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Effect of temperature fluctuations during frozen storage on the quality of potato tissue (cv. Monalisa)

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Abstract Results are presented on the effect of different ranges of temperature fluctuation (-24 to -18 °C, -18 to -12 °C, -12 to -6 °C, -24 to -12 °C and -18 to -6 °C) on the compression, shear and tension parameters of packed and unpacked frozen potato tissue. The initial temperature, duration and number (2, 4, 8, 16, 24 and 32) of fluctuations were varied. The highest parameter values occurred in samples subjected to fluctuations between -24 °C and -18 °C, and the lowest values in the range -18 to -6 °C. The mechanical strength of the frozen tissue decreased with an increase in the number of fluctuations and in most cases was lower in the packed samples. Moisture loss was greatest in the -18 to -6 °C range for pre-packed samples. Changes in the maximum compression force, as a measure mechanical damage, showed the greatest level of significance.

Key words Freezing · Temperature fluctuations · Rheological parameters · Structure · Potato

Introduction

Frozen vegetable tissue is unstable during storage and the quality deteriorates to a variable extent depending on the type of product and the storage temperature [1, 2]. Loss of quality is caused by physical and chemical changes taking place in the product as the result of recrystallization and sublimation of water. Canet [3] reported that the effect of recrystallization during storage and distribution of frozen products cancels out the beneficial effects of fast freezing.

Spain

The number, size, shape and orientation of the ice crystals alters during storage, resulting in successive melting on the surface of smaller crystals and recrystallization on larger ones.

Long periods of frozen storage are not necessarily harmful if a constant low temperature is maintained. Brown [4] examined the effect of constant low temperature on asparagus and green beans stored at -30 °C for 4-6 years and found no appreciable change in flavour or aroma, nor any visible increase in cell wall damage. Canet [5] reported that a number of mechanical properties of blanched and frozen potatoes were unaffected by storage at -25 °C. Similarly, Monzini et al. [6] showed that the cell structure of potato tissue did not deteriorate during 6 months' storage at -20 °C (± 1 °C). Fennema et al. [7] and Zaritzky et al. [8] detected no ice crystal growth below -10 °C.

The sublimation of water requires a reduction of the temperature and partial vapour pressure in the product, to values below those of the triple point of water (0.01 °C and 610.7 Pa for pure water, respectively). A supply of heat is also needed (2800 J/g of ice at 0 °C) for the change of phase [9]. A sufficient increase in temperature can occur if products are not properly packed, resulting in dehydration and accumulation of extracted water in the form of frost on the inside of the container. Excessive dehydration produces loss of weight and "freezer" burning on the product surface, which have negative effects on quality [3]. Reid [10] has noted that although temperature fluctuations produce temperature gradients with a periodic reversal in direction, this does not mean that moisture migrates in one direction then returns to the initial location. The structure, number of interfaces, and moisture concentration in different regions of the product all affect the way in which water moves towards, the surface, and from there to the surrounding atmosphere.

Recrystallization and surface drying are accelerated by temperature fluctuations during frozen storage, although the literature contains few references to quantification of the effects on vegetable tissue. Sebök et al. [11] studied the formation of agglomerates and blocks during storage of various vegetables and fruits and found that their formation

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was strongly influenced by oscillations in the storage temperature, as small as ± 0.2 to ± 1.5 °C.

The aim of this study was to investigate the effect of different ranges and frequencies of temperature fluctuation on compression, shear and tension parameters of frozen potato tissue, simulating frozen storage conditions. The experiments were performed on pre-packed and unpacked samples in order to take into account the influence of packing on tissue quality. Scanning electron microscopy (SEM) revealed the extent of the structural damage caused by such fluctuations.

Materials and methods

Test material. The potatoes (*Solanum tuberosum*, L., cv. Monalisa) same from Segovia, Spain and had weights within the confidence interval ($153.839 \le \mu \le 186.569$) and specific weights (g/cm³) within the interval ($1.0635 \le \mu \le 1.0796$); $P \le 0.01$. The material was stored at 4 °C and 85% relative humidity.

Freezing, thawing and temperature fluctuations. Loose potatoes were frozen by blasting with liquid nitrogen vapour in an Instron program-

Fig. 1 Thermal history of the product and air temperature in unpacked samples subjected to 4 and 16 fluctuations in the range -18 to -6 °C

mable chamber (model 3119-05, -70 °C/+250 °C) at -60 °C (-2 °C/min) until the temperature at the thermal centre reached -18 °C. Once -18 °C was attained, the chamber temperature was maintained at this temperature until lowered or raised to the minimum temperature specified for the fluctuations, i.e. -24, -18 and -12 °C. The latter were chosen as starting temperatures for fluctuations, as they represent the storage temperatures at different phases of the cold chain (production, -24 °C; transport, -18 °C; and distribution and sale, from -18 to -12 °C). Once all the fluctuations specified for each treatment pattern were completed, the product was thawed by blasting with air at +20 °C. For the pre-packed units, polyethylene bags were used, sealed under slight vacuum (-500 millibar) on a Multivac packing machine. Air and product temperatures, were monitored by K-type thermocouples using hardware and software systems which permitted real-time data gathering, storage and calculation of freezing rates [12].

Figure 1 shows the thermal history of the product and fluctuations in the air temperature in two fluctuation series performed between -18 and -6 °C on unpacked potatoes.

Rheological parameters. Compression, shear and tension tests were performed on an Instron food testing instrument, model 4501 (Instron, Canton, Mass., USA) using a 5-kN-load cell and Instron series IX software. Uniaxial compression (n = 10) and shear mechanical tests

100 800 80 700 Fc (N); Ft*10² (N) 60 600 ŝ 500 ŝ 40 400 300 20 200 100 0 2 Τ2 T3 4 8 16 24 32 Number of temperature fluctuations 📕 Fc 🔲 Fs 🗌 Ft

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Fig. 2 Effect of number of temperature fluctuations on rheological parameters and moisture content: T_1 fresh control, T_2 unpacked frozen control, T_3 packed frozen control

Table 1 Effect of temperature fluctuation range on frozen tissue. Values are means (n = 120). Different letters in the same column indicate significant differences

Range of fluctuation	Compression			Shear			Tension				
	<i>F</i> _c (N)	Ec (MPa)	Uc (µJ/mm ³)	<i>Fs</i> (N)	Gs (kPa)	Us (µJ/mm ³)	F_t (N)	<i>E</i> _t (MPa)	Ut (µJ/mm ³)	D _t (mm)	Mo (%)
−24 to −18 °C	330.45a	1.80a	152.06a	45.06a	7.07a	126.26a	13.65a	1.24a	67.24a	13.43a	69.15a
−18 to −12 °C	299.29b	1.73a, b	149.12a	44.26a	6.53b	122.46a	12.46b	1.13b	61.65a, b	13.25a	68.33b, c
-12 to -6 °C	289.07b	1.66b, c	139.87b	41.91b	6.43b	120.32a	11.24c	1.00c	57.14b, c	13.15a	67.96c
-24 to -12 °C	291.01b	1.62c, d	140.87b	41.74b	6.59a, b	121.86a	11.10c	1.12b	52.29c, d	12.32b	68.24c
-18 to -6° C	261.61c	1.55d	124.79c	41.09b	6.22b	112.79b	10.15d	0.95c	48.10d	11.71b	66.91d
LSD, 99%	11.9220	0.0993	7.6903	2.2359	0.4928	6.6847	0.9304	0.0771	6.2533	0.7728	0.8832

(n = 10) were carried out on cylindrical specimens (diameter, 25.4 mm; height, 10 mm). Tension tests (n = 10) were conducted on 5-mm-thick dog-bone-shaped specimens (dimensions: 75 mm long, 20 mm wide at the retaining ends and 8 mm wide at the neck). Samples were

compressed at a deformation rate of 200 mm/min to determine the maximum compression force (F_c), apparent modulus of elasticity (E_c) and energy required for breaking per unit of volume (U_c). The shear test was performed using a shear cell [5] at a deformation rate of

Table 2 Effect of number temperature fluctuations and packaging in the temperature fluctuation range -24 to -18 °C. T_1 fresh control, T_2 frozen control without packaging, T_3 frozen control with packaging,

NP unpacked samples, P pre-packed samples. Means (n = 10). Different letters in the same column indicate significant differences

Number of fluctuations	Compression			Shear			Tension				
	<i>F</i> _c (N)	<i>E</i> _c (MPa)	<i>U</i> _c (μJ/mm ³)	Fs (N)	Gs (kPa)	Us (μJ/mm ³)	F_t (N)	<i>E</i> _t (MPa)	U_t (µJ/mm ³)	D _t (mm)	$egin{array}{c} M_o \ (\%) \end{array}$
Fresh (T1) Frozen (T2) Frozen (T3) 2 (NP) 2 (P) 4 (NP) 4 (P) 8 (NP) 8 (P) 16 (NP) 16 (NP) 16 (P) 24 (NP) 24 (P)	697.89a 425.47b 375.26b-d 387.43b, c 369.07b-e 366.53b-e 353.03c-f 360.73b-e 308.35e-g 348.32c-f 290.58f, g 330.99c-f 289.61f, g	4.76a 3.13b 2.49c 2.40c, d 1.92e, f 2.07d, e 1.86e-g 1.79d 1.77e-g 1.70f, g 1.67f, g 1.67f, g	411.16a 330.46b 222.46c 198.66c, d 150.86e-h 177.78d, e 140.37f-h 173.92d-f 138.72g, h 166.29d-g 135.90g, h 149.32e-h 129.99h	92.60a 60.17b 53.22b, c 51.96c, d 47.24c-f 49.97c-e 44.95d-g 48.60c-f 43.35e-g 46.53c-f 41.27f, g 44.11e-g 41.01f, g	16.96a 11.35b 9.89b, c 9.21b-d 7.33d-g 8.81c-e 7.19d-g 8.14c-f 7.10d-g 6.93e-g 6.26f, g 6.24f, g 6.04f, g	247.26a 163.25b 158.43b, c 147.99b-d 135.87c-e 138.21c-e 125.66d-g 136.09c-e 120.62e-g 130.77d-f 119.31e-g 123.39e-g 110.00f, g	25.86a 19.36b 14.99c-e 17.60b, c 13.45e, f 16.77b-d 12.87e, f 15.17c-e 12.06e, f 14.82c-e 11.00f 14.62c-e 11.01f	3.34a 1.70b 1.31b-f 1.58b, c 1.27c-f 1.53b, c 1.25c-f 1.44b-d 1.11d-f 1.35b-e 1.04d-f 1.26c-f 0.97e, f	60.37a 100.95b 73.14c 77.37b, c 71.33c 76.60b, c 70.35c 72.35c 61.85c 71.09c 62.72c 63.01c 60.10c	10.45a 12.23a, b 14.01b 14.38b 14.09b 14.24b 13.98b 13.23b 13.75b 13.75b 13.35b 13.04b 12.90a, b	81.81a 72.87b 71.21c, d 72.62b, c 70.67d-f 70.96d, e 70.01d-g 69.23f, g 69.23f, g 69.46e-g 68.67g, h 68.98g 66.74i 66.88g, h
32 (NP) 32 (P) LSD, 99%	312.86d-g 247.98g 66.0684	1.59f, g 1.52g 0.3720	143,65e-h 118.78h 35.1555	43.12e-g 38.63g 7.8460	5.77g 5.93f, g 2.2526	121.52e-g 105.69g 24.2353	13.67d-f 10.86f 3.1197	1.19c-f 0.94f 0.3990	60.93c 59.19c 25.5654	12.86a, b 12.16a, b 2.5193	66.27i 67.35h, i 1.5869

Table 3 Decrease (%) in maximum compression breaking force with the corresponding number of temperature fluctuations with respect to samples frozen and thawed without fluctuations

Number of fluctuations	−24 to −18 °C		–18 to –12 °C		−12 to −6 °C		−24 to −12 °C		−18 to −6 °C	
	Unpacked	Packed	Unpacked	Packed	Unpacked	Packed	Unpacked	Packed	Unpacked	Packed
2	8.94	1.64	7.00	16.37	10.54	22.03	12.25	21.31	27.05	26.86
4	13.85	5.92	15.59	20.00	19.89	25.41	24.40	24.72	29.77	30.04
8	15.21	17.83	21.53	26.15	24.20	29.66	26.58	40.74	32.68	32.11
16	18.13	22.56	24.57	34.78	33.11	31.03	27.65	31.25	36.23	41.61
24	22.20	22.82	26.24	35.20	33.16	33.00	28.89	35.82	37.03	46.71
32	26.46	33.91	38.76	39.03	35.16	37.76	31.81	23.90	38.65	47.66

400 mm/min to give the maximum shear force (F_s) , modulus of rigidity (G_s) and shear energy required per unit of volume (U_s) . The tension test was performed at a deformation rate of 100 mm/min, using a cell consisting of two compressed-air clamps (1.5 bar) fitted to the specimen necks over filter paper to prevent slipping and cracking. This gave the maximum tension force (F_t) , apparent modulus of elasticity (E_t) , energy required for breaking per unit of volume (U_t) and maximum deformation (D_t) . Uniform stress was applied over a length of 30 mm.

Moisture content. Determinations were made by output power at 70% drying samples in a Philips microwave oven (model M-718, 700 W) set at 70%. Weighing was performed on a Mettler AT 100 analytical balance with metering precision of 0.00001 g. The initial weight of each sample was approximately 5 g. Samples were weighed every 5 min until a constant weight was attained. Ten determinations were performed for each treatment.

Tissue structure. Tissue structure was examined by output power at 70% scanning electron microscopy (SEM) using a Hitachi microscope, model S-2500. Tissue samples were fixed in 50% or 70% ethyl alcohol (90 ml), glacial acetic acid (5 ml), formol (5 ml) for 2 h and dehydrated in an increasing series of ethanol from 70% to 100%: a 15-min immersion in each ethanol concentration (70%, 80% and 90%) and 2 times 1 h in 100% ethanol. Finally, the specimens were preserved in acetone until processed in a critical-point drier, then mounted and sputter-coated with platinum (400 Å) in a P-S1 diode sputtering system

metallizer. Photomicrographs were taken with a Mamiya camera using Ilford FF-4 6 \times 9-cm film. Films were processed following the standard method; magnification \times 78 (1 cm = 130 µm).

Statistical analysis. Multifactorial analysis of variance was performed and the means compared by least significant difference (LSD, 99%), using the Statgraphics (v. 5.0) statistical package [13].

Results and discussion

Multifactorial analysis of variance showed that the temperature fluctuation range to which the frozen tissue was subjected (Table 1) significantly affected ($P \leq 0.01$) all rheological parameters and the moisture content of the thawed tissue. The highest parameter values were found in samples subjected to fluctuations in the range -24 to -18 °C, and the lowest in samples subjected to fluctuations in the range -18 to -6 °C. The differences between the other experimental ranges (-18 to -12 °C, -24 to -12 °C and -12 to -6 °C) were less significant, although the extent of the mechanical damage to the frozen tissue, in ascending order, was -24 to -18 °C < -18 to -12 °C < -24 to



Fig. 3 1 Fast-frozen tissue (-2 °C/min) with slow thawing (+0.5 °C/min). 2 Fast-frozen tissue (-2 °C/min), subjected to 4 fluctuations and slow thawing (+0.5 °C/min). 3 Fast-frozen tissue (-2 °C/min), subjected to 32 fluctuations in the range -18 to -6 °C and slow thawing (+0.5 °C/min) (1 cm = 130 μ m)

-12 °C < -12 to -6 °C < -18 to -6 °C, i.e., it increased where temperatures fluctuation ranges were higher or broader. Tissue dehydration (Table 1) was also significantly greater where the temperature fluctuations range limits were higher or more widely separated. Of the rheological parameters, compression was the most sensitive to temperature fluctuation showing the greatest level of significance. The shear test parameters showed the lowest significant difference.

Figure 2 shows the effect of the number of fluctuations on rheological parameters and moisture content. Again, the effect was significant ($P \leq 0.01$) in all the parameters considered, which decreased as the number of fluctuations increased. The compression energy required for breaking was less with 24 fluctuations than with 32, although these values were not significantly different. The compression parameters showed the greatest significant difference. Of all the parameters, maximum force changed with the number of fluctuations with the greatest level of significance, only showing no significant difference between 16 and 24 fluctuations. The decrease in moisture content was significant from the 8th fluctuation upwards (Fig. 2 d).

The effect of the packaging was significant ($P \le 0.01$) for moisture content and all the rheological parameters except maximum tension deformation. In pre-packed tissue, mechanical strength was lower and dehydration greater. Once again, it was the compression parameters which indicated this effect with the highest level of significance.

There were no significant interactions between effects on the parameters considered, which means that each effect was independently significant. Table 2 shows comparisons of the average results when the number of fluctuations and packaging for the -24 to -18 °C temperature fluctuation range were considered. There were significant differences between the rheological parameters and moisture content in fresh tissue (Table 2, T1) and processed tissue. The rheological parameters and moisture content in unpacked frozen tissue thawed without fluctuations (Table 2, T_2) were higher than those measured in packed frozen tissue thawed under identical conditions (Table 2, T₃). The differences between the two frozen controls were also significant for the apparent modulus of rigidity and breaking energy under compression, maximum tension force and energy required for breaking under tension, and moisture content. Structural damage caused by freezing was greater in pre-packed tissue, which may be attributed to the slower freezing rate [14]. Freezing of unpacked samples, in liquid nitrogen at -60 °C, proceeded at a maximum rate of -2 °C/min, whereas the average freezing rate in comparable packed samples was -1.25 °C/min.

Within this temperature fluctuation range, maximum compression force values did not differ significantly from the unpacked frozen control until after 16 fluctuations. The tension parameters in both packed and unpacked samples did not differ significantly from the controls until after 8 or 16 fluctuations. All other rheological parameters differed significantly from the controls after only 2 or 4 temperature fluctuations.

Tension energy in packed samples decreased with temperature fluctuations, but not significantly so. The behaviour of maximum breaking deformation under tension was different. Values of this parameter were higher in the frozen controls (Table 2, T_2 and T_3) than in the fresh sample (Table 2, T_1), indicating loss of tissue elasticity on freezing. The highest maximum deformation value was registered in samples subjected to 2 fluctuations, decreasing with increasing numbers of fluctuations up to 32. This indicates softening of the tissue after 4 fluctuations. Moisture content was higher in unpacked samples up to 8 fluctuations; however, in all the other fluctuation ranges tested, tissue moisture content was higher in unpacked samples regardless of the number of fluctuations.

Table 3 shows the percentage decrease, with respect to controls T₂ and T₃, of maximum breaking compression force as the number of fluctuations increased, for all five ranges considered. It showed the highest level of significance for the three effects studied. Except for packed samples subjected to a fluctuation range of -24 to -18 °C, the decrease in maximum compression force was very fast in the first 2 or 4 temperature fluctuations, slowing down thereafter. As few as 4 fluctuations were enough to cause appreciable damage to the tissue structure. The damage caused by fluctuations was greater in the packed samples, and likewise greater in those fluctuation ranges coming close to the zone of maximum ice crystal formation in the freezing process. Maximum compression force in packed samples subjected to fluctuations in the range -24 to -12 °C was greater after 16 fluctuations than after 8. This could be due to dehydration of the tissue, although such an increase in maximum force was not found in the ranges -12 to -6 °C or 18 to 6 °C, where moisture loss was even greater.

The results show that recrystallization caused by temperature fluctuations in frozen stored tissue results in more mechanical damage where the fluctuation range, and hence the storage temperature of the product, is higher. At -12 to $-6 \,^{\circ}$ C and -18 to $-6 \,^{\circ}$ C, the tissues attained temperatures very close to the zone of maximum ice crystal formation. Fluctuations of up to $-6 \,^{\circ}$ C accelerated melting of small ice crystals, thus increasing the amount of available water, which re-froze immediately, causing an increase in the size but a decrease in the number of ice crystals. Even though the ranges were broader, fluctuations of -24 to $-12 \,^{\circ}$ C caused less mechanical damage than did fluctuations of -12 to $-6 \,^{\circ}$ C.

The high degree of structural deterioration resulting from temperature fluctuations in packed samples may have been due to sublimation of ice on the sample surface. This caused greater drying of the tissue, as the moisture content results confirmed. The damage caused by recrystallization and sublimation was cumulative.

Photomicrographs 2 and 3 (Fig. 3) show potato tissue subjected to 4 fluctuations in the range -24 to -18 °C and 32 fluctuations in the range -18 to -6 °C, respectively. Photomicrograph 1 shows potato tissue frozen under identical conditions and thawed without fluctuation. On com-

parison more broken cell walls are seen in 2 than in 1. Photomicrograph 3 shows structural damage caused by 32 temperature fluctuations of -18 to -6 °C. There is absolute loss of cell integrity and the cells appear contracted owing to intense tissue dehydration.

The results demonstrate that by ascertaining the effect of temperature fluctuations at each stage of the cold chain, it is possible to estimate cumulative loss of texture quality in a product during storage and distribution. The rheological behaviour of the vegetable structure throughout the entire freezing process can be characterized. In conclusion, the combined effect of time and temperature in the course of storage is cumulative and irreversible and can determine the textural quality of a frozen product.

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