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Prefermented frozen lean wheat doughs

Janne Räsänen

VTT Biotechnology and Food Research

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Valtion teknillinen tutkimuskeskus (VTT), Vuorimiehentie 5, PL 2000, 02044 VTT
puh. vaihde (09) 4561, faksi (09) 456 4374

Statens tekniska forskningscentral (VTT), Bergsmansvägen 5, PB 2000, 02044 VTT
tel. växel (09) 4561, fax (09) 456 4374

Technical Research Centre of Finland (VTT), Vuorimiehentie 5, P.O. Box 2000, FIN–02044 VTT, Finland
phone internat. + 358 9 4561, fax + 358 9 456 4374

VTT Bio- ja elintarviketekniikka, Elintarviketekniikka, Biologinkuja 1, PL 1500, 02044 VTT
puh. vaihde (09) 4561, faksi (09) 455 2103

VTT Bio- och livsmedelsforskning, Livsmedelsteknik, Biologgränden 1, PB 1500, 02044 VTT
tel. växel (09) 4561, fax (09) 455 2103

VTT Biotechnology and Food Research, Food Technology,
Biologinkuja 1. P.O. Box 1500, FIN–02044 VTT, Finland
phone internat. +358 9 4561, fax +358 9 455 2103

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ABSTRACT

The baking properties of prefermented frozen doughs were examined with frozen storage times up to 14 days at -20°C. Different types of flour, prefermentation times, water contents, and hydrocolloids were investigated. The factors used to explain the observed improvements were yeasted dough rheology, pore structure, and water state.

The deterioration in loaf properties was observed to fall into two categories: those due to freezing and subsequent thawing (freeze-thaw stability), and those occurring over longer frozen storages (frozen storage stability). Shorter prefermentation time (25 vs. 40 min) improved the freeze-thaw stability of frozen doughs and increased the loaf volumes on average by 20%. In the same way the baking properties became more independent of flour quality, and extra-strong flours were not needed to achieve loaf volumes similar to those of fresh baking. In the pore structure studies, shorter prefermentation time was observed to change the structure for more even. Smaller air bubbles with thicker cell walls were not so sensitive to ice crystal damage.

Shorter prefermentation time did not significantly improve the frozen storage stability of prefermented frozen doughs. The major decrease in loaf volumes during frozen storage occurred during the first week, after which there was little change. For the achievement of fresh-like loaf properties after 14 days frozen storage, lower water contents were needed (2 percentage units reduction from the fresh baking optimum). The role of water became clear in the analyses of water state in frozen doughs. The self-diffusion coefficient and the amount of liquid phase increased during frozen storage because of ice crystal growth, but the increase could be minimized by reducing the water content and adding hydrocolloids. Thus, the major deteriorations in prefermented frozen doughs are caused by ice crystals. When shorter prefermentation time was combined with reduced water content, yeasted dough rheology after frozen storage was similar to that of fresh dough.

PREFACE

Most of the present work was carried out at VTT Biotechnology and Food Research during the years 1994 - 1997. The academic year 1995 - 1996 I spent at the Department of Food Science, University of Nottingham, in England. Financial support was provided by the Finnish Food Research Foundation, and is gratefully acknowledged.

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Very special thanks go to my colleagues at VTT – Maarit Fabritius, Helena Härkönen, Taru Laurikainen, and Teija Parkkonen – and to Leena Pulkki for her skillful technical assistance. There are many others to thank: Professor Kaisa Poutanen for undertaking a critical reading of the manuscript, Marja Siitari-Kauppi and the staff at the Laboratory of Radiochemistry, University of Helsinki, for providing support and cooperation in the autoradiographic analyses of frozen doughs, and Ph.D. Imad Farhat, Samil Kök, Ph.D. Jenny Melvin, Ph.D. Wan Aida Wan Mustapha, and Ph.D. Malcolm Robertson for encouraging and assisting me during my studies at the University of Nottingham.

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Finally, I would like to express my warmest gratitude to my dear wife Sanna for her great patience and support during the several years it took to complete this work.

LIST OF PUBLICATIONS

This dissertation is based on the following original articles, referred to as Publications I - V.

I Räsänen, J., Härkönen, H. and Autio, K. 1995. Freeze-Thaw Stability of Prefermented Frozen Lean Wheat Doughs: The Effect of Flour Quality and Fermentation Time. Cereal Chemistry 72(6), pp. 637 - 642.

II Räsänen, J., Laurikainen, T. and Autio, K. 1997. Fermentation Stability and Pore Size Distribution of Frozen Prefermented Lean Wheat Doughs. Cereal Chemistry 74(1), pp. 56 - 62.

III Räsänen, J., Blanshard, J. M. V., Mitchell, J. R., Derbyshire, W. and Autio, K. 1998. Properties of Frozen Wheat Doughs at Subzero Temperatures. Journal of Cereal Science. In press.

IV Räsänen, J., Blanshard, J. M. V., Siitari-Kauppi, M. and Autio, K. 1997. Water Distribution in Frozen Lean Wheat Doughs. Cereal Chemistry 74(6), pp. 806 - 813.

V Räsänen, J. and Autio, K. 1998. Effect of Stabilisers and Water Content on the Rheological Properties of Prefermented Frozen Wheat Doughs. Gums and Stabilisers for Food Industry 9. London: Elsevier Applied Science Publishers. In press.

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1 INTRODUCTION

Baking has traditionally been a highly labor intensive business. This together with low product prices, and substantial equipment investments, especially in breadmaking, keep profit margins low. The low profitability of baking is further exacerbated by the necessity to operate during night hours (from 3 till 9 am) so that fresh products will be available when supermarkets open in the morning. Most customers nevertheless do their shopping after working hours, when bread has already staled for at least 12 hours. This kind of production also places considerable demands on transportation, as products should be moved to the retailer as soon as possible after production. If customers are to obtain fresh products and producers higher profits, baking times must be extended. A most interesting solution for this is frozen doughs, the use of which has increased enormously during the past two or three decades.

Figure 1 shows how average weekly sales per full-time employee equivalent for in-store bakeries have been rising in the United States since 1988 (Litwak and Maline 1993). This has occurred even though the nominal cost of labor has increased at the same time. Between 1991 and 1992, for example, weekly sales per in-store bakery unit increased by 7.4%, from $7,117 to $7,643. The in-store baking consists of 43% bake-off preparation,

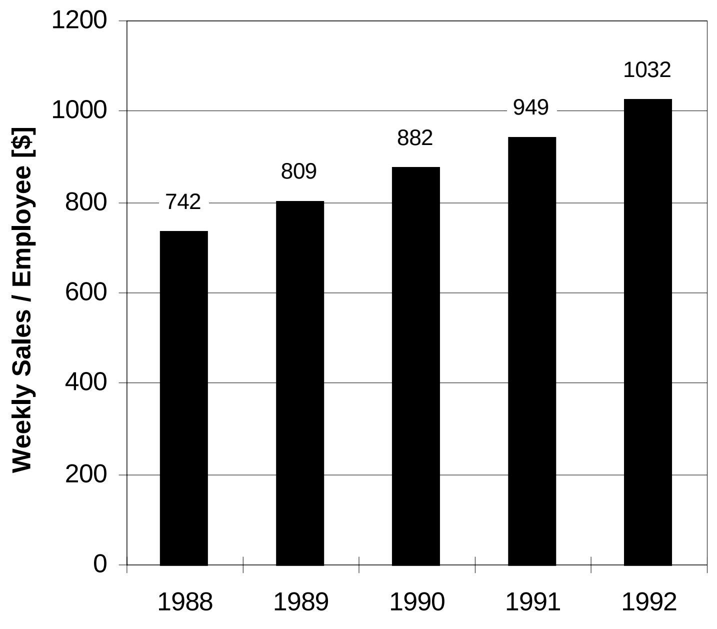

Figure 1. Weekly sales per in-store bakery employee (Liwak and Maline 1993).

37% combination of methods, and 20% scratch or mix baking (Krumrei 1992, Lee 1992). Bake-off refers to the process where refrigerated or frozen doughs are thawed, proofed, and baked in supermarkets (Best 1995).

In addition to bake-off, in-store bakeries also thaw and slightly reheat or sell as is, ready-to-eat fully baked products that they receive in refrigerated or frozen form, or they complete the baking of partially baked frozen products. The partially baked products are baked at the head bakery until the crumb has settled without crust formation, and the baking is completed at the in-store bakery by a quick heating to form an attractive brown crust. However, the completed partially baked products stale considerably faster than fresh baked ones.

In bake-off products, fermentation is retarded by lowering the temperature or decreasing the amount of yeast. As can be seen from the temperature dependence of yeast viability depicted in Figure 2, the optimal fermentation temperature lies between 25°C and 45°C. At lower temperatures the yeast viability is reduced; e.g. at 10°C the viability is only 75% of optimum. Refrigerated doughs are used after short storage times, for example overnight or over the weekend, supplying extra resources for the coming day. The economic benefits are considerably greater for frozen doughs (e.g. Best 1995).

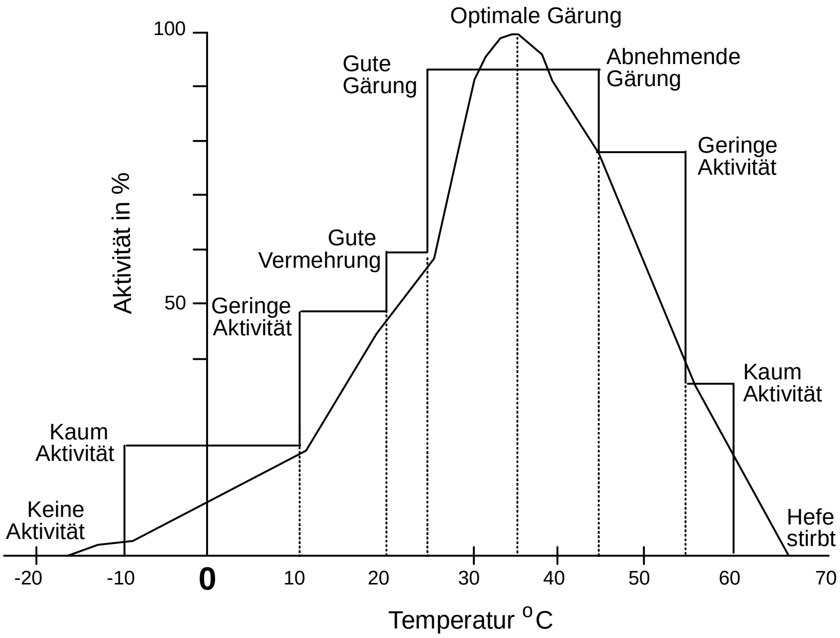

Figure 2. Temperature dependence of yeast viability (Heckelmann 1993).

1.1 FROZEN DOUGHS

1.1.1 Background

The use of frozen doughs has been of great interest since the 1960's and they are now widely used in industrial bakeries. However, loaf volumes are usually smaller and quality is poorer for breads baked from frozen doughs than in fresh baking. This is especially seen for doughs with low fat content. The advantages of frozen doughs are summarized in Table 1. Because of the many things recommending them, the use of frozen doughs is growing at a rapid pace. The need for research in this area is correspondingly great.

Table 1. Advantages of frozen doughs as a review from literature.

1. Fresh products are available around the clock
2. Production costs are lower
3. Use of equipment in more cost-effective
   (in best cases 24 h per day)
4. Labour costs are reduced:
   a) in bakeries (fewer night hours)
   b) in store bakeries (no need for skilled bakers)
5. Transportation is facilitated (once a week delivery)

Frozen doughs are of two different types depending on when fermentation takes place: doughs that are fermented after freezing, called *nonfermented frozen doughs*, and doughs that are fermented before freezing, called *prefermented frozen doughs*. For the most part it is the nonfermented frozen doughs that are used in industrial baking.

1.1.2 Nonfermented frozen doughs

Nonfermented frozen doughs are frozen immediately after mixing and scaling, and the time for yeast activation before freezing is preferably set at minimum. Thus, there is a great need for gas production, in other words for yeast viability, after frozen storage. Two fundamental problems encountered in the commercial development of frozen dough technology are the following:

1) freezing affects the ability of the **gluten network** to retain gases and

2) freezing affects the viability of **yeast** and its subsequent gassing power.

Many hypotheses have been presented as to why these changes occur. The deterioration of the gluten network has been attributed to the ice crystals formed in freezing, which cause physical breakage of the gluten, weakening hydrophobic bonding, and redistributing the water in the gluten structure (Varriano-Marston et al. 1980, Wolt and D'Appolonia 1984b, Berglund et al. 1991, Inoue and Bushuk 1991, Autio and Sinda 1992). The water redistribution also increases inhomogeneity in thawed doughs and the drying of some components. Changes in the gluten network of frozen dough are also suggested to result from the effect of reducing substances (e.g. glutathione) leached out from yeast cells, which by chemical reduction weaken gluten disulfide groups (Kline and Sugihara 1968, Hsu et al. 1979). There is no general agreement regarding these hypotheses for the loss of gas retention power; do these factors work together or is one more important than the other one.

The loss of yeast viability could be caused by ice crystals that physically puncture the outer membrane of the yeast cells, or by the accumulation of metabolic products resulting in the autolysis of the cells (Kline and Sugihara 1968, Hsu et al. 1979).

Hosomi et al. (1992) suggest three different ways to solve the above-mentioned problems with frozen doughs:

1) find a new yeast strain or improve old ones to make them more resistant to freezing
2) use prefermented doughs
3) find suitable additives and ingredients for frozen doughs.

The research on frozen doughs has been concentrated on new yeast strains and additives. These are discussed in more detail in Section 1.1.4 *Baking properties of frozen doughs*. However, the use of prefermentation before freezing decreases the need for yeast viability after frozen storage.

1.1.3 Prefermented frozen doughs

Prefermented frozen doughs are frozen after fermentation and prefermentation may be the best solution for the problem of decreased yeast viability after frozen storage, since the need for the dough to be fermented after thawing is then reduced. In this way, processing after frozen storage is also less time-consuming. This is shown in Table 2, in which various frozen dough processes are compared. Prefermentation reduces the time required for processing after frozen storage from 120 min to 75 min (Table 2). In fact, prefermented frozen doughs can be processed directly in a programmed oven (Brümmer and Neumann 1993), so that only baking is required after frozen storage (Table 2). On the other hand, the gluten network of prefermented doughs, especially at the air-cell interface, is under extension and highly sensitive to damage from ice crystals. Thus, the baking properties of prefermented frozen doughs are not so good as those of nonfermented frozen doughs. Table 3 summarizes the advantages of prefermented frozen doughs over nonfermented ones.

Table 2. Time saving obtained with prefermented frozen doughs (Brümmer et al. 1993).

	Nonfermented Doughs	Prefermented Doughs	Prefermented + Programmed Oven
Prefermentation, min	0	30	30
Thawing (~20°C), min	60[a]	30	0
Proofing (32°C 65% RH), min	60[a]	45	0
Total time after freezing, min	120[a]	75	0

[a] the time needed is longer if thawing is at +4°C

Table 3. Advantages of prefermented frozen doughs over nonfermented according to variety sources.

1. Reduced need for yeast viability after frozen storage
2. Less time-consuming production after freezing
3. Improved heat transfer:
   a) more economical freezing and thawing
   b) faster production
4. Cheaper bake-off stations (no proofing ovens)

1.1.4 Baking properties of frozen doughs

Figure 3 describes the general effect of frozen storage on loaf volumes of breads baked from frozen doughs (Brümmer et al. 1993). As can be seen, the greatest decrease in baking quality occurs during the first day of storage at -20°C, in other words during freezing and subsequent thawing. The loaf volumes decrease from 730 ml to 670 ml with nonfermented frozen doughs and to 560 ml with prefermented frozen doughs. This property is later referred to as *freeze-thaw stability.*

It has been generally found (e.g. Brümmer et al. 1993) another dramatic decrease in loaf volumes to occur during the first week of storage -20°C

(Fig. 3). After this the deterioration in loaf volumes occurs with an obviously slower rate. The trend was the same for nonfermented and prefermented frozen doughs. After seven days storage, the volumes were, respectively, 15% and 30% smaller than those of fresh baked breads. The changes in baking properties during longer frozen storage times are referred to below as *frozen storage stability*. Attempts have been made to improve the baking stability by using new yeast strains and additives and there are some generally accepted recommendations for frozen doughs, which are discussed below.

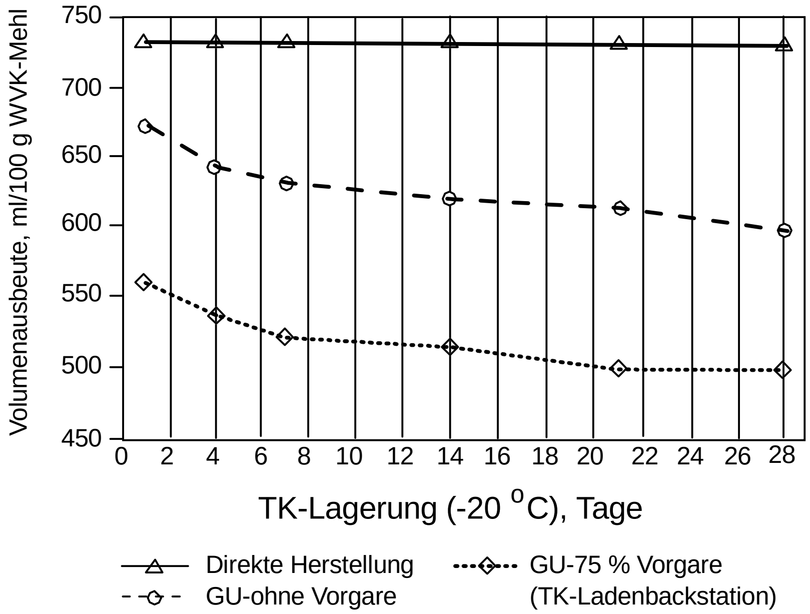

Figure 3. Decrease of loaf volumes of breads baked after frozen storage at -20°C. The top line is the control values for fresh baking, the middle values are for nonfermented frozen doughs, and the bottom ones are for prefermented frozen doughs (75% of optimal fermentation time for fresh baking). Prefermented doughs were thawed and baked in a programmed oven (from Brümmer et al. 1993).

Flour

High-protein flours from hard wheat varieties are normally recommended for frozen doughs because they ensure dough strength for gas retention during thawing and final proof. Thus, the protein content should be 12 - 14% (on water-free basis) (Marston 1978, Sideleau 1987) or even greater. Benjamin et al. (1985) suggest a protein content of at least 16%. Flours with lower protein content need to be strengthened with vital wheat gluten when used for frozen baking (Wang and Ponte 1994). However, there has been no evidence of a direct correlation between baking properties and the absolute value of protein content. The protein quality is as important as the protein content (Kulp 1995).

Other recommendations for flours used in frozen doughs are an oxidation level higher than in fresh baking, since reducing agents (glutathione) leach out from yeast cells and weaken the gluten structure (disulfide bridges), or ice crystals damage the gluten structure. A low level of starch damage and low proteolytic activity are also recommended (Marston 1978).

Water absorption

Lower water absorption levels than normally used for fresh baking are desirable for nonfermented frozen doughs, since low levels limit the amount of water not absorbed by the system (Lorenz and Kulp 1995, Brack and Hanneforth 1995). In the publications this is referred as the amount of “free” water. A large amount of “free” water is damaging to the dough and yeast during freezing and thawing cycles (Javes 1971, Sideleau 1987). Actual water absorption depends on the variety of product desired, the formulation, and the machining requirements (Sideleu 1987). Chilled water is used to reduce the dough temperature (20°C) to slow yeast activation and accelerate freezing (Javes 1971). For prefermented frozen doughs, in contrast, higher absorption levels than in fresh baking have been recommended (Hanneforth et al. 1994).

Yeast

Higher levels of yeast (5 - 6% on flour basis) are normally used in nonfermented frozen doughs to compensate for losses in yeast viability during extended storage (Meritt 1960, Drake 1970, Javes 1971, Lorenz 1974, Marston 1978). Yeast is essential for proper gas production for dough leavening, and to give good loaf volumes and crumb quality. Not surprisingly, yeast is the most studied of all ingredients in frozen doughs (Bruinsma and Giesenschlag 1984).

The retention of sufficient yeast viability and gassing power during frozen storage is described as the major problem in nonfermented frozen doughs, and only minor improvements in quality can be achieved through changes in formulation and ingredients, change in type of yeast, addition of dough conditioners, decrease in absorption, addition of oxidizing agents, or reworking of the dough after thawing (Lorenz and Bechtel 1964, 1965, Davis 1981, Bruinsma and Giesenschlag 1984). Yeast for frozen doughs should be osmotolerant and have high heat-resistance (Casey and Foy 1995). However, these characteristics are polygenic and unlinked, and thus result from more than one genetic spread over several chromosomes. This, together with the low price of traditional baking yeast, recommends the use of the traditional yeast, *Saccharomyches,* in frozen baking (Casey and Foy 1995).

Three different types of yeast are available for frozen baking: compressed yeast, instant dry yeast, and active dry yeast. Compressed yeast is widely used for products to be stored two to four weeks (Casey and Foy 1995). The drying of yeast is now generally accepted to affect the structure and functional integrity of the cytoplasmic membrane in a manner that increases the sensitivity of yeasts to freezing (Kline and Sugihara 1968, Javes 1971, Bruinsma and Giesenschlag 1984, Wolt and D'Appolonia 1984b). Because active dry yeast must be prehydrated in 43 - 46°C water for 5 - 15 min, and this produces fermentation compounds before freezing, active dry yeast also has a lowered ability to resist freezing.

Nonfermented frozen doughs are generally prepared at temperatures lower than used for fresh baking (i.e. 20 vs. 24°C, Casey and Foy 1995). In this way the yeast activation before freezing is minimized. Dough temperatures below 20°C diminish frozen dough performance by not allowing for sufficient conditioning of gluten in mixing (Casey and Foy 1995). During prefermentation, metabolic by-products are formed, which are believed to make yeast cells less cryoresistant, resulting in increased yeast cell death upon freezing (Hsu et al. 1979). Thus, the factor considered to be the most important in frozen stability of nonfermented frozen doughs is the inverse relationship between the time of active fermentation before freezing and the yeast stability in frozen doughs (Meritt 1960, Kline and Sugihara 1968, Tanaka et al. 1976, Hsu et al. 1979, Hino et al. 1987, 1990, Holmes and Hoseney 1987).

Shortening

It is well known that shortening in the formulation improves dough processing and crumb properties of breads (De Stefanis 1995). According to De Stefanis at least 1% of shortening is required for nonfermented frozen doughs, with maximum benefits at 2% (on flour basis). Lorenz and Kulp (1995), on the other hand, recommend 4 - 5% for fine grain quality in frozen doughs. The recent study of Brooker (1996) also notes the effect of fat crystals (solid shortening) on stabilizing the air bubble structure in fresh fermented doughs. Unsaturated triglycerides (oils) have no positive effects on baking properties, however (De Stefanis 1995, Brooker 1996).

Surfactants

Surfactants are categorized into two general classes: dough strengtheners (e.g. mono- or diglycerides, sodium or calcium strearoyl lactylate) and crumb softeners (e.g. monoglycerides, De Stefanis 1995). Dough strengtheners interact with the gluten proteins, improving the frozen stability of the doughs. Sodium stearoyl lactylate (SSL) and diacetyl tartaric acid esters of monoglycerides (DATEM), in particular, have proved to be valuable for extended frozen storage stability, producing breads with greater loaf volumes because of better oven rise (De Stefanis et al. 1977, Marston 1978, Varriano-Marston et al. 1980, Davis 1981, Dubois and Blockcolsky 1986, Hosomi et al. 1992).

Sweeteners

Sugar levels (saccharose) in frozen doughs depend on the type of product and crust characteristics required, but they need to be slightly higher than in fresh baking (Heid 1968, Dubois and Dreese 1984). Levels of 8 - 10% are recommended because of the hygroscopic properties of sugar, which decreases the amount of water not absorbed in dough and reduces yeast damages (Bruinsma and Giesenschlag 1984). Sucrose has been used in most studies of frozen doughs. As reported by Dubois and Dreese (1984), however, the type of sweetener (sugars, syrups etc.) can also have an effect on the survival of yeast after frozen storage.

Oxidants

Oxidants have been shown to be a key ingredient together with yeast for producing good quality, nonfermented frozen doughs (De Stefanis 1995). Oxidants are used in frozen doughs because the damaged yeast cells leach out reducing substances (glutathione) and, thus, weaken the disulfide bridges that stabilize the gluten network (Kline and Sugihara 1968, Hsu et al. 1979). Potassium bromate has been found particularly effective in improving the stability of frozen doughs (Lorenz and Bechtel 1965). In many countries, however, the use of potassium bromate is either limited or prohibited by law. Various other oxidants are used instead, most notably potassium iodate, azodicarbonamide, and ascorbic acid (De Stefanis 1995). A satisfactory substitute has not yet been found, however, for the slow-acting potassium bromate.

Other ingredients

Other ingredients have also been studied in frozen doughs (enzymes etc.). However, there is no generally accepted recommendations on them as in the above mentioned cases.

1.2 AIMS OF THE STUDY

The aims of the present study were to improve the baking properties of prefermented frozen doughs and to determine the reasons for the structural collapse occurring during thawing. The changes in the state of water and the role of dough porosity were of particular interest.

The study was based on the master's thesis ”Rheological and structural changes in frozen wheat flour doughs” (Räsänen 1994), in which the generally recognized facts on prefermented doughs were observed (Fig. 4). Figure 4 presents the poor baking properties of prefermented doughs, which were a little improved when a dough strengthener was used (S-kimo from Puratos, Belgium).

In this thesis the first aim was to improve the baking behavior of prefermented frozen doughs according to flour quality and process parameters. In the beginning the frozen storage time at -20°C was selected to be short enough (for one day) to observe the most critical changes. However, in the latter studies the frozen storage time was lengthened up to 14 days. The reasons for the observed baking results were studied in dough rheology (non-yeasted as well as yeasted doughs), microstructure, and water state. Finally the dough recipe was improved according to all studies and tested with a frozen storage time up to 14 days.

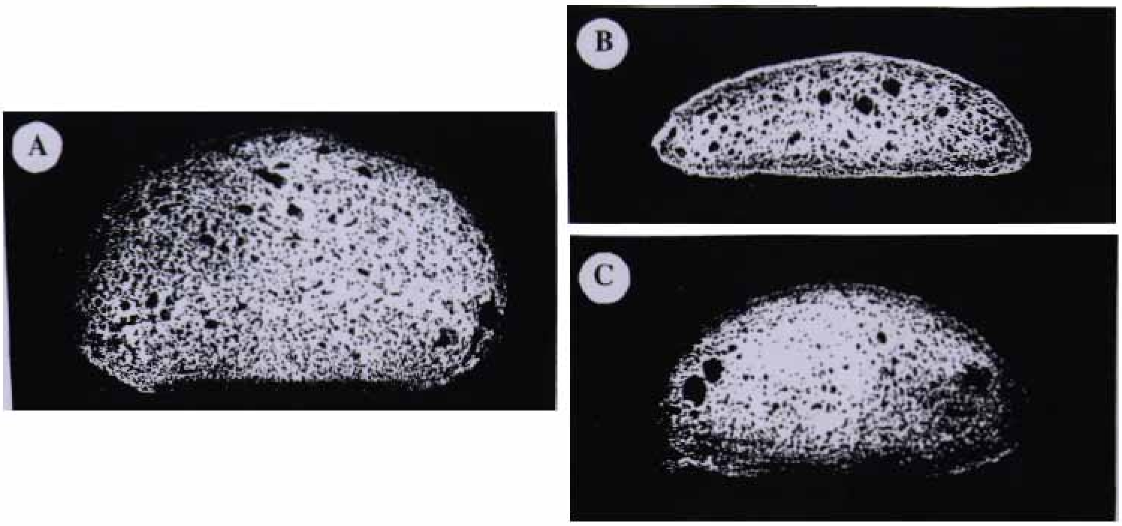

Figure 4. Baking properties of prefermented frozen doughs after one week frozen storage at -20℃. (A) fresh reference, (B) bread baked from frozen dough, and (C) case B with a dough strengthener (S-kimo from Puratos, Belgium) (Räsänen 1994).

2 MATERIALS AND METHODS

2.1 RAW MATERIALS AND PROCESS CONDITIONS

2.1.1 Flour samples

Effect of flour quality on the properties of prefermented frozen doughs was reported in publications I - IV. In general, six different flours were used, although the further studies concentrated on four of them (Publications III - IV). After Publication I the flour samples had to be changed for a new set of flours due to the fact that the distributor could not provide more of those flours. Tables 4 and 5 summarize the characteristics of the flours. Flour numbering 1 - 6, based on Publication II, was used through out the thesis for clarity, although the numbering changed in Publications III and IV (Table 5).

The flours were milled from pure wheat cultivars by Bühler MLU-202, Switzerland, with an average 60% flour yield. Determinations were made of moisture, protein content (N x 5.7), falling number, wet gluten content, farinograph absorption at 500 BU (AACC 1995), and extensibility and resistance to extension in an extensigraph (AACC 1995). All the analyses were carried out in duplicate and the results were calculated on a dry matter basis.

Table 4. Results of flour analysis for the six flours used in the first study (I).

Quality Tests	Flour A	Flour B	Flour C	Flour D	Flour E	Flour F
Protein content (N x 5.7), %	11.35	12.74	17.29	11.67	12.43	14.10
Ash content, %	0.54	0.58	0.54	0.49	0.49	0.47
Falling number value	222	304	508	317	236	316
Wet gluten, % (a)	28.4	27.2	40.7	33.8	30.7	44.2
Water soluble index, % (b)	5.15	5.64	4.64	4.63	4.67	4.79
b / a	0.18	0.21	0.11	0.14	0.15	0.11
Farinograph						
Absorption, %	50.0	58.8	62.5	53.5	54.0	56.0
Dough development time, min	2.0	2.5	12.0	2.3	3.0	2.5
Stability, min	6.0	16.5	12.0	9.0	12.5	18.8

Table 5. Characteristics of the six flours studied in Publications II - IV.

Quality Tests	Flour 1	Flour 2	Flour 3	Flour 4	Flour 5	Flour 6
Protein content (N x 5.7), %	12.93	12.55	11.43	12.93	17.89	10.84
Ash content, %	0.51	0.51	0.48	0.45	0.56	0.54
Falling number value	470	525	315	395	290	407
Wet gluten, % (a)	29.9	27.2	26.8	29.8	40.5	27.5
Water soluble index, % (b)	4.15	3.63	3.79	3.53	4.22	4.54
b / a	0.14	0.13	0.14	0.12	0.10	0.17
Farinograph						
Absorption, %	58.7	55.4	54.0	55.5	62.8	59.0
Dough development time, min	10.3	7.0	2.2	2.3	17.4	2.3
Stability, min	17.7	18.3	9.8	4.5	16.5	4.0
Extensograph (45 min)						
Maximum resistance, BU	810	695	770	815	915	390
Extensibility, mm	157	153	146	142	191	127
Publications III - IV	Flour 1		Flour 2	Flour 3	Flour 4	

The amount of water solubles was determined according to Izidorczyk et al. (1991) by adding 15 ml 30°C distilled water to 5 g flour. After 3 min shaking and centrifuging the supernatant was evaporated and the water soluble index (WSI) was calculated.

2.1.2 Recipe and other raw materials

Dough formulation was 100% flour, 4% yeast (compressed baker's yeast, *Saccharomyces cerevisiae*, from Finnish Yeast Ltd.), 2% sugar, 1.5% salt (NaCl), 4% shortening (Sunnuntai, Raisio Group, Finland), and 4% S-kimo (dough strengthener from Puratos, Belgium). Two different water contents were studied: normal, to achieve optimal farinograph consistency of 500 BU, and normal minus 2 percentage units. Figure 5 shows the scheme of the steps used in processing and analyzing the doughs and baked breads.

Hydrocolloids (soluble dietary fibers) were investigated in the study reported in publication V with the aim of improving water distribution and the frozen storage stability of prefermented frozen doughs. The use of six different hydrocolloids was studied. Table 6 describes the manufacturers and main components of these hydrocolloids. Additions were made at two different levels: 0.5% and 1.5% on a flour basis. In all cases the optimal water absorption was determined for different additive levels with a farinograph (Table 6). Hydrocolloids were hydrated in part of the water to form a uniform gel, and mixed with the dry ingredients. After this, the yeast was suspended in the rest of the water and added into the dough.

The effect of hydrocolloids was analyzed at water levels that were reduced by 2 and by 4 percentage units from normal. All the analyses were performed after 14 days frozen storage at -20°C, and all were performed at least twice (Publication V).

Table 6. Hydrocolloids and water absorption ability on flour basis.

Hydrocolloid, Manufacturer (Main Component)	Amount [%]	Optimal Absorption [%]
A Stabilizer XC-8444, TIC GUMS	0	56.5
(Blend, standardized with dextrin)	0.5	59.0
	1.5	63.5
B Colloid 1023 T, TIC GUMS	0.5	62.5
(Blend)	1.5	66.0
C Cekol 700 P, Metsä-Serla	0.5	61.0
(CMC)	1.5	67.5
D Cekol 30000 P, Metsä-Serla	0.5	64.5
(CMC)	1.5	71.0
E Alginate FD 155, Danisco Ingred.	0.5	61.0
(Sodium alginate)	1.5	67.5

2.1.3 Process conditions

Figure 5 summarizes the steps used in processing and analyzing the doughs and baked breads. Yeast was added as a suspension in 37°C water. The mixing was done with a blade mixer (Original Diosna) or a fork mixer (John Holmström) to the optimum mixing time determined with a farinograph. Small amounts of dough (15 or 30 g flour) were mixed in a 50-g bowl with a minorpin mixer (Henry Simon Ltd., UK) or a mixograph (National MFG Co., USA) to obtain optimal dough development. Small amounts of dough were used in fundamental rheological tests, ultracentrifugation, and NMR experiments. To minimize the differences that arise from mixing, the same dough was used for fresh breads and prefermented frozen doughs (large doughs).

After 20 min floor time at 28°C the dough was divided into pieces of 150 g, which were molded into rolls with an extensigraph. The final proofing was carried out at 34°C and 80% RH, for either 40 min or 25 min. The dough pieces were frozen with a blast freezer (-30°C and 1.5 m/s) to a final core temperature of -20°C. Frozen samples were stored in a chest freezer at -20°C ± 2°C. The frozen storage condition was chosen according the freezer capasity available in the bakeries. In major cases -20°C has also been used as storage temperature in the scientific papers on frozen doughs. This can be explained by the fact that the amount of ice at -20°C is not critical for thawing and subsequent ice crystal growth (Fig. 6).

After frozen storage the doughs were thawed in a fermentation cabinet at 34°C and 80% RH and then baked at 200°C for 25 min (internal temperature at 10 min over 98°C). Thawing time was 1 hour, and postfermentation time 0.5 hour for doughs with normal water content and 1 hour for doughs with reduced water content. After 2 hour cooling the bread loaf volumes (determined by rape seed displacement), weight, and form ratio (maximum height / width) were measured. The specific volume was calculated by dividing volume by weight. The baking tests were performed at least twice for all flours.

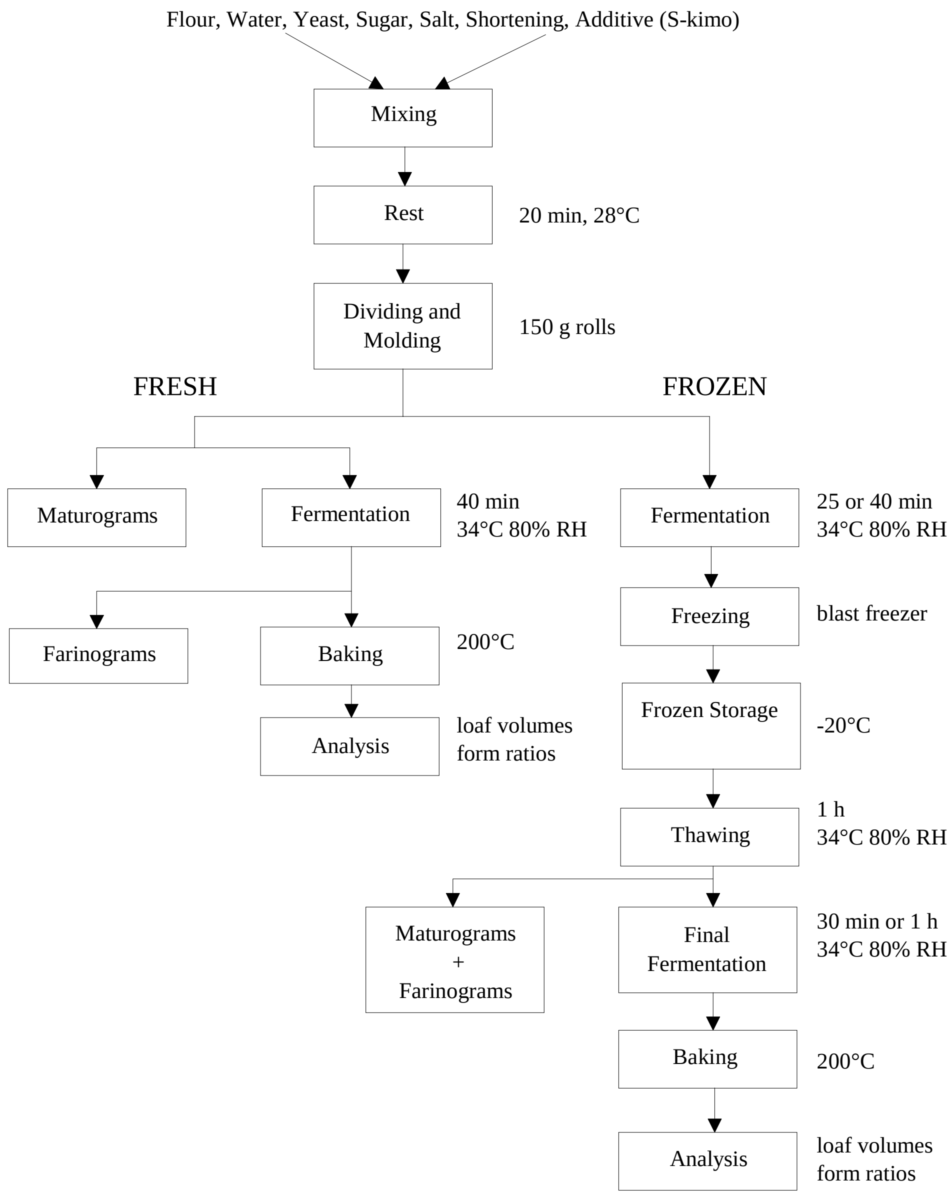

Figure 5. Scheme for processing and analyzing of fresh and prefermented frozen doughs.

Figure 6. Amount of ice fraction (%) in dough on total water content as a function of temperature (Lind 1988).

2.2 RHEOLOGICAL MEASUREMENTS

2.2.1 Empirical methods

Empirical methods – farinograph mixing and maturograph fermentation— simulate parts of the baking process. Figure 5 shows where these methods were applied in the general scheme of the study. In order to improve the comparability of the results of empirical and baking tests identical sample sizes and dough contents were used in the experiments. The empirical rheology of frozen dough was reported in Publication II (effect of water content and flour quality) and in Publication V (effect of hydrocolloids).

Farinograph experiments

The mixing tolerance of fermented doughs was analyzed with a Brabender farinograph. The sample weight was 400 g before fermentation, which is smaller than the amount normally used in measuring water absorption (300 g flour + ~ 60% water on flour basis). Figure 7 presents an example of a farinogram for fermented dough. The lowest point occurs after 1.5 min mixing, after which the dough becomes stronger because of water redistribution and the formation of new bonds. The lowest point was used to analyze the rheological properties of samples which had been thawed for one hour at 34°C and 80% RH before measurement. This point was chosen because of the high correlation with the results of baking tests (Voivala 1998).

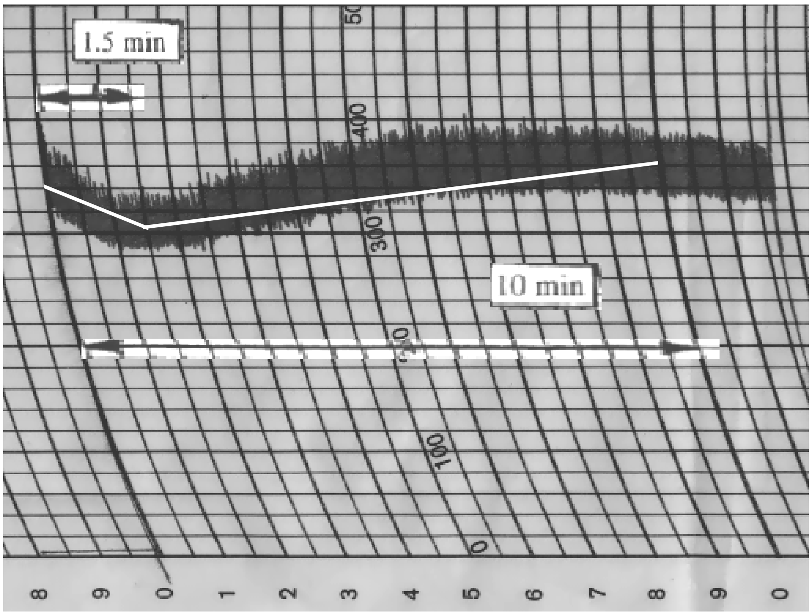

Figure 7. An example of a farinogram for fermented dough.

Maturograph experiments

The maturograph measurements were carried out according to Seibel and Crommentuyn (1963a,b) and Mettler (1990). The maturograph is designed to analyze the fermentation properties of dough in a two-step process, which is repeated until the peak of the curve is observed (Fig. 8). In the first step the dough is expanding and the plunger, which is in contact with the dough, is moving upwards. After 2 min expansion the plunger is forced down. The dough level (height of the highest peak), elasticity (effect of weight constraint in the peak), and final proof time (time required to reach the highest peak) are established according to Figure 8.

Temperature and humidity in the maturograph were adjusted to 34°C and 80% RH, which were the proofing conditions during baking. The fresh control doughs (150 g pieces) were measured immediately after flooring and molding, whereas the prefermented frozen doughs were measured after one hour thawing at 34°C, 80% RH. The doughs were thawed in the measuring pan, because partly or totally thawed doughs could not be transferred to the pan without causing the dough structure to collapse. All measurements were carried out two to four times.

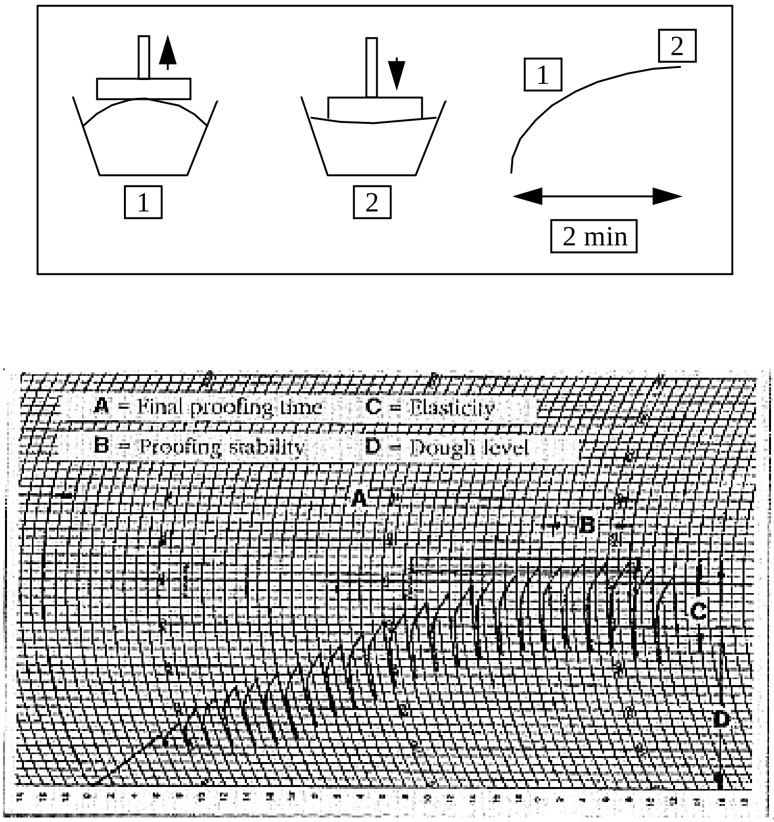

Figure 8. Maturograph principle and a sample curve.

2.2.2 Fundamental methods

Fundamental rheological properties were studied in both water-flour doughs and yeasted doughs. Effect of the raw materials on rheology was investigated for fresh dough (Publication IV). All conditions used in the baking tests were monitored in yeasted dough rheology with frozen storage times up to 14 days: prefermentation time (Publications I, IV, and V), water content (Publications IV and V), and a dough strengthener, S-kimo (Publications IV and V).

In Publication I, the rheological parameters of the yeasted frozen doughs after thawing were measured with a Bohlin rheometer (VOR, Sweden). The rheometer was equipped with a parallel plate system with a constant gab, and thus the expansion of the dough had to be minimized by reducing the measuring time to 10 s. In Publications IV and V the fundamental rheological parameters of yeasted doughs were measured with a StressTech rheometer (ReoLogica Instruments AB, Sweden). The StressTech includes a gas cylinder, which allows change in the gap and monitoring of the normal force during viscoelastic measurements. Measuring conditions were as described below.

Principle of dynamic oscillation measurements

In dynamic oscillation measurements the potential energy and the energy dissipated as heat are measured separately as storage modulus (G') and loss modulus (G''). Measurement is based on a sinusoidal strain ($\gamma = \gamma_0 \sin\omega\, t$) that is applied to the sample. The material responds to the strain with a sinusoidal stress ($\sigma = \sigma_0 \sin\omega\, t$), which is dependent on the properties of the sample (ω = angular frequency, σ_0 = shear stress, γ_0 = shear strain). The phase angel (δ) gives information on the phase shift, and thus on the ratio of the viscous to elastic properties in the sinusoidal deformation (e.g. mentioned Levine and Slade 1990):

$$\tan\delta = \frac{G''}{G'} = \frac{\sigma_0/\gamma_0 \sin\delta}{\sigma_0/\gamma_0 \cos\delta}$$

For an elastic solid the resulting stress is in phase with the strain, and all absorbed energy is transferred as potential energy (δ = 0), but for a viscous liquid the stress is 90° ahead of the strain (Figure 9). A viscoelastic material exhibits a stress between these two extremes. The viscoelastic measurement is done in "the linear region", or in other words the modulus is not dependent on the strain. The measurement can be performed at either constant strain or constant stress.

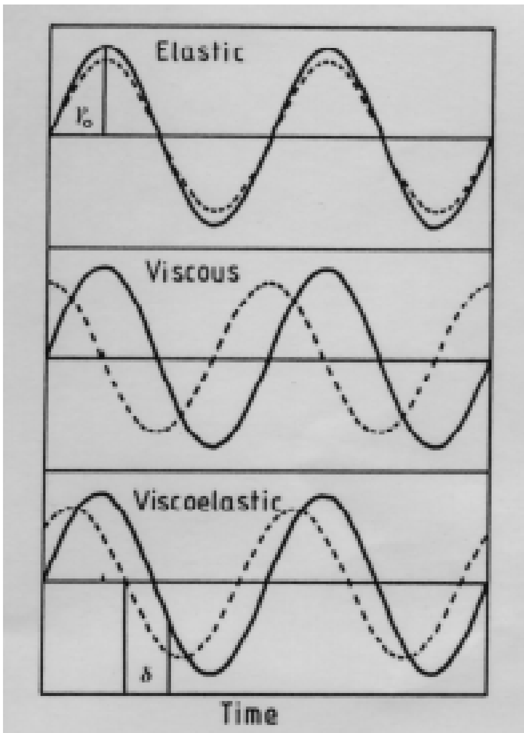

Figure 9. The applied sinusoidal oscillatory shear strain (solid curve) and the dynamic responses for elastic, viscous, and viscoelastic shear stress (dashed lines).

Bohlin rheometer (VOR)

Samples (1.5 g) weighed from doughs thawed 30 min at room temperature were slowly compressed with the upper plate until the gap between the plates (diameter 25 mm) was 1.5 mm. To prevent the samples from drying, an O-ring was used on the lower plate together with silicon oil on the sides of dough pieces. The measurements were carried out at 25°C in a high temperature cell, where the strain was 0.6 x 10^{-3} and frequency 1 Hz. Each measurement took 10 s. The average storage modulus (G') of at least four measurements is reported.

StressTech rheometer

The frozen doughs were thawed for ½ hour at room temperature before samples were taken. Circular samples, diameter 20 mm and thickness 2.0 mm (non-yeasted dough) or 3.0 mm (yeasted dough), were prepared from dough sheets and measured with a parallel plate system. The samples were compressed with the upper plate, the normal force being less than 2.0 N during compression. Before the measurements, which took 80 s, the normal force was 1.0 N or less. Drying of the samples during the measurements, was prevented by applying silicon oil. The measurements were made at 25°C and with a constant stress of 10.0 Pa (corresponds to a strain ~ 1.5 x 10^{-3}). Non-yeasted doughs were measured with constant gap, but an autotension, limit of normal force 0.1 N was used with yeasted doughs. Thus, for yeasted doughs not only was the storage modulus (G') but the change in the gap during the measurement was measured. The tests were carried out at least four times from separate samples.

2.3 WATER DISTRIBUTION

Freezing and frozen storage have a marked effect on water distribution, because of the formation and growth of ice crystals. In this study the changes in water distribution were analyzed by two different methods, ultracentrifugation and ^1H NMR spectroscopy (Publications III and IV).

2.3.1 Ultracentrifugation studies

Ultracentrifugation followed the procedure of Larsson and Eliasson (1996a). However, the amount of liquid phase was increased by using a larger sample (≈20 g). Thawed dough samples were placed in closable test tubes (diameter 25 mm and height 89 mm), and were centrifuged for 1 hour at 100 000 x g in a Beckman L8-55M ultracentrifuge (USA). The amount of liquid phase was determined as percentage weight change after one, seven, and 14 days frozen storage for normal and reduced water content. The results were compared with the values for fresh doughs. The experiments were repeated twice for all conditions using replicate samples.

2.3.2 ^{1}H NMR studies

Relaxation times

The ^{1}H NMR T_2 relaxation behavior of the dough (water-flour mixtures) was studied at different water contents (normal and reduced) over the temperature range -45 to 0°C after one and 14 days frozen storage. The experiments were made with a Maran NMR spectrometer (Resonance Instruments, UK) running at 20 MHz (^{1}H) and equipped with a temperature control unit. The sample temperature was manipulated by changing the temperature of the nitrogen gas flow around the sample tube. The magnet temperature was held constant at 30°C.

The samples were analyzed by a free induction decay (FID) and by a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. The conditions were: 90° pulses of 2.8 - 2.9 μs, a dwell time of 1 μs, a delay of 100 μs between the 90° and 180° pulses and a recycle delay of 2 seconds. The experiments involved heating the sample from -45 to 0°C (hereafter called Heating) and cooling it from 0 to -45°C (hereafter Cooling) in 5°C steps. The samples were allowed to equilibrate for 25 min before measurements were made.

The amount of ice in the dough was calculated at -10 and -40°C on the basis of the change in the liquid amplitude ratio from 0°C. The data of decay times and amplitude ratios were plotted as a function of temperature, and used to derive the ice melting and glass transitions of dough in the Publication III.

Self-diffusion

The self-diffusion of water in water-flour doughs was analyzed at +40°C three water contents (optimal, +3, and -3 percentage units) after frozen storage times at -20°C up to 19 days. NMR spin-echo techniques have long been established as a valuable method for measuring the apparent self-diffusion coefficient D of mobile spins in a static magnetic field gradient. Variants of the spin echo techniques have been developed using a pulse field gradient. The Minispec NMS 120 NMR Analyzer (Brucker, Germany) with an operating frequency of 20 MHz (^{1}H) was used with pulsed field gradient spin-echo (PFGSE) as defined by Tanner and Stejskal (1968). The conditions were: 100 μs duration of magnetic field gradient, delay of 4 ms between the 90° and 180° pulses, and recycle delay of 2 seconds. The gradient amplitude was set at 5 (Bruker arbitrary units). The operation temperature was +40°C. Measurements were begun with frozen sample, and the stabilized values were recorded. The experiments were repeated twice under all conditions and the self-diffusion coefficient D was compared with D_0, the self-diffusion coefficient of water.

3 RESULTS AND DISCUSSION

As was discussed in the Introduction, the decline in the baking quality of frozen doughs trends to be most marked during freezing and subsequent thawing. These changes are discussed below under the concept *freeze-thaw stability* in Section 3.1.1. Another dramatic decrease is usually observed during the first week of storage, after which the baking quality decreased at obviously slower rate. These changes in baking properties during storage are discussed under the concept *frozen storage stability* in Section 3.1.2 and the phenomena behind the improvements obtained in baking properties are analyzed in Sections 3.2 - 3.6.

3.1 BAKING PROPERTIES OF FROZEN DOUGHS

3.1.1 Freeze-thaw stability

Effect of prefermentation time on breads baked from prefermented frozen doughs is discussed in Publication I. Figures 10 and 11 present the results for loaf volumes and form ratios, respectively. The optimal fermentation time for fresh baking was 40 min, and 25 min was chosen as an example of interrupted fermentation (i.e. shorter prefermentation time, also referred to as partly fermented). According to a paper by Hanneforth et al. (1994) published simultaneously with our studies, the fermentation time for partly fermented frozen doughs should be one-half or two-thirds of the optimal time for fresh baking.

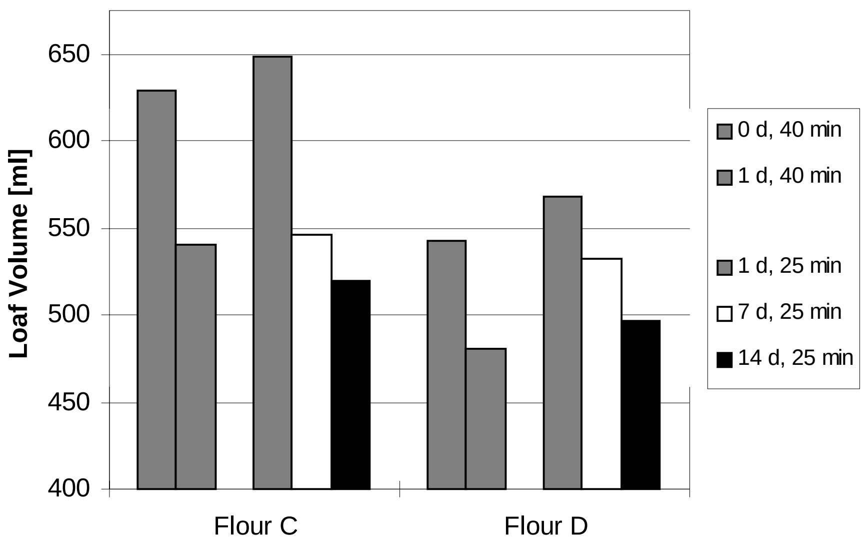

Figure 10. Effect of prefermentation time (40 and 25 min) on loaf volumes during frozen storage up to 14 days at -20℃.

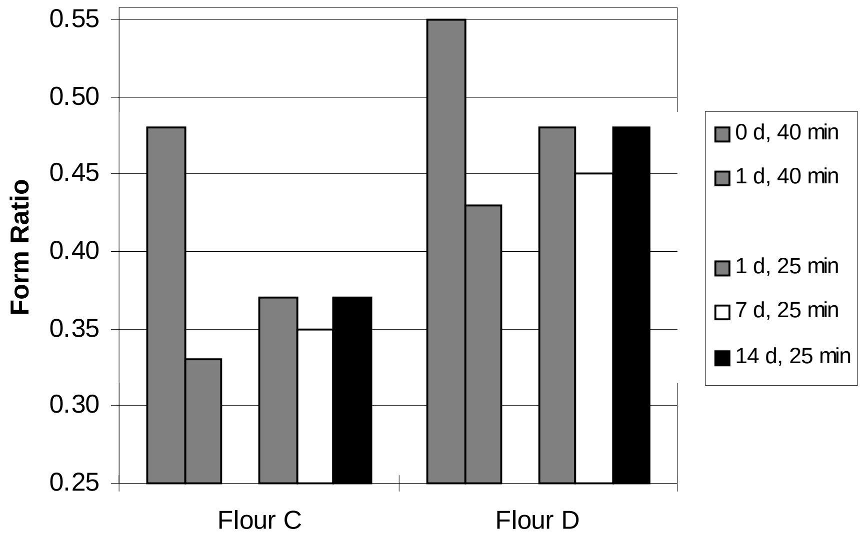

Figure 11. Effect of prefermentation time (40 and 25 min) on form ratios during frozen storage up to 14 days at -20°C.

The prefermentation time had a dramatic effect on the freeze-thaw stability of doughs: the shorter fermentation resulted in larger loaf volumes and better form ratios (Figs. 10 and 11). The loaf volumes of breads baked from prefermented frozen doughs after one day frozen storage improved on average by 20% when the prefermentation time was decreased from 40 min to 25 min. This improvement was almost independent of the flour quality (Fig. 10). Also the loaf volumes relative to fresh baking were seen to be retained, or even increased at the shorter prefermentation time. This kind of result has not been reported earlier. Kräft et al. (1994) reported that the loaf volumes of breads baked using partly fermented (80%) frozen doughs were on average 87.5% of the volumes of fresh baked breads. Brümmer et al. reported an even greater effect of freezing on 75% fermented frozen doughs, the loaf volumes of which were only 77% of the loaf volumes of fresh breads (1993).

Improved freeze-thaw stability of partly fermented (25 min) frozen doughs was also observed as higher form ratios, although the values remained clearly lower than in fresh baking (Fig. 11). The flattening of breads baked from frozen doughs was less when a shorter proofing before freezing was used. The great difference in form ratios of fresh and frozen baking may have been due to high temperature gradient in thawing and over-proofing of the outer part of the dough (Dubois and Blockcolsky 1986).

Although shorter prefermentation time (25 min) was a good solution to increase the freeze-thaw stability of prefermented frozen doughs, it could not prevent the deterioration of loaf volumes in breads baked from frozen doughs with longer frozen storage (Fig. 10). The reduction in loaf volumes was greatest during the first week of storage, on average 16%, after which the volumes remained almost constant. This was consistent with the earlier findings of Brümmer et al. (1993). Frozen storage time had no significant effect on the form ratio of breads baked using partly fermented frozen doughs (Fig. 11).

3.1.2 Frozen storage stability

Effect of reduced water content

Water content of prefermented frozen doughs was decreased after experiments with the maturograph showed that frozen storage softened the dough structure (Publication II). The dough structure could not stand the weight of the plunger of the maturograph, and collapsed with a release of fermentation gases. Figure 12 summarizes the changes in maturographs and bread sections, and Table 7 presents the loaf properties after 14 days frozen storage. The results of maturograms are discussed in more detail in Section 3.2.1 *Empirical methods, Maturograph*. The positive effect of lower water absorption levels on frozen dough has also been reported earlier for nonfermented frozen doughs (Lorenz 1974, Brümmer 1988). In contrast, Hanneforth et al. recommend higher water absorption levels for prefermented frozen doughs (1994).

Table 7. Effect of water content (normal and reduced by 2 percentage units) and final fermentation time on baking properties of flours 4 and 5 after 14 days frozen storage at -20°C.

	Water Content	Frozen Storage [d]	Loaf Volume [ml]		Form Ratio	
				±		±
Flour 4	normal	0	517	36	0.59	0.02
		14	457	14	0.48	0.02
	reduced	14	462	4	0.52	0.04
		14[a]	593	8	0.56	0.00
Flour 5	normal	0	589	16	0.49	0.02
		14	562	34	0.39	0.02
	reduced	14	530	22	0.39	0.03
		14[a]	710	10	0.42	0.02

[a] ½h longer final fermentation

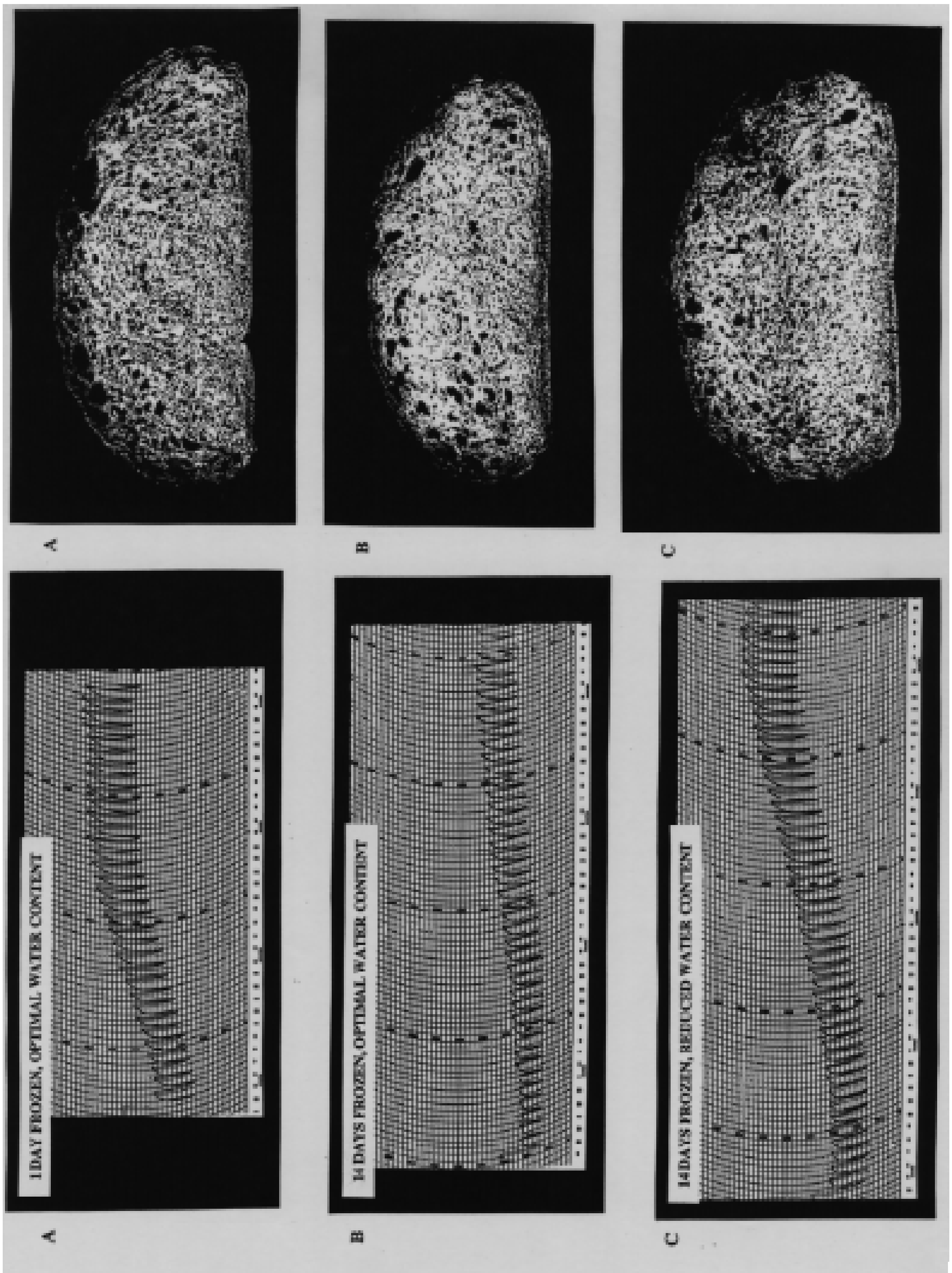

Figure 12. Maturograms and internal appearance of breads prepared under the following conditions: (A) normal water content, one day frozen storage, (B) normal water content, 14 days frozen storage, and (C) reduced water content, 14 days frozen storage. Prefermentation time was 25 min and storage temperature -20℃ in all cases.

The form ratio of breads baked from doughs frozen 14 days was greatly improved by reducing the water content (Table 7). However, no improvement was seen in loaf volumes (Publication II). The lack of improvement can be explained by the equally long fermentation for doughs with normal and reduced water contents after frozen storage. Thus, the more elastic dough (less water) did not expand as much as the dough with normal water content. Figures 12a and 12c describe well the need for longer postfermentation (fermentation after frozen storage). The dough level of a sample with reduced water content frozen 14 days (Fig. 12c) reached the same level as the sample stored one day (Fig. 12a). However, a longer time was needed to reach this. Thus, the postfermentation of frozen doughs with reduced water content was extended by 30 min to a total thawing time of 2 hours.

Extended postfermentation had a positive effect on the baking properties of prefermented frozen doughs with reduced water content (Table 7 and Fig. 12). After 14 days frozen storage the loaf volumes were equal to or even larger than the volumes in fresh baking, but form ratios, although they improved, remained under the fresh level (Table 7). The frozen storage stability of prefermented frozen dough could be resolved by shorter prefermentation time (25 vs. 40 min) and reduced water content (2 percentage units from the optimum of fresh baking).

Effect of hydrocolloids

Hydrocolloids are well known for their high water absorption capability and potential to improve the gas holding capacity of dough (Anderson and Andon 1988). They are also classified as dietary fibres, thus improving the nutritional value of bread. Effect of hydrocolloids on frozen storage stability of prefermented frozen doughs is discussed in Section 3.6 *Hydrocolloids in frozen doughs*.

3.2 RHEOLOGICAL PROPERTIES OF FROZEN DOUGHS

3.2.1 Background

Kulp has written a comprehensive review on the rheological studies of frozen bread doughs (1995). The usual method to analyze the empirical rheology of dough is to test extensibility and resistance to extension with Brabender’s extensigraph. Varriano-Marston and co-workers (1980) and Wolt and D’Appolonia (1984a) reported dough strengthening during frozen storage, whereas Inoue and Bushuk (1991) and Inoue and co-workers (1994) reported just the opposite. All these studies were carried out with a modified extensigraphic procedure. Kulp attributed (1995) the difference to the action of the oxidants: Inoue and Bushuk used ascorbic acid instead of potassium bromate, which was used in the previous studies. The extensigraphic experiments were performed with both non-yeasted and yeasted doughs.

The changes in the rheology of dough frozen storage and thawing have been attributed to the reducing substances leached out from yeast cells (Kline and Sugihara 1968, Hsu et al. 1979) and to ice crystal formation and subsequent redistribution of water (Varriano-Marston et al. 1980, Wolt and D'Appolonia 1984b, Berglund et al. 1991, Inoue and Bushuk 1991, Autio and Sinda 1992). However, there is no general agreement regarding these chemical and mechanical reasons for the loss of gas retention power: Are they both involved or is one more important than the other?

The changes in dough structure have also been studied by fundamental methods (viscoelastic measurements). Autio and Sinda (1992) found a decrease in storage modulus (G') and an increase in tan δ of non-yeasted dough during frozen storage. They also showed the relaxation modulus and relaxation half-life to decrease as a result of weakening of the gluten network during freezing. However, the experiments were carried out with non-yeasted doughs and the structural changes of non-yeasted doughs differ markedly from those of yeasted doughs. Yeast-fermented doughs are difficult to study because of their complexity, and the dimensions and physical properties of the dough change with time (Szczesniak 1988, Bloksma 1990). Probably the only study on the viscoelastic properties of yeasted doughs has been published by Kaufmann and Kuhn (1994). They studied the effect of yeast and fermentation time on dough rheology and found higher yeast addition (0 - 4% on flour basis) and longer fermentation time (higher than 30 min) to soften the doughs.

Our work concentrated on the rheological properties of yeasted doughs. Doughs were analyzed by both empirical (farinograph and maturograph) and fundamental (Bohlin VOR and StressTech rheometers) methods. Explanations for the observed changes are discussed in Sections 3.4 *Ice crystal damage* and 3.5 *Water distribution in frozen doughs*.

3.2.2 Empirical studies

Maturograph results

The most pronounced change in the dough level (height of maturogram) of prefermented frozen doughs with normal water content occurred during the first week of storage (Fig. 13 and Table 8). This result was highly significant for all studied flours (Publication II). During the measurement, the dough structure was extremely soft, and it collapsed during the measurement when the fermentation gases were released. Gas production was still sufficient after seven days of frozen storage, which was seen as the ability of the dough to move the plunger upwards. However, the second step resulted in the escape of gases, evidently because the gluten network could not retain them. This kind of phenomenon was not observed after one day frozen storage, when the baking quality was equal to that of fresh baked breads (Publication I).

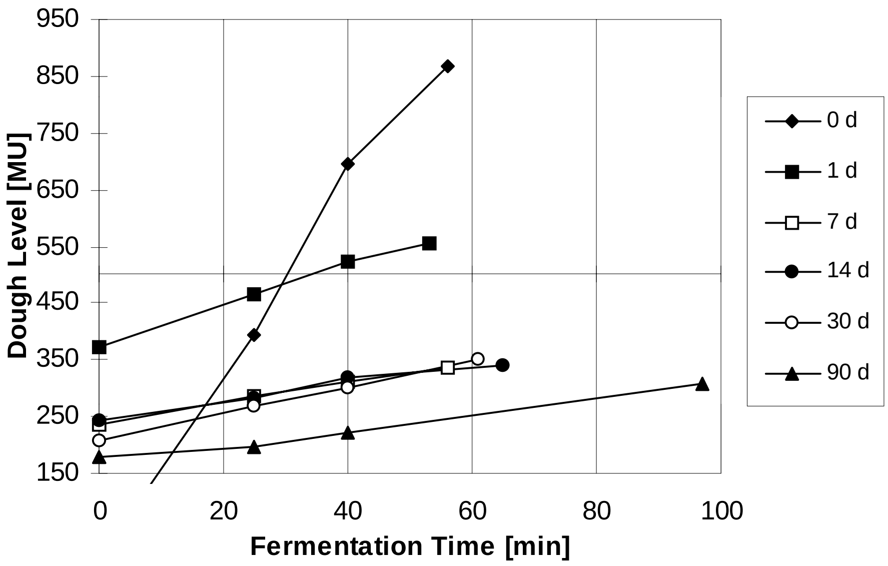

Figure 13. Average dough levels of the six flours, measured with the maturograph after different frozen storage times at -20°C.

Longer frozen storage, up to 30 days, did not further decrease the dough expansion during proofing, and maturograms were almost the same after seven and 30 days frozen storage (Fig. 13). After 90 days frozen storage, the dough level at peak dropped slightly, and a clear change was observed in the final proof time (time to the peak, Fig. 13). The most likely explanation for this is the decrease in yeast viability. Decreased yeast viability during longer frozen storage times has been reported in the number of earlier studies (Kline and Sugihara 1968, Inoue and Bushuk 1992, Takasaki and Karasawa 1992, Inoue et al. 1994).

Reduced water content increased the elasticity and rigidity of prefermented frozen doughs, which was seen as higher dough levels (Table 8). The change in dough levels was most pronounced after seven days frozen storage, when the peak values were almost the same as the average of all

Table 8. Effect of frozen storage time (-20°C) and water content (normal and reduced by 2 percentage units) on the maturograph properties (dough level and elasticity) of flours 4 and 5.

	Water Content	Frozen Storage [d]	Dough Level [MU]	±	Elasticity [MU]	±
Flour 4	reduced	1	805	25	280	20
		7	610	21	225	23
		14	598	65	205	23
	normal	14	428	53	185	9
Flour 5	reduced	1	385	15	185	5
		7	290	29	155	15
		14	298	33	160	16
	normal	14	310	34	170	16

flours after one day storage (Publication II). Since reduced water content (2 percentage units from normal) did not improve the dough level of all flours, the effect was flour dependent (Table 8). Evidently every flour has a unique optimal water absorption for freezing (as in fresh baking), which is lower than the optimum in fresh baking. Longer postfermentation was needed to achieve the positive effect of reduced water content also in loaf volumes, as was discussed in 3.1.2 *Frozen storage stability*. The positive effect of lower absorption levels on frozen dough has been reported earlier for nonfermented frozen doughs (Lorenz 1974, Brümmer 1988). However, higher absorption levels than in fresh baking have been recommended for prefermented frozen doughs (Hanneforth et al. 1994).

Farinograph results

Farinograph analysis proved to be a fast and reliable way to analyze the rheological properties of yeasted doughs (Publication V). The lowest point of the farinogram, after 1.5 min mixing, was used as a measure of dough rigidity, since this was the transfer point for the formation of new dough structure. Figure 14 shows the effect of frozen storage on farinograms of yeasted doughs. As can be observed the dough weakened during frozen storage, exhibiting a lower consistency than the fresh dough. Shorter prefermentation time increased dough rigidity, and lower water content increased it still further, to an almost fresh-like response. There was a strong correlation between farinograms and baking properties in the lower consistency value, the smaller loaf volume, and the smaller form ratio (Voivala 1998).

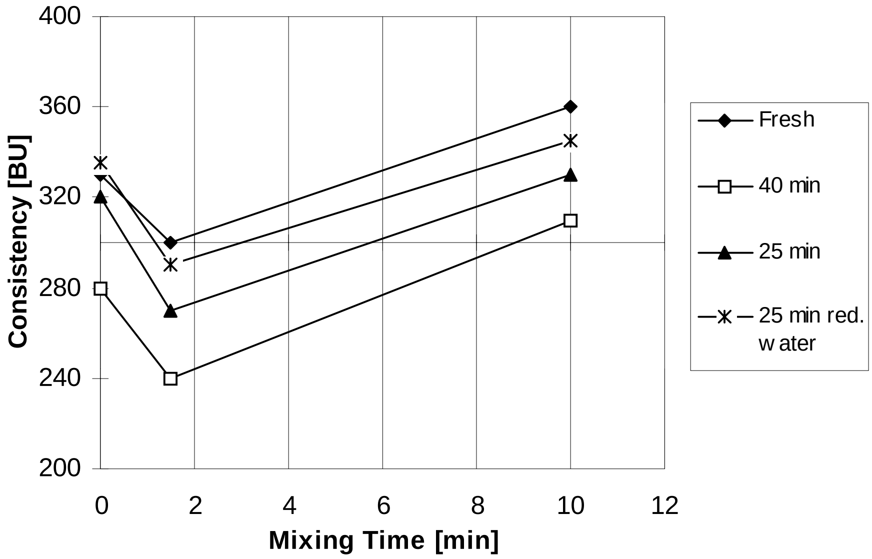

Figure 14. Effect of prefermentation time (40 and 25 min) and water content (normal and reduced) on doughs frozen 14 days at -20°C, as seen in farinograms.

3.2.3 Fundamental studies

Bohlin rheometer (VOR)

In Publication I a Bohlin rheometer was used to compare the viscoelastic properties of yeasted frozen doughs with those of non-yeasted fresh doughs (Table 9). Yeast addition and fermentation resulted in dough softening, and longer prefermentation time further softened dough. This is consistent with the results of Kaufmann and Kuhn (1994). Longer frozen storage also resulted in further decrease of dough rigidity. The differences in G' values between non-yeasted and yeasted doughs measured by Bohlin and StressTech rheometers were comparable, even though flours were different (Tables 9 vs. 10a).

StressTech rheometer

Effects of S-kimo (a dough strengthener from Puratos), prefermentation time, and water content on prefermented frozen doughs were studied as storage modulus (G') values with a StressTech rheometer (Figure 15a, Publications IV and V). Doughs were softer when S-kimo was added and at longer prefermentation time and higher water content (Fig. 15a).

Table 9. G' values (storage modulus) at different fermentation and frozen storage times at -20°C for flours C and D.

	Prefermentation [min]	Frozen Storage [d]	G' [kPa] Flour C		Flour D	
				±		±
Non-yeasted doughs	0	1	13.03	0.38	25.13	0.91
Yeasted doughs	40	1	8.04	0.33	18.18	0.38
	25	1	9.65	0.15	20.28	0.90
	25	7	9.10	0.13	19.58	0.58

Kaufmann and Kuhn (1994) report the same effect: that fresh wheat doughs are softer at longer fermentation time. Frozen storage did not appear to have any statistically significant effect on dough rigidity (G' values, Publication IV). Figure 16 shows the effect of frozen storage on G' values of water-flour doughs. The result was now totally opposite to that for yeasted doughs: frozen storage greatly decreased the rigidity, thus explaining the lower gas-holding capacity of frozen doughs. This kind of deterioration could be prevented by reducing the water content of doughs (Fig. 16). Decrease in G' values for non-yeasted doughs during frozen storage has also been reported by Autio and Sinda (1992).

The StressTech rheometer, which is equipped with a gas cylinder, allows the measurement of change in the gap during monitoring of the storage modulus. The conditions for measuring this expansion potential (ΔGap, Fig. 15b) were the same as for the measurement of G' (Fig. 15a). When no S-kimo was added freezing decreased the expansion potential of dough, which further decreased during longer frozen storage. A response similar to that of fresh dough was observed for ΔGap with lower water content and shorter prefermentation time. In general, frozen storage from 7 to 14 days did not have any statistically significant effect, as was also seen in the earlier baking tests (Publications I and II). The expansion potential of yeasted doughs (ΔGap) correlated better with baking results than did the small deformation measurement (G' values). This can be explained by the fact that the rheological changes in baking occur at larger deformations. Table 10a and b summarizes the rheological properties for flours 4 and 5 (both non-yeasted and yeasted doughs, Publication IV).

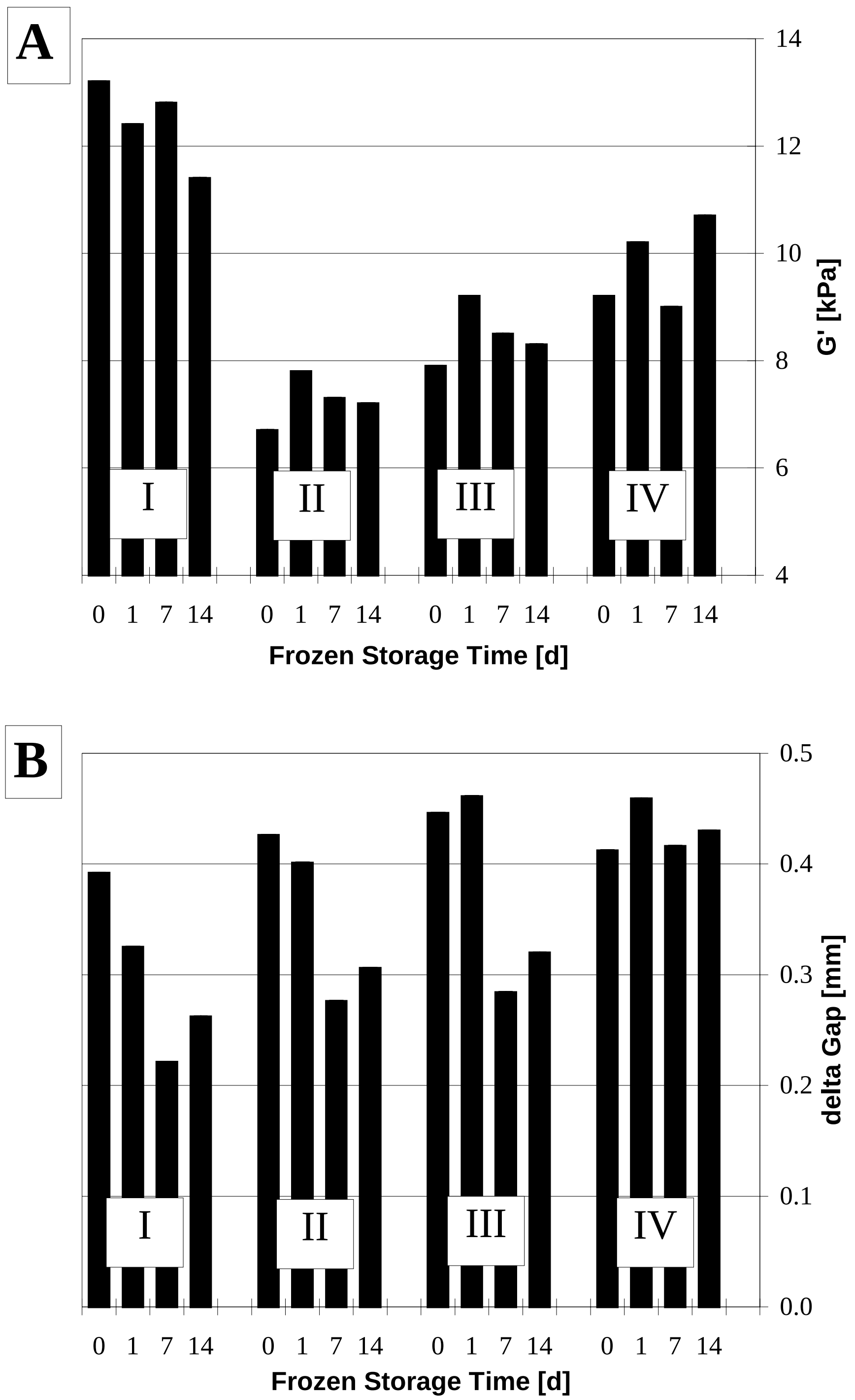

Figure 15. (A) G' values and (B) ΔGap of fermented frozen doughs under different conditions: I no S-kimo, prefermentation time 40 min, II S-kimo, 40 min, III S-kimo, 25 min, and IV S-kimo, 25 min, and reduced water content. Samples were stored at -20℃ before measuring.

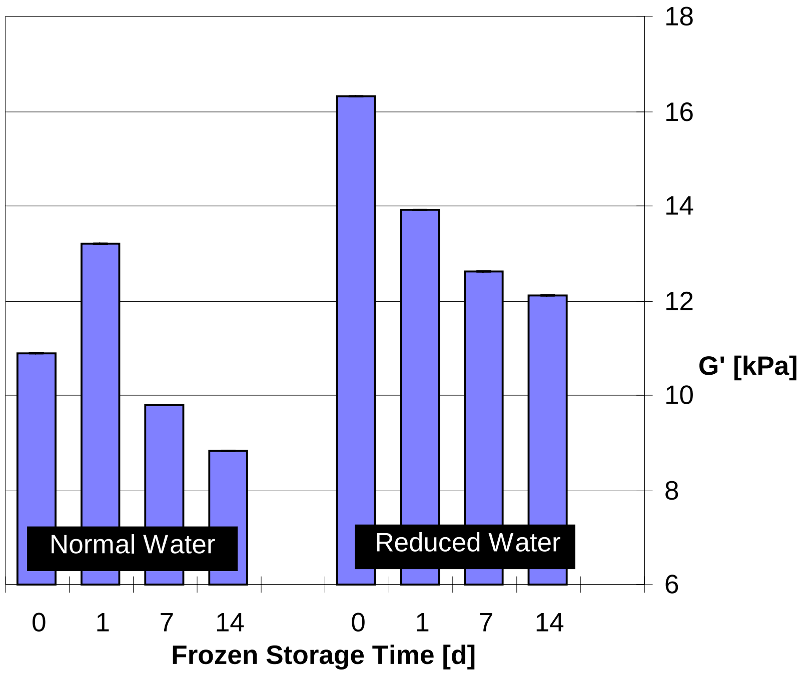

Figure 16. Effect of water content and frozen storage time (at -20°C) on the storage modulus (G') in water-flour mixtures.

3.3 EFFECT OF FLOUR QUALITY ON FROZEN DOUGHS

The experiments reported in the Sections 3.1 *Baking properties of frozen doughs* and 3.2 *Rheological properties of frozen doughs* were carried out with both high and normal protein flours, because high protein flours are usually recommended for frozen baking (e.g. Marston 1978, Sideleau 1987). Flours C and 5 can be described as extra strong flour (protein content ≈17%, N * 5.7 as dry basis) and flours D and 4 as normal flour (≈12%, N x 5.7 protein). Flour numbering 1 - 6, based on Publication II, was used through out the thesis for clarity, although the numbering was changed in Publications III and IV (see Table 5).

<u>Effect on baking properties</u>

Figures 10 and 11 show that the baking properties of prefermented frozen doughs cannot be predicted from protein content. Although the loaf volumes for fresh baking and after one day frozen storage were larger for the flour with the higher protein content (flour C), they were equal with longer frozen storage times (Fig. 10). In all cases, form ratios were higher for the flour with lower protein content (flour D, Fig. 11). The only flour characteristic that was found to correlate with the baking properties was the ratio of water solubles to wet gluten (Fig. 17, Publication I).

Slade et al. (1988) reported the loaf volumes of fully prefermented frozen doughs (i.e. prefermentation time as long as in fresh baking) to increase as the ratio of water solubles to wet gluten decreased. They obtained a correlation of r = -0.84 between the log of loaf volume and the ratio of water solubles to wet gluten after three months of frozen storage. In our study (Fig. 17) the correlation was higher for 40 min fermented doughs (i.e. fully fermented) after one day storage than for fresh breads (r = -0.90 vs. r = -0.78). Thus, in the case of 40 min fermented frozen doughs the flours with a lower ratio of water solubles to wet gluten provided more resistant doughs to changes caused by freezing and thawing.

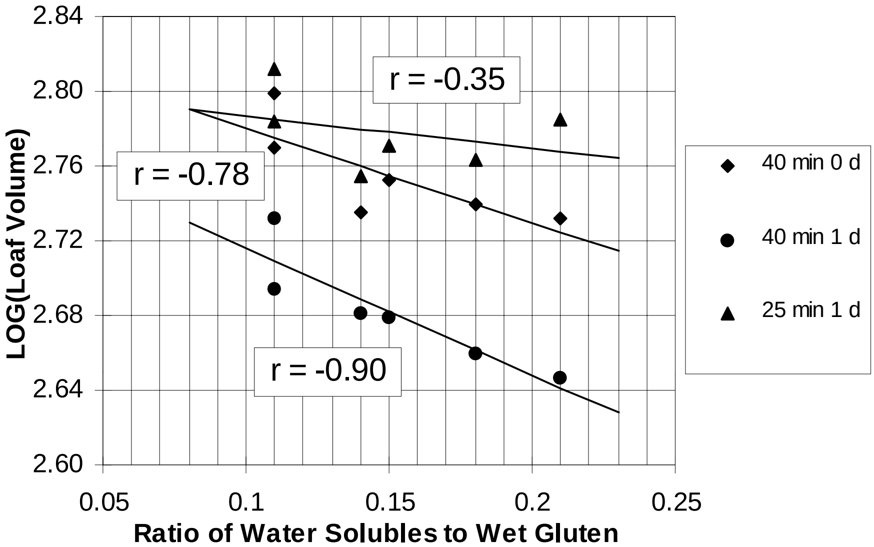

Figure 17. Correlations of log(loaf volume) and ratio of water solubles to wet gluten in bread baked after different prefermentation times (40 and 25 min) and frozen storage times (0 and 1 day) at -20°C.

Shorter prefermentation improved the loaf volumes of breads baked using prefermented frozen doughs independently of the flour quality (Publication I). This was also seen as clearly weaker correlation between the loaf volumes and the ratio of water solubles to wet gluten, r = -0.35 (Fig. 17). Thus, the effect of flour quality on prefermented frozen doughs can be minimized by optimizing the processing conditions.

Table 10a. G' values (storage modulus) of prefermented frozen doughs for flours 4 and 5. Samples were stored at -20°C.

	Conditions[a]	Water Content	Frozen Storage [d]	G' [kPa] Flour 4	±	Flour 5	±
Non-yeasted doughs		normal	1	22.1	1.10	7.7	0.35
			14	14.1	1.08	6.1	0.40
		reduced	1	26.2	0.78	8.5	0.25
			14	20.6	0.99	6.8	0.57
Yeasted doughs	no S-kimo, 40 min	normal	1	12.0	0.62	4.9	0.29
			14	7.5	0.24	5.8	0.36
	S-kimo, 40 min	normal	1	8.9	0.66	5.1	0.43
			14	7.6	0.42	5.2	0.45
	S-kimo, 25 min	normal	1	9.0	0.55	5.3	0.43
			14	8.3	0.51	5.1	0.27
	S-kimo, 25 min	reduced	1	16.0	0.80	5.5	0.21
			14	12.7	0.92	6.6	0.38

[a] time presents prefermentation time

Table 10b. ΔGap (expansion potential) of prefermented frozen doughs for flours 4 and 5. Samples were stored at -20°C.

	Conditions[a]	Water Content	Frozen Storage [d]	Delta Gap [mm] Flour 4	±	Flour 5	±
Yeasted doughs	no S-kimo, 40 min	normal	1	0.25	0.01	0.33	0.02
			14	0.12	0.01	0.26	0.01
	S-kimo, 40 min	normal	1	0.27	0.03	0.40	0.02
			14	0.16	0.01	0.31	0.02
	S-kimo, 25 min	normal	1	0.28	0.03	0.46	0.03
			14	0.19	0.02	0.32	0.03
	S-kimo, 25 min	reduced	1	0.31	0.02	0.46	0.02
			14	0.21	0.01	0.43	0.01

[a] time presents prefermentation time

<u>Effect on rheological properties</u>

In the rheological experiments the flours with a higher protein content (Flours C and 5) always gave the softer doughs. Changes in recipe or frozen storage time of dough had only a minor effect, if any, on the rheological properties (G’ values) of the dough prepared from the strong flour (Tables 8, 10a and 10b). This was not as obvious for the flours in the first series (Table 9). Expansion potential, which was studied with the StressTech rheometer, however, correlated well with the baking properties for all flour types (Publication IV).

3.4 ICE CRYSTAL DAMAGE

3.4.1 Background

Food structure is always affected by freezing. The structure modification of protein gels is well illustrated in Figure 18, where the gel is cooled from one direction (from the bottom of the container). In this way the structure of the gel becomes fibrous, like meat, as a result of ice crystal growth and concentration of protein zones. The structure modification of protein gels consists of (Lawrence et al. 1986):

1. Phase separation
   (ice crystals and concentrated solution or suspension)

2. Ice crystal orientation
   (at the same time the orientation of concentrated phase)

3. Stabilization of new structure by chemical bonding.

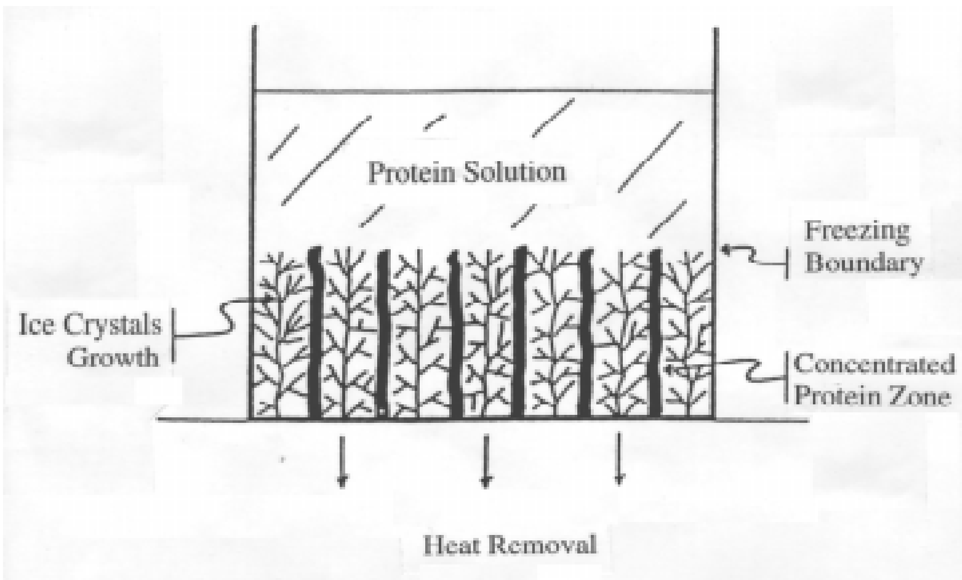

Figure 18. Structure modification of protein gel by one-way directed freezing (freezing from the bottom of container).

When a protein solution freezes, the volume of water will increase on average by 9 per cent (Lawrence et al. 1986). After ice crystals nucleate (homogeneous in the absence of solid interfaces, or heterogeneous in the presence of solid interfaces), they still have potential to grow. The growth of the crystals is limited either by mass transfer or by heat transfer, whichever is slower. In *mass transfer,* water molecules must move from the liquid phase to a stable site on the crystals for the crystal growth, and in *heat transfer,* the latent heat of crystallization must be removed. Thus, a faster freezing will result in a larger amount of small ice crystals formed through heat transfer. The size of ice crystals will be mostly determined by the ice crystals nucleation, which is followed by crystals growth. The size and shape can also change during frozen storage, and this phenomenon is called *recrystallization*. Enlargement of ice crystals during frozen storage is also known as "Ostwald ripening" (Blanshard and Franks 1987). Ice crystals and recrystallization are discussed in considerable detail by Fennema et al. 1973, MacKenzie 1973, Heldman and Singh 1981, Franks 1982, Blanshard and Franks 1987, Donhowe et al. 1991, and George 1993.

3.4.2 Ice crystals in frozen doughs

The major changes occurring in frozen doughs, both in gluten structure and in yeast viability, are due to ice crystals. The damage is both direct (physical) and consequent (water distribution). Stauffer (1993) has emphasized the role of ice crystals in damaging the gluten structure, but also concedes the lack of convincing experimental support. Nevertheless, in the studies on fully hydrated frozen doughs by low-temperature electron scanning microscopy, Berglund and co-workers (1991) found that less water is associated with both gluten and starch fractions than in corresponding fresh doughs. The water is instead concentrated into large patches of ice crystals. They also observed gluten strands to become thinner and starch granules to separate from the gluten matrix during frozen storage.

In our work, the physical effect of ice crystals on dough structure was studied by light microscopy, whereas the changes in water distribution were studied by ultracentrifuge as the amount of liquid phase, and by ^{1}H NMR methods as the amount of ice and self-diffusion coefficient. Physical effects are discussed in Section 3.4.3 *Porosity of dough* and water distribution is treated in Section 3.5 *Water distribution in frozen doughs.*

3.4.3 Porosity of dough

Effect of prefermentation time

Shorter fermentation before freezing resulted in a thicker network of gluten around the air bubbles, and the average size of the gas bubbles was smaller (Fig. 19 and Publication I). Thus, the walls of the air bubbles were more resistant to the stress of freezing (for example, the formation of ice crystals) than were those of optimally fermented doughs. The pore structure correlated very well with the baking results discussed in Section 3.1.1 *Freeze-thaw stability*. Shorter prefermentation time improved the loaf volumes on average by 20% and also prevented the collapse of doughs during thawing (Figs. 10 and 11). Differences between the flour samples C and D could also be explained by the pore structure; for flour D seemed to contain fewer large bubbles and had a denser structure of gluten (Publication I). Thus, flour D (normal flour) showed better stability during freezing and frozen storage than flour C (strong flour). Micrographs of the doughs stored frozen for seven days revealed no new information.

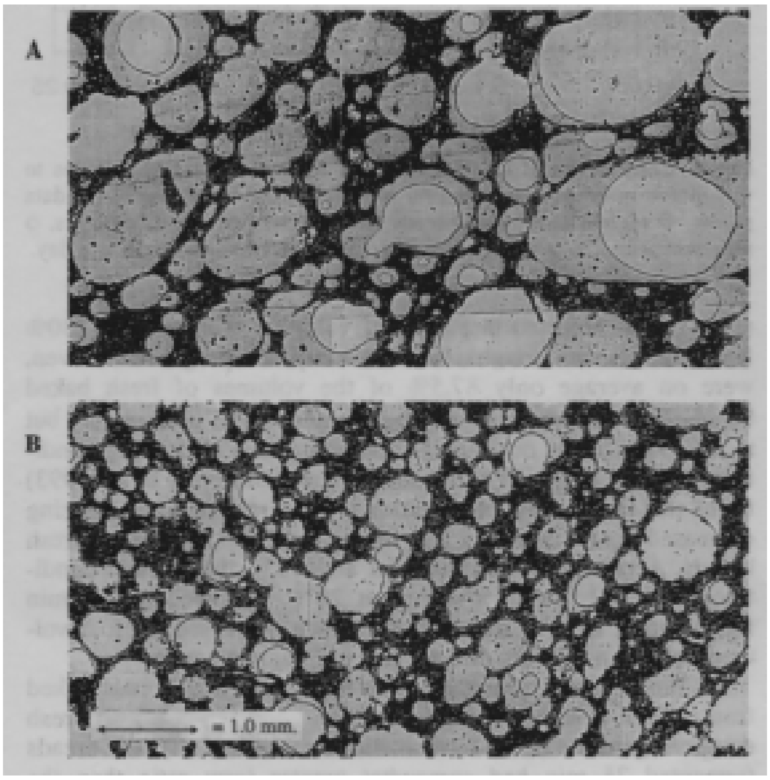

Figure 19. Pore structure of prefermented doughs after one day frozen storage at -20°C with (A) 40 min and (B) 25 min prefermentation.

Effect of reduced water content

Relative to frozen doughs with normal water content, the dough prepared from flour 4 exhibited the greatest improvement in dough level when the water content was decreased (Table 8 and Publication II). After seven days frozen storage, the porosity of doughs with normal and reduced water contents was 56.5 to 46.4% (area of pores), respectively (Table 11). The decreased area of pores per total area was due to the thicker wall around air bubbles and the smaller amount of large cells (1 - 10 mm^2). Since the total number of air cells did not decrease dramatically, the number of small air bubbles must have increased. In part, the more compact microstructure with reduced water content explains the higher elasticity and loaf volumes of the dough with lower water content (Tables 8 and 7, respectively).

Table 11. Pore size distribution (%) and total area of pores in dough (%) for flours 4 and 5 after seven days of frozen storage at -20°C. [a] Effect of reduced water content is reported as percentage change from the values at normal water content.

	Water Content	Pore Size [%] [a]			Total Area of Pores [%]
		0.001-0.1 mm^2	0.1-1 mm^2	1-10 mm^2	
Flour 4	normal	21.6	40.4	38.0	56.5
	reduced	9.7	7.2	-13.2	46.4
Flour 5	normal	20.4	42.8	36.0	49.1
	reduced	22.1	18.7	-32.5	44.5

The total porosity of all doughs decreased when the water content was reduced (Table 11 and Publication II). The number of 0.1 - 1 mm^2 pores increased, while the number of 1 - 10 mm^2 pores decreased. However, the greatest change in pore size distribution was for flours 3, 5, and 6, which showed almost no improvement in the dough levels of maturograph curves when water content was reduced (Publication II). Thus, the pore size distribution cannot alone explain the improved frozen storage stability of prefermented doughs with reduced water content, but there must be an interactive effect between pore size distribution and the stretching properties of gluten, which then together determine the stability. Study of the correlation between loaf volumes and the ratio of total porosity to extensibility of flour showed a correlation as high as r = 0.87. After freezing, the doughs become more extensible in a manner unique to each flour (Inoue and Bushuk 1992). Thus, it can be thought that the correlation between these parameters could have been even better than the measured values suggested. On the other hand, the stability of frozen dough is also dependent on other parameters, such as the amount of water not absorbed by the system.

Liquid phase hypothesis

Gan et al. (1995) presented a revised model for dough expansion and pore structure on the basis of their studies by scanning electron microscopy. In their liquid phase hypothesis, two consecutive stages occur during dough expansion (Fig. 20). First, gas cells are embedded in a continuous starch-protein matrix, which becomes thinner during gas cells expansion. The behavior of the dough at this stage is primarily determined by the rheological properties (Fig. 20a). In the second stage, liquid film maintains the integrity of gas cells, as discontinuities in the starch-protein matrix become increasingly frequent during expansion (Fig. 20b). Oven rise will end as the liquid phase ruptures and gases will be lost rapidly (Fig. 20c). Thus, the baking properties of dough in the final stages of baking are primarily determined by the stability of the liquid phase. Air bubble structure has also been shown to be especially susceptible to damage during uniaxial extension (Levine and Slade 1990).

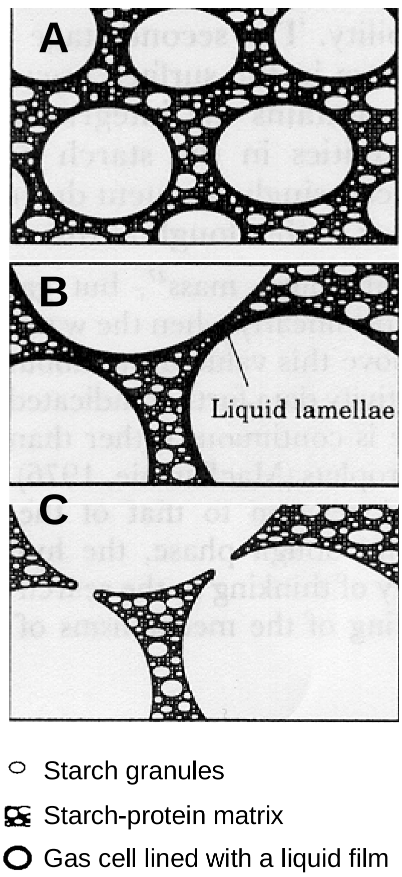

Figure 20. A. revised model of dough expansion. A) At early stages of fermentation, the expanding gas cells are embedded in a starch-protein matrix, B) at advanced stages of fermentation and early stage of baking, starch-protein matrix fails to enclose the gas cells completely, leaving areas with a very thin liquid film, and C) at the end of oven rise the liquid film will rupture (Gan et al. 1995).

The liquid phase hypothesis presents an excellent explanation for the observed improvements in prefermented frozen doughs with shorter prefermentation time and reduced water content. If the fermentation before freezing proceeds to the second stage, where gas cells are stabilized only by liquid phase, freezing and thawing will change the structure of the frozen dough dramatically. During frozen storage the frozen liquid phase may absorb more water from its surroundings or the liquid phase may lose water to ice crystals in the surroundings. In both cases the gas cells will rupture because of freezing and the thawed dough will collapse. However, if gas cells are surrounded by starch-protein matrix (the first stage of expansion) they will better withstand the stress of freezing and frozen storage.

3.5 WATER DISTRIBUTION IN FROZEN DOUGHS

Ice crystal damage is both direct (physical) and consequent (water distribution) as was noted above. Berglund and co-workers (1991) observed in their studies that, after frozen storage, less water is associated with both gluten and starch fractions, and the water instead is concentrated into large patches of ice crystals in dough. Physical changes in the structure of prefermented frozen doughs were described above in Section 3.4.3 *Porosity of dough*.

3.5.1 Amount of liquid phase

Wheat flour dough has been described by Eliasson and Larsson (1993) as bicontinuous and phase separated. It consists of two aqueous phases, the water-swelled protein phase (gluten) and the liquid phase (dispersed starch granules and solubles). Larsson and Eliasson (1996a) suggest a new model of phase separation for wheat dough based on ultracentrifugation studies. Five different phases are proposed – liquid, gel, gluten, starch, and unseparated dough – with the relative amount of each depending on the water content of the dough. The importance of the liquid phase in wheat flour doughs was originally noted by MacRitchie (1976). He reported the electrical conductivity and gas retention of dough to be zero until appearance of the liquid phase separated by ultracentrifugation. In our work, the amount of liquid phase determined by ultracentrifugation was used as a measure of water distribution in frozen doughs (Publications III and IV).

<u>Effect of freezing and frozen storage</u>

Ultracentrifugation followed the method of Larsson and Eliasson (1996a), but only the total amount of liquid phase in water-flour doughs was analyzed as a function of frozen storage time at -20°C (Figure 21 and Table 12). The longer frozen storage time resulted in a larger amount of liquid phase in water-flour mixtures, as shown in Figure 21. This is an obvious consequence of the growth of ice crystals. During frozen storage the ice crystals physically puncture the structure of the dough, weakening the gluten network and yeast viability. The growth of ice crystals also causes a concentration of polymers resulting in a higher glass transition. This was observed in DMTA studies (dynamic mechanical thermal analysis): with normal water content the glass transition temperature (T_g) of dough moved to higher temperatures during frozen storage, whereas reduced water content prevented this effect (Publication III). When water content was reduced, the change in the amount of water not absorbed by the system was much slower, and the amount of liquid phase remained almost constant during frozen storage (Fig. 21). After 14 days frozen storage the amount of liquid phase was lower in the dough with reduced water content than in that with normal water content for fresh dough (Fig. 21 and Table 12). In baking tests, reduced water content was observed to improve the frozen storage stability of prefermented frozen doughs, as discussed in Section 3.1.2 *Frozen storage stability*.

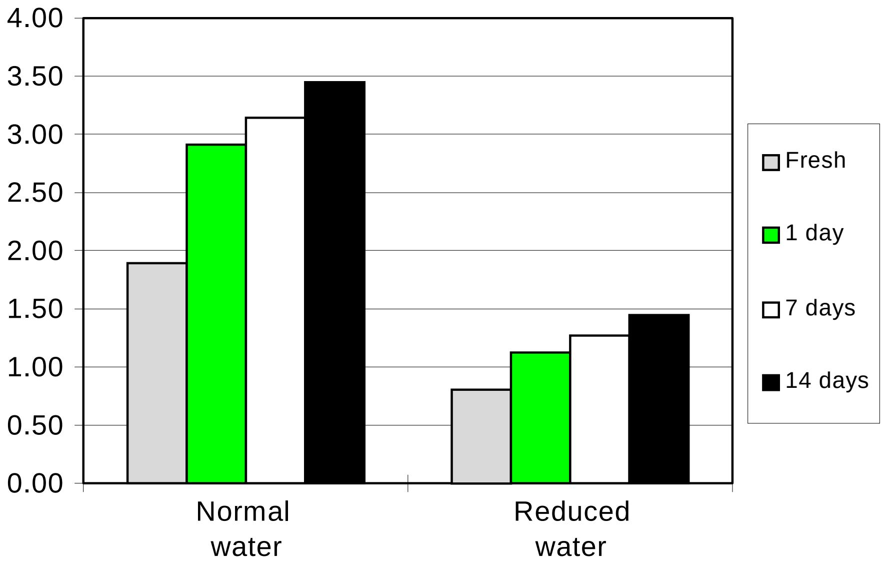

Figure 21. Amount of liquid phase in dough (water-flour mixtures) at different water contents and frozen storage times at -20°C.

The increase in the amount of liquid phase during the first day of storage is due to nucleation and subsequent growth of ice crystals in doughs (Fig. 21 and Table 12). Although the amount and size of ice crystals will be largely determined at freezing, the crystals have a strong tendency to grow (i.e. recrystalize) during frozen storage. Since the growth of ice crystals during frozen storage is dependent on the amount of water not absorbed in the surroundings, this water need to be minimized by reducing the total water content (Fig. 21). No statistically significant changes in the amount of liquid phase were observed during frozen storage from seven to 14 days

(Publications III and IV). Thus, most of the recrystallization must have occurred during the first week of storage. This is consistent with the loaf properties of breads baked from prefermented frozen doughs (Publications I and II).

Table 12. Amount of liquid phase in water-flour mixtures prepared from flours 4 and 5, stored at -20°C.

Water Content	Frozen Storage [d]	Amount of Liquid Phase [%]			
		Flour 4		Flour 5	
			±		±
Normal	0	5.11	0.10	3.47	0.04
	1	4.54	0.28	2.14	0.06
	7	5.28	0.01	4.62	0.14
	14	5.39	0.13	4.80	0.22
Reduced	0	1.88	0.05	2.31	0.15
	1	2.40	0.11	2.16	0.02
	7	3.13	0.08	3.05	0.06
	14	3.31	0.06	3.05	0.06

Effect of flour quality

Flour quality had a great effect on the amount of liquid phase in the frozen doughs (Publications III and IV). Flour 1 gave the least and flour 3 the most liquid phase in all cases. Flour 3 had a relatively low water soluble index and a relatively low wet gluten content (Table 5). When the water content in the doughs was reduced, the amount of liquid phase decreased ($P < 0.01$). The weakest statistical significance was seen for flour 5, which had the highest water content. Reduced water content improved the postfermentation stability of flours 1 and 4, but not that of flours 3 and 5 (Publication II). An explanation for this result could be that other ingredients (sugar, salt, shortening etc.) change the water distribution in dough. Larsson and Eliasson found in their ultracentrifugation studies, for example, that ascorbic acid and lipids affect water distribution in dough (1996a,b).

3.5.2 Amount of ice

Figure 22 shows typical liquid amplitudes of FID (free induction decay) for dough (flour-water mixture) as a function of temperature from 0°C to -45°C (Publication III). When the temperature is decreased the amount of the more rapidly decaying component (solid) increases (change in amplitude from 23000 to 9000, Publication III). This is a consequence of ice formation. The dough can be considered to be practically frozen at -10°C. However, there seem to be some other changes at lower temperatures, as was suggested, for example, by the development of a small shoulder in the relaxation curve (Publication III).

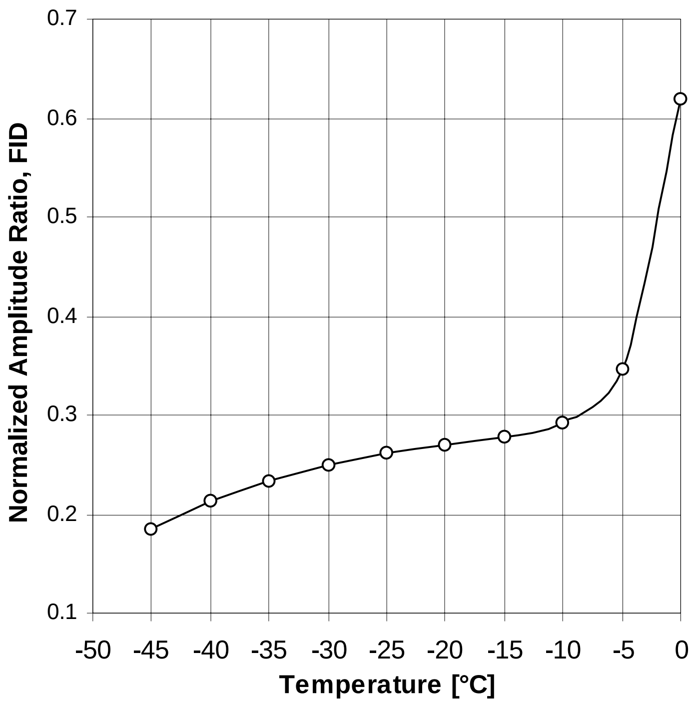

Figure 22. Effect of temperature on the normalized amplitude ratio of liquid amplitude, FID.

Studies on the CPMG (Carr-Purcell-Meiboom-Gill) relaxation of dough also showed that the greatest change to occur in the temperature range 0 to -10°C (Publication III). This was observed from as a decrease both in amplitude and in decay time. The liquid signal at -10°C represents the “nonfrozen” water and the change in the solid signal is caused by ice. The amount of ice can be calculated from phase amplitudes (Fig. 22 and Table 13).

Lind (1988) reported the amount of ice in dough to be 56% of the total water content at -10°C and 63% at -40°C. This result was obtained by DSC (differential scanning calorimetry) using the melting enthalpy. In the present study, the percentage change in the liquid amplitude ratio from 0°C to -10 and -40°C was used to calculate the amount of ice in doughs (Table 13). The choice of -10°C was based on the observation that samples were practically frozen at this temperature. The temperature of -40°C was chosen because phase transition (glass transition) was observed near -30°C. There was a general consistency with the values reported by Lind, especially at -10°C. At this temperature the average amount of ice was 55% of the total water content (observations varied from 52 to 57%). Further freezing from -10 to -40°C increased the amount of ice to 68% on average (observations varied from 64 to 74%). The difference between our values and Lind (56% at -10°C and 63% at -40°C, 1988) could be explained by the different recipes and flours used (in this thesis flour-water dough). Sugar, salt and shortening (used by Lind) have a great effect on freezing properties, decreasing the freezing temperature. The general finding for the effect of water content in dough is the expected one that reduced water content results in a smaller amount of ice (Table 13).

Table 13. Amount of ice of the total water content at -10 and -40°C in water-flour mixtures for flours 4 and 5. Samples were stored at -20°C.

Water Content	Frozen Storage [d]	Amount of Ice [%]			
		Flour 4		Flour 5	
		-10 °C	-40 °C	-10 °C	-40 °C
Normal	1	52.8	65.7	57.7	74.0
	14	53.9	64.2	57.3	69.2
Reduced	1	52.4	65.6	56.0	70.2
	14	52.9	64.7	56.5	67.7

Effect of flour quality

NMR study of the amount of ice in doughs frozen at -10°C revealed a clear order of the flours from highest to lowest ice content: 5, 1, 4, and 3 (Publication III). The ice content appeared to correlate well with the absorption of doughs measured by farinograph (r = 0.98). Thus, more ice was observed at higher water absorption levels. However, experiments using the ultracentrifuge revealed a different order for the amount of liquid phase in dough: the order from highest to lowest was flours 3, 4, 5, and 1 (Publication III). Two possible explanations for the difference could be that, in the ultracentrifugation, the amount of liquid phase was monitored as change in weight of the liquid fraction, and the temperatures of the NMR and ultracentrifugation analyses were different (-10/-40°C and +20°C, respectively). Thus, water solubles and other components in water could influence the order of flours. On the other hand, the liquid phase recorded with the ultracentrifuge at room temperature represents the water frozen at -10°C plus water in the unfreezable matrix and, thus, the results are not comparable with the NMR values. Ultracentrifugation may also cause the release of absorbed water in dough.

The amount of ice was clearly greater at -40°C than at -10°C (Table 13). The increase was dependent on flour quality, and the order of flours from highest to lowest ice content changed to 1, 5, 3, and 4 (Publication III). Because the amount of ice was calculated from the change in the liquid amplitude ratio, temperature had a flour dependent effect on liquid amplitudes.

Self-diffusion

The self-diffusion coefficient (D) of water in water-flour doughs was measured for three different water contents (optimal, +3, and -3 percentage units) at +40°C. Frozen samples were measured after frozen storage up to

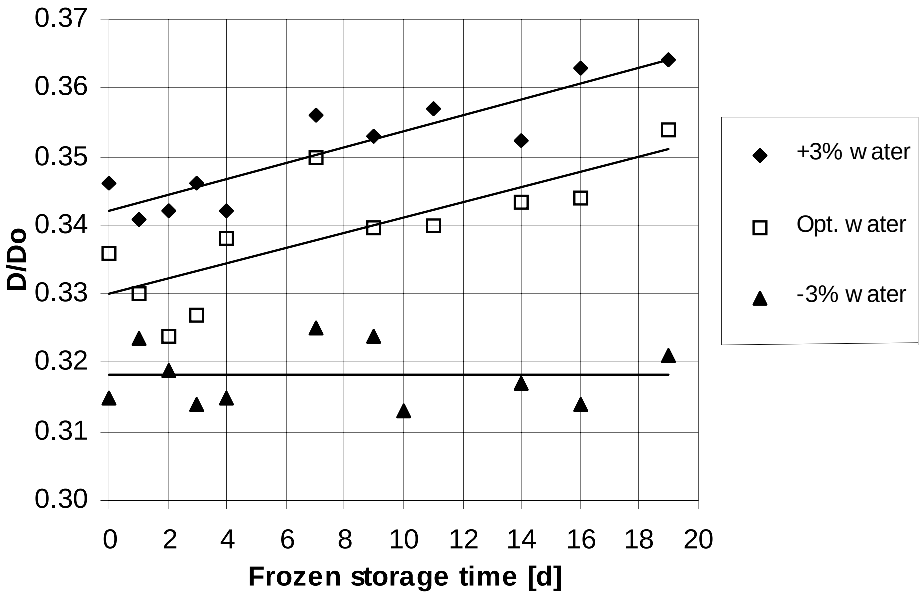

Figure 23. Self-diffusion of dough at different water contents and frozen storage times. Measured at +40°C.

19 days, at which point the self-diffusion was stabilized at +40°C and considered to correspond to that of fresh doughs. Figure 23 shows the self-diffusion coefficient D relative to D_0, the self-diffusion coefficient of water. The self-diffusion coefficient increased during frozen storage with optimal and +3 percentage units water content, but remained constant with reduced water content. Self-diffusion was always faster at the higher water contents. The self-diffusion in water-flour mixtures correlated well with the amount of liquid phase. Thus, the self-diffusion, as well as the amount of liquid phase, increased during frozen storage because of the growth of ice crystals. This in turn resulted in drying of polymers and in large water patches. Reduced water content can be used to control the growth of ice crystals and the negative changes in dough rheology.

3.6 HYDROCOLLOIDS IN FROZEN DOUGHS

Hydrocolloids were chosen to improve the frozen storage stability of prefermented frozen doughs because of their high water absorption ability and potential to improve the gas holding capacity of dough (Anderson and Andon 1988). As was discussed above, the amount of water not absorbed by the system has an enormous effect on the growth of ice crystals and subsequent deterioration in the baking properties of frozen doughs. Dubois and Dreese (1984) have described the positive effect of larger amounts ofsweeteners on frozen doughs (8 - 10%). Sweeteners increase the amount of absorbed water in doughs, but they also affect the color of bread (Maillard reaction). For this reason, the sugar content was kept constant (2% on flour basis) in the present study.

Effect on water absorption

In investigating the effect of six different hydrocolloids on water absorption in doughs, they were tested at two levels each (0.5% and 1.5% on flour basis). The increase in water absorption is described in Table 6 and Publication V. At higher content of hydrocolloids, the water absorption as well as the dough development time increased in all cases (see Fig. 24 for Cekol 700 P, CMC).

Effect on baking properties

Baking quality after 14 days of frozen storage at -20°C with Cekol 700 P (CMC) is shown in Table 14 and Figure 25. The loaf volumes of breads baked from prefermented frozen doughs were clearly increased by the use of hydrocolloids. The effect was evident even when the water content of doughs was increased. The amounts of water added to the doughs represented in Table 14 and Figure 25 were (A) 54.5% (the reference), (B) 59.0%, (C) 57.0%, (D) 65.5% and (E) 63.5%. The empirical rheological experiments showed the effect of Cekol 700 P (CMC) to be much greater at the 0.5% level than the 1.5% level (Publication V). This was seen as higher form ratio at the 0.5% level of hydrocolloid, but effect on the loaf volume was clearer at the 1.5% level (Table 14).

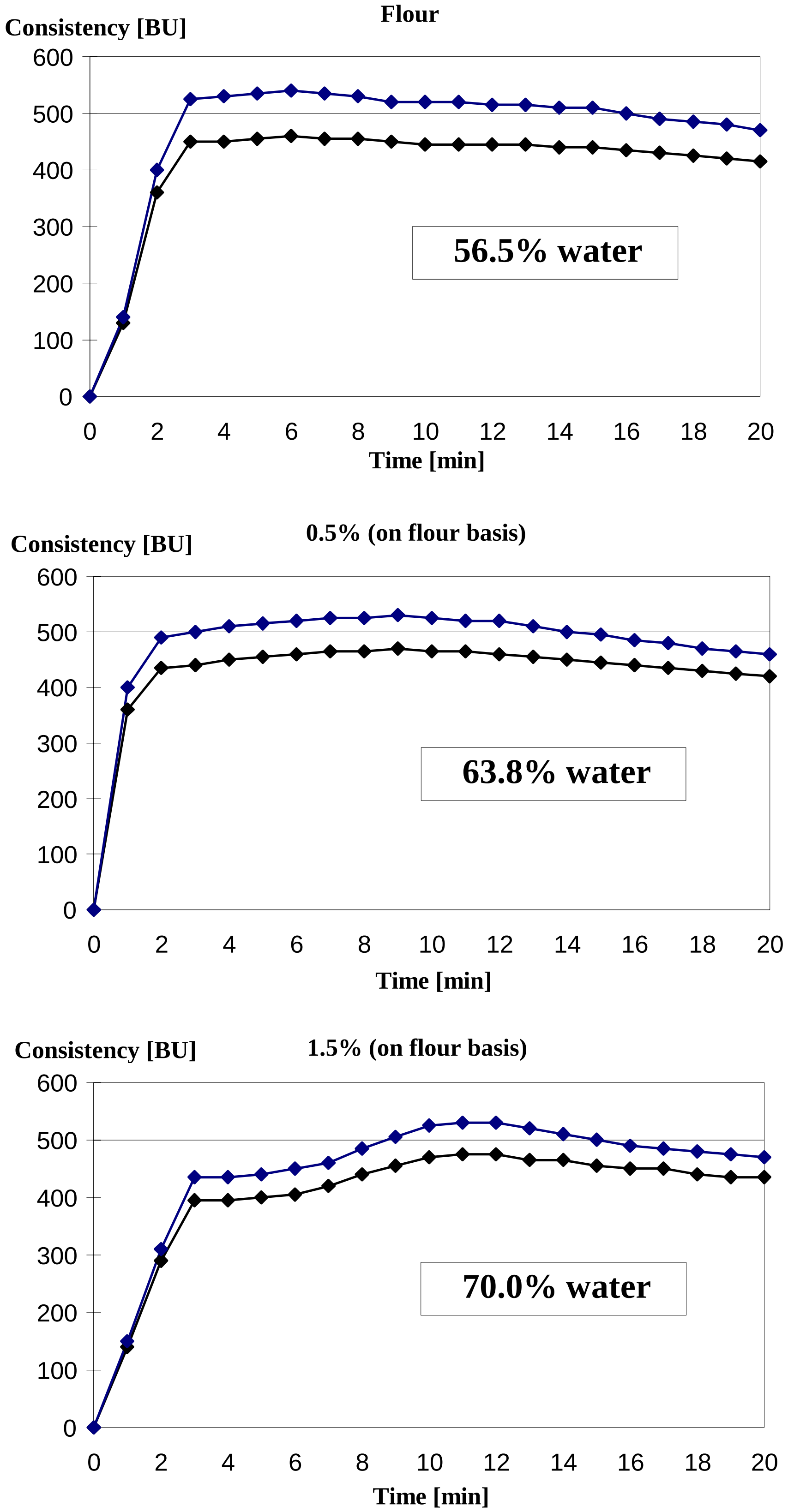

Figure 24. Increased water absorption ability of hydrocolloids with different levels of Cekol 700 P (CMC).

Table 14. Effect of hydrocolloid Cekol 700 P (CMC) on the baking properties of prefermented doughs stored frozen for 14 days at -20°C.

	Hydrocolloid [%]	Water[a]	Loaf Volume [ml]	±	Form Ratio	±
A	0	-2	573	9	0.55	0.01
B	0.5	-2	590	14	0.53	0.02
C	0.5	-4	600	22	0.60	0.01
D	1.5	-2	660	22	0.46	0.01
E	1.5	-4	720	8	0.47	0.01

[a] percentage units

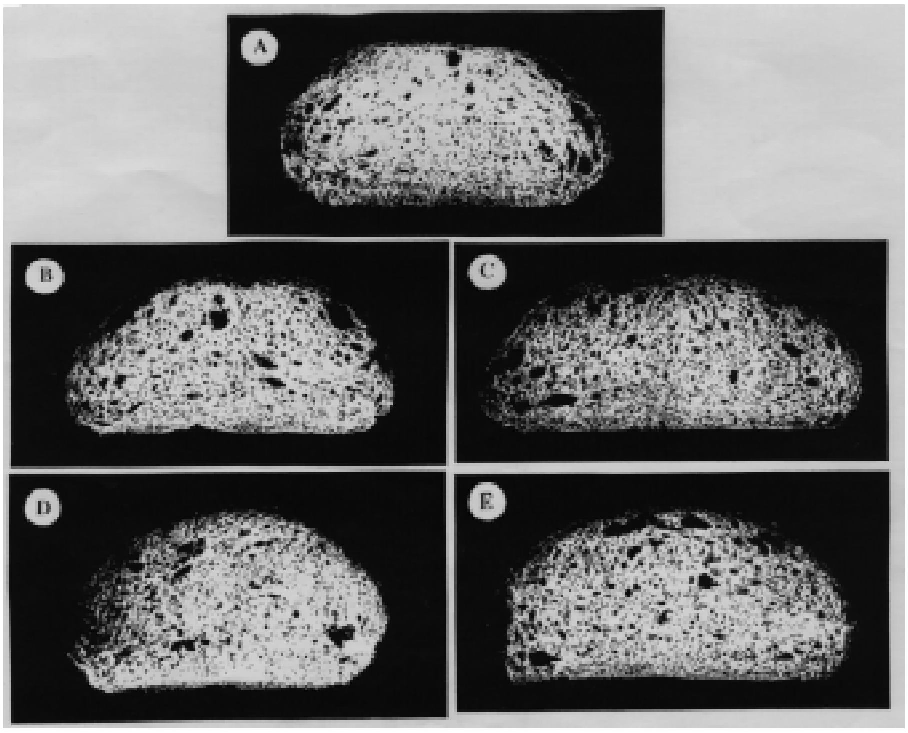

Figure 25. Effect of hydrocolloid Cekol 700 P (CMC) on the baking properties of prefermented doughs stored frozen for 14 days at -20°C. A) Reference, no gums, B) and D) additions at 0.5% level, C) and E) addition at 1.5% level. Water content was reduced in A - C by 2 percentage units and in D and E by 4 percentage units.

4 CONCLUSIONS

Most earlier studies have recommended minimizing fermentation before freezing for maximal baking properties of frozen doughs. This work shows, however, that breads with acceptable and fresh-like properties can be produced from prefermented frozen doughs. The profitability and flexibility of frozen baking can in this way be increased.

The preparation of prefermented frozen doughs requires some modifications to be made to fresh baking:

1. Prefermentation time should be shorter than fermentation time in fresh baking

2. The amount of water not absorbed in dough should be decreased by
   a) reducing the total water content of dough
   b) adding ingredients with high water absorption ability (for example, hydrocolloids).

Shorter prefermentation time and reduced water content reduce the great demand that frozen baking normally puts on flour quality. Thus, the baking properties (deterioration during frozen storage) of partly prefermented frozen doughs are almost independent of the flour quality. However, yeast viability after frozen storage is still needed for high quality breads baked from partly fermented frozen doughs, because the needed thawing/ postfermentation time was from 1.5 to 2 hours.

Figure 26 summarizes the observed phenomena behind the deterioration of frozen doughs. According to the present studies the major changes are caused by ice crystals, which physically break gluten and yeast cells, but also cause redistribution of water. Thus, thawed dough contains water-poor and water-rich areas. The extensibility of gluten is highly dependent on the water content. Although the amount and size of ice crystals will largely be determined by the freezing step, the crystals have a strong tendency to grow during frozen storage, in a process known as recrystallization. The growth

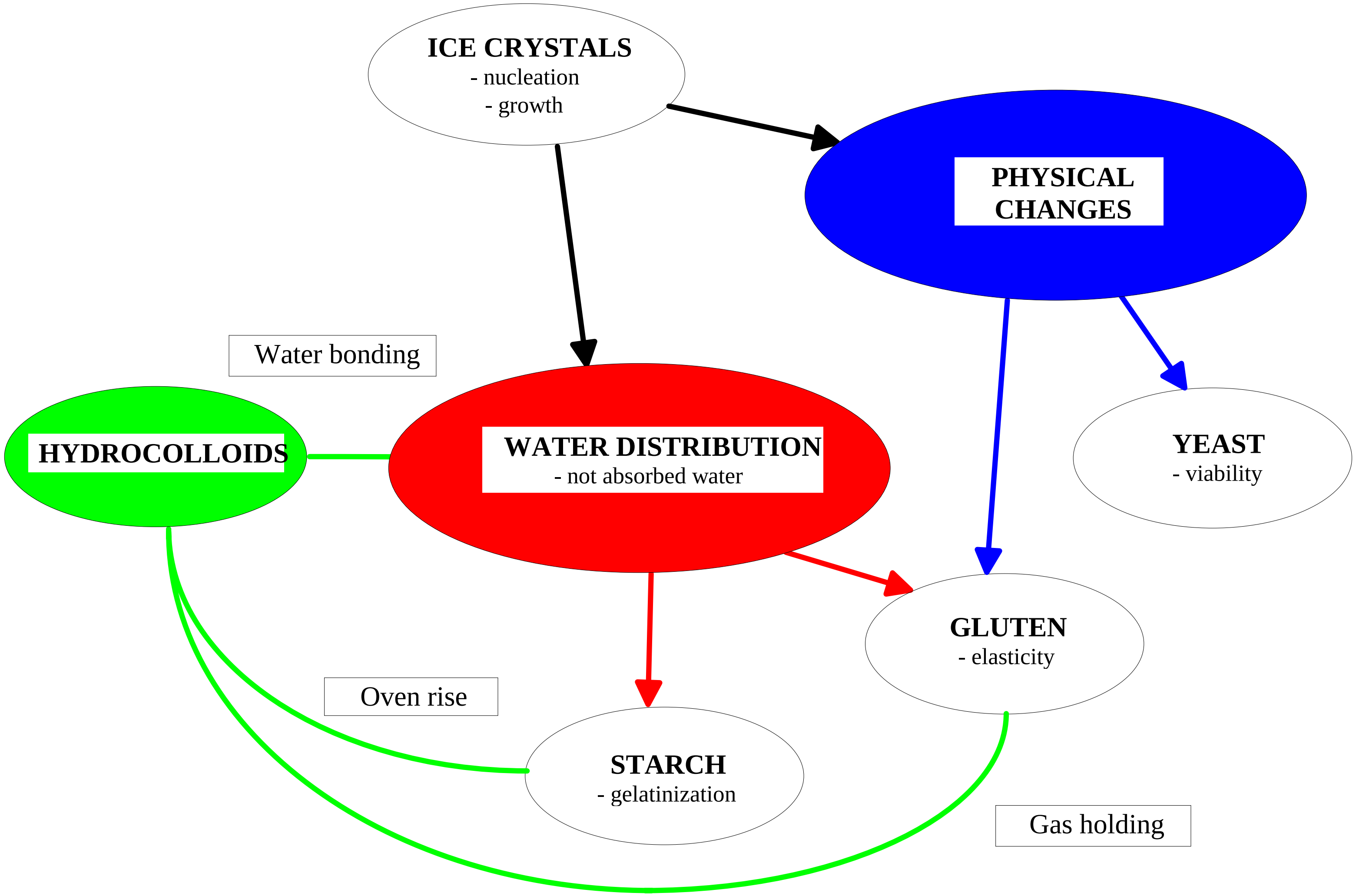

Figure 26. Ice crystal damage in frozen doughs and the effectiveness of hydrocolloids in preventing deterioration.

of ice crystals during frozen storage is dependent on the amount of water absorbed in the surroundings. Thus, the amount of water not absorbed by the system has to be minimized by reducing water content or adding water absorbing ingredients such as hydrocolloids (Fig. 26).

Pore structure of prefermented frozen dough is another critical factor observed in this study together with water distribution in determining baking quality. If the fermentation extends till the stage where the stability of air cells is dependent on the liquid phase stability before freezing (Gan et al. 1995), the structure will collapse before baking, resulting in flat breads. Shorter prefermentation time and reduced water content were observed to increase the amount of small air bubbles, which have a thicker wall around them (starch-gluten matrix). Thus, the air walls are not so sensitive to ice crystals damages.

This study showed that, with the use of modified conditions, breads having the same properties as fresh baked products can be produced from prefermented frozen doughs. Although the experiments were carried out under specific conditions, which included relatively long thawing and postfermentation time, the findings are relevant to all types of frozen dough baking, thus providing the information needed for developing frozen doughs that can be baked without a separate thawing step and without quality deterioration in programmed ovens. Pore size distribution, water redistribution, and consequent extensibility of the dough will determine the loaf volumes and other baking properties of frozen prefermented doughs.

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