C. Hoseney, 1991. A mechanism of bread firming. II. Role of starch hydrolyzing enzymes. Cereal Chem., 68: 503-508.

- Davidou, S., M. Le Meste, E. Debever and D. Bekaert, 1996. A contribution to the studyof staling of white bread: Effect of water and hydrocolloid. Food Hydrocoll., 10: 375-383.
- Rogers, D.E., K.J. Zeleznak, C.S. Lai and R.C. Hoseney, 1988. Effect of native lipids, shortening and bread moisture on bread firming. Cereal Chem., 65: 398-401.
- Schiraldi, A., L. Piazza, O. Brenna and E. Vittadini, 1996. Structure and properties of bread dough and crumb. J. Therm. Anal., 47: 1339-1345.
- Armero, E. and C. Collar, 1998. Crumb firming kinetics of wheat breads with antistaling additives. J. Cereal Sci., 28: 165-174.
- Russell, P.L., 1983. Kinetic study of bread staling by differential scanning calorimetry. The effect of painting loaves with ethanol. Starch, 3: 5277-5282.
- Russell, P.L., 1983. A kinetic study of bread staling by differential scanning calorimetry and compressibility measurements. The effect of added monoglyceride. J. Cereal Sci., 1: 297-303.
- LeMeste, M., V.T. Huang, J. Panama, G. Anderson and R. Lentz, 1992. Glass transition of bread. Cereal Foods World, 37: 264-267.
- Champenois, Y., P. Colonna, A. Buléon, G. Della Valle and A. Renault, 1995. Starch gelatinization and retrogradation in white pan bread. Sci. Aliments, 15: 593-614.
- Vodovotz, Y., L. Hallberg and P. Chinachoti, 1996.
 Effect of aging and drying on thermomechanical properties of white bread as characterized by Dynamic Mechanical Analysis (DMA) and Differential Scanning Calorimetry (DSC). Cereal Chem., 73: 264-270.
- Marsh, R.D.L and J.M.V. Blanshard, 1988. The application of polymer crystal growth theory to the kinetics of formation of the B-amylose polymorph in a 50% wheat starch gel. Carbohydrate Poly., 9: 301-317.
- 14. Baik, M.Y. and P. Chinachoti, 2000. Moisture redistribution and phase transitions duringbread staling. Cereal Chem., 77: 484-488.
- Karim, A.A., M.H. Norziah and C.C. Seow, 2000. Methods for the study of starch retrogradation. Food Chem., 71: 9-36.

- Jagannath, J.H., K.S. Jayaraman and S.S. Arya, 1999.
 Studies on glass transition temperature during staling of bread containing different monomeric and polymeric additives. J. Applied Poly. Sci., 71: 1147-1152.
- 17. Zobel, H.F., 1973. A review of bread staling. Bakers Digest, 47: 53-58.
- Vodovotz, Y., M. Baik, E. Vittadini and P. Chinachoti, 2001. Instrumental Techniques Usedin Bread Staling Analysis. In Chinachoti P, Vodovotz Y, (Edn.) Instrumental Techniques Used in Bread Staling Analysis. CRC Press, New York, pp. 93-111.
- Varriano-Marston, E., G. Huang and J.J. Ponte, 1980.
 Comparison of methods to determine starch gelatinization in bakery foods. Cereal Chem., 57: 242-246.
- Sidhu, J.S., P.G. Caceres and M. Behbehani, 1997.
 Measurement of starch properties during staling of Arabic bread. Starch, 49: 180-186.
- Jagannath, J.H., K.S. Jayaraman, S.S. Arya and R. Somashekar, 1998. Differential scanning calorimetry and wide-angle X-ray scattering studies of bread staling. J. Applied Poly. Sci., 67: 1597-1603.
- Lee, M.H., M.H. Baek, D.S.H.J. Cha Park and S.T. Lim, 2002. Freeze—thaw stabilization of sweet potato starch gel by polysaccharide gums. Food Hydrocoll., 16: 345-352.
- Smits, A.L.M., F.C. Ruhnau, J.F.G. Vliegenthart and J.J.G. Van Soest, 1998. Ageing of starch based systems as observed with FT-IR and solid state NMR spectroscopy. Starch, 50: 478-483.
- Czuchajowska, Z. and Y. Pomeranz, 1989. DSC, water activity and moisture contents in crumb center and near-crust zones of bread during storage. Cereal Chem., 66: 305-309.
- 25. Vidal, F.D. and A.B. Gerrity, 1979. Antistaling agent for baking products. U.S. Patent 4160848.
- Zeleznak, K.J. and R.C. Hoseney, 1986. The role of water in the retrogradation of wheat starch gels and bread crumb. Cereal Chem., 63: 407-411.
- 27. Zobel, H.F., S.N. Young and L.A. Rocca, 1988. Starch gelatinization: An x-ray diffraction. Cereal Chem., 65:443-446.