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Oscillatory Properties of Fresh and Frozen/Thawed Mashed Potatoes as Modified by Mixtures of Amidated Low-Methoxyl Pectin and Xanthan Gum

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ABSTRACT

Freezing and thawing of mashed potatoes has a detrimental effect on their physical and water-holding properties. This study deals with the ability of mixtures of amidated low-methoxyl (ALM) pectin and xanthan gum (XG) to ameliorate these effects in fresh (F) and frozen/thawed (F/T) mashed potatoes. Viscoelastic properties were monitored by oscillatory measurements. A parameter that characterizes the fluid behaviour for the nonlinear viscoelastic range (α, fluid-like relative angle) was also determined. The effect of ALM and XG concentration on the dynamic rheological parameters was studied using response surface methodology (RSM). A central composite rotatable experimental design was used with ALM concentration ranging between 1.5 and 4.5 g kg^{-1} and XG concentration ranging between 0.5 and 2.5 g kg^{-1} as independent variables. The effects were highly dependent on the levels of ALM and XG added, although the effect of XG concentration on the oscillatory measurements was more significant. When comparing the effect of processing on a particular formulation, although F samples presented a spongier, more rigid structure over the linear viscoelastic range (higher elastic modulus values (G')) than their F/T counterparts, they were more fluid-like after breakdown. For F mashed potatoes, the optimum condition for α showing maximum fluid-like character after breakdown was found at 3.32 g kg^{-1} ALM pectin and 1.65 g kg^{-1} XG, whereas the response surface for α was saddle-shaped after freezing and thawing. For F/T mashed potatoes, the optimum condition for δ showing maximum structural weakening in the linear viscoelastic range was found at 3.06 g kg^{-1} ALM pectin and 2.38 g kg^{-1} XG. In spite of the fact that no enhancement of oscillatory properties was observed, this approach may have potential for designing F and F/T mashed potatoes with specified dynamic properties.

Keywords: cryoprotectant mixtures, processing, puréed cooked potatoes, response surface, viscoelastic properties
Abbreviations: **ALM**, amidated low-methoxyl pectin; **DA**, degree of amidation; **DM**, degree of methylation; **F**, fresh mashed potatoes; **F/T**, frozen/thawed mashed potatoes; **HM**, high-methoxyl pectin; **LM**, low-methoxyl pectin; **LSD**, least significant difference; **RSM**, response surface methodology; **XG**, xanthan gum

INTRODUCTION

Freezing and thawing of foods can have a detrimental effect on their sensory and water-holding properties as a result of physical disruption of cells or cell components or changes in the structure of certain macromolecules (Downey 2002, 2003). The quality of frozen foods is influenced by the size and the number of ice crystals produced during freezing. It is well known that the formation of large ice crystals during freezing negatively affects sensory properties and texture of frozen foods. One strategy to minimize damage arising from freezing and thawing is to incorporate compounds that interact with water and offer protection against the deleterious effects of thawing in particular, i.e., cryoprotectants (Sych *et al*. 1990), which have been reported to slow down the rate of ice crystal growth and alter crystal shapes (Bolliger *et al*. 2000).

Hydrocolloids are widely used in the ice-cream and frozen dessert industries to limit ice crystal size and protect the product from heat shock and dryness. Ice crystals may be smaller or not depending on the hydrocolloid's ability to bind water and to increase the viscosity of the mixture (Regand and Goff 2003). Amidated low-methoxyl (ALM) and high-methoxyl (HM) pectins were added at five different concentrations to fresh and frozen/thawed mashed potatoes (Alvarez *et al*. 2008, 2009). In this study, authors found that ALM pectin exhibited water-holding capability, whereas HM did not.

Buyong and Fenema (1988) reported that in amounts of less than 2% (w/w), hydrocolloids such as carboxymethylcellulose, sodium alginate, guar gum, locust bean gum and carrageenans reduced the amount of ice by less than 3%, while gelatine had no effect at all. Increasing the concentration of hydrocolloids reduced the amount of water that could be frozen. Non-gelling hydrocolloids (i.e. xanthan) inhibit the formation of elongated ice crystals in frozen desserts, preventing growth in crystal size at low temperatures in abusive storage with temperature fluctuations (Fernández *et al*. 2007).

Starch and pectin are among the most important plant polysaccharides. Pectin, found for example in fruits (apples, lemons) and other fibrous sources (sugar beet), as the intercellular cement within the plant cell wall, consists predominantly of sequences of galacturonic acid with occasional interruptions by rhamnose residues (Ross-Murphy *et al*. 1998). Pectins with a low degree of esterification gel with divalent ions. Nowadays, there is demand for functional foods. The intake of pectin has been reported to be healthful for people at risk of cardiovascular diseases. Moreover, this is a fibre that is known to be able to reduce plasmatic cholesterol.

Amidated low methoxyl (ALM) pectins have been reported to be suitable for enhancing mechanical properties of restructured fish products (Ramírez *et al*. 2007). For its part, xanthan gum (XG) induces cooking and cooling stability in wheat flour and improves the freeze/thaw stability of

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starch-thickened frozen foods. Water-binding agents, including hydrocolloids such as XG and guar gum, offer an alternative for improving bread quality both in frozen storage and in thawing by microwave. Increased water-holding capacity is desirable in the microwave process to hinder rapid water loss and render the product less tough (Mandala 2005).

Mashed potatoes as prepared in this study are themselves combined systems of native potato starch–denatured milk protein–water–salt, and therefore complex interactions can influence the properties of these mixtures. There are few published articles about the effects of hydrocolloids on the consistency of mashed potatoes which have been frozen and directly thawed using microwave appliances (Alvarez *et al*. 2007a). Gelatinized starch systems are complex materials and worth analysing given that they are highly filled suspensions of swollen deformable particles immersed in an amylase network (Navarro *et al*. 1997).

The starch paste is subjected to both thermal and mechanical treatment, thus making it difficult to relate viscous behaviour to the single-parameter viscoamylograph measurement (Ahmed and Ramaswamy 2006a). Foods can exhibit viscous or elastic behaviour or a combination of the two, which are generally recognized as viscoelastic properties. The method most commonly used to study the viscoelastic property of foods is oscillatory viscometry, which provides more details about the rheological behaviour of foods than conventional rheometric parameters such as the flow-behaviour index or consistency coefficient (Ahmed and Ramaswamy 2006b). Small-amplitude oscillatory (dynamic) tests allow researchers to relate dynamic rheological parameters to the molecular structure and glass transition temperatures of the sample (Gunasekaran and Ak 2000).

The theory for small stresses and deformations corresponding to the linear viscoelastic range is well developed (Kokini *et al*. 1995). While assays performed within the linear range are not destructive, elastic or viscoelastic materials obtained outside this range may suffer irreversible structural changes. Thus, data obtained within the nonlinear range cease to be material constants because they are greatly influenced by the test apparatus and the chosen experimental conditions (Navarro *et al*. 1997). In real production processes, viscoelastic fluids are subjected most of the time to high shear deformation conditions which are related to the nonlinear viscoelastic behaviour of the material.

Therefore, considering the technological interest in polysaccharide mixtures, the aim of this work was to study the linear and nonlinear viscoelastic behaviour of both F and F/T mashed potatoes with added mixtures of ALM pectin-XG, in order to determine how the presence of gelling (pectin) and non-gelling (xanthan) hydrocolloids modifies the viscoelastic behaviour of mashed potatoes and to investigate the probable existence of synergistic or incompatibility effects. It is expected that the rheological behaviour of the systems studied will provide useful information for possible technological applications in mashed potato-hydrocolloid systems.

MATERIALS AND METHODS

Test material

The potatoes used were fresh tubers (cv. 'Kennebec') from Aguilar de Campoo (Burgos), Spain cultivated in 2006 and having weights (g) within the confidence interval ($95.69 \leq \mu \leq 111.81$) and specific weights (g cm^{-3}) within the interval ($1.0721 \leq \mu \leq 1.0787$); $P \leq 0.01$. Raw material was stored in a chamber at 4 ± 1°C and 85% relative humidity throughout the experiment (Smith 1987; Nourian *et al*. 2003).

Preparation of mashed potatoes

Tubers were manually washed, peeled and diced. Mashed potatoes were prepared in 650-g batches from 607.7 g kg^{-1} of potatoes, 230.8 g kg^{-1} of semi skimmed in-bottle sterilized milk (calcium content, 0.12 g kg^{-1}; fat content, 15.5 g kg^{-1}), 153.8 g kg^{-1} of water, and 7.7 g kg^{-1} of salt (NaCl) using a Thermomix TM 21 apparatus (Vorwerk España, M.S.L., S.C., Madrid, Spain). Hydrocolloids were added at this point; the appropriate amount of ALM and XG was added to the rest of ingredients in the form of a dry powder and all the ingredients were then cooked for 20 min at 100°C (blade speed, 100 rpm), and the amount of liquid evaporated was determined by weighing the ingredients before and after boiling. The evaporated liquid was then replaced by an equal weight of boiling water, and the ingredients were again cooked at 100°C for 5 min. The mash was immediately ground for 40 s (blade speed, 2000 rpm) and homogenized through a stainless steel sieve (diameter, 1.5 mm). The final pH of the F mashed potatoes without added cryoprotectants was 6.05.

After preparation, half of each F mashed potato sample was immediately analyzed and the other half was packed in 300×200 mm^2 rectangular polyethylene plastic bags, sealed under light vacuum (−0.05 MPa) on a Multivac packing machine (Sepp Haggenmüller KG, Wolfertschwenden, Germany), and frozen and thawed according to the procedures indicated next.

Cryoprotectants

Amidated low-methoxyl (ALM) pectin (GENU pectin type LM-104 A; pectin was methylated to a degree of 27%, and in addition, a further 20% of the residues was amidated (DA = 20%)) and xanthan gum (XG) (Keltrol F [E]) were donated by Premium Ingredients, S.L. (Girona, Spain). Powders were stored at room temperature. Range-finding experiments were performed at the outset of this work to ascertain the maximum acceptable amount of each biopolymer that could be added to the mashed potato on the basis of flavour, viscosity, and colour (Alvarez *et al*. 2008, 2009; Fernández *et al*. 2008). From these preliminary results, the lower and upper levels of each hydrocolloid to be used in mixtures were set at 1.5 and 4.5 g kg^{-1} for AML and at 0.5 and 2.5 g kg^{-1} for XG. **Table 1** shows cryoprotectant concentrations of the F and F/T mashed potatoes tested, together with the notations used to refer to each of the samples.

Table 1 Notation system for F and F/T mashed potatoes and cryoprotectant contents.

System notation	Description and biopolymer content (g kg^{-1})
F, F/T	F and F/T mashed potatoes without added biopolymers
F-ALM3, F/T-ALM3	F and F/T mashed potatoes with 3 g kg^{-1} added amidated low methoxyl (ALM) pectin
F-XG1.5, F/T-XG1.5	F and F/T mashed potatoes with 1.5 g kg^{-1} added xanthan gum (XG)
F-ALM0.88/XG1.5, F/T-ALM0.88/XG1.5	F and F/T mashed potatoes with 0.88 g kg^{-1} added ALM pectin and 1.5 g kg^{-1} added XG
F-ALM1.5/XG0.5, F/T-ALM1.5/XG0.5	F and F/T mashed potatoes with 1.5 g kg^{-1} added ALM pectin and 0.5 g kg^{-1} added XG
F-ALM1.5/XG2.5, F/T-ALM1.5/XG2.5	F and F/T mashed potatoes with 1.5 g kg^{-1} added ALM pectin and 2.5 g kg^{-1} added XG
F-ALM3/XG0.09, F/T-ALM3/XG0.09	F and F/T mashed potatoes with 3 g kg^{-1} added ALM pectin and 0.09 g kg^{-1} added XG
F-ALM3/XG1.5, F/T-ALM3/XG1.5	F and F/T mashed potatoes with 3 g kg^{-1} added ALM pectin and 1.5 g kg^{-1} added XG
F-ALM3/XG2.91, F/T-ALM3/XG2.91	F and F/T mashed potatoes with 3 g kg^{-1} added ALM pectin and 2.91 g kg^{-1} added XG
F-ALM4.5/XG0.5, F/T-ALM4.5/XG0.5	F and F/T mashed potatoes with 4.5 g kg^{-1} added ALM pectin and 0.5 g kg^{-1} added XG
F-ALM4.5/XG2.5, F/T-ALM4.5/XG2.5	F and F/T mashed potatoes with 4.5 g kg^{-1} added ALM pectin and 2.5 g kg^{-1} added XG
F-ALM5.12/XG1.5, F/T-ALM5.12/XG1.5	F and F/T mashed potatoes with 5.12 g kg^{-1} added ALM pectin and 1.5 g kg^{-1} added XG
F-ALM1.5/XG1.5, F/T-ALM1.5/XG1.5	F and F/T mashed potatoes with 1.5 g kg^{-1} added ALM pectin and 1.5 g kg^{-1} added XG

Freezing and thawing procedures

Mashed potatoes were frozen by forced convection with liquid nitrogen vapour in an Instron programmable chamber (model 3119-05, −70/+250°C) at −60°C until their thermal centres reached −24°C (freezing rate, 1 ± 0.10°C min^{-1}). Air and product temperatures were monitored by T-type thermocouples (NiCr/NiAl; −200 to +1000°C) using the MMS3000™ Multi Measurement System™ (Mod. T4, Commtest Instruments, Christchurch, New Zealand). After freezing, the samples were placed in a domestic freezer for storage at −24°C and left there for at least 1 month before thawing. For microwave thawing, frozen mashed potato samples were unpacked and then thawed in a Samsung M1712N microwave oven (Samsung Electronics S.A., Madrid, Spain). Samples were irradiated for a total of 20 min with output power ratings of 600 W. Samples were first irradiated for 15 min, and then removed from the microwave and stirred manually and gently with a spoon for 1 min to achieve a uniform temperature distribution. Next, the samples were irradiated for an additional 5 min under the same conditions. After thawing, the temperature reached at the product thermal centre was measured in all cases (+50 ± 5°C) (Alvarez *et al*. 2005).

Heating of samples

All the F and F/T samples were brought up to 55°C by placing them in the Hetofrig CB60VS water bath (Heto Lab Equipment A/S, Birker.d, Denmark), where again water and product temperatures were monitored by T-type thermocouples using a hardware and software system developed with the LabWindows/CVI package (National Instruments Spain S.L., Madrid, Spain) for the automation of the thermal process control (Rico *et al*. 1995). Sample testing temperature was 55°C, as previous studies showed that this is the preferred temperature for consumption of mashed potato (Alvarez *et al*. 2005).

Oscillatory rheological measurements

Small amplitude oscillatory shear experiments (SAOS) were carried out with a controlled stress rheometer (Bohlin CVR 50, Bohlin Instruments, Gloucestershire, UK) at 55°C with smooth plates (40 mm diameter and 2 mm gap) and a solvent trap to prevent water evaporation. Samples were allowed to relax for 5 min before conducting rheological measurements such as equilibration time after loading the sample on the sensor system. Temperature control was carried out with a Peltier Plate system (-40 to +180°C; Bohlin Instruments, Gloucestershire, UK).

From stress sweeps, the linear viscoelastic domain for each sample was determined at 1 rad s^{-1} over a strain amplitude range of 10^{-4}-10^{0} which covers the linear and nonlinear ranges of the systems. A sinusoidal shear strain γ was applied to the sample, and a sinusoidal stress wave was also obtained. This shear stress response of the material and the phase shift (δ) between the applied strain and the stress response were monitored every 16 s. The linear viscoelastic range is limited to that amplitude range for which the complex modulus (G^*) is constant. Next, three frequency sweeps were carried out over the range 0.1-100 rad s^{-1} at very small strains, mostly below 10^{-3}. A new sample was used each time for rheological measurements, which are therefore average values of four determinations.

The dynamic rheological parameters used to evaluate the viscoelastic properties of the mashed potatoes were the phase angle (δ), the complex modulus (G^*), the storage or elastic modulus (G'), the loss or viscous modulus (G'') and the complex viscosity (η^*) at 1 rad s^{-1}. A power-law type relationship was verified for the dynamic rheological data of mashed potatoes (Alvarez *et al*. 2004, 2007b). Linear regressions of ln (G') and ln (G'') versus ln (ω) were carried out in each experimental condition and the magnitudes of slope and intercepts were computed from the following equations:

$$G' = K'(\omega)^{n'} \quad (1)$$

$$G'' = K''(\omega)^{n''} \quad (2)$$

where n', ln (K'), n'', and ln (K'') are regression coefficients relating G and ω. In addition, a parameter was defined from the stress sweeps to characterise the fluid behaviour for the nonlinear viscoelastic range (α, fluid-like relative angle), namely the ratio between the phase angle (δ) measured at $\gamma = 2\ 10^{-1}$ to the phase angle corresponding to a pure fluid ($\delta = 90°$) (Navarro *et al*. 1997). All the rheological measurements in each experimental combination were carried out in duplicate. For each replicate, the preparation of mashed potatoes as described above was repeated twice.

Experimental design and data analysis

The effect of ALM and XG concentration on the dynamic rheological parameters used to evaluate the viscoelastic properties of both F and F/T mashed potatoes was studied using RSM. This made it possible to establish optimum ALM and XG concentrations so as to produce mashed potato with different optimum rheological parameters. The upper and lower levels of the two factors ALM and XG concentration were initially based on published information from mashed potatoes (Alvarez *et al*. 2008, 2009; Fernández *et al*. 2008). Statgraphics® software version 5.0 (STSC Inc., Rockville, MD, USA) was used to provide the experimental designs, calculate equations, do statistical evaluation and print out data.

A central composite rotatable experimental design was used with ALM concentration ranging between 1.5 and 4.5 g kg^{-1} and XG concentration ranging between 0.5 and 2.5 g kg^{-1} as independent variables (**Table 3**). In the design, coded variables are related to uncoded ones by equations: $X_1 = (\xi_1\text{-}a)/b$ and $X_2 = (\xi_2\text{-}c)/d$, where X_1, X_2, ξ_1 and ξ_2 are ALM and XG concentrations in coded and uncoded mode respectively; a, c are the central points of the uncoded ALM and XG concentrations ranges studied (3 and 1.5 g kg^{-1}, respectively); b, d are calculated as the difference between mentioned central points and the upper and lower conditions of the uncoded ALM and XG concentrations ranges studied (1.5 and 1 g kg^{-1}, respectively).

The design required 13 variable combinations that were performed in random order, including five replicates of the centre region to generate a quadratic response surface (Myers and Montgomery 1995; Alvarez and Canet 1999a; Alvarez *et al*. 1999; Fernández *et al*. 2006). In both F and F/T mashed potatoes, each combination of concentrations was repeated twice and all the results averaged. The following dependent variables (responses) were analysed by RSM: the phase angle (δ), the storage modulus (G'), the loss modulus (G''), the complex viscosity (η^*), the slopes of storage and loss moduli ($n'$and n'', respectively), the ln of intercepts ln(K') and ln(K''), and the fluid-like relative angle (α).

Data were analysed for coefficient of determination (R^2) value, probability, lack-of-fit test, and regression coefficients (b_0, b_1, b_2, b_{11}, b_{22} and b_{12}). The relationship between the dependent and independent variables was expressed in terms of a second order polynomial equation having the form:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2$$

where Y = response, X_1 = ALM concentration (g kg^{-1}), X_2 = XG concentration (g kg^{-1}) and b_0, b_1, b_2, b_{11}, b_{22}, b_{12} = coefficients (constants) which measure linear, quadratic and interaction effects (Sim *et al*. 2004). The optimum ranges for the two factors tested (ALM and XG concentrations) were interpreted from response surfaces. Thus as possible, stationary points of X_1 and X_2 respectively, which give the optimum response, were calculated, as well as the value of the estimated response at one random point (Myers and Montgomery 1995).

For both F and F/T mashed potatoes, the differences in dynamic rheological parameters for the different ALM/XG concentrations of the central composite design and controls were studied prior to optimization by means of one-way analysis of variance. The least significant difference tests were used with a 99% confidence interval for the comparison of dynamic parameters. The effect of each added ingredient on specific oscillatory parameters was also studied by means of correlation analysis. F and F/T mashed potatoes without and with individually added cryoprotectants at the centre points of the range studied for each biopolymer (i.e. ALM at 3 g kg^{-1} and XG at 1.5 g kg^{-1}) were used as controls to study the effect of ALM and XG mixtures on the rheology of the mashed potatoes.

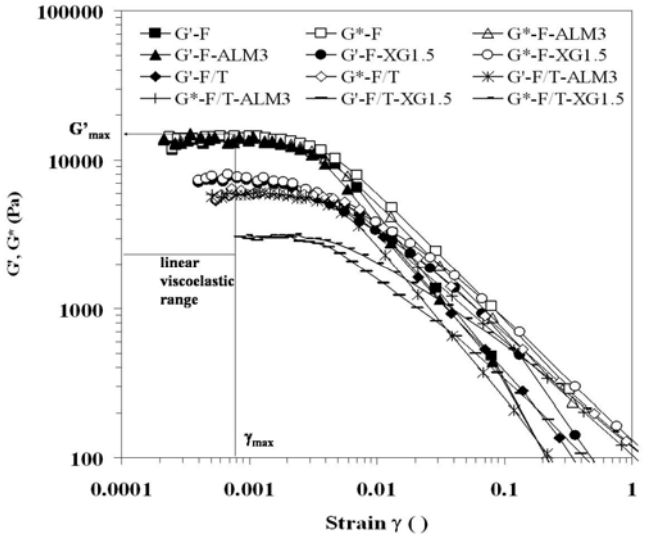

Fig. 1 Typical dynamic curves showing the changes in storage *G*' and complex modulus *G** with strain (frequency 1 rad s^{-1}) for both F and F/T mashed potatoes without added hydrocolloids (G'/G*-F, G'/G*-F/T), for both F and F/T mashed potatoes with 3 g kg^{-1} added ALM pectin (G'/G*-F-ALM3, G'/G*-F/T-ALM3) and for both F and F/T mashed potatoes with 1.5 g kg^{-1} added XG. Log-log scale.

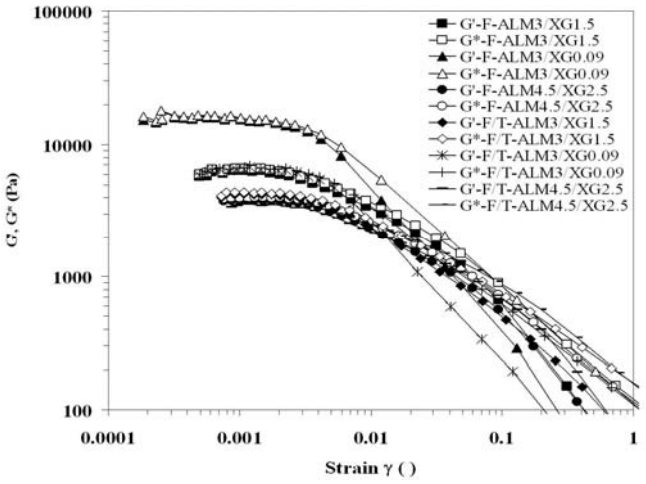

Fig. 2 Typical dynamic curves showing the changes in storage *G*' and complex modulus *G** with strain (frequency 1 rad s^{-1}) for both F and F/T mashed potatoes with 3 g kg^{-1} added ALM pectin and 1.5 g kg^{-1} added XG (G'/G*-F-ALM3/XG1.5, G'/G*-F/T-ALM3/XG1.5), for both F and F/T mashed potatoes with 3 g kg^{-1} added ALM pectin and 0.09 g kg^{-1} added XG (G'/G*-F-ALM3/XG0.09, G'/G*-F/T-ALM3/XG0.09), and for both F and F/T mashed potatoes with 4.5 g kg^{-1} added ALM pectin and 2.5 g kg^{-1} added XG (G'/G*-F-ALM4.5/XG2.5, G'/G*-F/T-ALM4.5/XG2.5). Log-log scale.

RESULTS AND DISCUSSION

Rheological behaviour of mashed potatoes using dynamic oscillatory test

Fig. 1 shows dynamic curves produced by the oscillatory rheometer for both F and F/T mashed potatoes made without added hydrocolloids and with added single biopolymers. In turn, **Fig. 2** shows dynamic curves for both F and F/T mashed potatoes made with three selected added ALM pectin and XG mixtures. Curves represent storage modulus *G*' (elastic component) and complex modulus *G** as functions of strain γ over four decades of strain at a constant oscillation frequency of 1 rad s^{-1}. From **Figs. 1** and **2**, it would appear that in all mashed potatoes, both moduli show similar values at low deformations (< 210^{-3}), indicative of the low contribution of the viscous component *G*" to the viscoelastic properties of the mashed potatoes, although a more exhaustive analysis revealed some differences between samples in that respect. In all the mashed potatoes, *G** values were slightly higher than *G*' over the complete range of strain shown (**Figs. 1, 2**), but when XG was added to the mashed potatoes, either individually or mixed with ALM pectin, the differences between *G** and *G*' values were considerably greater (**Table 2**). Note how the average value of the ratio *G**/*G*' calculated for the complete linear viscoelastic domain ranged between 1.03 and 1.04 in both F and F/T samples with added XG but was lower for the rest of the samples.

This result indicates that the addition of XG increased the contribution of *G*" to the viscoelastic properties of the mashed potatoes in the linear viscoelastic range. Analogously, Rodríguez-Hernández and Tecante (1999) found that xanthan exerted a greater effect on *G*", while i-carrageenan exerted a greater effect on *G*'. This is logical if we consider that XG does not form gels and therefore its presence has a greater impact on the viscose response than on the elastic response.

As noted earlier, the range of strain where the value of *G** is constant corresponds to the linear viscoelastic range of the system (Navarro *et al*. 1997). The linear viscoelastic range is limited by G'_{max} and $\gamma_{max.}$ The linear viscoelastic domain determined for each curve plotted in **Fig. 1** and **Fig. 2** is also shown in **Table 2**. The biopolymer concentration had no great effect on the maximum strain, and similar results were found in all the mashed potato combinations. However, when comparing the effect of processing on a particular formulation, fresh and frozen/thawed samples differed in terms of fragility. It can be seen (**Table 2**) that except for F and F/T, and F-ALM4.5/XG2.5 and F/T-ALM4.5/XG2.5 samples, γ_{max} was lower in the fresh samples than in their F/T counterparts. We may therefore conclude in general that the frozen/thawed mashed potatoes with added selected cryoprotectant combinations can withstand higher

Table 2 Dynamic measurements for linear and nonlinear viscoelastic ranges of both F and F/T mashed potatoes without added hydrocolloids, with single added ALM and XG hydrocolloids, and with some selected added ALM and XG hydrocolloid mixtures.

System notation	G^*_{max} (Pa)	G'_{max} (Pa)	γ_{max} ( )	G^*/G'[a]	α
F	14550 ± 5	14280 ± 45	$7.74\ 10^{-4} \pm 9.01\ 10^{-5}$	1.02 ± 0.00	0.1631 ± 0.0030
F/T	6485 ± 82	6339 ± 47	$7.29\ 10^{-4} \pm 7.11\ 10^{-5}$	1.02 ± 0.00	0.1113 ± 0.0010
F-ALM3	15030 ± 105	14630 ± 70	$3.44\ 10^{-4} \pm 9.87\ 10^{-5}$	1.03 ± 0.00	0.1670 ± 0.0020
F/T-ALM3	6170 ± 95	6070 ± 97	$1.21\ 10^{-3} \pm 1.22\ 10^{-4}$	1.02 ± 0.00	0.1284 ± 0.0100
F-XG1.5	8000 ± 67	7730 ± 175	$6.79\ 10^{-4} \pm 8.31\ 10^{-5}$	1.04 ± 0.00	0.2343 ± 0.0040
F/T-XG1.5	3580 ± 1	3470 ± 8	$2.12\ 10^{-3} \pm 1.79\ 10^{-4}$	1.03 ± 0.00	0.1610 ± 0.0100
F-ALM3/XG1.5	6440 ± 74	6180 ± 71	$7.17\ 10^{-4} \pm 4.11\ 10^{-5}$	1.04 ± 0.00	0.2402 ± 0.0020
F/T-ALM3/XG1.5	4400 ± 7	4300 ± 32	$1.08\ 10^{-3} \pm 7.85\ 10^{-5}$	1.03 ± 0.00	0.1616 ± 0.0004
F-ALM3/XG0.09	16100 ± 75	15800 ± 105	$3.74\ 10^{-4} \pm 3.01\ 10^{-5}$	1.02 ± 0.00	0.1540 ± 0.0040
F/T-ALM3/XG0.09	6950 ± 133	6780 ± 117	$1.20\ 10^{-3} \pm 6.10\ 10^{-5}$	1.02 ± 0.00	0.1501 ± 0.0010
F-ALM4.5/XG2.5	4020 ± 8	3850 ± 10	$1.32\ 10^{-3} \pm 1.03\ 10^{-4}$	1.04 ± 0.00	0.1913 ± 0.0100
F/T-ALM4.5/XG2.5	3730 ± 12	3590 ± 5	$1.07\ 10^{-3} \pm 8.70\ 10^{-5}$	1.04 ± 0.00	0.1213 ± 0.0010

[a] Ratio value corresponds to the average value at the linear viscoelastic range.

strains without undergoing irreversible modifications than their F counterparts.

When dynamic rheological curves are compared in the linear viscoelastic domain, both F and F-ALM3 samples showed high values of *G*' for the linear viscoelastic range of the dynamic assays (**Fig. 1, Table 2**). Moreover, F mashed potatoes with 3 g kg^{-1} added ALM pectin and no more than 0.09 g kg^{-1} added XG (F-ALM/XG0.09 sample) presented the largest *G*' value (**Fig. 2, Table 2**). Large elastic modulus values (*G*') are associated with rigid structures (Edwards *et al*. 1993). Therefore, the addition of 3 g kg^{-1} ALM pectin had the effect of thickening the mashed potatoes as compared to F samples without added biopolymers, corroborating previous findings (Alvarez *et al*. 2009).

Generally, pectin is characterized by its degree of methylation (DM) and in some cases also by its degree of amidation (DA) (Capel *et al*. 2006), as the methoxyl groups can be converted to amide groups, which modify some properties of the pectin gels that are useful in certain applications (Racape *et al*. 1989). It is known that low-methoxyl (LM) pectins usually form gels in the presence of Ca^{2+} ions over a wider range of pH values, with or without sugar (Axelos and Thibault 1991). Gelling is caused by complexation of sections of two different pectin chains with the ions, and the efficient Ca^{2+} binding is an important factor both at high and low pH values (Cardoso *et al*. 2003). However, the gel forming ability of LM pectin is a combination of several mechanisms and under acidic conditions cross-links supported by hydrophobic interactions and hydrogen bonds may also enhance the gel formation of LM pectin (Gilsenan *et al*. 2000). Racape *et al*. (1989) showed that ALM pectins need less calcium for gel formation, and they are also less prone to precipitation at high Ca^{2+} concentrations. ALM pectin used in this study had a DM = 27% and a DA = 20%, which it may possibly favour gelling of mashed in presence of Ca ions, supplied mainly by the added milk. By contrast, it has been shown that amidation has little influence on the sensitivity to Ca^{2+}, but strongly favours acid-induced gelation (Lootens *et al*. 2003).

On the contrary, adding XG at 1.5 g kg^{-1} and 2.5 g kg^{-1} (either alone or combined with ALM) significantly reduced the rigidity of both F and F/T mashed potatoes. The lowest *G*' values were found in the F and F/T mashed potatoes with 4.5 g kg^{-1} added ALM pectin and 2.5 g kg^{-1} added XG (F-ALM4.5/XG2.5 and F-ALM4.5/XG2.5 samples), i.e., corresponding to the highest XG concentration used. The addition of 0 to 2.5 g kg^{-1} XG, then, had the effect of softening the mashed potatoes, monotonically with increasing concentration. Mashed potatoes are systems containing anionic potato starch granules, and so the repelling forces between the negatively charged phosphate groups on the anionic potato starch granules and the negative charges on the XG molecules could be the cause, according to Shi and BeMiller (2002), who concluded that retardation of granule destruction and leaching of amylase seem to be the cause of the reduction in peak viscosity when negatively charged starches are heated in solutions of anionic gums.

For their part, Lai *et al*. (1999) stated that there is a thermodynamic incompatibility between starch polysaccharides and XG, as exclusion effects of swollen granules increase the concentration of other polysaccharides in the continuous phase. The promotion and inhibition of xanthan "weak-gel" rheology by calcium ions has also been studied (Mohammed *et al*. 2007). Authors found an anomalous reduction in gel-like character at Ca^{2+} concentration between stoichiometric and twice stoichiometric equivalence to the carboxyl groups of the polymer, which was tentatively ascribed to partial replacement of intermolecular site-binding of calcium ions by binding to individual carboxyl groups, thus maximizing the degree of complexation. Studies of cation activity in the presence of xanthan (Lambert *et al*. 1985) indicate that the particular effectiveness of Ca^{2+} involves specific site-binding to the carboxyl groups of the polymer.

On the other hand, note that *G*' values were much lower in all the processed samples than in the fresh ones (**Table 2**). This suggests that in all cases, freezing and thawing processes weakened the gel structure of the products in the linear viscoelastic range as compared to F counterparts. Curiously, addition of XG at the highest concentration (2.5 g kg^{-1}) significantly reduced the differences between F and F/T counterparts (for instance see F-ALM4.5/XG2.5 and F/T-ALM4.5/XG2.5 samples, **Table 2**), evidencing the ability of XG to improve freeze/thaw stability.

It has been found that much stronger and more cohesive networks are formed when solutions of XG are frozen and thawed (Giannouli and Morris 2003). During freezing, xanthan chains are forced to align and associate by conversion of solvent (water) to ice crystals. The forced associations survive upon thawing, to produce the cryogel network. Addition of sugars or incorporation of Ca^{2+} restricts conversion of liquid water to ice or alignment and association during freezing, thus reducing or eliminating network formation. On the other hand, the ice crystals in samples with mixtures of locust bean and xanthan gums were found to be smaller than in the other samples for different freezing methods assayed (Fernández *et al*. 2007). This effect was attributed by the authors to the formation of a gel-like structure by the locust bean and xanthan gums, which would limit water molecule diffusion and hence ice crystal growth. The mashed potatoes presented here contain either sugars, supplied mainly by the potato and the milk, or Ca ions, supplied mainly by the added milk. Their presence in the systems may possibly have partially reduced the gel-like structure formation, but the latter would still have been enough to limit ice crystal growth, which resulted in less cellular damage in the F/T mashed potatoes containing high concentrations of XG.

Outside the linear viscoelastic region, the viscous component gained in importance and *G** values were much greater than *G*' in all systems. Above the mentioned linear viscoelastic limit, *G** and *G*' decreased rapidly in all samples, indicating a high sensitivity of the structure to deformation (**Figs. 1, 2**). After structural breakdown, dynamic measurements quantified the liquid-like character of the mashed potatoes. In dynamic assays, outside the viscoelastic range, the viscous behaviour of the systems was characterized by the fluid-like relative angle α as previously defined (**Table 2**). The highest α values were found in the F samples with added XG at 1.5 g kg^{-1} and 2.5 g kg^{-1}, as one single component or mixed with ALM pectin (F-XG1.5, F-ALM3/XG1.5 and F-ALM4.5/XG2.5 samples). The mashed potatoes with added XG that showed a weak structure during the linear viscoelastic range, then, also had a more fluid-like character with low viscosity after breakdown ($\alpha \rightarrow 1$). Note that although F mashed potatoes presented a spongier, more rigid structure than their F/T counterparts within the linear viscoelastic range (higher *G*' values), they had more fluid-like characteristics than F/T samples after breakdown. Lower α values in the processed samples corresponded to high rigidity outside the linear viscoelastic range.

Since foodstuffs are submitted to large deformations, it is definitely important to analyse both linear and nonlinear viscoelastic ranges to determine a product's performance under actual processing conditions (Navarro *et al*. 1997). Thus, any rheological material testing should therefore explore how samples behave inside and outside the range of linear viscoelasticity. Results obtained within the nonlinear range serve mainly for relative comparison of samples subjected to a particular set of stress-strain conditions (Eliasson 1986; Schramm 1994).

Data analysis of dynamic oscillatory measurements

The effect of each supplementary cryoprotectant on the specific dynamic parameters of mashed potatoes with added ALM pectin and XG mixtures can be seen in **Table 3**. Addition of XG to F mashed potatoes increased phase shift (δ) and rheological characteristic *n*' (slope of storage modulus),

Table 3 Correlation matrix of cryoprotectant and response data for ALM and XG mixtures (bold figures are significant, $P < 0.05$).

	ALM	XG	ALM*ALM	XG*XG	ALM*XG	δ	G'	G''	η^*	n'	Ln(K')	n''	Ln(K'')	α
F mashed potatoes														
ALM	1	-	-	-	-	-0.18	-0.08	-0.23	-0.08	-0.01	-0.06	0.61	-0.21	0.25
XG	-	1	-	-	-	0.82	-0.81	-0.76	-0.81	0.84	-0.85	0.62	-0.80	0.29
ALM*ALM	-	-	1	-	-	-0.16	-0.13	-0.31	-0.14	0.02	-0.11	0.65	-0.29	0.16
XG*XG	-	-	-	1	-	0.63	-0.62	-0.64	-0.63	0.65	-0.68	0.52	-0.71	0.07
ALM*XG	-	-	-	-	1	0.51	-0.65	-0.72	-0.66	0.61	-0.68	0.79	-0.76	0.32
F/T mashed potatoes														
ALM	1	-	-	-	-	0.14	0.09	0.14	0.10	0.22	0.12	0.26	0.23	-0.10
XG	-	1	-	-	-	0.77	-0.21	0.40	-0.17	0.74	-0.17	-0.26	0.46	0.18
ALM*ALM	-	-	1	-	-	0.21	-0.08	-0.09	-0.06	0.28	-0.06	0.35	0.08	-0.07
XG*XG	-	-	-	1	-	0.60	-0.06	0.40	0.00	0.56	-0.02	-0.22	0.47	0.17
ALM*XG	-	-	-	-	1	0.65	-0.15	0.34	-0.09	0.71	-0.08	0.01	0.44	-0.17

while increasing XG levels correlated significantly with reduced G', G'', η^* and rheological characteristics lnK' and lnK'' (ln of intercepts of ln(ω) versus ln(G') and ln(G'') regressions (Alvarez *et al*. 2006). In the case of G', G'', η^*, n', lnK' and lnK'', quadratic and interaction terms for XG were significant. The results show and corroborate that with added XG, the F mashed potatoes behaves like a weaker gel structure, confirming previous findings (Alvarez *et al*. 2009). Interestingly, both ALM and XG concentrations correlated significantly with rheological characteristic n'' (slope of viscose response); the quadratic term for ALM and interaction also correlated significantly with this rheological parameter.

The calculated correlation matrix for the F/T dataset (**Table 3**) showed that only δ and n' had a significant positive linear and quadratic correlation with XG content, while the interaction term for ALM and XG also correlated significantly with the rheological parameter and the characteristic respectively. Neither linear, quadratic nor interaction terms showed a significant correlation with the rest of the dynamic parameters and characteristics in the F/T products. Processing significantly reduced the effect of adding ALM pectin and XG on the gel structure of the mashed potatoes. The contribution of XG to the viscoelastic behaviour of the mashed potatoes with added ALM pectin and XG mixtures was greater than that of ALM pectin, above all in the F mashed potatoes. Results also evidence non-synergistic interactions in the added mixtures.

Data were compiled for ALM and XG combinations; mean values of all the dynamic properties and rheological characteristics obtained for the F and F/T mashed potatoes are shown in **Table 4**. Both fresh and frozen/thawed samples without added cryoprotectants (F and F/T), with 3 g kg^{-1} individually added ALM pectin (F-ALM3 and F/T-ALM3) and with 1.5 g kg^{-1} individually added XG (F-XG1.5 and F/T-XG1.5) were treated as controls. The different concentrations constituting each added ALM pectin and XG mixture significantly affected all the oscillatory measurements ($P < 0.01$) in both F and F/T mashed potatoes. Results were similar for G^* and G' in the linear viscoelastic range, and therefore data for G^* have been omitted. In all cases, G' values were much higher than G'' indicating that the mashed potatoes behaved like a weak gel. Such behaviour has been reported elsewhere in samples of fresh and frozen mashed potatoes reconstituted from potato flakes or made from potato tubers (Alvarez and Canet 1999b; Alvarez *et al*. 2004), and likewise in tomato-, corn-starch paste-, sweet-potato puree- and vegetable puree-based baby foods (Ahmed and Ramaswamy 2006a, 2006b).

In both F and F/T mashed potatoes, the lowest δ values were recorded in control samples F-ALM3 and F/T-ALM3 and in the samples corresponding to design point 4 (F-ALM3/XG0.09 and F/T-ALM3/XG0.09), indicating that the mashed potatoes with added individually ALM pectin were more solid-like. In any case, both F and F/T controls without added cryoprotectants also had low phase angles. In the fresh samples, the highest G', G'' and η^* values were again recorded in F-ALM3/XG0.09, F and F-ALM3 samples. Analogously, in the F/T samples the highest G' and η^* values were found in F/T-ALM3/XG0.09, F/T-ALM3 and F/T samples without added cryoprotectants, in that order. In the processed samples, the highest G'' value was recorded for design point 10 (F/T-ALM3/XG2.91), although the differences with the G'' values recorded for the replicated design point 5 (F/T-ALM3/XG1.5) and design point 4 (F/T-ALM3/XG0.09) were not significant.

Recently, LM pectin gels have been characterized in the presence of Ca^{2+} by oscillatory measurements (Löfgren *et al*. 2006). In that study, the authors investigated the rheological properties of nonamidated pectin, amidated pectin, and saponified pectin gels at different pH values, both with and without sucrose. However, real food formulations will usually involve the addition of other ingredients. As mentioned above, mashed potatoes include potato starch (containing negatively charged phosphate groups), salt (NaCl), water and semi-skimmed in-bottle sterilized milk, containing either calcium ions or fat. Therefore, in these systems, the gel formation ability of ALM pectin is influenced by different complex mechanisms. The strengthening of the gel network of the F mashed potatoes associated with the addition of ALM pectin individually was lower than expected. The reason for this could be competition between potato starch and ALM pectin for the added salt, available water, and calcium. A large proportion of ions could be trapped by the potato starch, so that more ions or higher levels of ALM pectin need to be added to the system than would be required to achieve gelation of the hydrocolloid in an aqueous system.

On the other hand, fat content can also be considered as factor likely to contribute to the viscoelastic properties of F and F/T mashed potatoes obtained from oscillatory shear tests. For example, in spreadable-type processed cheese samples, fat acted as a lubricant contributing to a more liquid-like behaviour of the samples (Dimetreli and Thomareis 2008).

The high degree of substitution in ALM pectin may also cause steric hindrance of the pectin strands, rendering the gel structure more flexible and thus limiting the possibility of long Ca^{2+}- mediated assemblies (Löfgren *et al*. 2006). Also, in this study, the final pH of the F mashed potatoes without and with added hydrocolloids ranged between 6 and 6.1. For the ALM pectin, the highest storage modulus was recorded at pH 3. At this pH it is likely that the amide groups strengthen the gel network by hydrogen bonds. At pH 4, 5, and 7 the storage moduli are considerably lower, which might be a consequence of increased electrostatic repulsions between the pectin chains, preventing the formation of hydrogen bonds.

In the case of the F product, G', G'' and η^* values recorded at the replicated centre points 5-9 (F-ALM3/XG1.5) were significantly lower than those recorded in the three controls, although there were non-significant differences between the complex viscosity corresponding to F-XG1.5 control and that recorded at four replicated centre points. In fact, of the other samples containing added ALM pectin and XG mixtures, only the ones with the lowest XG concentra-

Table 4 Coded and uncoded variables of the response surface design and oscillatory measurements: F and F/T mashed potatoes with added different concentration combinations, and controls.

Design point and system notation	Coded		Uncoded		δ(°)	*G'* (Pa)	*G"* (Pa)	η^* (Pa s)	*n'*	ln *(K')*	*n"*	ln *(K")*	α
	X_1	X_2	ξ_1: ALM (g kg^{-1})	ξ_2: XG (g kg^{-1})									
F mashed potatoes													
F*					11.65 b	14580.75 b	3010.70 a	13950.50 b	0.1228 c	9.52 a	0.0228 a	8.09 a	0.1633 c
F-ALM3**					10.32 a	14039.00 c	2554.22 c	13375.75 b	0.1134 a, b	9.47 a	0.0306 b	7.98 a	0.1678 d
F-XG1.5***					18.22 h	7186.85 f	2367.02 d	7095.10 e	0.1794 f, g	8.76 d	0.0785 e	7.77 b	0.2333 n
1 (F-ALM0.88/XG1.5)	-1.41	0	0.88	1.5	16.55 f	6105.52 h	1809.82 g	5971.92 g, h	0.1730 e, f	8.60 e, f	0.0789 e	7.55 d-f	0.1711 e
2 (F-ALM1.5/XG0.5)	-1	-1	1.5	0.5	12.40 c	10600.50 d	2135.52 e	10128.77 c	0.1210 b, c	9.21 b	0.0505 c	7.73 b, c	0.1411 a
3 (F-ALM1.5/XG2.5)	-1	1	1.5	2.5	17.87 h	4715.5 j	1523.75 i	4640.50 j	0.1932 h	8.36 g, h	0.0985 g	7.35 g	0.1948 i
4 (F-ALM3/XG0.09)	0	-1.41	3	0.09	10.45 a	15702.50 a	2713.25 b	14880.00 a	0.1099 a	8.59 e, f	0.0655 d	8.05 a	0.1544 b
5 (F-ALM3/XG1.5)	0	0	3	1.5	17.07 g	6592.25 g	2027.00 e, f	6460.00 f, g	0.1742 e-g	8.71 d, e	0.0865 f	7.65 c, d	0.2422 n
6 (F-ALM3/XG1.5)	0	0	3	1.5	15.35 d	6653.25 g	1901.75 f, g	6744.50 e, f	0.1680 d, e	8.77 d	0.0888 f	7.62 c, d	0.2044 j
7 (F-ALM3/XG1.5)	0	0	3	1.5	15.55 d	6665.00 g	1853.50 g	6490.75 e-g	0.1640 d	8.70 d, e	0.0844 e, f	7.56 d-f	0.2333 m
8 (F-ALM3/XG1.5)	0	0	3	1.5	15.80 d, e	6663.50 g	1906.50 f, g	6592.25 e-g	0.1746 e-g	8.74 d	0.0864 f	7.62 c, d	0.2252 l
9 (F-ALM3/XG1.5)	0	0	3	1.5	16.25 e, f	6644.00 g	1885.25 g	6574.50 e-g	0.1667 d, e	8.67 d, e	0.0869 f	7.59 d, e	0.2422 n
10 (F-ALM3/XG2.91)	0	1.41	3	2.91	15.75 d	6500.25 g	1832.25 g	6333.25 f-h	0.1667 d, e	8.70 d, e	0.0840 e, f	7.51 e, f	0.1722 f
11 (F-ALM4.5/XG0.5)	1	-1	4.5	0.5	11.82 b	9012.50 e	1887.00 g	8613.75 d	0.1284 c	9.08 c	0.0886 f	7.62 c, d	0.1756 g
12 (F-ALM4.5/XG2.5)	1	1	4.5	2.5	16.30 f	4283.00 k	1254.00 j	4175.25 j	0.1820 g	8.30 h	0.1216 i	7.15 h	0.1911 h
13 (F-ALM5.12/XG1.5)	1.41	0	5.12	1.5	15.37 d	5883.00 h	1656.75 h	5770.50 h, i	0.1747 e-g	8.60 e, f	0.1107 h	7.47 f	0.2067 k
Random point (F-ALM1.5/XG1.5)	-1	0	1.5	1.5	15.70 d	5507.75 i	1487.75 i	5337.25 i	0.1625 d	8.48 f, g	0.0825	7.26 g, h	0.1910 h
LSD (99%)					0.4586	334.054	132.158	621.81	0.0086	0.1230	0.0072	0.1074	0.0010
F/T mashed potatoes													
F/T*					11.37 b	5948.00 g	1191.00 e, f	5640.75 i	0.1237 b	8.62 i	0.0818 b-d	7.19 d-f	0.1111 a
F/T-ALM3**					10.42 a	6748.25 h	1211.50 e-g	6003.50 j	0.1158 a, b	8.74 j	0.0659 a, b	7.22 e, f	0.1289 c
F/T-XG1.5***					15.77 i	3644.25 b	1018.50 c	3565.50 b, c	0.1741 g, h	8.13 b, c	0.0909 d	7.02 b, c	0.1600 i
1 (F/T-ALM0.88/XG1.5)	-1.41	0	0.88	1.5	15.35 g-i	3229.25 a	903.62 b	3139.75 a	0.1646 e-g	7.98 a	0.0790 b-d	6.88 a, b	0.1644 j
2 (F/T-ALM1.5/XG0.5)	-1	-1	1.5	0.5	11.00 a, b	3843.50 b, c	751.27 a	3780.25 c, d	0.1194 b	8.24 e, f	0.0796 b-d	6.75 a	0.1311 d
3 (F/T-ALM1.5/XG2.5)	-1	1	1.5	2.5	15.57 h, i	4392.25 d	1224.00 e-h	4271.00 e, f	0.1586 d-f	8.32 f, g	0.0718 a-c	7.14 c-e	0.1878 o
4 (F/T-ALM3/XG0.09)	0	-1.41	3	0.09	10.65 a, b	6858.75 h	1304.10 g-i	6738.75 k	0.1081 a	8.82 j	0.0862 c, d	7.21 d-f	0.1511 f
5 (F/T-ALM3/XG1.5)	0	0	3	1.5	14.47 e-g	4890.00 e	1333.75 h, i	4748.75 h	0.1623 d-f	8.44 h	0.0849 c, d	7.21 d-f	0.1511 f
6 (F/T-ALM3/XG1.5)	0	0	3	1.5	13.35 c, d	4621.75 d, e	1136.35 d, e	4290.00 e-g	0.1382 c	8.40 g, h	0.0611 a	7.09 c-e	0.1656 k
7 (F/T-ALM3/XG1.5)	0	0	3	1.5	14.72 f-h	4809.00 e	1231.25 e-h	4541.75 f-h	0.1627 d-f	8.38 g, h	0.0681 a, b	7.18 d-f	0.1500 e
8 (F/T-ALM3/XG1.5)	0	0	3	1.5	14.18 d-f	4775.50 e	1233.75 e-h	4526.75 f-h	0.1544 d, e	8.41 g, h	0.0713 a-c	7.16 c-f	0.1556 h
9 (F/T-ALM3/XG1.5)	0	0	3	1.5	13.77 d, e	4831.75 e	1283.77 f-i	4637.75 g, h	0.1585 d-f	8.42 g, h	0.0781 b-d	7.18 d-f	0.1528 g
10 (F/T-ALM3/XG2.91)	0	1.41	3	2.91	13.95 d-f	5341.00 f	1362.00 i	5295.75 i	0.1528 d	8.54 i	0.0723 a-c	7.29 f	0.1722 m
11 (F/T-ALM4.5/XG0.5)	1	-1	4.5	0.5	12.60 c	4065.00 c	845.92 a, b	3795.25 c, d	0.1355 c	8.22 d-f	0.0742 a-c	6.89 a, b	0.1767 n
12 (F/T-ALM4.5/XG2.5)	1	1	4.5	2.5	16.10 i	3782.25 b, c	1066.77 c, d	3903.00 c, d	0.1814 h	8.21 c, d	0.0807 b-d	7.08 c-e	0.1211 b
13 (F/T-ALM5.12/XG1.5)	1.41	0	5.12	1.5	15.47 h, i	4067.25 c	1138.00 d, e	4005.00 d, e	0.1691 f, g	8.23 e, f	0.0910 d	7.07 c, d	0.1667 l
Random point (F/T-ALM1.5/XG1.5)	-1	0	1.5	1.5	14.30 e, f	3293.75 a	881.92 b	3239.25 a, b	0.1579 d, e	8.06 a, b	0.0850 c, d	6.84 a	0.1844 ñ
LSD (99%)					0.9123	289.6450	111.7170	352.0690	0.0111	0.1025	0.0159	0.1455	0.0008

*F and F/T mashed potatoes without added cryoprotectants; **F and F/T mashed potatoes with 3 g kg^{-1} added amidated low-methoxyl (ALM) pectin; ***F and F/T mashed potatoes with 1.5 g kg^{-1} added xanthan gum (XG). Values are given as mean score values of eight determinations. Different letters in the same column indicate significant differences $P < 0.01$. LSD, least significant difference.

tions (F-ALM1.5/XG0.5, F-ALM3/XG0.09 and F-ALM4.5/XG0.5) had *G*' and η^* values higher than F-XG1.5 control. Also, the replicated F/T-ALM3/XG1.5 samples presented higher phase angles and lower *G*', *G*" and η^* values than F/T and F/T-ALM3 controls, and only F/T-ALM3/XG0.09 sample had higher *G*', *G*" and η^* values than the three control used. In mashed potatoes with mixtures, the presence of a second hydrocolloid (XG) resulted in a lower *G*' than in the corresponding sample with an equal concentration of ALM pectin alone; this effect was noticeable in both F and F/T mashed potatoes. Therefore, there was no enhancement of oscillatory properties. Also, the loss of gel-likeness over the ranges of ALM and XG concentrations used suggests that there is a repulsive effect or incompatibility between ALM pectin and XG when added to mashed potatoes, on top of the known tendency to greater intermolecular association when ALM pectin is added as a single component.

It is generally accepted that enhancement of mixture modulus results from the existence of interpenetrating networks (Rodríguez-Hernández and Tecante 1999) in a single non separated phase, and on that basis it seems certain that no such phenomenon occurred in these systems. It is likely that in mashed potatoes including potato starch, when the proportion of either ALM pectin or XG increased, the cations added with the milk gradually became insufficient to promote junction zones in ALM pectin as their numbers were reduced by competition among polymers for cations and solvent. It is well known that the stiffness of ALM pectin gels (Löfgren *et al*. 2006) and XG "weak-gels" (Mohammed *et al*. 2007) peaks depending on ion concentration. In the presence of another polysaccharide fewer ions will be available for ALM pectin.

Table 4 also shows the effect of ALM and XG concentrations on the slopes (*n*' and *n*") and ln of intercepts of ln(ω) versus ln(*G*') and ln(*G*") regressions, and likewise on the α parameter characterizing the nonlinear viscoelastic domain. In both F and F/T samples, *n*' values were higher than *n*" values, indicating that *G*' was more frequency-dependent than *G*". In both F and F/T samples, the magnitudes of ln(*K*') were higher than those of ln(*K*") under all the combinations used. For example, *n*' values were higher at centre points than in F, F/T, F-AML3 and F/T-ALM3 controls, indicating that the replicated mashed potatoes (F-ALM3/XG1.5 and F/T-ALM3/XG1.5) had a weaker gel structure. Similarly, the lower values of the slopes of ln(ω) versus ln(*G*") in F samples indicate that the frequency de-

pendence of *G*" was considerably lower in F and F-ALM3 controls. However, at the replicated centre points 5-9, *n*' and *n*" values were lower in the F/T samples, indicating that *G*' and *G*" were more independent of frequency in the processed samples.

For their part, α values were lower in all the F/T samples than in their F counterparts, evidencing that F products were more fluid-like after breakdown, especially F-XG1.05 control and replicated F-ALM3/XG1.05 samples. Of the processed products, F/T-ALM1.5/XG2.5 and F/T-ALM1.5/XG1.5 had the highest α values, which were again associated respectively with low and high ALM pectin and XG concentrations.

Optimization of cryoprotectant concentrations

Based on the results of the first statistical analysis, RSM was used to identify any optimum ALM and XG concentrations for some oscillatory measurements in the F and F/T mashed potatoes. Regression coefficients of each response model fitted were tested for significance. They are presented in **Table 5**, together with their coefficients of determination, R^2, *F*-Ratios and *P*-values, and lack-of-fit tests. Response models of instrumental parameters which gave R^2-values < 0.75 have been omitted, as these models showed very low percentages of explained variability, indicating a significant lack-of-fit (Henika 1982). In F mashed potatoes, independent variables had approximately the same effect on *G*', η^* and *n*", with significant interaction (b_{12}), linear and quadratic terms for ALM (b_1 and b_{11} respectively) and XG concentrations (b_2 and b_{22} respectively), and also relatively high R^2-values (> 0.75), but with significant lack-of-fit tests. Models with high R^2-values and significant lack-of-fit tests indicate that higher-order models are probably required to describe the effects of the independent variables and would be used only for trend analysis (Henika 1982; Alvarez *et al*. 1999a).

In F samples, δ and *n*' models presented significant linear and quadratic terms for XG concentration (b_2 and b_{22} respectively), whereas in the case of the α model the quadratic term for ALM concentration (b_{11}) was also significant. In F/T mashed potatoes, δ and *n*' models presented significant linear and quadratic terms for XG concentration (b_2 and b_{22} respectively), while in the case of the δ model the quadratic term for ALM concentration (b_{11}) was also significant. The R^2-value for *n*' and δ was very high (> 0.85), and the lack-of-fit tests were non-significant. In the processed samples, for their part, the ln (*K*') model presented significant linear and quadratic terms for ALM and XG concentrations. In the case of ln (*K*') model, the R^2-value was good (almost 0.80), but the lack-of-fit test was significant. In the case of the α model the interaction term (b_{12}) was the only significant one; however, the R^2-value was relatively high (0.87), with no significant lack-of-fit test. Most of the models fitted that presented high R^2-values (> 0.85) also had significant lack-of-fit tests. Among the common causes of poor modelling are a skewed response distribution, curvature in the relationship between a response variable and a design factor, large between-replicate variation and outlying experiments (Downey 2003).

Examination of the standardized residuals produced by the models showed no outlying experimental points, while ANOVA demonstrated the significance of the fitted regression models. The high between-replicate variation is the most likely cause of the poor modelling. Stepwise regression analysis was performed for the dependent variables. This analysis eliminates the insignificant coefficients on the basis of *P*-values so that the models can be reduced. Reduced models did not present higher R^2-values; however, when the interaction term was eliminated the lack-of-fit tests were not significant for ln (*K*") in the F product (**Table 5**), and therefore a reduced model was utilized for this dependent variable. Only models with high percentages of explained variability (R^2 > 0.85) and non-significant lack-of-fit tests would be considered sufficiently accurate to make predictions (Henika 1982). Of the models fitted for oscillatory parameters, only δ, *n*' and α models in the F and F/T products definitely fulfil both conditions.

Therefore, only the full models fitted for δ, *n*' and α were used for further analysis in order to be able to obtain stationary points (Myers and Montgomery 1995). In this way, the δ, *n*' and α models were used in both F and F/T mashed potatoes to generate surface responses to identify the main effects of ALM and XG concentrations (**Fig. 3**). As **Fig. 3** shows, only in F mashed potatoes did the fluid-index α (**Fig. 3C**) increase with ALM and XG concentrations up to certain levels beyond which the independent variable decreased, thus defining an obvious optimum region. In the case of F product, the phase angle (**Fig. 3A**) and slope of storage modulus (**Fig. 3B**) showed a moderate sad-

Table 5 Regression coefficients, coefficient of determination (R^2) and analysis of variance of the quadratic models for oscillatory measurements of F and F/T mashed potatoes at the design response surface.

F mashed potatoes									
Coefficient	**δ (°)**	***G*' (Pa s)**	***G*" (Pa s)**	**η^***	***n'***	**ln *(K')***	***n"***	**ln *(K")***	**α**
b_0	16.00	6643.60	1914.80	6572.40	0.17	8.72	0.09	7.61	6.54E-3
b_1	-0.48	-291.90**	-91.84*	-283.14**	-1.75E-4	-0.02	0.01**	-0.05*	0.07
b_2	2.18**	-2953.56**	-306.92**	-2751.71**	0.03**	-0.36**	0.01**	-0.20**	0.13**
b_{11}	-5.12E-3	-673.40**	-164.93**	-687.93**	2.19E-3	-0.09**	5.36E-3**	-0.10**	-9.06E-3*
b_{22}	-1.44**	1880.15**	98.55*	1679.77**	-0.02**	0.18**	-4.69E-3**	0.04*	-0.03**
b_{12}	-0.25	288.87**	-5.31	262.44**	-4.65E-3	0.02	-3.75E-3**	-	-6.37E-3
R^2	0.95	0.95	0.84	0.91	0.95	0.95	0.88	0.85	0.90
F-Ratio	28.35	28.50	7.60	26.27	28.60	28.48	9.86	11.41	12.94
P-value	0.000	0.000	0.009	0.000	0.000	0.000	0.004	0.002	0.002
Lack of fit	0.667	0.000**	0.013*	0.000**	0.108	0.013*	0.000**	0.011*	0.765
F/T mashed potatoes									
Coefficient	**δ (°)**				***n'***	**ln *(K')***			**α**
b_0	14.1				0.16	8.41			0.16
b_1	0.29				5.66E-3	0.03*			-2.23E-3
b_2	1.59**				0.02**	-0.04**			3.87E-3
b_{11}	0.65*				5.84E-3	-0.19**			2.91E-3
b_{22}	-0.91*				-0.01*	0.10**			9.59E-4
b_{12}	-0.27				1.68E-3	-0.02			-0.03**
R^2	0.91				0.88	0.79			0.87
F-Ratio	13.882				10.448	5.320			9.210
P-value	0.002				0.004	0.025			0.006
Lack of fit	0.240				0.632	0.000**			0.158

Subscripts: 1 = ALM pectin concentration; 2 = XG concentration. Significant level: *0.05; **0.01.

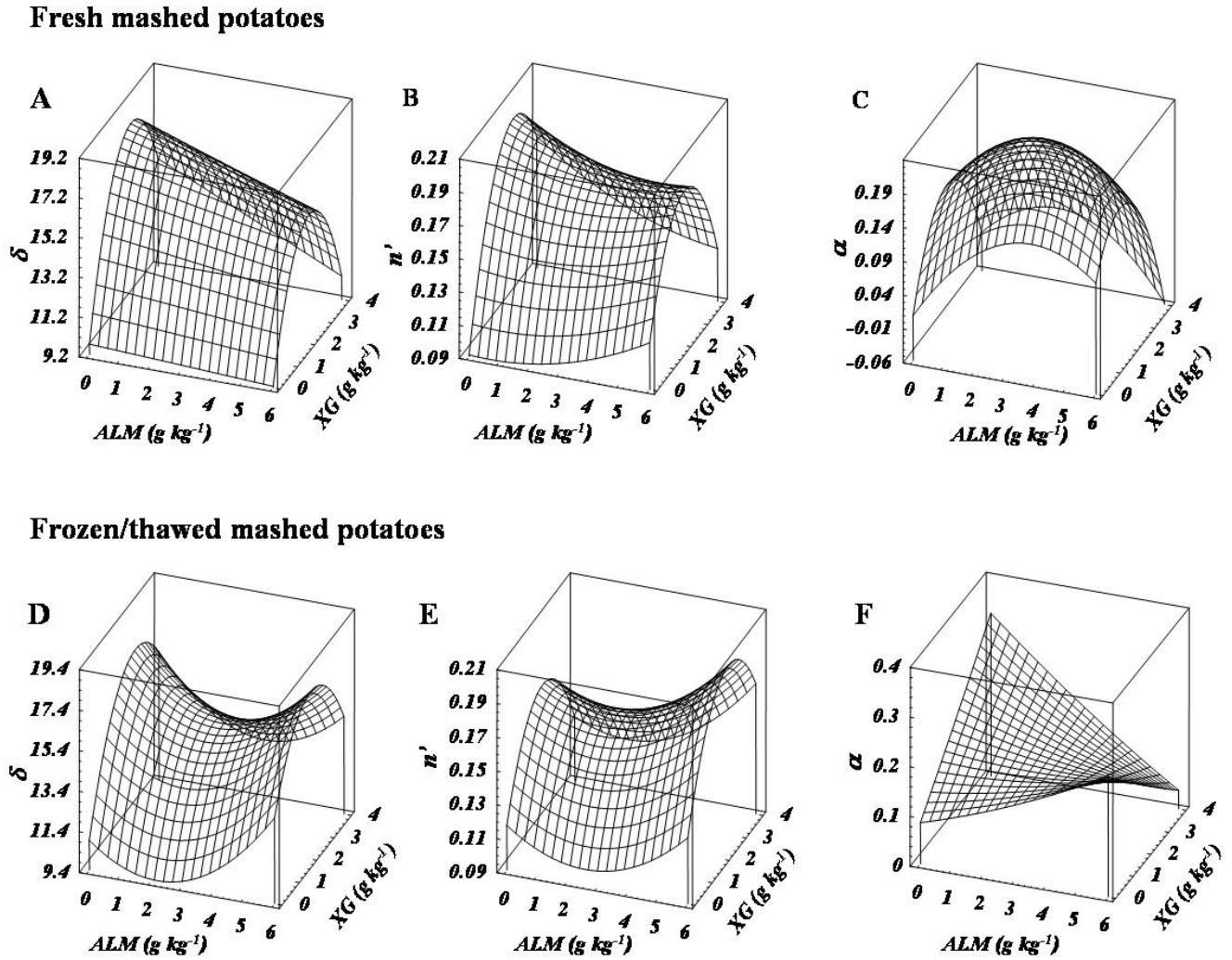

Fig. 3 Oscillatory parameter response surfaces as functions of ALM pectin and XG concentrations for F and F/T mashed potatoes: (**A, D**) phase angle (δ) from linear viscoelastic range; (**B, E**) slope of storage modulus (n') from linear viscoelastic range; (**C, F**) fluid-like relative angle (α) from nonlinear viscoelastic range.

dle effect caused by the incorporation of ALM pectin. Saddle-shaped topologies are one of the surface types characteristic of models involving quadratic terms (Downey 2003). In the case of F/T product, the three response surfaces for δ, n', and α (**Figs. 3D-F**) were also saddle-shaped, thus identifying a set of ALM and XG concentration values which will produce the maximum phase angle, slope of storage modulus and fluid-likeness in F/T mashed potatoes.

In both F and F/T mashed potatoes, comparison of the response surfaces for δ and α (**Figs. 3A, 3C** and **Figs. 3D, 3F** respectively) revealed a change in topology, mainly along the ALM pectin axis in the F samples and along both ALM and XG axes in the F/T samples, between the phase angle determined in the linear viscoelastic domain and the fluid-like relative angle calculated in the nonlinear viscoelastic range. This result again highlights the importance of analysing both linear and nonlinear viscoelastic ranges. Also, for the same fluid-index α parameter **Fig. 3F** shows a clear change in topology as compared to the F product (**Fig. 3C**) along the ALM and XG axes as the mashed potatoes are processed. These differences are entirely attributable to processing in this case.

The fact that ALM pectin and XG concentrations had a quadratic effect on fluid-index α in the F product and on phase angle δ in the F/T product (**Table 5, Fig. 3**) indicated that there is an optimum region for both independent variables; therefore the stationary points for these responses were calculated and the closeness or distance of the optimum responses were tested for the two dependent variables. In F mashed potatoes, the critical values of α showing maximum fluid-like characteristics after structural breakdown in the nonlinear viscoelastic range lay in the region delimited by the ranges studied; these were 3.32 g kg^{-1} for ALM pectin and 1.65 g kg^{-1} for XG. When ALM pectin and XG are added in the latter concentrations, the resulting product relaxes rapidly after structural breakdown (Navarro *et al*. 1997). The estimated response at the stationary point for α was 0.2310.

In F/T mashed potatoes, the critical values of stationary points for δ indicating maximum structural weakening in the linear viscoelastic range were 3.06 g kg^{-1} for ALM pectin and 2.38 g kg^{-1} for XG, and the estimated response at stationary point for δ was 14.80. Adding 1.5 g kg^{-1} of both ALM pectin and XG (F-ALM1.5/XG1.5 and F/T-ALM1.5/XG1.5 samples, **Table 4**) further tested the accuracy of the models for both rheological parameters. The predicted value (0.1990) using the α model was quite close to the experimental value (0.1910, **Table 4**) in the case of the F mashed potatoes, with a precentage gap between predicted and experimental values of -4.52. The predicted value (14.46) using the δ model was very close to the experimental value (14.30, **Table 4**) in the case of F/T mashed potatoes, with a percentage gap between predicted and experimental values of -1.10. The models fitted for fluid-like relative angle (α) in F mashed potatoes and for phase angle (δ) in F/T mashed potatoes presented high R^2, non-significant lack-of-.tests and a small gap between experimental and predicted values; these therefore appear to be suitable as oscillatory parameters to represent the rheological behaviour of F mashed potatoes after structural breakdown and of F/T mashed

potatoes in the linear viscoelastic range, when ALM pectin and XG mixtures are added.

CONCLUSIONS

The addition of XG (either individually or mixed with ALM pectin) increased the contribution of *G*" to the viscoelastic properties of the mashed potatoes in the linear viscoelastic range. F/T mashed potatoes with added ALM pectin and XG mixtures can withstand higher strains without undergoing irreversible modifications than can their F counterparts. Freezing and thawing processes weakened the gel structure of the systems in the linear viscoelastic range as compared to F counterparts, but addition of 2.5 g kg^{-1} XG significantly reduced the differences between F and F/T counterparts, tentatively by limiting ice crystal growth. XG contributed more to the viscoelastic behaviour of the mashed potatoes with added mixtures than ALM pectin, particularly in the F mashed potatoes since processing significantly reduced the effect of adding ALM pectin and XG on the gel structure of the mashed potatoes. Optimum responses obtained for the fluid-like relative angle (α) in F and for the phase angle (δ) in F/T mashed potatoes demonstrate that there was no enhancement of oscillatory properties in the systems with added ALM pectin and XG mixtures.

The negative effect of adding ALM pectin and XG to mashed potatoes suggests that there is no interaction between xanthan gum, potato starch and ALM pectin, while each gelling polysaccharide forms its own junction zones and there is no interaction between chains. Authors suggest research into mixtures of XG with others non-gelling (galactomannan family) or gelling (carrageenan family) hydrocolloids or proteins (sodium caseinate) to achieve optimum effects.

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