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Investigation of physicochemical properties of breads baked in microwave and infrared-microwave combination ovens during storage

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Abstract Staling of breads baked in different ovens (microwave, infrared-microwave combination and conventional) was investigated with the help of mechanical (compression measurements), physicochemical (DSC, X-ray, FTIR) and rheological (RVA) methods. The effect of xanthan-guar gum blend addition on bread staling was also studied. Xanthan-guar gum blend at 0.5% concentration was used in bread formulation. The gums were mixed at equal concentrations to obtain the blend. After baking, the staling parameters of breads were monitored over 5 days storage. During storage, it was seen that hardness, retrogradation enthalpies, setback viscosity, crystallinity values, and FTIR outputs related to starch retrogradation of bread samples increased, whereas FTIR outputs related to moisture content of samples decreased significantly with time. The hardness, retrogradation enthalpy, setback viscosity, and crystallinity values of microwave-baked samples were found to be highest among other heating modes. Using IR-microwave combination heating made it possible to produce breads with similar staling degrees as conventionally baked ones in terms of retrogradation enthalpy and FTIR outputs related to starch retrogradation. Addition of xanthan-guar gum blend decreased hardness, retrogradation enthalpy and total mass crystallinity values of bread samples showing that staling was delayed.

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Introduction

Bread staling refers to all changes, rather than microbiological deterioration, which take place at different rates and intensities after removal of the sample from the oven [1]. These serial changes cannot be explained by a single effect, and include amylopectin retrogradation, reorganization of polymers within the amorphous region, loss of moisture content, distribution of water content between the amorphous and crystalline zone, and the crumb macroscopic structure [2, 3]. Bread staling is associated with some typical sensorial changes such as loss of flavour, loss of crispness in the crust and increased crumb firmness. Since staling has considerable economic importance to the baking industry, it is important to concentrate on this subject.

Characterization of bread and starch-gel systems from macro- to nanoscale is required to get information about the staling mechanism. When investigating the staling phenomena, the mechanical properties, microstructure and physicochemical properties have been measured respectively, by the help of compression measurements, microscopic monitoring methods, DSC and X-ray analysis [4]. Studies on bread staling demonstrated that changes in starch structure, such as gelatinization and retrogradation of starch, contribute to firm texture [5]. If the physicochemical properties are taken into consideration, among the thermoanalytical methods differential scanning calorimetry (DSC) has been widely used in providing basic information on starch retrogradation [6, 7]. As storage time increases, the retrogradation enthalpy of samples increases [8]. Moreover, changes in crystallinity during ageing can be shown in the

X-ray diffraction patterns [9, 10]. Crystallization of amorphous starch into B-type crystalline structure is observed during bread ageing, where V-type crystalline structure, which is indicative of amylose complexing with fatty acids, remains unchanged [8]. Fourier Transform Infrared (FTIR) spectroscopy, which has the advantage of being a noninvasive method, has also been used to monitor staling in bread [11]. FTIR spectroscopy measures the degree of short-range ordering in a system. Conformational changes brought about by starch retrogradation can be monitored with this method, since the system becomes more ordered upon staling [9, 11]. The tendency of a starch to retrograde can also be studied from its pasting behaviour, usually by observing changes in viscosity related to starch crystallization [12] using Rapid Viscoanalyser [6, 9]. Setback viscosity was related with the retrogradation or re-ordering of the starch molecules [13].

Gums are widely used in baked goods to enhance dough handling properties, to increase overall quality of the fresh products [14, 15] and to extend their shelf-life [16, 17]. Seyhun et al. [16] demonstrated in their studies that use of gums (xanthan gum, guar gum and MC) helped to retard staling of microwave-baked cakes. The effect of hydrocolloids (sodium alginate, κ-carrageenan, xanthan gum and HPMC) on conventionally baked fresh bread quality and bread staling were studied by Guarda et al. [17] and it was found that bread quality was improved with the usage of these hydrocolloids. Keskin et al. [15], demonstrated in their studies that xanthan-guar blend addition to the formulation improved quality of fresh breads (high-specific volume and porosity, low hardness values) baked in infrared-microwave combination oven.

Rapid staling is one of the disadvantages of microwave baked products. Rapid staling mechanism in microwave baking is not clear yet. Infrared-microwave combination baking may be a promising method to retard staling of baked products. Infrared-microwave combination heating combines the time-saving advantage of microwave heating by rapid heating, with the browning and crisping advantages of infrared heating, and by providing additional heat flux on the surface [18]. Breads baked in combination oven had comparable quality with the conventionally baked ones in terms of colour, textural characteristics, specific volume and porosity [19] and may be an alternative to conventionally baked ones.

There is no study in literature investigating the staling of breads baked in microwave and infrared-microwave combination oven. The objective of this study was to investigate the physicochemical properties of breads baked in different ovens (microwave, infrared-microwave combination and conventional) during staling by using FTIR, X-ray, DSC and RVA. It was also aimed to study the effects of xanthan-guar blend on retardation of staling of breads. This study will provide insights into the staling mechanism of microwave baked breads.

Materials and methods

Dough preparation

Bread flour containing 30% wet gluten, 13.5% moisture and 0.54% ash was used in the study. The dough was prepared according to the hamburger bread formulation, which is 100% flour, 8% sugar, 6% milk powder, 2% salt, 3% compressed yeast (Pakmaya, Turkey), 8% margarine, 55% water on flour weight basis. Gum blend made of guar gum (Guar Gum Powder HV-101 FCC, AEP Colloids Inc., NY, USA) and xanthan gum (XAN-80 NF FCC, AEP Colloids Inc., NY, USA) at equal amounts was added to the formulation at 0.5% concentration to see its effect as compared to the control formulation which contains no gum. Dough was prepared by using straight dough method. That is, the dry ingredients were mixed first. Yeast was dissolved in water at 30 °C. Margarine was melted and added to the dry ingredients in liquid phase together with dissolved yeast. All the ingredients were mixed by a mixer (Kitchen Aid, 5K45SS, USA). After complete mixing of the dough, it was placed into the incubator at 30 °C for fermentation. Total duration of the fermentation was 125 min. After the first 70 min, the dough was taken out of the incubator, punched and placed into the incubator again. A second punch took place after 35 min. After fermentation, the dough was divided into 50-g pieces. Each piece was shaped and placed into the incubator for the last time for 20 min under the same incubation conditions.

Conventional baking

Conventional baking was performed in a commercial electrical oven (Arçelik ARMF 4 Plus, Turkey). The prepared dough samples were baked at 200 °C for 13 min. Four breads were baked at a time.

Microwave baking

The infrared-microwave combination oven (Advantium oven[TM], General Electrics, USA) was used by only operating the microwave power. The power of microwave oven has been determined as 706 W by using IMPI 2-L test. The frequency of the oven was 2450 MHz. Dough samples were baked at 100% power for 2.0 min. Four breads were baked at a time.

Infrared-microwave combination baking

Infrared-microwave baking was performed in combination oven (Advantium oven[TM], General Electric Company, Louisville, KY, USA). There were three 1,500-W lamps, two at the top and one at the bottom. Four breads were baked using 70% halogen-lamp power both at the top and

at the bottom and 20% microwave power for 8 min which was the optimum condition determined by preliminary experiments. Two beakers, each containing 400 ml water, were placed at the back corners of the oven to provide required humidity during baking [19].

Storage of bread

After baking, breads were covered with stretch film, and kept in a plastic bag at 22 ± 2 °C for 120 h. Moisture content test, hardness test, RVA, DSC, X-ray and FTIR analysis of breads were performed at different storage times, such as RVA, X-ray, FTIR for 1 and 120 h; DSC for 24, 72, 120 h; moisture content for 0, 1, 24, 48, 72, 120 h; hardness for 1, 24, 48, 72, 120 h.

Analysis of bread

Moisture content

Moisture content of whole bread samples were determined by drying the samples in an oven at 105 °C until constant weight was obtained (AACC, 2000). Five replications were done.

Hardness

The hardness of bread crumbs were measured with Texture Analyser (TA Plus, Lloyd Instruments, UK) equipped with a 50 N load cell. Breads with the dimension of 20 mm × 25 mm × 15 mm were compressed for 25% at a speed of 55 mm/min. A cylindrical probe with a diameter of 10 mm was used. For the fresh bread, the hardness was measured 1 h after baking to allow it to cool to room temperature. Five replications were done.

RVA analysis

Rapid Visco™ Analyzer (RVA) (Newport Scientiric PTY. Ltd, Warriewood, NSW, Australia) was used to study gelatinization and retrogradation of starch in bread. The freeze–dried bread samples were ground in a coffee grinder and sieved through a 212-μm screen. Ground sample of 4 g (14% moisture basis) was added to 25 g distilled water in an RVA sample canister. The heating and cooling cycles were programmed in the following manner: The samples were held at 50 °C for 1 min, heated to 95 °C within 3.5 min and then held at 95 °C for 2.5 min. It was subsequently cooled to 50 °C within 3.5 min and then held at this temperature for 2 min. The peak viscosity, i.e. the maximum viscosity during pasting, break down viscosity, i.e. the difference between the peak viscosity and the minimum viscosity during pasting, setback viscosity,

i.e. the difference between the maximum viscosity during cooling and the minimum viscosity during pasting, final viscosity, i.e. the viscosity at the end of the RVA run, pasting temperature (°C), i.e. the temperature indicating an initial increase in viscosity and peak time (min), i.e. time to reach the peak viscosity were determined from the RVA plots using Termocline for Windows, Version 2.0. Two replications were done.

DSC analysis

Differential scanning calorimeter (DSC) (Perkin Elmer Jade DSC, Shelton, USA) was used to measure the retrogradation enthalpies of starch in breads during storage. 10 ± 1 mg of freeze–dried bread crumb samples were loaded into the pans and water was added at 1:2 (w/v, sample: water ratio). The pans were hermetically sealed and kept at room temperature for 1 h. Then, the samples were scanned by DSC from 10 to 90 °C at a heating rate of 10 °C/min. Two replications were done.

X-ray analysis

X-ray diffraction analysis was done using Rigaku Miniflex (Rigaku Americas Corp., The Woodlands, USA) with CuKα (30 kV, 15 mA, $\lambda = 1.542$Å) radiation. The scanning region of the diffraction angle (2θ) was 0°–40° with the scanning speed of 1°/min. The curve fitting analysis were done by the help of PeakFit V4.12 software. The freeze–dried samples were compressed to thin disks of 1–2 mm thickness and a diameter of 13 mm.The pressed sample was mounted on a sample holder. The measurements were carried out at 22 ± 2 °C. Two replications were done. Crystalline peaks were analysed as pseudo-Voight-form and the amorphous ones as Gaussian-form peaks [10]. The crystallinity levels in the samples were determined by the separation and integration of the areas under the crystalline and amorphous X-ray diffraction peaks [20]. The quantification of relative crystallinity was performed using the total mass crystallinity grade (TC), which is the ratio of area of the crystalline fraction to the area of crystalline fraction plus the amorphous fraction.

$$TC = \frac{I_c}{I_c + I_a}$$

where I_c is the integrated intensity of crystalline phase, and I_a is the integrated intensity of the amorphous phase [10].

FTIR analysis

ATR–FTIR experiments were conducted on a Bruker Vertex 70 Spectrometer using Diamond w/KRS-5 lens single reflection ATR plate (MIRacle ATR, Pike

Table 1 Moisture content of control and gum-added breads baked in different ovens during staling

Oven type	Storage time (h)					
	0	1	24	48	72	120
Microwave-control	35.2 ± 0.12	31.4 ± 0.17	30.9 ± 0.19	30.7 ± 0.12	30.5 ± 0.19	30.1 ± 0.08
Combination-control	36.0 ± 0.17	34.0 ± 0.19	33.6 ± 0.17	33.3 ± 0.07	33.1 ± 0.06	33.1 ± 0.14
Conventional-control	38.2 ± 0.11	36.8 ± 0.09	36.8 ± 0.11	36.7 ± 0.12	36.7 ± 0.09	36.5 ± 0.16
Microwave-gum	35.6 ± 0.07	31.6 ± 0.11	31.3 ± 0.12	30.8 ± 0.15	30.6 ± 0.08	30.3 ± 0.07
Combination-gum	36.0 ± 0.17	34.2 ± 0.15	33.9 ± 0.16	33.7 ± 0.09	33.4 ± 0.10	33.0 ± 0.11
Conventional-gum	38.3 ± 0.06	36.9 ± 0.09	36.8 ± 0.10	36.6 ± 0.10	36.6 ± 0.09	36.3 ± 0.20

Technologies, Madison, WI, USA), operating in the middle-IR region, 600–4,000 cm^{-1}. The measurements were done at a resolution of 2 cm^{-1} with 32 scans. Freeze–dried breads were placed onto the surface of the crystal and contact of ATR crystal with the sample was provided. Two replications were done. The curve fitting analysis was done by the help of PeakFit V4.12 software.

Statistical analysis

Analysis of variance (ANOVA) was performed to determine whether there was significant difference between storage time, gum and oven types ($P < 0.05$). Variable means were compared by Tukey Single Range test by using Minitab, statistics programme (MINITAB for Windows, Version 14, Minitab Inc., State College, PA, USA).

Results and discussion

Moisture content

ANOVA results demonstrated that moisture content of samples were dependent on storage time and oven type (Table 1). The rapid decrease in moisture content of samples was seen during the first 1 h cooling period (Table 1). During storage, the variation of moisture content with storage time decreased more slowly.

The moisture content of microwave-baked breads were found to be the lowest among other heating modes (Table 1). During microwave heating, relative to conventional baking, larger amounts of interior heating result in increased moisture vapour generation inside the food material, which creates significant interior pressure and concentration gradients. This results in higher rate of moisture losses during microwave heating, creating an outward flux of rapidly escaping vapour [21]. In early studies, it was shown that breads baked in microwave oven lost more moisture as compared to conventionally baked ones [18, 19].

In Table 1, it was seen that the addition of xanthan-guar blend to the formulation did not affect the moisture content of samples during storage significantly. It is stated that the overall increase in dough water absorption due to the addition of a gum can be relatively small since it is used at low amounts (typically from 0.01 to 0.5% total formula basis); the additional water may be insignificant, but the viscous, slippery mouth feel that the gums retain even after baking can be perceived as a beneficial increase in product moistness [22].

Hardness

The hardness values of microwave-baked samples were found to be highest among other heating modes, which was in accordance with early studies [18, 19]. During 5 days of storage, hardness of bread samples increased significantly with time (Fig. 1). The increase in firmness may be related to the decrease in moisture content. Moisture content has
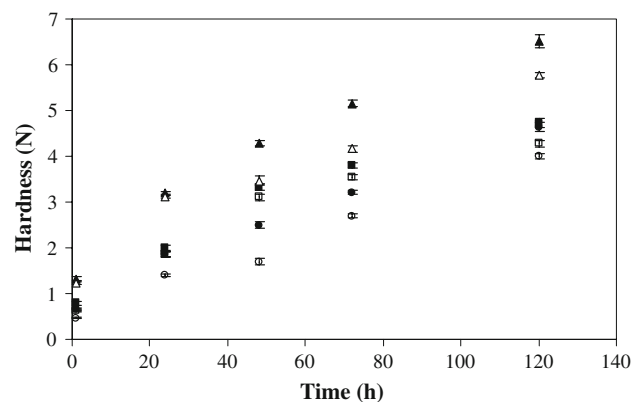

Fig. 1 Variation in hardness of control and gum-added breads baked in different ovens during storage (*filled triangle* control breads baked in microwave oven; *filled square* control breads baked in infrared-microwave combination oven; *filled circle* control breads baked in conventional oven; *open triangle* gum-added breads baked in microwave oven; *open square* gum-added breads baked in infrared-microwave combination oven; *open circle* gum-added breads baked in conventional oven)

been shown to be inversely proportional to the rate of firming [23].

Several factors play a role in the bread firming process, but the large volume of data implicates that amylopectin retrogradation is a key factor, and gluten is also involved and cannot be ignored [24]. One theory states that bread firming is a result of hydrogen bonding between gelatinized starch granules and the gluten network. It could also involve hydrogen bonding between retrograded starch molecules and the gluten network with retrogradation occurring either before or after association of amylopectin and/or amylose molecules with the protein network [24]. In bread, water acts as a plasticizer [25]. When moisture decreases, it accelerates the starch (gelatinized or retro-graded)–protein interactions, and also starch-starch interactions, resulting in firmer texture. Therefore, crumb moisture and firmness are closely related. According to three-way ANOVA results, it was found that hardness values were dependent on storage time, oven and gum types. Since the moisture content of microwave-baked samples was the lowest among other heating modes (Table 1), it was not surprising that the hardness values of microwave-baked samples were the highest (Fig. 1) [18, 19]. Moreover, the hardness of infrared-microwave combination baked bread samples were in between that of conventionally and microwave-baked ones, meaning that combination heating partially solved the rapid staling problem of microwave baking in terms of one of the indicator parameters of staling.

It was found that the addition of xanthan-guar blend to the formulation resulted in a significant decrease in the hardness values of samples baked in all types of ovens (Fig. 1), meaning that gum addition retarded staling in terms of hardness values. Gums are able to modify starch gelatinization and retard starch retrogradation by interacting with starch components; amylose and amylopectin, or gluten [14]. It was previously shown that gums reduced the firmness of bread crumb [14].

Viscosity (RVA) profiles

Among RVA data, setback viscosity values have been related to staling in literature [26]. When gelatinized starch cools, an increase in viscosity is observed until the for-mation of gel due to the ordering of starch molecule [13]. The increase in viscosity is known as setback viscosity in RVA profile [26].

As can be seen in Table 2, the setback viscosity of the samples baked in microwave and IR-microwave combi-nation oven increased significantly during storage. Amylose and amylopectin affect the setback viscosity together. Setback viscosity is related to the amylose chains mainly during cooling of bread but the effect of amylose chain entanglement may also be seen after 5 days of stor-age. Since amylose-amylopectin aggregation is known to be responsible for staling, the interchain association of the amylose and amylopectin fraction that might have increased the setback viscosity value after 5 days of stor-age. It was found that the setback viscosities of the samples baked in combination oven were in between the values for conventionally and microwave-baked ones (Table 2). Thus, the samples baked in microwave oven had higher setback viscosities.

The results showed that gum addition to the formulation resulted in an increase in viscosity values of most of the samples baked in different ovens during storage which cannot be related to starch retrogradation (Table 2). It was stated by some researchers [27–29] that viscosity of starch/hydrocolloid systems after heating and cooling was greater than in systems containing only starch.

Table 2 RVA profile of control and gum-added breads baked in different ovens during staling

Oven type	Presence of gum	Storage time (h)	Peak viscosity (cP)	Break down viscosity (cP)	Setback viscosity (cP)	Final viscosity (cP)
Microwave	No	1	663 ± 24	91 ± 9	1023 ± 27	1023 ± 16
Microwave	No	120	1248 ± 35	157 ± 11	2160 ± 25	2160 ± 15
Combination	No	1	290 ± 19	9 ± 5	644 ± 19	644 ± 21
Combination	No	120	919 ± 15	52 ± 7	1645 ± 32	1645 ± 24
Conventional	No	1	286 ± 21	11 ± 4	664 ± 23	664 ± 17
Conventional	No	120	344 ± 17	8 ± 2	673 ± 13	673 ± 9
Microwave	Yes	1	1493 ± 39	214 ± 16	2195 ± 35	2195 ± 31
Microwave	Yes	120	1595 ± 27	259 ± 20	2275 ± 30	2275 ± 20
Combination	Yes	1	1219 ± 33	172 ± 13	1683 ± 9	1683 ± 25
Combination	Yes	120	1520 ± 36	493 ± 31	1883 ± 11	1883 ± 28
Conventional	Yes	1	968 ± 23	40 ± 14	1675 ± 18	1675 ± 15
Conventional	Yes	120	1103 ± 18	75 ± 12	1839 ± 13	1839 ± 23

Table 2 also demonstrates the peak, break down and final viscosities of breads baked in different ovens. It was observed that the viscosity values increased as storage time increased. The peak viscosity values of fresh samples (stored for 1 h) baked in microwave oven were higher than that of baked in other ovens. It was previously shown by Palav and Seetharaman [30] that the peak viscosity in the microwave-heated samples was higher than that in conduction-heated samples following 2 or 120 h of storage. The higher peak viscosity in microwave-heated samples suggested that the granular integrity was not completely destroyed during microwave heating while the granules were more pasted following conduction heating. Incomplete destruction in granular integrity may be because of high moisture loss, affecting all reactions during swelling, gelatinization and retrogradation. There was no difference between peak viscosity values of breads baked in conventional and combination ovens.

DSC

The results of ANOVA demonstrated that retrogradation enthalpies of samples were dependent on storage time, gum and oven types. It can be seen from Fig. 2 that retrogradation enthalpy of samples increased significantly as storage time increased. The significant increase in retrogradation enthalpies can be clearly seen for 120 h stored of control breads baked in all types of ovens.

Moreover, the retrogradation enthalpies of microwave-baked breads were the highest, due to the rapid staling problem of microwave heating. On the other hand, the retrogradation enthalpies of samples baked in infrared-
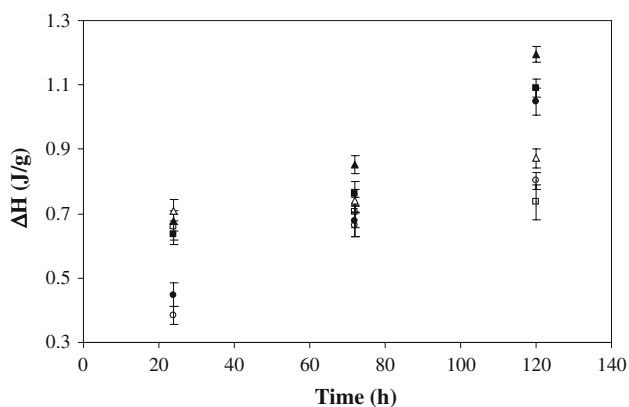

Fig. 2 Variation in retrogradation enthalpy of control and gum-added breads baked in different ovens during storage (*filled triangle* control breads baked in microwave oven; *filled square* control breads baked in infrared-microwave combination oven; *filled circle* control breads baked in conventional oven; *open triangle* gum-added breads baked in microwave oven; *open square* gum-added breads baked in infrared-microwave combination oven; *open circle* gum-added breads baked in conventional oven)

microwave combination oven were in between the values of conventionally and microwave-baked breads, which means combination heating partially solved the rapid staling problem of microwave heating in terms of one of the indicator parameters of staling.

It can be easily seen from Fig. 2 that gum addition reduced retrogradation enthalpy meaning that amylopectin retrogradation was retarded. Chaisawang and Suphantharika [29], found that the retrogradation enthalpy values of gum-added starch samples were significantly ($P < 0.05$) lower than samples containing only starch. They associated their results with a reduction in water availability causing partial gelatinization of crystalline regions in the starch granules and starch-gum interactions [29].

X-ray

The diffraction pattern analysis showed that fresh bread stored for only 1 h contained only a peak around 20.7° corresponding to a V-type structure (Fig. 3a, c, e). This is indicative of amylose complexing with fatty acids, which remains virtually unchanged during ageing [31]. Peaks at 15.8°, 17.7°–18° and 22.8° indicating B-type structure appearing during storage (Fig. 3b, d, f). In the case of microwave-baked samples, the physical orientation of the branched amylopectin molecules of starch within the swollen granule may be different than that of the other samples baked in conventional and combination ovens. This results in appearence of an additional peak at 15.8°, indicating more crystalline structure since the swelling, hydration and gelatinization degree of starch in the samples baked in microwave oven is different from the ones baked in conventional and combination ovens.

The different types of crystals influence the distribution of water within the crumb differently. The A-type crystal contains eight water molecules, whereas the B-type crystal contains 36 water molecules. As a result, in breads recrystallization of amylopectin develops B-type crystalline regions and the crumb becomes firmer because more water has migrated into the crystalline region. This water which participated in the formation of the crystal is no longer available as a plasticizer of the starch-gluten. Macroscopically, the lack of the plasticizing effect from water results in firmer bread [32]. This result is supported by the firm texture of microwave-baked breads (Fig. 1). B-type crystalline structure is larger for microwave-baked breads.

The total mass crystallinity grades of samples baked in different ovens can be seen in Fig. 4. According to ANOVA, total mass crystallinity grades of samples were dependent on storage time, gum and oven types. As storage time increased, crystallinity values of all samples increased significantly (Fig. 4). The formation of gel structure due to

Fig. 3 X-ray pattern change
after 1 and 120 h storage for
control breads baked in different
ovens (**a** conventional 1 h;
b conventional 120 h;
c microwave 1 h; **d** microwave
120 h; **e** infrared-microwave
combination 1 h; **f** infrared-
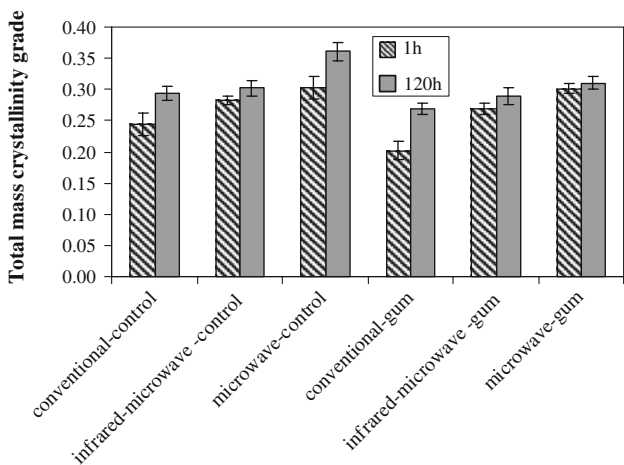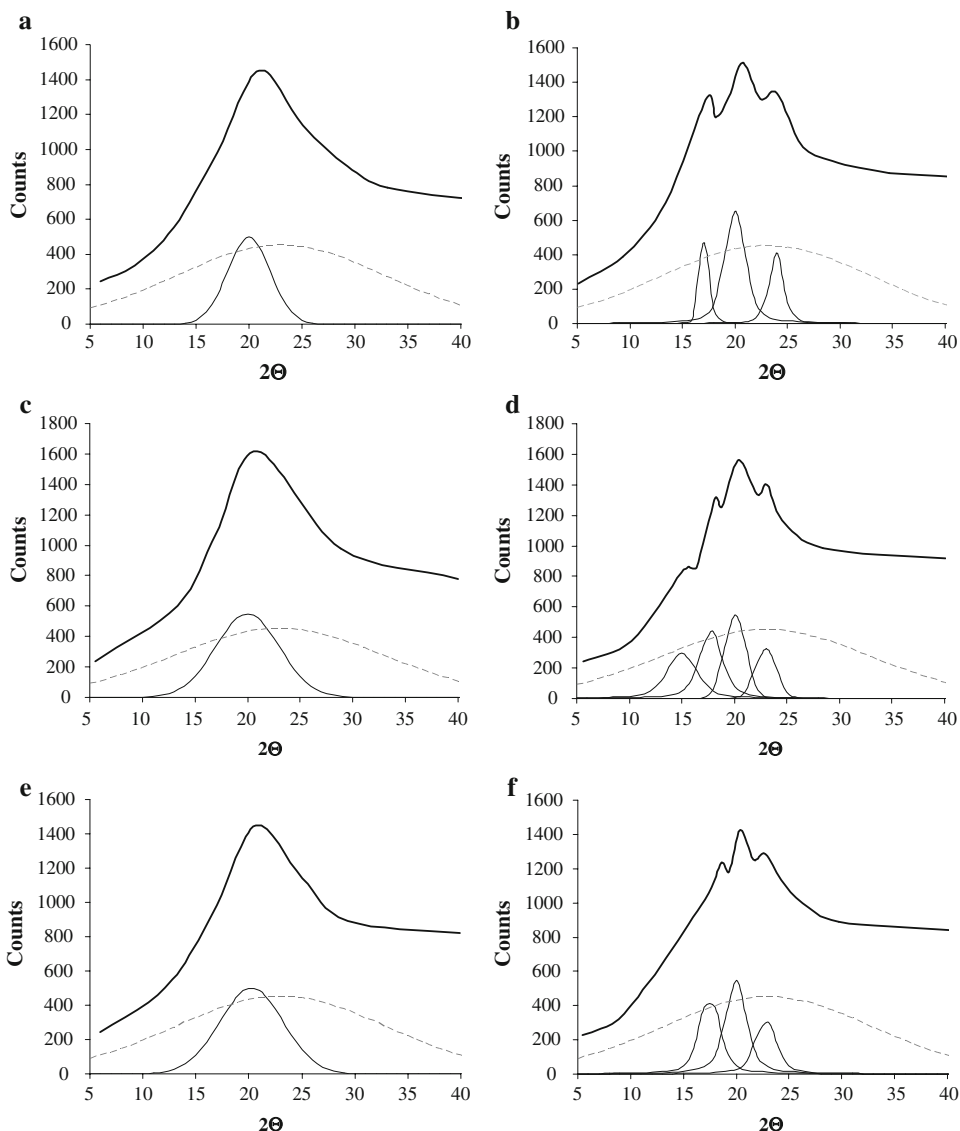microwave combination 120 h)

Fig. 4 Variation in total mass crystallinity of control and gum-added breads baked in different ovens during storage

the starch retrogradation during storage is linked to the development of crystallites, which is considered to be the interchain association of the amylose and amylopectin fraction [33].

When the crystallinity values of samples baked in different ovens were considered, it was found that the samples baked in microwave oven had significantly higher crystallinity values than the ones baked in conventional and combination ovens (Fig. 4). It is known that high temperatures can cause larger starch granule modification and disruption and as a result, larger amount of starch can be expelled from the granule [3, 34]. Since microwave-heated samples may reach higher temperatures than conventionally heated ones in a shorter time, the leached starch amount of breads baked in microwave oven might be higher than that of conventionally baked ones which might increase the crystallinity values.

When the effect of gum addition on total mass crystallinity values of samples were considered, it was found that gum addition decreased crystallinity values of all samples (Fig. 4), resulting in retardation of staling in terms of starch retrogradation, one of the indicator parameter of staling. On the other hand, it was seen that there was no change in number of peaks appearing in X-ray pattern of gum-added samples baked in different ovens (Fig. 5).

FTIR

Water-related variations such as drying and water redistribution, have an influence on the measured spectra. In Fig. 6a–f the water-related variations, lying in the 3,000–3,600 cm^{-1} wavenumber interval, which corresponds to the O–H bond stretching vibration, can be easily seen. This fact is due to the lower water content of breads in the storage period and probably due to the subsequent reorganisation of the water molecules into the protein-polisaccharide

network [35]. Progressive intensity reduction in that region of the spectra with staling was suggested by Cocchi et al. [36].

The integral area of peaks appearing at 2,980–3,600 cm^{-1}, which represents water-related variations and changes during storage, was proportionate to the 2,810–2,970 cm^{-1} loadings region, which is almost exactly related to the "C–H strech in saturated lipids" (2,806–2,840 cm^{-1}) [36], to make the measurements independent of uncontrollable factors. The variation in contact surface between the ATR crystal and sample at every measurement can be regarded as uncontrollable factors in FTIR analysis [36, 37].

It can be seen from Tables 3 and 4, that as storage time increased the ratio of peaks appearing at 2,980–3,600 cm^{-1} (A_1) and 2,810–2,970 cm^{-1} (A_2) significantly decreased, which was because of the decrease in moisture content of crumb of bread samples during storage and reorganization of water molecules in protein–starch network, resulting in

Fig. 5 X-ray pattern change after 1 and 120 h storage for gum-added breads baked in different ovens (**a** conventional 1 h; **b** conventional 120 h; **c** microwave 1 h; **d** microwave 120 h; **e** infrared-microwave combination 1 h; **f** infrared-microwave combination 120 h)
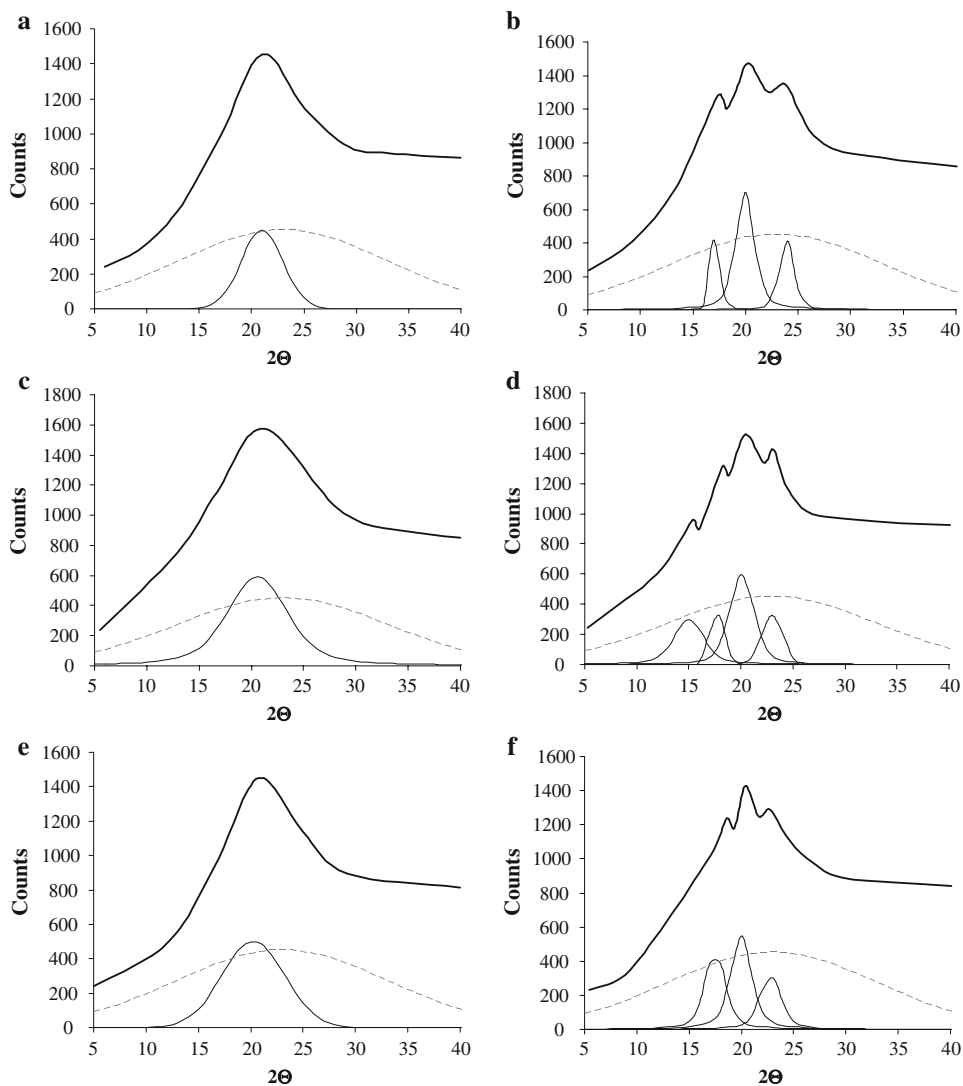
Fig. 6 a–f FTIR spectra of control and gum-added breads baked in different ovens after 1 h (*continuous line*) and 120 h (*dashed line*) storage (**a** conventional, control; **b** conventional, gum; **c** microwave, control; **d** microwave, gum; **e** infrared-microwave combination, control; **f** infrared-microwave combination, gum)
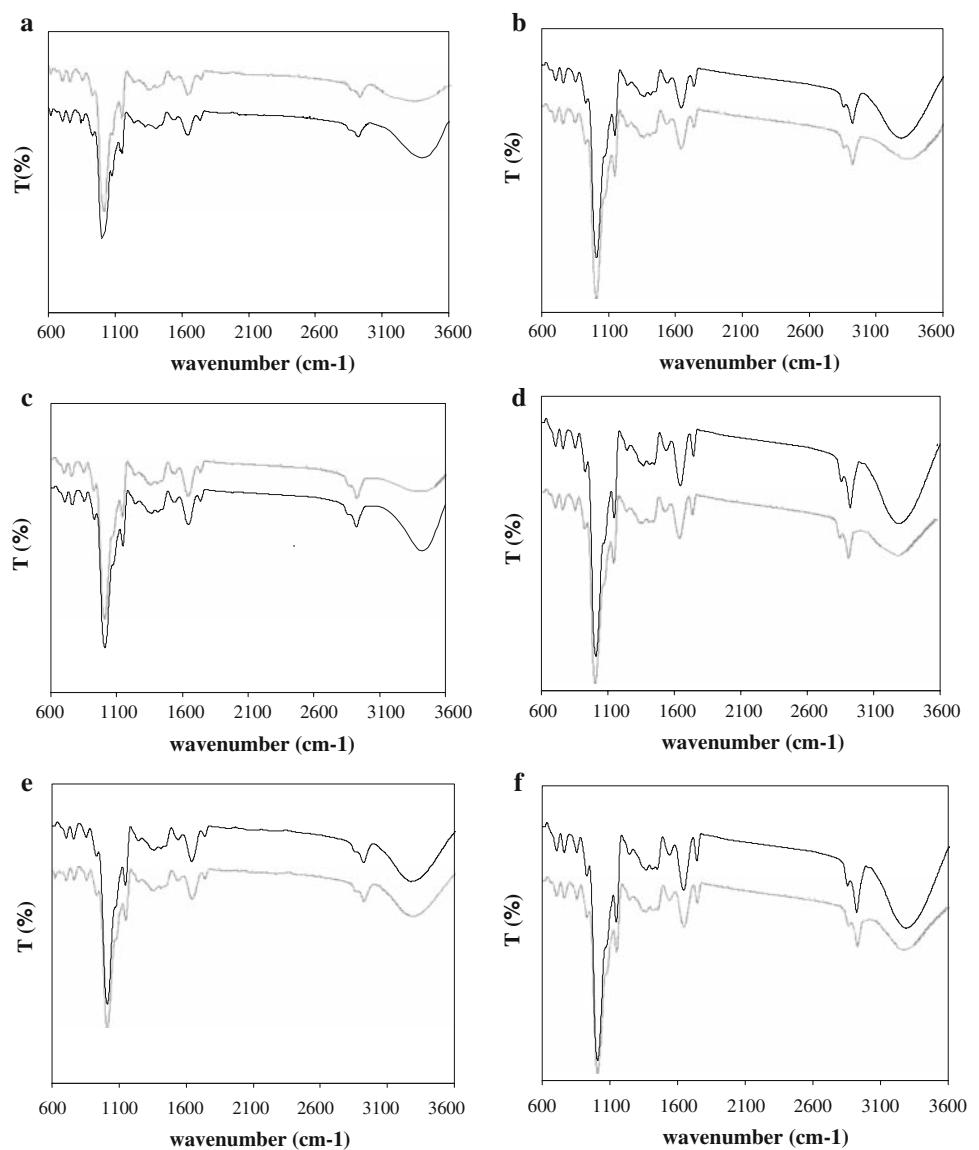

Table 3 The integral area ratios of peaks appearing at 2,980–3,600 cm^{-1} (A_1) and 2,810–2,970 cm^{-1} (A_2); appearing around 1,060–1,070 cm^{-1} (A_3) and $\sim$1,151 cm^{-1} (A_4) related to control breads

Peak ratios/storage time (h)	Oven type					
	Conventional		Microwave		Infrared-microwave combination	
	A1/A2	A3/A4	A1/A2	A3/A4	A1/A2	A3/A4
1	5.1 ± 0.3	0.89 ± 0.05	1.8 ± 0.20	1.25 ± 0.32	3.5 ± 0.40	0.96 ± 0.07
120	3.5 ± 0.7	1.07 ± 0.09	1.4 ± 0.30	1.27 ± 0.18	2.1 ± 0.50	1.03 ± 0.11

change in band intensities. The ratio of the peak intensities of samples baked in microwave and combination ovens were found to be significantly lower than that of conventionally baked ones. Additionally, the effect of gum addition in decreasing moisture loss during storage was especially seen for breads baked in microwave oven (Table 4). However, the addition of xanthan-guar blend to the formulation did not affect the moisture content of whole samples (crust and crumb together) during storage significantly (Table 1). An explanation to that result was that in FTIR analysis, only crumb of bread samples were used while both crumb and crust of bread were used in moisture determination by AACC method. Thus, addition of gum to the formulation may prevent moisture migration

Table 4 The integral area ratios of peaks appearing at 2,980–3,600 cm^{-1} (A$_1$) and 2,810–2,970 cm^{-1} (A$_2$); appearing around 1,060–1,070 cm^{-1} (A$_3$) and $\sim$1,151 cm^{-1} (A$_4$) related to gum added breads

Peak ratios/storage time (h)	Oven type					
	Conventional		Microwave		Infrared-microwave combination	
	A1/A2	A3/A4	A1/A2	A3/A4	A1/A2	A3/A4
1	5.0 ± 0.8	0.91 ± 0.09	3.3 ± 0.3	1.22 ± 0.07	3.6 ± 0.2	0.97 ± 0.03
120	3.8 ± 0.4	1.09 ± 0.04	2.1 ± 0.4	1.30 ± 0.05	2.4 ± 0.3	1.09 ± 0.06

from crumb to crust resulting in decrease in moisture loss. Therefore, a decrease in moisture loss was observed in the bread crumb formulated with gum.

The spectral region 1,200–800 cm^{-1}, which has been shown to be sensitive to the degree of molecular order in starch, was used [37] in analysing starch related variations. The modification with ageing of the absorption values in this spectral region, consisting in the variation of the relative intensities of overlapped bands at $\sim$1,000 cm^{-1}, has been observed by other researchers [36], relating it to the progressive ordering of the amylopectin polymer present in bread. Peaks at 1,047 cm^{-1} are related to crystalline regions of starch [9, 38]. The band at $\sim$1,151 cm^{-1} is often used as an "internal correction standard peak" [37, 39], to make the measurements independent of uncontrollable factors. The ratio of peak intensities at 1,047 and 1,151 cm^{-1}, which was assigned in literature [37], was used to monitor starch retrogradation.

The peak intensity ratios of samples around 1,060–1,070 cm^{-1} (A$_3$) and 1,151 cm^{-1} (A$_4$) can be seen in Tables 3 and 4. ANOVA results demonstrated that A3/A4 was dependent on oven type and storage time. Since increase in the ratio of peak intensities around 1,060−1,070 cm^{-1} (A$_3$) and 1,151 cm^{-1} (A$_4$) is related to starch retrogradation, A3/A4 of samples baked in microwave oven was found to be the highest among other heating modes (Tables 3, 4). Additionally, it was found that A3/A4 of samples increased as storage time increased (Tables 3, 4). FTIR analysis was not found to be as capable as the other methods [i.e. DSC, compression (hardness), X-ray], in demonstrating the effect of gum addition in decreasing starch retrogradation.

Conclusion

The retrogradation enthalpy values and FTIR outputs related to starch retrogradation of breads baked in combination oven were not found to be statistically different than that of conventionally baked ones, which means that it is possible to produce breads by combination heating with similar staling degrees as conventionally baked ones. Moreover, the hardness, setback viscosity and total mass crystallinity values of infrared-microwave combination baked bread samples were lower than those of microwave-baked ones, meaning that combination heating partially solved the rapid staling problem of microwave baking. X-ray analysis demonstrated that microwave heating resulted in appearence of an additional peak at 15.8°, indicating more crystalline structure. On the other hand, the number of peaks appearing in X-ray pattern of infrared-microwave combination baked samples was found to be similar to that of conventionally baked ones. The addition of xanthan-guar blend to the formulation retarded staling of breads.

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