UNIVERSIDAD POLITECNICA DE VALENCIA
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— Instituto de Agroquímica y Tecnología de Alimentos —

LA REVALORIZACIÓN DEL USO DE ALMIDÓN DE TAPIOCA. ESTRATEGIA MULTIENFOQUE EN SU APLICACIÓN EN RELLENOS DE FRUTA

TESIS DOCTORAL
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Valencia, Noviembre de 2014

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HACEN CONSTAR QUE:

El trabajo de investigación titulado **"La revalorización del uso de almidón de tapioca. Estrategia multienfoque en su aplicación en rellenos de fruta"** que presenta Dña. Maria Alejandra Agudelo Motato por la Universidad Politécnica de Valencia, ha sido realizado en el Instituto de Agroquímica y Tecnología de alimentos (IATA-CSIC) bajo nuestra dirección y que reúne las condiciones para optar al grado de Doctor.

Valencia, Noviembre de 2014

Fdo: Dra. Susana Fiszman Dal Santo

Fdo: Dra. Paula Varela Tomasco

A mi familia especialmente a mi
madre a mi esposo y a mi hijo,

Agradecimientos

Gracias a Dios por guiar mis pasos en cada momento, para estar en el lugar indicado y en el tiempo adecuado para vivir cada etapa de mi vida, como esta que hoy termina con la elaboración de esta tesis.

A Sucromiles S.A, hoy Sucroal S.A: A Orlando Castaño, desde el principio de mi vida profesional y laboral, siempre pendiente de mí, ayudándome en todo, has sido más que un padre para mí, como te digo de cariño "mi angelito". Este viaje ha sido en gran parte tu obra, Gracias

Al Doctor Colmenares

Gracias por ser más que un Gerente, el padre de una gran familia, por confiar en mí y en mis capacidades, por todo su apoyo y cariño y por poner siempre los medios necesarios para que mi entrenamiento y capacitación fuera el mejor y en todos las áreas, no solo a nivel profesional sino también a nivel personal. Sucromiles fue mi sueño como ingeniera química y ha sido la plataforma para lanzarme por muchos sueños más, que hoy son una realidad en mi vida.

A mis compañeros en Sucroal: Andrés, Nhora, Iber y Luis Fernando, gracias por su amistad y gran ayuda enviando materias primas, información y por los análisis de muestras realizados cuando fue requerido.

A mis directoras de tesis en el IATA,

Susana, eres la mejor, no tengo palabras para expresar todo mi agradecimiento por toda tu contribución a mi tesis, a mi crecimiento profesional y personal, eres más que mi directora una gran amiga y una persona muy especial a la que admiro no solo por su gran labor y logros científicos y profesionales, sino también por sus grandes virtudes como mujer y madre.

Paula V, gracias por dirigir mi tesis al lado de Susana, son un gran equipo y sobre todo gracias por tu alegría, tus consejos tanto en mi vida profesional como en mi vida personal. Eres un ejemplo a seguir, por tu arduo trabajo el cual te ha llevado donde estas ahora con todos tus logros profesionales y lo más importante sin dejar de lado tu vida personal como esposa y como madre.

A Isabel Hernando, porque gracias a ti tuve la oportunidad de conocer a Susana y hacer mi tesis en el IATA. Gracias por tu alegría, tu apoyo y por ser mi tutora en la universidad.

A mis compañeras

Johanna, gracias por tu sincera amistad desde la universidad y ahora en el laboratorio, que buenos momentos hemos compartido.

Eli, Laura y Pau T, gracias porque fueron la mayor compañía y alegría mientras estuvieron en el laboratorio, cuanto las echo de menos, son personas muy especiales, gracias por catar mi comida colombiana especialmente mi Lau y por enseñarme gran parte de la cultura valenciana (española), bueno y también de la ecuatoriana mi Eli y de la árabe y las expresiones y dichos que tanto compartimos con Pau.

Teresa, Ana y Amparo, gracias por su colaboración y ayuda, por la información aportada para mi tesis, por sus enseñanzas sobre el manejo de equipos, por todos sus consejos y por brindarme su amistad.

Antonio, Iñaqui y Andrea Fantini, gracias por su valiosa colaboración en el trabajo experimental de mi tesis, por hacer mil y un rellenos de fruta y/o las largas horas en el reómetro o en las salas de análisis sensorial.

A todas las personas que pasaron por el laboratorio durante mi estadía allí, por las risas y los buenos ratos, a Vicenta, Aurora, Myrna, Ángela, Julián, Carolina, Dimitar, Natalia, a la alegre Gabriela y a la dulce Mary jane

Al IATA, por poner los medios para la realización de mi tesis, y en especial al personal y compañeros de otros laboratorios que he conocido en estos años. Al panel de catadores entrenados, y al resto de catadores que participaron en la tesis, por su tiempo y colaboración desinteresada.

A mis amigos y amigas, porque forman parte de mi vida porque compartimos penas y alegrías, y porque siempre me apoyan y están ahí cuando los necesito. Muy especialmente A mi July y a mi Annita, estuvieron allí justo cuando más necesitada una mano amiga en medio de la distancia, la soledad y el no encontrar a nadie que me orientara en medio de la selva de cemento donde el lenguaje español parecía ser un idioma diferente. Estaban aquí desde Colombia para estar junto a mí, orientarme, ayudarme en todo, pero sobre todo para darme su valiosa amistad y compañía.

A Maria Estella Matos por mostrarme el camino para hacer mis sueños realidad con la fuerza y la luz que hay en mi interior, por enseñarme a comunicarme mejor y a vivir el aquí y el ahora, gracias amiga.

A mis padres, porque sin duda no estaría aquí sin ellos, Al resto de mi familia porque todos han tratado de ayudarme y los he tenido cuando los he necesitado. Y también a la familia de mi esposo que ahora es mi familia.

A mis dos príncipes porque son el amor de mi vida,

A mi José (hermoso), por estar a mi lado, queriéndome y cuidándome, por entender y respetar mi trabajo, por hacer realidad mis sueños y por hacerme sentir la mujer más feliz del mundo.

A mi Samuel, un milagro hecho realidad, por ser un aliciente más en mi vida para cumplir todos mis sueños y proyectos.

Alejandra

Resumen

La identificación de nuevos nichos de mercado para productos procesados que contenga almidón de tapioca (yuca) se hace indispensable para favorecer el desarrollo de esta agroindustria en Colombia y en otros países productores. Los consumidores perciben los almidones nativos como "naturales" o "de menor riesgo" que otros ingredientes/ aditivos, como los almidones modificados; esta percepción y la tendencia del mercado hacia los alimentos naturales y de etiqueta limpia hace prometedor el uso de los almidones nativos. No obstante, los almidones nativos tienen limitaciones en algunas aplicaciones en la industria alimentaria, debido a su inestabilidad a altas temperaturas, a altas fuerzas de cizallamiento, a bajos pH y a su tendencia a retrogradar a bajas temperaturas, causando un descenso en la calidad de los productos finales.

El objetivo principal de esta Tesis es la evaluación del desempeño del almidón de tapioca nativo en rellenos de fruta y propuesta de un sistema mixto con pectina que admita las condiciones de pH, temperatura y proceso. Se han desarrollado sistemas basados en almidón nativo de tapioca para esta aplicación con el fin de revalorizarlo en la industria de alimentos.

Primero se evaluó la adición de un hidrocoloide como modelo principal (sistema mixto) basado en almidón nativo de tapioca con adición de pectina de bajo metoxilo; se comparó con un control, elaborado con un almidón modificado que se utiliza normalmente en rellenos de fruta industriales. Se estudiaron las propiedades de formación de pasta de los almidones y las propiedades viscoelásticas, los parámetros de textura instrumental (extrusión) y sinéresis de los diferentes sistemas modelo. En el diseño y formulación también se consideraron diversos factores inherentes a las condiciones experimentales de proceso de los rellenos de fruta donde se usa el sistema espesante; como la adición de fruta y la estabilidad frente a

los tratamientos térmicos como el horneado y a la congelación. Se evaluó el efecto de la cocción sobre la textura en dos aplicaciones de panadería (sistemas abiertos y cerrados). La adición de pectina aumentó significativamente la firmeza y la consistencia de los geles analizados y los rellenos con y sin fruta preparados con el sistema propuesto, fueron más resistentes a los tratamientos térmicos que los preparados con almidón de tapioca solo, mostrando propiedades reológicas y texturales estables durante los diferentes procesos y similares a las del almidón de maíz modificado, usado como control.

Teniendo en cuenta que en la actualidad, el mercado de los alimentos se encuentra cada vez más segmentado y los consumidores buscan productos no solo de buena calidad sino que sean más saludables, satisfagan necesidades y gustos personales, se evaluaron rellenos de fruta reducidos en azúcar, se aplicaron técnicas instrumentales (reológicas y de textura) y técnicas sensoriales (estudios de análisis sensorial descriptivo (QDA) clásico con panel entrenado y estudios con consumidores no entrenados para evaluar su aceptabilidad); y mediante escalas JAR se evaluó el gusto y la adecuación de algunos atributos sensoriales. Los resultados instrumentales y sensoriales estuvieron altamente correlacionados entre sí y se encontró segmentación en la percepción y gusto de los consumidores por los rellenos de fruta en tres grupos. Un grupo al que no le gustan los edulcorantes intensos en absoluto, otro grupo, que notablemente, prefiere las características de las muestras que contienen almidón de tapioca y un tercero intermedio en sus tendencias. Estos resultados sugieren que las formulaciones pueden ser adaptadas a cada escenario. Por último, sabiendo que una serie de características texturales se evalúan durante el consumo y la masticación del producto, que a su vez modulan la percepción del sabor, se aplicaron dos técnicas sensoriales relativamente nuevas: Dominio temporal de las sensaciones (TDS) evaluando textura y sabor por separado y análisis CATA (Check-all-that-apply) incluyendo la evaluación de un "relleno de fruta ideal".

Por último, los resultados se relacionaron con la aceptabilidad. Estas técnicas sensoriales permiten que sea el consumidor quien dirija y sugiera qué aspectos de la formulación pueden ser rediseñados.

Resum

La identificació de nous nínxols de mercat per a productes processats que continguen midó de tapioca (yuca) es fa indispensable per afavorir el desenvolupament d'aquesta agroindústria a Colòmbia i en altres països productors. Els consumidors perceben els midons nadius com "naturals" o "de menor risc" que altres ingredients / additius, com els midons modificats; aquesta percepció i la tendència del mercat cap als aliments naturals i d'etiqueta neta fa prometedor l'ús dels midons nadius. No obstant això, els midons nadius tenen limitacions en algunes aplicacions en la indústria alimentària, per la seua inestabilitat a altes temperatures, a altes forces de cisallament, a baixos pH i a la seua tendència a retrogradar a baixes temperatures, causant un descens en la qualitat dels productes finals.

L'objectiu principal d'aquesta Tesi és l'avaluació de l'acompliment del midó de tapioca natiu en farcits de fruita i proposta d'un sistema mixt amb pectina que admiteixca les condicions de pH, temperatura i procés. S'han desenvolupat sistemes basats en midó natiu de tapioca per a aquesta aplicació per tal de revaloritzar en la indústria d'aliments.

Primer es va avaluar l'addició d'un hidrocol·loide com a model principal (sistema mixt) basat en midó natiu de tapioca amb addició de pectina de baix metoxil; es va comparar amb un control, elaborat amb un midó modificat que s'utilitza normalment en farcits de fruita industrials. Es van estudiar les propietats de formació de pasta dels midons i les propietats viscoelàstiques, els paràmetres de textura instrumental (extrusió) i sinèresi dels diferents sistemes model. En el disseny i formulació també es van considerar diversos factors inherents a les condicions experimentals de procés dels farcits de fruita on s'usa el sistema espessidor; com l'addició de fruita i l'estabilitat enfront dels tractaments tèrmics com l'enfornat i a la congelació. Es va avaluar l'efecte de la cocció sobre la textura en dues

aplicacions de forn (sistemes oberts i tancats). L'addició de pectina va augmentar significativament la fermesa i la consistència dels gels analitzats i els farcits amb i sense fruita preparats amb el sistema proposat, van ser més resistents als tractaments tèrmics que els preparats amb midó de tapioca sol, mostrant propietats reològiques i texturals estables durant els diferents processos i similars a les del midó de blat de moro modificat, usat com a control.

Tenint en compte que en l'actualitat, el mercat dels aliments es troba cada vegada més segmentat i els consumidors busquen productes no només de bona qualitat sinó que siguen més saludables, satisfacin necessitats i gustos personals, es van avaluar farcits de fruita reduïts en sucre, es van aplicar tècniques instrumentals (reològiques i de textura) i tècniques sensorials (estudis d'anàlisi sensorial descriptiu (QDA) clàssic amb panell entrenat i estudis amb consumidors no entrenats per avaluar la seua acceptabilitat); i mitjançant escales JAR es va avaluar el gust i l'adequació d'alguns atributs sensorials.

Els resultats instrumentals i sensorials van estar altament correlacionats entre si i es va trobar segmentació en la percepció i gust dels consumidors pels farcits de fruita en tres grups. Un grup al qual no li agraden els edulcorants intensos en absolut, un altre grup, que notablement, prefereix les característiques de les mostres que contenen midó de tapioca i un tercer intermedi en les seves tendències. Aquests resultats suggereixen que les formulacions poden ser adaptades a cada escenari. Finalment, sabent que una sèrie de característiques texturals s'avaluen durant el consum i la masticació del producte, que al seu torn modulen la percepció del gust, es van aplicar dues tècniques sensorials relativament noves: Domini temporal de les sensacions (TDS) avaluant textura i gust per separat i anàlisi CATA (Check-all-that-apply) incloent l'avaluació d'un "farcit de fruita ideal".

Finalment, els resultats es van relacionar amb l'acceptabilitat. Aquestes tècniques sensorials permeten que siga el consumidor qui dirigeixi i suggereixi quins aspectes de la formulació poden ser redissenyats.

Summary

Identifying niche markets for products that use native tapioca starch is essential to promote the development of this agro-industry in Colombia and in other producing countries. Native starches are perceived by consumers as “natural” or “less risky” than other ingredients/ additives; this perception and the market trend towards natural foods and clean labels make the use of native starches look promising. However, native starches have limitations in some applications in the food industry because of their instability at high temperatures, high shear forces, low pH values and its tendency to retrogradation at low temperatures, leading to lower end-product quality.

The main objective of this thesis is to evaluate the performance of native tapioca starch in fruit fillings and to develop a starch plus low-methoxyl pectin mixed system able to support pH, nigh temperature and process conditions, adding value to the starch alone because of its improved properties.

First, the addition of pectin to the starch, as the main mixed system, was developed. It was compared to a control of modified starch commonly used in industrially prepared fruit fillings. Starch pasting and viscoelastic properties, instrumental texture parameters (extrusion) and syneresis of the different systems were studied. A number of factors inherent to the conditions of the preparation processes of fruit fillings, such as addition of fruit and stability at different temperature conditions (baking and freezing), were also studied. The effect of cooking in two bakery applications (open and closed systems) was evaluated. The addition of pectin caused a significant increase in the firmness and consistency of the gels analyzed and the fillings without fruit prepared with the proposed system were more resistant to heat treatment than those prepared with tapioca starch alone, showing stable rheological and textural properties during the different processes and similar to those of the modified corn starch, used as control.

Given that at present, the food market is increasingly segmented and consumers seek products not only of good quality but also healthier, satisfying needs, and personal tastes, reduced-sugar fruit fillings were also formulated. Instrumental (rheological and texture) and sensory techniques (quantitative descriptive analysis, QDA) and untrained consumer hedonic studies were performed. Liking and adequacy of some sensory attributes were also evaluated using just-about-right (JAR) scales.

The instrumental and sensory results were highly correlated, and a segmentation into three consumer groups was found in fruit fillings' perception and consumer liking. One group did not like intense sweeteners at all. Another, remarkably, preferred the characteristics of the tapioca starch samples. The third group (the most numerous) did not show these marked tendencies, suggesting that formulations should be adapted to each scenario.

Finally, knowing that a number of textural features are assessed during the consumption of the fillings, which in turn can modulate their flavour perception, two relatively new sensory techniques were applied: Temporal Dominance of Sensations (TDS) with trained assessors (with texture and flavour modalities separately performed) and a check-all-that-apply (CATA) questionnaire with consumers, including the evaluation of an "ideal fruit filling". The results were then correlated with consumers' liking. These sensory techniques allowed the consumer to drive and suggest what aspects of the formulation should be redesigned.

ÍNDICE

INTRODUCCIÓN

INTRODUCCIÓN

1. Almidón nativo de tapioca

Se obtiene de las raíces de la planta cassava (*Manihot esculenta*) que se encuentra en las regiones ecuatoriales. Recibe diferentes nombres dependiendo de la región, en Centro América y norte de Sur América se la denomina yuca, en Brasil mandioca o manioca, en India y Malasia tapioca, en África y suroeste de Asia, cassava. En Norte América y Europa el nombre cassava se aplica a las raíces de la planta y tapioca al almidón y otros productos procesados (Aristizabal 2007; Breuninger et al 2009). El alto contenido de almidón del tubérculo y su proporción de amilosa, en comparación con otras fuentes de almidón, hace de éste un importante cultivo industrial, además de ser una fuente de alimentación rica en calorías. El almidón de tapioca es la segunda fuente de almidón más importante en el mundo después del maíz.

El almidón se encuentra en las plantas en forma de gránulos y presenta diferentes características, dependiendo de la especie vegetal de la que proceda. Químicamente es un polisacárido de glucosa anhidra constituido por dos componentes: amilosa y amilopectina; en las figuras 1 y 2 se pueden observar las estructuras químicas de estos dos componentes. La proporción amilosa - amilopectina, también depende de la fuente vegetal. Los almidones contienen entre un 17-28 por ciento de amilosa; el maíz y el trigo están en el extremo alto del intervalo, mientras la patata y la tapioca están en el extremo más bajo. El almidón de tapioca tiene entre 17-22 por ciento de amilosa. La estructura y la cantidad relativa de ambos componentes del almidón desempeñan un papel importante en la determinación de sus propiedades fisicoquímicas.

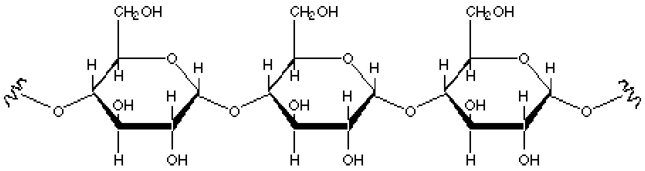

Figura 1. Estructura química de la Amilosa

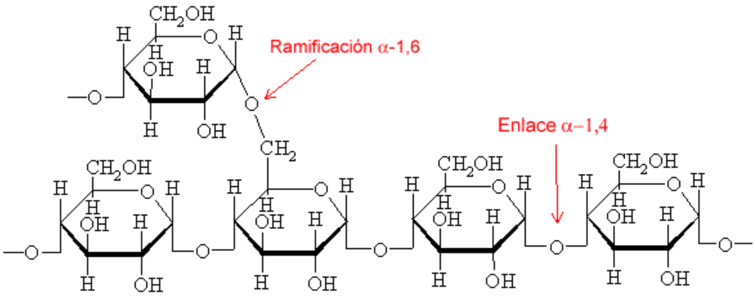

Figura 2. Estructura química de la Amilopectina

1.2. Composición y propiedades fisicoquímicas del almidón nativo de tapioca

La composición (contenido de proteína cruda, fibra cruda, cenizas y humedad), las características del gránulo (tamaño, color, forma y naturaleza cristalina), el peso molecular y el contenido de amilosa determinan el comportamiento del almidón en sus aplicaciones.

El contenido de proteínas de los almidones de tapioca y de patata es bajo, cerca del 0,1 por ciento, comparado con el de los almidones de arroz y de maíz (0,45 y 0,35 por ciento, respectivamente). En general los almidones nativos están empaquetados en gránulos. Los gránulos del almidón de tapioca contienen un pequeño porcentaje de lípidos, comparados con los almidones de cereales como el de maíz y arroz. Esta composición favorece la solubilización del almidón de tapioca, ya que los lípidos forman un complejo con la amilosa, que tiende a inhibir el hinchamiento y la solubilización de los gránulos del almidón. Los gránulos del almidón de tapioca no son uniformes en tamaño y forma: son redondos con terminaciones truncadas, y con un núcleo bien definido; su tamaño varía entre 4-35 mm, con un promedio de 20 mm. Las características de hinchamiento del granulo, gelatinización y formación de pasta, son funciones importantes del almidón cuando se utilizan como ingrediente en sistemas alimenticios para controlar o modificar sus propiedades reológicas (Pongsawatmanit et al 2007). La gelatinización es el mejor proceso para definir las características de un almidón; este proceso induce cambios en los gránulos como el hinchamiento, lixiviación de amilosa y amilopectina, rompimiento de los gránulos, pérdida de birrefringencia; e incremento en la viscosidad (Babic et al. 2006). Diferentes almidones muestran diferentes características de hinchamiento, en términos de volumen final del gel obtenido y en términos de temperatura de respuesta. Los almidones de tubérculos (patata y tapioca) presentan grandes volúmenes de gel, comparados con los que presentan los almidones de cereales. También muestran un fuerte aumento en la viscosidad durante la cocción y tienen picos de viscosidad más altos que los almidones de cereales (Biliaderis, 2009). Por su bajo contenido en amilosa, el almidón de tapioca presenta poca tendencia a la retrogradación, lo cual le confiere potencial para mejorar los ciclos de estabilidad al congelamiento y descongelamiento y la textura en algunos alimentos (Hoover, 2001). El almidón de tapioca gelatiniza a temperaturas relativamente bajas (62-73 ºC); el pico máximo se alcanza rápidamente, lo que implica que es un almidón fácil de cocinar y requiere menor consumo de energía. Sin embargo, aunque la viscosidad de la pasta es inicialmente alta, ésta decae bruscamente cuando continúa la agitación por encima de 90ºC y después de un enfriamiento posterior no hay formación de gel. Las propiedades de claridad y baja retrogradación del almidón de tapioca son útiles en muchos productos alimenticios. Las pastas de almidón de tapioca no son estables en medios muy ácidos, a pH por debajo de 2,4, hay destrucción del gránulo e hidrólisis parcial o total del almidón.

El almidón nativo se utiliza en numerosas aplicaciones industriales; en alimentos se usa para espesar, gelificar, estabilizar, proveer control de humedad y movilidad de agua, mejorar textura y reducir costos (Shi y BeMiller, 2002).

1.3. Aplicaciones del almidón de tapioca en la industria de alimentos

En la industria de alimentos el almidón, tanto nativo como modificado, tiene un papel importante en la textura de varios preparados al aportar palatabilidad y aceptabilidad como:

- Protege contra la humedad; en diversos productos en polvo –como azúcares– pues los almidones absorben humedad sin apelmazarse.
- Imparte textura y estabilidad a caramelos como agente para espolvorear, combinado con azúcar pulverizada en gominolas, caramelos y gomas de mascar.
- Espesa y da cuerpo y textura al alimento preparado; para sopas, alimentos infantiles, salsas, “gelatinas” no animales.
- Confiere textura, sabor y apariencia. La cocción del almidón produce una solución coloidal estable, compatible con muchos ingredientes en productos alimenticios.
- Aglutina y liga componentes. En la preparación de salchichas y embutidos cocidos.
- Emulsifica y produce emulsiones estables en la preparación de mayonesas y salsas similares.
- Estabiliza debido su elevada capacidad de retención de agua se usa en productos mantecados y helados. En la mezcla con harinas para bajar el contenido de proteínas y la fuerza del gluten en panadería.

- En la fabricación de galletas aumenta su capacidad de extenderse y carácter crujiente, además de ablandar, mejorar el sabor y evitar que adherencia.
- Como ingrediente en la preparación de snacks extruidos y expandidos.

En los últimos años hay una tendencia hacia la utilización de almidón de tapioca modificado e hidrolizado en preferencia a la utilización de almidón nativo, para obtener productos de mayor valor agregado; por ejemplo por hidrólisis, se obtienen almidones de baja solubilidad en agua fría y alta solubilidad en agua caliente, logrando geles de baja viscosidad utilizados en la industria alimentaria como espesantes, o para dotar a los alimentos de una película protectora o como estabilizantes en la preparación de jaleas, también para obtener dextrosa y jarabes de glucosa muy empleados en la industria de bebidas. Las tecnologías de modificación surgen como una alternativa rentable para el desarrollo del cultivo de cassava (Aristizabal, 2007). La identificación de nuevos nichos de mercado para productos procesados se hace indispensable para favorecer el desarrollo de la agroindustria de la yuca en Colombia (FAO, 2006). Por otro lado, el incremento del precio del maíz por su uso como sustrato en biocombustible, también hace que se favorezca la oportunidad de reemplazar el maíz y sus derivados por productos de “tapioca” (Jaramillo et al., 2011).

Los consumidores perciben los almidones nativos como “naturales” o “de menor riesgo” que otros ingredientes/ aditivos, como son los almidones modificados (Varela y Fiszman, 2013). Esta percepción y la tendencia del mercado hacia los alimentos naturales y de etiqueta limpia hace prometedor el uso de los almidones nativos (Arocas et al., 2010). No obstante, los almidones nativos tienen limitaciones en las algunas aplicaciones en la industria alimentaria, debido a su inestabilidad a altas temperaturas, a altas fuerzas de cizallamiento, a bajos valores de pH y a su tendencia a retrogradar a bajas temperaturas, causando un descenso en la calidad de los productos finales (Miyazaki et al., 2006). En muchas de estas aplicaciones el almidón interactúa con otros componentes de las formulaciones como azúcares, sales, otros hidrocoloides, etc. que afectan el proceso su gelatinización y el comportamiento durante la formación de pasta, entre otras propiedades (Pongsawatmanit et al 2007).

Por esta razón en el presente trabajo se seleccionó una aplicación alimentaria (relleno de fruta) que supone un reto para el almidón nativo de tapioca por las condiciones adversas de uso, buscando reformulaciones que permitan mejorar su comportamiento, y su tecnofuncionalidad, revalorizando el uso del almidón nativo de tapioca en la industria de alimentos.

2. Rellenos de fruta

Los rellenos de fruta son alimentos semisólidos similares a una mermelada; pueden contener menor cantidad de fruta, menor cantidad de sólidos y en su formulación pueden llevar almidones y otros hidrocoloides para mejorar su estabilidad a las temperaturas de horneado a las que se someten en sus aplicaciones finales. En su formulación contienen fruta, agua, azúcar o edulcorantes, acidulantes y espesantes. Los espesantes más usados son pectinas, almidones modificados y mezclas de hidrocoloides. La principal aplicación de los rellenos es en muy diversos productos de panadería y sus factores de calidad son la estabilidad, buen aspecto, y sabor agradable (Ulinsky, 1989). Por eso es importante conocer el comportamiento de los sistemas que forman y sus interacciones con el resto de los componentes para obtener una formulación adaptada a las aplicaciones finales.

2.1. Agentes de textura o espesante en rellenos de fruta

Un requisito importante a la hora de valorar la idoneidad de un espesante para su aplicación en rellenos de fruta es su estabilidad a pH ácido. La estabilidad de los almidones a diferentes valores bajos de pH es a menudo un punto crítico porque pueden sufrir hidrólisis con cierta facilidad. Los rellenos de fruta presentan valores de pH entre 3 y 4; (Wei et al 2001) estudiaron las propiedades de varios rellenos de fruta comerciales y encontraron intervalos de valores de pH entre 2,6 y 3,5. Los almidones que tradicionalmente se utilizan en aplicaciones a pH ácido son los modificados por entrecruzamiento. En general, a mayor grado de modificación por entrecruzamiento mayor resistencia al pH ácido.

Otro reto importante para el espesante es la estabilidad a altas temperaturas. Cuando se formulan rellenos de frutas deben considerarse dos etapas de calentamiento: el calentamiento durante la preparación del propio relleno (un paso intermedio en la industria) y el calentamiento en el horno durante la cocción de los pasteles. La temperatura afecta la calidad de los rellenos de fruta basados en almidón nativo, debido a su degradación a altas temperaturas que se ve favorecido por los valores bajos de pH. La viscosidad de la pasta de almidón de tapioca nativo también puede disminuir después de varios ciclos de calentamiento; este hecho afectará a su aplicación en rellenos de frutas, ya que conduce a la inestabilidad de la textura durante el almacenamiento (Temsiripong, Pongsawatmanit, Ikedab y Nishinari, 2005; Biliaderis, 2009).

Debido a esta inestabilidad los almidones modificados son los más indicados para esta aplicación. Por esta razón, en el presente trabajo, se seleccionó como control un relleno de fruta elaborado con almidón modificado altamente entrecruzado, hidroxipropilado y fosfatado de maíz waxy (MWCS) que se utiliza normalmente en rellenos de fruta elaborados industrialmente por su estabilidad mejorada. Las modificaciones químicas se realizan sometiendo los almidones nativos a una serie de reacciones asociadas con los grupos hidroxilos de sus polímeros; las más empleadas son el entrecruzamiento, la sustitución y la conversión (Mitolo, 2006). El almidón waxy, seleccionado como control, presenta doble modificación: la primera, por entrecruzamiento en la cual se introducen enlaces covalentes inter e intramoleculares en el polímero de almidón reforzando la estructura granular del mismo; esto permite un mejor control del hinchamiento granular y provee estabilidad ante el medio ácido y ante la degradación térmica y mecánica. La segunda modificación es por sustitución (eterificación), que consiste en la sustitución de los grupos hidroxilos del almidón por grupos monofuncionales como el acetilo o grupos hidroxipropilos. Esta modificación minimiza o previene la retrogradación por impedimento del acercamiento de las moléculas del polímero (Singh et al., 2007).

2.2. La fruta y sus interacciones con los demás componentes

La fruta, es el principal componente de los rellenos. Algunos resultados previos indican que la adición de pulpa de fruta en sistemas que contienen almidones o hidrocoloides, modifica las propiedades reológicas y provoca cambios de textura de los productos finales; los efectos son dependientes de numerosos factores: pH, cantidad de fruta adicionada, tipo de fruta, tamaño de partícula del puré, cantidad de sólidos (azúcares), tipo y concentración de hidrocoloides, y las interacciones entre todos estos factores. En general, existe poca información sobre el efecto de la adición de fruta a sistemas basados en almidón / hidrocoloides (Carbonell, Costell y Duran, 1991a; Carbonell, Costell y Duran, 1991b; Fiszman y Duran, 1992; Wei et al., 2001; Basu y Shivhare, 2010, Baiano, Mastromatteo y Del Nobile, 2012). En particular, en los sistemas que contienen pectina el calcio disponible en la fruta también es un factor importante (Young, Kappel y Bladt, 2003).

2.3. Efecto de la cocción en los rellenos de fruta

Los rellenos de fruta sufren diversos procesos de calentamiento durante su preparación y también en su aplicación final durante el horneado, en su aplicación final como pasteles rellenos, tartaletas, empanadillas, tartas, etc. Los rellenos deben demostrar principalmente estabilidad frente a estos procesos de calentamiento; no deben adquirir una consistencia muy fluida. Cuando existe gran fluidificación el relleno puede derramarse o salirse del pastel y se requemarán en el horno, creando una apariencia que no será aceptable, además de crear humos y suciedad.

El calentamiento afecta la calidad de los rellenos de fruta basados en almidón nativo, debido a la degradación del almidón por calentamiento a valores bajos de pH. La viscosidad de la pasta de almidón de tapioca nativo disminuye después de un ciclo de calentamiento; conduciendo a la inestabilidad de la textura hacia el final de la cocción o durante el almacenamiento (Biliaderis, 2009; Temsiripong, Pongsawatmanit, Ikeda, y Nishinari, 2005). Por esta razón es importante evaluar el comportamiento durante el calentamiento de los diferentes sistemas espesantes usados en los rellenos de fruta.

Por medio de estudios termoreológicos, se pueden determinar los efectos de aumento de temperatura. En el presente estudio, se valoró el efecto de la cocción sobre los rellenos (geles) aplicando barridos de temperatura en ensayos de reología dinámica (descrita en la sesión 4.1.1) y también se desarrolló un método para valorar el comportamiento en aplicaciones reales de los rellenos de fruta. Se estudiaron las características de textura de diferentes alimentos horneados que incluyen el relleno de fruta con el fin de evaluar el comportamiento y la estabilidad durante el horneado.

2.4. Rellenos de fruta reducidos en azúcar

El azúcar en rellenos de fruta contribuye a los sólidos solubles totales, un efecto que es esencial para su estabilidad física, química y microbiológica, así como para sus características sensoriales. Proporciona: dulzor, cuerpo y sensación en boca (*mouthfeel*); mejora el aspecto (color y brillo); y hace posible la gelificación de la pectina (Hyvonen y Torma, 1983; Basu, Shivhare y Singh, 2013). Los azúcares y los polialcoholes en general impiden el hinchamiento del granulo y en consecuencia aumentan la temperatura de gelatinización de los almidones (Sharma 2009; Biliaderis 2009). Pongsawatmanit et al (2007) encontraron que la adición de azúcar retarda el proceso de gelatinización de mezclas de almidón de tapioca y goma xantana resultando en altas temperaturas y entalpias de gelatinización; el pico de viscosidad final del almidón de tapioca se incrementa al incrementar la cantidad de goma xantana y azúcar. La adición de azúcar resulta en un incremento de la retrogradación y mejora el comportamiento viscoelástico de los geles preparados con estas mezclas.

Hoy en día, debido al crecimiento del sector de "alimentos saludables", la reducción del contenido de azúcar en los productos alimenticios mediante su sustitución total o parcial por edulcorantes alternativos se ha convertido en una opción viable para la producción de alimentos bajos en calorías. La sustitución del azúcar por otros edulcorantes es un desafío para los investigadores y para la industria, ya que por su adición suelen modificarse otros atributos sensoriales además del sabor dulce (Cadena, Cruz, Neto, Castro, Faria, y Bolini, 2013).

Cada vez con más frecuencia se utilizan edulcorantes de alta intensidad ya sea por su menor contenido en energía o debido a la relación entre el consumo de azúcar y la diabetes u otras enfermedades (Cadena y Bolini, 2011). La industria utiliza frecuentemente mezclas de edulcorantes para superar las limitaciones sensoriales de los edulcorantes individuales (Zhao y Tepper, 2007). Con las mezclas se aprovecha las sinergias que puedan presentarse; éstas se observan típicamente en edulcorantes que muestran diferentes perfiles de sabor, especialmente si uno de los edulcorantes es amargo. La mezcla tiende a crear un perfil de sabor mejorado.

El esteviósido (stevia) y la sucralosa son dos edulcorantes de alta intensidad no nutritivos, estables al calor y a los ácidos, y se pueden utilizar en combinación para la elaboración de productos como las mermeladas sin comprometer el sabor (Basu et al., 2013). En varios estudios se ha encontrado que la stevia aporta sabor amargo residual, común a muchas especies de stevia (Melo, Bolini, y Efraim, 2009; Prakash, DuBois, Clos, Wilkens, y Fosdick, 2008). Se sugirió que para reducirlo, es importante obtener la stevia con más rebaudiósido (Cadena, Cruz, Neto, Castro, Faria, y Bolini, 2013)). También se ha sugerido que la sucralosa tiene un sabor dulce relativamente limpio y persistente con poca persistencia de amargo (Nabors, 2002; Zhao, y Tepper, 2007).

Sin embargo, los edulcorantes de alta potencia no contribuyen a la textura del producto (se adicionan en muy pequeña cantidad); para mantener las características estructurales que aporta el azúcar se deben usar otras sustancias como sustitutos de la sacarosa en términos de agente de carga, tales como polidextrosa, que presenta propiedades tecnológicas similares a la sacarosa, excepto en el dulzor. La polidextrosa carece de sabor dulce, y ofrece 1 kcal / g en comparación con la sacarosa que tiene 4 kcal / g (Schirmer, Jekle, Arendt y Becker, 2012). La polidextrosa se ha incorporado con éxito en una amplia gama de alimentos, incluidos los productos de panadería, bebidas, confitería y postres congelados y se sabe que proporcionan las cualidades de cuerpo, textura y sensación en boca apropiados (Aidoo, Afoakwa, y Dewettinck, 2014); no aporta retrogusto, ni color y la interacción con el almidón y la proteína se dan de forma similar a la de la sacarosa (Pereira, Ríos de Souza, Teixeira, Queiroz, Borges y Souza, 2013).

3. Uso de hidrocoloides en mezcla con almidones

Los almidones se utilizan en mezclas con diferentes aditivos o ingredientes para mejoren su tecnofuncionalidad (Ortega et al 2001; Babic et al., 2006). Una alternativa para mejorar sus propiedades tecnofuncionales, especialmente la mejora en la textura, es la adición de hidrocoloides, que pueden interactuar con los almidones a través de interacciones moleculares (Ojijo y Shimoni, 2007; Babic et al., 2006).

Los hidrocoloides se pueden definir como polímeros solubles en agua que poseen la habilidad de conferir viscosidad o gelificar sistemas acuosos. Según esta definición los propios almidones son hidrocoloides, sin embargo, suele reservarse esta denominación a los que producen viscosidad a muy bajas concentraciones.

El uso de hidrocoloides como espesantes ha sido estudiado ampliamente, por su diversidad y su funcionalidad. Existe una gran cantidad de información acerca de cómo afectan ciertos hidrocoloides a las propiedades del almidón; sin embargo aún hay aspectos desconocidos en los sistemas almidón – hidrocoloides por la complejidad de sus efectos. Respecto a las propiedades reológicas del almidón de tapioca, es bien conocido que determinados hidrocoloides las afectan en diferentes formas (Breuninger, et al., 2009); principalmente debido a la interacción de las estructuras moleculares de los hidrocoloides y/o a las cargas iónicas del almidón y de ciertos hidrocoloides (Shi y Bemiller, 2002; Bemiller, 2011).

Diversos estudios han mostrado que algunas mezclas de hidrocoloides con almidones conducen a la mejora de ciertas propiedades tecnofuncionales deseables debido al desarrollo de interacciones macromoleculares (Ojijo y Shimoni 2007). (Lim et al 2002) sugirieron que ciertas gomas iónicas pueden actuar como agentes de entrecruzamiento, como también formar copolímeros a través de la formación de ésteres por inducción con calor. Arocha (2011) observó que una pectina de bajo metoxilo inducía un decrecimiento significativo en el pico de viscosidad, estabilidad (*breakdown*), viscosidad final y retrogradación del almidón de patata. Chaisawang et al (2006) investigaron el efecto de goma guar (no iónica) y goma xantana (cargada negativamente) sobre el comportamiento reológico y propiedades de almidón nativo de tapioca (no iónico) y sobre almidón aniónico de tapioca (cargado negativamente); encontraron que hubo tres factores que influenciaron las características de gelatinización; el primero, la estructura morfológica de la goma extendida en la matriz (fase continua) en la cual se encuentran embebidos los gránulos de almidón. La segunda, por el propio poder de hinchamiento de los gránulos de almidón. Y tercera, la interacción electrostática entre los gránulos de almidón y las moléculas de goma.

Khondkar et al (2007) estudiaron el efecto de la pectina sobre las propiedades del almidón de maíz waxy entrecruzado y no entrecruzado; encontraron un aumento en módulo de almacenamiento (G') y el módulo de perdida (G") con la adición de pectina. Además G" fue mayor que G" indicando que estos geles tenían un comportamiento predominantemente elástico con buena estructuración. Con estos datos sugirieron que podía tener lugar un cierto nivel de entrecruzamiento almidón- pectina en los sistemas mixtos.

3.1. Pectinas

Son hidrocoloides que en solución acuosa presentan propiedades espesantes, estabilizantes y sobre todo gelificantes en determinadas condiciones. Están presentes en mayor o menor grado en todas las frutas y plantas superiores, son solubles en agua caliente, insolubles en alcoholes y parcialmente solubles en jarabes ricos en azúcares. Son polímeros del ácido galacturónico, con un contenido medio de éster metílico (figura 3). La principal característica es su capacidad de formar geles en presencia de sólidos solubles suficientes y ácidos o iones polivalentes. Se clasifican de acuerdo con su grado de esterificación en pectinas de alto metoxilo (grado de esterificación superior al 50%) y pectinas de bajo metoxilo (grado de esterificación inferior al 50%). En el presente trabajo se utilizó una pectina de bajo metoxilo, por lo que sus propiedades se discuten en más detalle.

Las pectinas de bajo metoxilo (LMP) al contrario que las pectinas de alto metoxilo forman geles termorreversibles por interacción con el ión calcio presente en el medio; el pH y la concentración de sólidos son factores secundarios que influyen en la velocidad y la temperatura de gelificación y además en la textura final del gel. El comportamiento de estas pectinas está influenciado por varios factores: grado de esterificación de la pectina, su peso molecular, los grados Brix del producto, el valor del pH del producto y la cantidad de sales de calcio presentes (Ahmed, 1981).

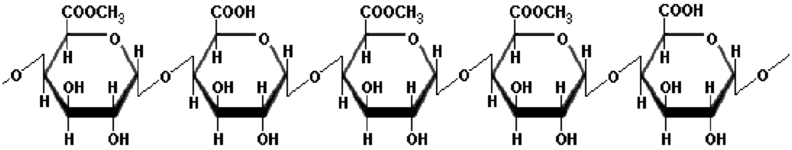

Figura 3. Estructura química de la pectina

Las características que se han tenido en cuenta para seleccionar la pectina de bajo metoxilo como hidrocoloide apto para la mezcla con el almidón de tapioca en el presente trabajo fueron:

- Esta clase de pectinas no requieren azúcares para su gelificación, pueden gelificar en ausencia de sólidos solubles y sólo por la interacción con iones de calcio de acuerdo con el modelo denominado *egg-box* (Young et al 2003). Este factor es muy importante para la elaboración de productos reducidos en azúcar.

- Las pectinas son ampliamente usadas en productos elaborados con frutas como las mermeladas, por ser un componente natural de las mismas.

- Al igual que los almidones nativos, los consumidores perciben las pectinas como un componente de bajo riesgo para la salud por provenir de una fuente natural y familiar para ellos, como lo son las frutas (Varela y Fiszman, 2013). Este factor es importante para el uso en productos de etiqueta limpia.

- Son estables a valores de pH entre 3 y 4, intervalo en el cual se encuentran los rellenos de frutas.

4. Control y desarrollo de los rellenos de fruta

El desarrollo y formulación de productos, al igual que en otras industrias, es una actividad sumamente importante para la industria de mermeladas y rellenos de frutas. La calidad del producto final es el principal determinante de la elección del consumidor. Evidentemente, son los ingredientes los que determinan dicha calidad tanto en términos subjetivos (calidad sensorial) como objetivos (composición, valor nutricional, etc.) (Basu y Shivhare, 2010).

La comprensión de las interacciones de los componentes del sistema o matriz que contiene el almidón será de máxima importancia para el control del proceso y para mejorar la textura y otros atributos de calidad de los productos finales (Biliaderis 2009). En los rellenos de fruta como se ha visto se añaden ingredientes (almidones, hidrocoloides, azúcares, ácidos y fruta entre otros) que pueden desarrollar interacciones, y que sumados a ciertos factores de proceso pueden alterar la calidad final del producto. Es necesario, por tanto, un conocimiento claro de las propiedades reológicas, texturales y sensoriales, con el objetivo de desarrollar nuevos productos y equipos y mejorar los procesos así como ayudar en el control de calidad (Steffe, 1996).

4.1. Textura de los rellenos de fruta

La textura de los alimentos es una percepción sensorial derivada de su estructura (a niveles moleculares, microestructurales y macroscópicos). La apreciación de la textura, atributo multiparamétrico, puede incluir uno o varios estímulos, como el visual, auditivo, táctil y cinestésico, trabajando en combinación (Chen, 2009). La percepción y la apreciación de la textura es un proceso dinámico, basado en las sensaciones generadas durante la deformación y ruptura oral del material alimenticio. Relacionar la textura sensorial de un alimento con sus propiedades microestructurales, reológicas y a grandes deformaciones no es una tarea fácil (Foegeding, 2007). La reología clásica y los ensayos mecánicos (a bajas y a altas deformaciones respectivamente) siguen siendo útiles y esenciales en la evaluación de las propiedades del material de los alimentos (Chen, 2009); pero el instrumento último es el ser humano, cuya percepción debe correlacionarse con los parámetros medidos por medios instrumentales.

4.1.1. Textura instrumental a bajas deformaciones

La mayoría de los alimentos no pueden clasificarse dentro del comportamiento típico de un líquido (viscosidad) ni el de un sólido (elasticidad) ya que presentan componentes de ambos comportamientos, llamado comportamiento viscoelástico. La medida de estas propiedades se realiza mediante ensayos reológicos dentro del intervalo o zona de viscoelasticidad lineal (ZVL). En ésta, la relación entre el esfuerzo y la deformación es lineal, de forma que la respuesta del material en este régimen está fuertemente condicionada por su estructura molecular; por ello se convierte en una buena herramienta de caracterización.

Debido a que los geles (rellenos de fruta) son materiales viscoelásticos, los ensayos reológicos dinámicos a bajas deformaciones resultan adecuados para evaluar sus características. De las pruebas de reología dinámica en la ZVL, se pueden obtener los valores del módulo de almacenamiento, G’, del módulo de pérdida G”, y del factor de pérdida tanδ = (G”/G’). El valor G’ es una medida de la energía de deformación almacenada en la muestra durante el proceso de cizallamiento, que representa la componente elástica de una muestra. El valor que G” es una medida de la energía disipada por la muestra, que representa la componente viscosa (Mezger, 2002). Si G’ es mucho mayor que G”, el material se comporta con mayor característica de sólido; es decir, las deformaciones serán esencialmente elásticas o recuperables. Por el contrario, si G” es mucho mayor que G’, la energía utilizada para deformar el material se disipa fluyendo y el comportamiento del material tiene mayores características de líquido (Rao, 1999). La relación entre los valores de G’ y G’’ define la tangente de pérdidas tanδ, en la que δ representa el desfase existente entre el esfuerzo y la deformación; es un parámetro indicativo de la relación entre la energía disipada y la almacenada por el sistema y de su viscoelasticidad. Si el material fuera totalmente elástico el esfuerzo y la deformación estarían en fase y en ángulo sería de 0º, mientras que si fuera totalmente viscoso habría un desfase de 90º. Los materiales viscoelásticos presentan valores entre 0 y 90º por lo que se tangente varía entre 1 y 0 y da indicación del grado de viscoelasticidad.

4.1.2. Textura instrumental a altas deformaciones

Las grandes deformaciones se aplican para revelar las propiedades mecánicas de los sistemas; con ellas se intenta simular las condiciones de deformación a las que pueden someterse cuando se manipulan en la boca durante la ingestión, o durante la preparación y procesado (Angioloni, y Collar, 2009). En alimentos tipo gel, los resultados de la aplicación de este tipo de ensayos se utiliza para relacionarlos con los atributos sensoriales, ya que las deformaciones aplicadas son del mismo orden (Roopa y Bhattacharya, 2008). Por ejemplo, datos de penetración del gel o de extrusión inversa proporcionan información que puede relacionarse con parámetros de textura como dureza, firmeza, o cohesividad en boca. Estos ensayos mecánicos a alta deformación proporcionan información que también puede estar relacionada con las mediciones dinámicas a bajas deformaciones, pero dicha relación normalmente no es directa.

4.2. Análisis sensorial

El análisis sensorial permite evaluar las sensaciones que se producen cuando se prueba un producto y ofrece una dimensión muy importante en el estudio de la calidad de productos alimenticios. La evaluación sensorial se puede definir como “la disciplina científica utilizada para evocar, medir, analizar e interpretar las reacciones a aquellas características de los alimentos y otras sustancias, percibidas por los sentidos de la vista, olfato, gusto, tacto y oído” (IFT, 2009).

Existen diversas herramientas de análisis sensorial que ayudan en el desarrollo y creación de productos, así como a su reformulación con el objetivo de satisfacer a los consumidores. La investigación cuantitativa del consumidor suele implicar la obtención de sus respuestas a través de métodos de recolección de datos apropiados. Los métodos sensoriales son relevantes en el desarrollo y diseño de productos, y las fases de optimización previas al lanzamiento (Van Kleef van Trijp, y Luning, 2005; Costa, y Jongen, 2006) pero también durante los controles de calidad.

4.2.1. Análisis descriptivo (QDA)

El análisis descriptivo o QDA (*Quantitative Descriptive Analysis)* (Stone y Sidel, 2004), es una herramienta de gran utilidad en el estudio de productos alimenticios. Este ensayo utiliza una metodología que conduce a una descripción completa de los productos y provee la base para determinar cuáles son las características sensoriales clave de los productos, y, en consecuencia, muy probablemente los que estarán relacionados con su aceptabilidad. Las características más importantes de este método son las siguientes:

- Mide todas las características sensoriales
- Puede analizar varios productos a la vez
- Emplea un número limitado de evaluadores altamente entrenados
- Los evaluadores se seleccionan y se monitoriza su actuación
- Emplea descriptores obtenidos por consenso

- Es un método cuantitativo en el que los resultados se analizan estadísticamente

La calidad sensorial de los rellenos de fruta incluye un gran número de características sensoriales. Son particularmente importantes el equilibrio de dulzor y acidez, color, sabor de fruta y una textura de gel homogéneo. Estas características están definidas por muchos atributos, que a su vez estarán relacionadas con las preferencias del consumidor.

Para un producto como los rellenos de fruta es importante entender las relaciones entre la percepción de la textura de gel y estructura (Renard et al., 2006). La textura del producto suele relacionarse con la excelencia de la preparación y debe ser idealmente constante una vez que el producto esté en el mercado. La variación en los tipos de ingredientes o sus niveles de concentración por lo general conduce a cambios en la estructura de gel que los consumidores percibirán como cambios en la textura o en las sensaciones en la boca. Esta “sensación en la boca” es la experiencia sensorial que se deriva durante y después de la ingestión. Los consumidores suelen apreciar términos de calidad (fresco, rancio, tierno, maduro) a partir de sensaciones físicas en la boca (duro, suave, húmedo, seco, etc.) (Basu y Shivhare, 2010). En general, los consumidores prefieren tener control total del alimento cuando se encuentra en su boca; en general, se rechaza un alimento grumoso, o demasiado viscoso, o que contienen trozos inesperados o partículas duras (Grujić et al., 2010).

4.2.2 Predominio temporal de las sensaciones (TDS, Temporal Dominance of Sensations)

Es una metodología sensorial desarrollada recientemente para evaluar la evolución temporal de las percepciones sensoriales en la boca durante la ingestión del producto que se está probando (Pineau et al. 2009). Mientras el análisis descriptivo clásico realiza medidas “estáticas” de la percepción, esta metodología ha ganado gran interés en el campo sensorial debido a su enfoque único que permite la descripción de la secuencia de las percepciones sensoriales predominantes a lo largo de la degustación de un producto. Se ha utilizado para describir diversos productos. El procedimiento de TDS es muy diferente de las metodologías sensoriales estándar. A lo largo de la evaluación, los panelistas tienen que hacer secuencialmente una elección entre varios atributos para determinar cuál de ellos es el que predomina sobre los demás. Por ello, la definición de la lista de atributos a evaluar es el elemento clave (Pineau 2012). Este método se ha utilizado para productos con diferentes propiedades de textura, tales como aguas y bebidas (Reverend et al. 2008; Teillet et al. 2010), cereales (Lenfant et al. 2009), vinos parcialmente desalcoholizados (Meillon et al. 2009), geles sólidos (Labbe et al. 2009), productos lácteos (Pineau et al. 2009), productos rebozados (Albert et al., 2010) o helados (Varela et al., 2014). Hasta ahora no se ha usado en geles suaves como rellenos de fruta o mermeladas

4.2.3 Pruebas con consumidores.

Escalas de adecuación (Just-about-right o JAR)

Las escalas de adecuación, son unas de las más usadas durante el desarrollo de productos (optimización), en conjunto con medidas de aceptabilidad, para ajustar las formulaciones de acuerdo con la preferencia del consumidor. Estas pruebas ayudan a entender qué atributos del producto es necesario modificar para mejorar la aceptabilidad o preferencia (Rhotman, 2007). Las escalas JAR se utilizan en la ciencia de los consumidores para identificar si un atributo es demasiado alto o demasiado bajo en un producto, o si es "justo el adecuado". Las calificaciones de los consumidores proporcionan una indicación de las posibilidades de mejorar el prototipo y la dirección del cambio en la formulación. Se utilizan con frecuencia en los estudios de optimización de producto (Popper, 2014).

En el diseño del producto, un paso clave es la selección de una formulación de producto que se ajusta en la medida de lo posible a las preferencias sensoriales de los consumidores (van Kleef, van Trijp, y Luning, 2006). En este contexto, uno de los principales desafíos para la ciencia sensorial y del consumidor es proporcionar información útil para la decisión de cambios específicos en la formulación del producto (Moskowitz y Hartmann, 2008). Uno de los pasos más importantes del proceso es la identificación del producto ideal para los consumidores y el camino a seguir para la reformulación. En el presente trabajo se utilizó la técnica cuestionario CATA con el fin de profundizar en este conocimiento sobre las percepciones del consumidor. Así, se obtuvo información para una adecuada orientación hacia la diversificación y reformulación de los rellenos de fruta usando almidón de tapioca.

Cuestionario CATA (Check-all-that-apply)

CATA es un método accesible y de uso fácil para el consumidor; se utiliza cada vez con mayor frecuencia para obtener la percepción de los consumidores sobre las características sensoriales y no sensoriales de los productos alimenticios. Ha ido ganando popularidad debido a su simplicidad y facilidad de uso (Adams, Williams, Lancaster, y Foley, 2007; Ares, Barreiro, Deliza, Giménez y Gámbaro, 2010; Ares, Varela, Rado y Giménez, 2011a; Dooley, Lee y Meullenet, 2010; Plaehn, 2012). En este método se presenta a los consumidores una lista de términos y se les pide que seleccionen todos los que consideren apropiados para describir el producto que están evaluando. La relevancia de cada término para cada producto se determina calculando la frecuencia de selección que hace el conjunto de consumidores encuestados. Este método de análisis puede usarse para identificar qué características del producto son importantes para el consumidor y su relación con los determinantes de la aceptación o la preferencia, en combinación con datos de aceptabilidad.

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OBJETIVOS

OBJETIVO PRINCIPAL

El objetivo principal de esta Tesis Doctoral es la evaluación del desempeño del almidón de tapioca nativo en rellenos de fruta y propuesta de un sistema mixto con pectina que admita las correspondientes condiciones de pH, de temperatura y de proceso.

Objetivos específicos

- Evaluar el efecto de la adición de pectina de bajo metoxilo sobre las propiedades reológicas y de textura del almidón de tapioca nativo y comparar su tecnofuncionalidad con almidón de maíz waxy modificado, usado como control.

- Investigar el efecto de los tratamientos de calentamiento y congelación/ descongelación sobre las propiedades reológicas de los sistemas propuestos para la elaboración de rellenos de fruta. Estudiar los efectos de la cantidad de fruta y del horneado en aplicaciones de pastelería.

- Evaluar el efecto de la cantidad de fruta y del reemplazo de azúcar con polidextrosa y edulcorantes de alta intensidad sobre las propiedades reológicas, la textura instrumental y las características sensoriales de los rellenos de fruta y sobre la percepción oral dinámica de los rellenos de fruta

- Evaluar las características de los rellenos de fruta propuestos con técnicas que estudian la percepción del consumidor, estudiando posibles nichos de preferencia.

ESTRUCTURA DE LA TESIS DOCTORAL

El trabajo de investigación realizado ha dado origen a diversas publicaciones científicas, cuyo contenido se presenta en los distintos capítulos de la presente Tesis Doctoral. Las referencias de las publicaciones y el capítulo en que aparecen son:

Capítulo I.

Agudelo, A., Varela, P., Sanz, T., y Fiszman, S. (2014). Native tapioca starch as a potential thickener for fruit fillings. Evaluation of mixed models containing low-methoxyl pectin**.** *Food Hydrocolloids*, 35, 297-304

Capítulo II.

Agudelo, A., Varela, P., Sanz, T., y Fiszman, S. (2014). Formulating fruit fillings. Freezing and baking stability of a tapioca Starch-pectin mixture model. *Food Hydrocolloids*, 40, 203-213

Capítulo III.

Agudelo, A., Varela, P., y Fiszman, S. (2014).Fruit fillings development: a multiparametric approach. Aceptado con cambios menores en *LWT*

Capítulo IV.

Agudelo, A., Varela, P., y Fiszman, S. (2014). Methods for a deeper understanding of the sensory perception of soft gelled systems. Enviado a *Food Hydrocolloids*

En el capítulo 1 se evaluó la adición de pectina en combinación con el almidón de tapioca como sistema modelo de agente espesante en un relleno de fruta y se compararon las propiedades de formación de pasta, las propiedades viscoelásticas, los parámetros de textura instrumental (extrusión) y sinéresis del sistema propuesto con el almidón nativo de tapioca solo y con un control (almidón modificado de maíz waxy) usado en rellenos de fruta industrialmente

En el capítulo 2 se investigó la influencia de los tratamientos de calentamiento y congelamiento/ descongelamiento sobre las propiedades de formación de pasta, propiedades viscoelásticas, propiedades de textura (extrusión) y la sinéresis de los sistemas con y sin fruta (mezcla del almidón de tapioca y pectina, almidón control y almidón de tapioca). Además se evaluó el efecto de la cocción sobre la textura en dos aplicaciones de panadería (sistemas abiertos y cerrados).

En el capítulo 3 se evaluaron rellenos de fruta reducidos en azúcar, elaborados con diferente cantidad de fruta y remplazando el azúcar por polidextrosa como agente de carga y una mezcla de edulcorantes de alta intensidad. Para ello se aplicaron técnicas instrumentales (reológicas y de textura) y técnicas sensoriales (estudios de análisis sensorial descriptivo (QDA) clásico con panel entrenado y estudios con consumidores no entrenados para evaluar su aceptabilidad y adecuación (uso de escalas JAR).

En el último capítulo se aplicaron técnicas sensoriales relativamente nuevas para poder profundizar en la comprensión de la percepción de sistemas gelificados suaves como los rellenos de fruta. Las técnicas usadas fueron: Dominio temporal de las Sensaciones (TDS: *Temporal Dominance of Sensations*) evaluando textura y sabor por separado y análisis CATA (*Check-all-that-apply*) incluyendo la evaluación de un "relleno de fruta ideal". Los resultados se relacionaron con la aceptabilidad por los consumidores.

CAPÍTULO 1

Native tapioca starch as a potential thickener for fruit fillings. Evaluation of mixed models containing low-methoxyl pectin

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ABSTRACT

Fruit fillings for pastries are low-pH systems that have to withstand baking temperatures without loss of quality. The present study evaluated a mixed system based on native tapioca starch (NTS) with the addition of low-methoxyl pectin (LMP) as a model for use in an acid environment (pH 3.0-3.2). This system was compared with a modified (highly cross-linked, hydroxypropylated and phosphated) waxy corn starch (MWCS) commonly used in industrial fruit fillings. The starch pasting and viscoelastic properties, instrumental texture and syneresis were measured. The addition of LMP to replace 10% of the NTS significantly increased the peak viscosity (PV), hot paste viscosity (HPV), cold paste viscosity (CPV) and total relative setback of the NTS and reduced relative breakdown. The mixed system also made the gel stronger and more elastic, achieving similar levels of viscoelastic properties to those of the control starch. At a frequency of 1 Hz, in acid conditions and with 35% sugar, no significant differences in G', G" and tan G'/G" were found between the mixed system and the control (MWCS). The addition of pectin caused a significant increase in the firmness and consistency of the gels analyzed by extrusion tests.

Keywords: Tapioca starch, Pectin, Fruit fillings, Rheology, Pasting properties, Texture, Syneresis.

1. INTRODUCTION

Identifying niche markets for products that use native tapioca starch e which is extracted from cassava roots e and acquiring a deeper knowledge of its applications in food systems and matrices would boost the development of this agro-industry in Colombia and other South American countries (FAO, 2006). Native starches (NS) are perceived by consumers as “natural” or “less worrying” than other ingredients/additives (Varela y Fiszman, 2013); this perception and the market trend towards natural foods and clean labels make the use of native starches look promising (Arocas, Sanz, y Fiszman, 2010). However, in industrial applications such as in fruit fillings for pastries, which have low pH values because of the fruit and must withstand the baking temperatures, NS present limitations as they are unstable in these conditions and tend to retrograde at low temperatures, leading to lower end-product quality (Miyazaki, Van Hung, Maeda, y Morita, 2006). In these kinds of application modified starches are indicated.

For example, modification by etherification provides stability against retrogradation and modification by cross-linking provides stability against acid, thermal and mechanical degradation (Singh, Kaur, y McCarthy, 2007). Another alternative to improve the functional properties of NS is to use hydrocolloids, which could act with starches through macromolecular interactions (Babic et al., 2006; Ojijo y Shimoni, 2007). It has been shown that particular hydrocolloids affect the rheological properties of tapioca starch in different ways (Babic et al., 2006; Breuninger, Pyyachomkwan, y Siroth, 2009), largely owing to the molecular structure of the hydrocolloids and/or the ionic charges of the starch and the hydrocolloids (BeMiller, 2011; Shi y BeMiller, 2002). Pectin is the hydrocolloid most frequently used in systems containing fruit; for fruit fillings _ which normally contain less than 55% sugar _ low methoxyl pectin (LMP) with the addition of calcium ions would be indicated. Information on mixed starch/LMP systems is scarce. Khondkar, Tester, Hudson, Karkalas, and Morrow (2007) studied the effect of LMP on the dynamic rheological properties of crosslinked and uncross-linked waxy corn starch and found that G’ and G” increased when pectin was added. They suggested that there could be cross-linking between the starch and the pectin in this type of system. Lim, Han, Lim, and BeMiller (2002) also suggested that ion-charged gums could act as cross-linking agents in starch-gum systems.

The effects of other gums such as guar gum (non-ionic) and xanthan gum (negatively charged) on the properties and rheological behaviour of native tapioca starch (non-ionic) and of anionic (negatively charged) modified tapioca starch were researched by Chaisawang and Suphantharika (2006), who found that the system gelling characteristics were influenced by three factors: (a) the continuous phase of the gum extending through the matrix where the starch granules had collected, (b) the swelling ability of the starch granules themselves and (c) the electrostatic interaction between the starch granules and the gum molecules. The dominance of each factor was dependent on the combination of each specific starch and gum: xanthan gum totally wrapped around the NS granules and made it more difficult for them to swell and, in turn, to gelatinize. On the other hand, in the modified starche xanthan system gelatinization was retarded compared with the native starch due to repulsion between the starch granules and the gum. The guar gum, on the other hand, did not wrap round either the native or the anionic starch granules but allowed them to gelatinize freely.

Sugar, whether alone or in the presence of hydrocolloids, has well-know effects on starch gelatinization that have been studied by a number of authors (Babic et al., 2009; Baek, Yoo, y Lim, 2004; Chantaro y Pongsawatmanit, 2010; Eliasson, 1992; Perry y Donald, 2002; Rumpold, Bauer, y Knorr, 2005; Sharma, Oberoi, Sogi, y Gill, 2009). The presence of sugars and of polyols prevents the starch granules from swelling and increases their pasting temperature and gelatinization temperature, measured by a Rapid Visco Analyser (RVA) and by differential scanning calorimetry (DSC) respectively. In tapioca starch (TS) specifically, Pongsawatmanit, Temsiripong, and Suwonsichon (2007) studied mixtures of NTS and xyloglucan and found a higher pasting temperature in the presence of sugar, measured with an RVA. They also observed that the final viscosity peak rose when the quantities of sugar were increased. Chantaro and Pongsawatmanit (2010) observed the same effects in mixtures with xanthan gum.

The purpose of this study was to assess the effect that adding low-methoxyl pectin plus calcium would have on the rheology and consistency of native tapioca starch and to compare its performance with that of modified waxy corn starch, used as a control, in order to reappraise the use of native tapioca starch under the typical sugar concentration, pH, and temperature conditions of fruit fillings.

2. MATERIALS AND METHODS

2.1 Ingredients

The ingredients employed were native tapioca starch (NTS) (moisture content 13.7%, Sucroal S.A., Colombia), citric acid and sodium citrate (Sucroal S.A., Colombia), highly cross-linked waxy corn starch, hydroxypropylated and phosphated (MWCS) (moisture content 12.3%, Polartex 6716, Cargill, Spain), low-methoxyl pectin (LMP) (33-37% esterified, moisture content 12%, Unipectine OB700, Cargill, España), anhydrous calcium chloride (Panreac, Spain) and white sugar (Hacendado, Spain).

2.1.1. Native tapioca starch characterization

The moisture and ash content of the tapioca starch were measured using standard USP procedures (USP, 2009). The phosphate content was measured by an NTC (Norma Tecnica Colombiana) procedure (ICONTEC, 2001), the pH and acidity by procedure ISI 26-5e (ISI, 1999) and the amylose content by a colorimetric method employing visible UV spectrophotometry (Jarvis y Walter, 1993; Wuttisela, Shobsngob, Triampo, y Triampo, 2008). All the measurements of physical and chemical properties were carried out at the Sucroal S.A. Food Research and Development Laboratory in Colombia.

2.2 Sample preparation

The samples were prepared in a food processor-cooker (Thermomix TM 31, Wuppertal, Germany) equipped with temperature and stirring speed controls. All the samples were prepared at pH 3 and contained 35% sugar and 6% of the thickener system. The thickener model systems employed were the control starch (MWCS), native tapioca starch (NTS) and NTS with two levels of pectin e 0.3% and 0.6% of the total sample weight e and two levels of calcium ions in each, namely 40 mg and 60 mg of calcium ions per gram of pectin (Table 1). The sample preparation for the determination of the pasting properties is described in Section 2.3.

The first step in preparing the samples was to add the sugar to part of the water, heat to 60ºC and stir at 600 rpm for 5 min. In the formulations with pectin, this was first dispersed in water with the magnetic stirrer at 80ºC until it was totally dissolved, then allowed to cool to 60ºC before adding it to the sugar-water mixture. The starch was dispersed in another part of cold water and added to the sugar-water mixture, which continued to be stirred while heating for another 2 min. Once the mixtures had been prepared with these ingredients, the temperature was increased to 90ºC and heating and stirring continued for a further 30 min. The calcium chloride was then dissolved in a small amount of water and added to the mixtures containing pectin. The pH was adjusted to between 3 and 3.2, using citric acid and sodium citrate buffer solutions, and stirring and heating continued for a further 5 min. The samples were transferred to plastic containers and held in refrigeration (8ºC) for 24 h. Before each test, the samples were stabilized for 1h at ambient temperature.

Table 1. Ingredients of the thickener model system (expressed per 100 g formulation). All formulations contain 35% sugar

Sample	Ingredient*			
	NTS g	LMP g	$CaCl_2$ mg*	MWCS g
NTS	6	-	-	-
NTS+LMP 0.3+Ca60	5.65	0.30	0.050	-
NTS+LMP 0.3+Ca40	5.67	0.30	0.033	-
NTS+LMP 0.6+Ca60	5.30	0.60	0.100	-
NTS+LMP 0.6+Ca40	5.33	0.60	0.067	-
MWCS	-	-	-	6

NTS=Native Tapioca Starch, MWCS=Modified Waxy Corn Starch, LMP=Low Methoxyl Pectin, Ca=Calcium ion, $CaCl_2$=Calcium chloride
* The calcium salt dosages were 40 mg and 60 mg of calcium ion per g of pectin in each system (LMP 0.3 and LMP 0.6)

2.3 Starch pasting properties

Starch pasting properties were determined using a Starch Pasting Cell attached to a controlled stress rheometer (AR-G2, TA Instruments, Crawley, England). The measurements were made in starches dispersed at 6% (w/v) in water or in the corresponding water solution (with different levels of sugar, citric acid, calcium chloride or LMP). 25 g of the dispersion were placed in the cylindrical container and inserted into the base of the pasting cell. The sample was stirred vigorously at 100 s^{-1} for 10 s and the stirring speed was set to 30 s^{-1} until the end of the test. The samples were heated from 30ºC to 90ºC at a speed of 15 ºC/min, held at 90 ºC for 5 min, cooled to 30ºC at a speed of 15ºC/min and finally held at a constant temperature of 30ºC for 5 min. The data were collected with the software supplied with the equipment (TA Data Analysis, TA Instruments, Crawley, England).

The parameters extracted were pasting temperature (PT), taken as the temperature at which the viscosity begins to rise; peak viscosity (PV), taken as the highest viscosity achieved during heating; hot paste viscosity (HPV), taken as the viscosity value at the end of the isothermal period at 90ºC; cold paste viscosity (CPV), taken as the viscosity value at the end of the isothermal period at 30ºC; breakdown (PV-HPV); relative breakdown (PV-HPV)/PV; total setback (CPV-HPV); and relative total setback, (CPV-HPV)/CPV.

2.4 Viscoelastic properties

The linear viscoelastic properties were measured using a controlled stress rheometer (AR-G2, TA Instruments, Crawley, England) with Peltier temperature control, using a 60 mm diameter plate-plate geometry with a 1 mm gap. Before measurement began, the sample was left to stabilize between the plates for 10 min. The measurements were carried out at 20ºC. Stress sweeps were carried out to determine the linear viscoelastic region, followed by frequency sweeps from 10 to 0.01 Hz at stress amplitude inside the linear region. The storage modulus (G’), loss modulus (G”) and loss tangent (tanδ or tan G”/G’) were recorded with the software (TA Data analysis, TA Instruments, Crawley, England).

2.5 Extrusion test

The extrusion properties were measured with a texture analyzer (TA-XT Plus, Godalming, England) equipped with a 50 mm diameter back extrusion cell (A/BE Back Extrusion Rig) with a 10mmgap between the extrusion cylinder and the compression disk. The compression speed was 10 mm/s and the trigger point was 10 g. The duration of the test was set at 15 s (Arocas, Sanz, y Fiszman, 2009). The samples were placed in an extrusion cylinder and stabilized in a water bath at 25ºC for 10 min before making the measurements. The force-displacement profiles were recorded and the area under the curve (AUC, in N s) and maximum extrusion force (Fmax, in N) as a measure of consistency were obtained.

2.5 Syneresis

Two methods were used to measure syneresis: Centrifugation. The method used was adapted from Sanguansri, Orawan and Janya (2008). The sample was weighed and centrifuged (Sorvall RC-5B, DuPont Instruments, Wilmington, DE, USA) at 8000 g for 15 min. The liquid released was removed and weighed. After extrusion. The method used was adapted from Arocas et al. (2009). Syneresis was quantified 2 min after the extrusion test. The sample was weighed and transferred to a funnel lined with filter paper (Whatman 42) and the liquid released was collected for 15 min. This method is intended to reduce the degree of gel structure destruction that occurs during centrifuging. In both methods, syneresis was expressed as the amount of liquid released per 100 g of sample.

% Syneresis = (Weight of liquid released / Total initial weight of sample)*100

2.7 Statistical processing of the data

All the tests were carried out in duplicate with samples prepared on different days. Analyses of variance (ANOVA) were performed to compare the effect of adding the different ingredients on the pasting properties of the tapioca starch in comparison to the control starch (MWCS). Tukey's multiple comparison test was used to analyse inter-group differences with a 95% confidence interval. These analyses were performed with the XLSTAT statistics software package (Addinsoft-Barcelona-Spain, version 2009, 4.03).

3. RESULTS AND DISCUSSION

3.1 Physico-chemical properties of tapioca starch

The NTS assay results are shown in Table 2. The values were similar to those reported in other studies (Sriroth, Santisopasri, Petchalanuwat, Kurotjanawong, y Piyachomkwan, 1999). The 13.7% moisture content was high but acceptable. Nuwamanya, Baguma, Emmambux, and Rubaihayo (2010) reported starch moisture levels ranging from 14% to 16% and stated that the level depends on the process employed and the storage conditions. The 0.011% phosphate content was similar to the levels in tapioca starch reported by other authors: 0.016-0.018% (Moorthy y Ramanujam, 1986), 0.008% organic and 0.001% inorganic phosphate (Hoover, 2001) and 0.01% total phosphate content in tapioca starch (Breuninger et al., 2009). The 23.55% amylose content was in the high regions of the ranges reported by several authors (Freitas, Paula, Feitosa, Rocha, y Sierakowski, 2004; Nuwamanya et al., 2010; Sajeev, Sreekumar, Unnikrishnan, Moorthy, y Shanavas, 2010). A high amylose content has usually been linked to a greater tendency to retrogradation in starches, showing higher peak viscosities with consequently greater breakdown

(Hoover, 2001). Charles, Chang, Ko, Sriroth, y Huang (2005) identified the fine structures of five genotypes of TS and established that variations between the starches were due to altered amylose and amylopectin structural elements. They obtained the highest gelatinization temperatures in the starches with the highest amylose content and attributed this finding to the high level of interactions in the long branch chain amylopectin and the high amylose molecule sizes observed in these starches. Because of their structure, these starches formed gels that were slightly more independent of frequency in oscillatory tests and were firmer and more stable.

Table 2. Physico-chemical description of the native tapioca starch

Physico-chemical property	Value
Moisture (% w/w)*	13.70 (0.20)
Ash (% w/w)*	0.09 (0.01)
Phosphates (% w/w)*	0.01 (0.001)
Acidity (% w/w)	0.06 (0.007)
pH in solution (1% w/v)	5.58 (0.14)
Amylose (%)	23.55 (0.49)

Figures in brackets are standard deviations
* Dry bases

3.2 Starch pasting properties

3.2.1. Effect of pH

An important requisite when assessing the suitability of a starch for use in fruit fillings is its stability at an acidic pH. The starches traditionally used in acidic pH applications are ones that are modified by cross-linking. Generally speaking, the greater the modification by cross-linking the greater their resistance to acidic pH values. Table 3 shows the pasting parameters, PV, PT, HPV, CPV, relative total setback and relative breakdown values at different pH levels, comparing their effect in NTS and in a highly cross-linked modified starch that is appropriate for this application (MWCS, control). As expected, the pH values had completely different effects on the pasting parameters in the two types of starches. In the NTS, PT and PV decreased significantly as the pH fell. However, the most noticeable change at the lowest pH was a significant decrease in HPV and an associated increase in relative structure breakdown, showing the high level of starch structure breakdown which takes place during the heating step at a low pH. The CPV values were also significantly lower at pH 3, which again points to the inability of NTS to produce a gel at pH 3.

The effect of pH on MWCS was completely different, as the high level of cross-linking makes it resistant to low-pH levels. In this starch, the maximum viscosity developed at pH 3 and the PV, HPV and CPV levels all rose as the Ph decreased. One noticeable feature of the behaviour of the MWCS was that the viscosity values rose slightly during the isothermal stage at 90ºC, showing that because of its high degree of crosslinking, this starch needs high acidity and a high temperature in order to swell and develop maximum viscosity. The rise in viscosity during the isothermal period at 90ºC explains the negative relative breakdown values, which indicate that the granular structure of this starch most probably did not breakdown. The pasting temperature was altered very slightly by the pH in the range studied (Table 3). The instability of native starches to acidic conditions has been reported by many authors. Mali et al. (2003) compared the rheological behaviour of yam tuber starch and tapioca starch in solutions at pH 3 and 6, using a Brabender Viscograph, and obtained very similar results, although they did not find that the pH affected the pasting temperature. Sae-kang and Suphantharika (2006) studied the influence of pH on tapioca starch at pH 3, 6 and 9, using DSC, and found very low gelatinization enthalpy at pH 3, which indicated that the starch underwent acid hydrolysis.

Table 3. Effect of pH on mean pasting property values of native tapioca starch (NTS) and modified waxy corn starch (MWCS), measured in the starch pasting cell

Starch	pH value	PV (Pas)	PT (°C)	HPV (Pas)	CPV (Pas)	Relative total setback	Relative breakdown
NTS	3	0.505^{a} (0.011)	67.10^{b} (0.14)	0.166^{b} (0.000)	0.348^{c} (0.005)	$O.520^{b}$ (0.024)	0.672^{a} (0.006)
	4	0.505^{a} (0.001)	67.50^{b} (0.01)	0.269^{a} (0.005)	0.678^{b} (0.024)	1.518^{a} (0.041)	0.468^{b} (0.009)
	5	0.488^{a} (0.011)	68.60^{a} (0.14)	0.278^{a} (0.001)	0.735^{a} (0.114)	1.645^{a} (0.011)	0.430^{b} (0.006)
MWCS	3	0.293^{a} (0.002)	66.00^{b} (0.01)	0.381^{a} (0.001)	0.839^{a} (0.001)	0.546^{a} (0.001)	-0.301^{a} (0.014)
	4	0.216^{b} (0.007)	67.00^{a} (0.02)	0.273^{b} (0.010)	0.645^{b} (0.023)	0.576^{b} (0.001)	-0.263^{a} (0.094)
	5	0.181^{c} (0.001)	67.50^{a} (0.01)	0.215^{c} (0.001)	0.542^{c} (0.003)	0.602^{c} (0.003)	-0.194^{a} (0.002)

Figures in brackets are standard deviations

Different letters within the same column indicate significant differences ($p>0.05$) according to Tukey's multiple comparison test

NTS=Native Tapioca Starch, MWCS=Modified Waxy Corn Starch, PV= peak viscosity, PT= pasting temperature, HPV= hot paste viscosity, CPV= cold paste viscosity.

In the present work, no significant differences in pasting properties were found at pH 4, 5 or 6 (data not shown). These results are in agreement with those reported by Muhrbeck and Eliasson (1987), who observed that the rheological data for tapioca starch were not sensitive to pH levels of between 4.2 and 9.2. The starch hydrolysis mechanism presented two phases: the first corresponded to a faster degradation of the amorphous areas of granules and the second to a slower degradation of the crystalline regions. The acid hydrolysis rate of starch granules depends on the source of the starch and the amount of acid added (Campanha and Franco, 2011). In the present case, pH values from 4 to 6 did not have a significant effect on the pasting profile of NTS.

3.2.2. Effect of sucrose

Fruit fillings not only have low pH but also high sugar levels, so it is useful to know the effect of sugar concentrations on the gelatinization of starch at an acidic pH level (pH 3). The effect of sugar on the pasting parameter values of NTS and MWCS are shown in Table 4. The viscosity values and PT rose with the sugar concentration. Significant differences were found in PV, PT, HPV and CPV. Similar results have been reported in a number of papers dealing with tapioca starch. Pongsawatmanit et al. (2007), using an RVA, found that with higher sugar and xyloglucan contents, dispersions of NTS and xyloglucan in different proportions showed increases in the viscosity peak and final viscosity. According to Chantaro and Pongsawatmanit (2010), a higher sugar concentration increased the PT, PV, CPV, breakdown and setback values in mixtures of NTS and xanthan gum. Baek et al. (2004) and Babic et al. (2006) found that the gelatinization temperature and enthalpy of corn starch and tapioca starch with different types of sugar rose with increased sugar concentration. Rumpold et al. (2005) and Sharma et al. (2009) established that tapioca starch gelatinization is delayed by the addition of sugar. Eliasson (1992) and Baek et al. (2004) explained the effect of sugar on the gelatinization of starch in terms of two mechanisms. One is based on a reduction in the available water and water activity in the presence of sugar.

Table 4. Effect of sugar concentration on mean pasting property values of NTS and MWCS. All formulations at pH=3

Sample	Sugar level %(w/w)	PV (Pas)	PT (°C)	HPV (Pas)	CPV (Pas)	Relative total setback	Relative breakdown
NTS	0%	0.505^{c} (0.01)	67.10^{c} (0.14)	0.166^{c} (0.01)	0.348^{c} (0.01)	0.520^{c} (0.02)	0.672^{a} (0.01)
	15%	0.743^{b} (0.01)	73.10^{b} (0.14)	0.243^{b} (0.01)	0.667^{b} (0.01)	0.636^{b} (0.01)	0.673^{a} (0.01)
	35%	1.125^{a} (0.01)	80.40^{a} (0.01)	0.415^{a} (0.01)	1.546^{a} (0.01)	0.732^{a} (0.01)	0.631^{b} (0.004)
MWCS	0%	0.293^{c} (0.01)	66.00^{b} (0.02)	0.381^{b} (0.01)	0.839^{b} (0.01)	0.546^{b} (0.00)	-0.301^{a} (0.01)
	15%	0.39^{b} (0.01)	70.50^{ab} (0.01)	0.443^{b} (0.02)	0.996^{b} (0.05)	0.555^{b} (0.01)	-0.125^{a} (0.09)
	35%	1.173^{a} (0.01)	74.50^{a} (0.01)	1.43^{a} (0.16)	4.37^{a} (0.08)	0.673^{a} (0.03)	-0.218^{a} (0.14)

Figures in brackets are standard deviations
Different letters within the same column indicate significant differences ($p>0.05$) according to Tukey's multiple comparison test
NTS=Native Tapioca Starch, MWCS=Modified Waxy Corn Starch, PV= peak viscosity, PT= pasting temperature, HPV= hot paste viscosity, CPV= cold paste viscosity.

The second is based on sugar-starch interactions: as the volume of free solvent falls, its plastifying effect is reduced and its interaction with the molecules of starch is delayed, resulting in a delay in gelatinization. However, Perry and Donald (2002) reported that in presence of sugar, once gelatinization is initiated it progresses in an identical way to that found in pure water. The nature of the plasticizing solvent does not affect the mechanism but the greater the mean molecular weight of the solvent (whether by increasing the solution concentration or the molecular weight of the individual solute), the greater the extent to which gelatinization is shifted to higher temperatures. According to these authors, these variations in gelatinization appear to be caused not by specific starch-solute or solute-water interactions but by non-specific variation in thermodynamic and kinetic properties which affect the ability of granules to swell.

For both NTS and MWCS, the relative total setback rose when the sugar concentration increased but the relative breakdown was practically unaffected. A slight although significant reduction in relative breakdown was observed in the NTS when the sugar concentration rose, whereas the MWCS showed negative breakdown values because this modified starch did not present breakdown (Table 4): as cross-linking strengthens the bonds between the starch chains, causing resistance of the granules to swelling, they retained their integrity at 90ºC.

3.2.3. Effect of calcium and pectin

Table 5 presents the effects of adding LMP and calcium ions on the pasting parameters of NTS, with and without sugar. Adding calcium ions alone (in the form of CaCl2) at concentrations of 0.033% and 0.100% did not have a significant effect on the parameters that represent NTS gelatinization. These results agreed with the findings of Muhrbeck and Eliasson (1987) that adding electrolytes at low concentrations did not alter the gelatinization temperature or enthalpy of tapioca starch but did affect those of potato starch. The difference between these two starches is that the NTS has a lower proportion of phosphate groups than potato starch and they do not act in the same way during gel formation. The high degree of phosphate group substitution in the potato starch increases its negative charge, giving it different characteristics to those of other tuber starches (Karim et al., 2007; Noda et al., 2007). In rice starch, both native and hydroxypropylated, a fall in viscosity has been reported when calcium salts were added (Islam y Mohd, 1997). These authors suggested that the calcium and starches form chelates by means of intra- and inter-molecular hydrogen bonds or bridges that create cross-links between the molecules or within the same molecule through the coordination of two anionic oxygens (ionized hydroxyl groups), which affects the behaviour of the starch.

Table 5. Mean pasting property values of formulations containing 6% of thickener model systems

Sample*	mg Ca	Sugar level % (w/w)	PV (Pas)	PT (ºC)	HPV (Pas)	CPV (Pas)	Relative total setback	Relative breakdown
NTS	0	0	0.505^{d} (0.01)	67.10^{b} (0.14)	0.166^{d} (0.00)	0.348^{e} (0.01)	0.520^{e} (0.02)	0.672^{a} (0.01)
NTS	40	0	0.486^{d} (0.01)	67.40^{b} (0.01)	0.178^{cd} (0.01)	0.385^{e} (0.01)	1.169^{d} (0.01)	0.634^{b} (0.01)
NTS	60	0	0.502^{d} (0.02)	67.50^{b} (0.00)	0.179^{cd} (0.00)	0.382^{e} (0.02)	1.134^{d} (0.12)	0.644^{ab} (0.00)
NTS+LMP 0.3+Ca40	40	0	0.554^{c} (0.01)	67.10^{b} (0.14)	0.193^{c} (0.01)	0.471^{d} (0.01)	1.442^{c} (0.01)	0.652^{ab} (0.00)
NTS+LMP 0.6+Ca60	60	0	0.807^{b} (0.01)	67.20^{b} (0.14)	0.351^{b} (0.01)	0.881^{c} (0.01)	1.507^{b} (0.01)	0.565^{c} (0.01)
NTS+LMP 0.3+Ca40	40	35	1.359^{a} (0.01)	80.15^{a} (0.07)	0.551^{a} (0.003)	2.004^{a} (0.010)	2.636^{a} (0.00)	0.594^{bc} (0.00)
NTS+LMP 0.6+Ca60	60	35	1.366^{a} (0.01)	80.25^{a} (0.07)	0.526^{a} (0.002)	1.916^{b} (0.01)	2.641^{a} (0.01)	0.615^{b} (0.01)

Figures in brackets are standard deviations
Different letters within the same column indicate significant differences ($p>0.05$) according to Tukey's multiple comparison test
NTS=Native Tapioca Starch, MWCS=Modified Waxy Corn Starch, LMP=Low Methoxyl Pectin, Ca=Calcium ion, $CaCl_2$=Calcium chloride, PV= peak viscosity, PT= pasting temperature, HPV= hot paste viscosity, CPV= cold paste viscosity.

The addition of pectin brought a significant increase in the PV, HPV, CPV and total relative setback of the NTS (Table 5). These results are similar to those reported by Babic et al. (2006) for tapioca starch to which carrageenan and high methoxyl pectin had been added, where the effect of the carrageenan on viscosity was greater than that of the pectin.

The effects of hydrocolloids on the viscosity of mixed systems with starch have been interpreted by Alloncle, Lefebvre, Llamas, and Doublier (1989), who assumed two phases in the system, with the gum located in the continuous phase and the starch in the dispersed phase, and considered that the increased viscosity of the suspension is due to the contribution of both phases, which results in a sharp rise in the viscosity of the starche hydrocolloid combination. Sikora, Kowalsky, and Tomasik (2008) studied binary starche xanthan gum systems with potato, tapioca, oat and corn starches in a proportion of 9:1. These authors suggested that initially the starch and gum gel solution forms two separate phases which slowly combine into one phase, causing a rise in viscosity, after which the phases separate again, causing breakdown, and the viscosity falls.

They also observed that the separated phase of the starch and the gum combined to form a homogeneous phase more rapidly in the NTS solution than in the other starch mixtures. The pasting temperature did not change when pectin was added. This agrees with the results obtained by Hongsprabhas, Israkarn, and Rattanawattanaparkit (2007), who found that adding alginate and carrageenan to NTS did not significantly affect the pasting temperature obtained with an RVA. However, Chaisawang and Suphantharika (2006) found that the pasting temperature of potato and tapioca starches increased significantly when xanthan gum and guar gum were added. Rojas, Rosell, and de Barber (1999) concluded that adding different hydrocolloids to wheat flour promotes a great effect on the pasting properties of the resulting hydrocolloid-flour mixture and the extent of this variation is highly dependent on the chemical structure of the hydrocolloid added: the PT of the wheat flour rose slightly in the presence of pectin and HPMC at different concentrations, the addition of K-carrageenan, alginate and xanthan gum at different concentrations led to a fall in PT, and the effect of adding guar gum depended on the concentration.

3.3 Linear viscoelastic properties

As may be seen in Fig. 1a and b, a considerable difference in structure was observed between NTS and MWCS, which is recommended for use in fruit fillings. The mechanical spectra were recorded at a constant 35% sugar concentration for both starches on their own and for the mixtures of NTS with two concentrations of pectin and two levels of calcium ions at each of the pectin concentrations. The mechanical spectrum of NTS, with G' values only slightly higher than those of G" and quite frequency-dependent, reflected a weak gel structure with low viscoelasticity. The modified starch was more viscoelastic, as it had significantly higher modulus values than the native starch and the two moduli were further apart. Also, these values were much less frequency-dependent than those of the native starch, which again reflected the stronger gel structure of the modified starch.

The mixture of NTS with pectin and Ca ions considerably increased the values of G' and G" and the distance between the two, showing a sizeable increase in viscoelastic behaviour (Biliaderis, 2009; Steffe, 1996) and taking the NTS closer to the viscoelastic properties of the MWCS gel. Increasing the LMP concentration raised the modulus values and the gap between them and reduced the frequency-dependence. At 0.6% LMP (Fig. 1a), the shape of the mechanical spectra was very similar to that of the MWCS. Table 6 presents the mean values of G', G" and tanδ at a frequency of 1 Hz. It will be seen that increasing the concentration of LMP brought a significant rise in G' and G" and a significant drop in tanδ (closer to 0), reflecting increased viscoelasticity. The effect of the quantity of calcium depended on the concentration of LMP. At 0.3% LMP (Fig. 1b), increasing the calcium ions from 40 mg to 60 mg per g of pectin did not alter the G’, G” or tanδ. In other words, the structure of the gel was not affected. At the 0.6% LMP concentration, however, significant rises in the values of the viscoelastic moduli and in viscoelasticity were observed when the concentration of calcium ions was increased, showing that the lower concentration had not fully activated the gelling function of the LMP. It should be noted that with 0.6% LMP, no differences were found between the viscoelasticity (tanδ) of the modified starch and that of the native starch. Consequently, in both cases, in the presence of sugar and at pH 3 the NTS-LMP mixture appears to possess the same rheological properties as the control starch.

Khondkar et al. (2007) obtained an improvement in the rheological behaviour of cross-linked waxy corn starch by adding low methoxyl pectin and concluded that cross-linking can take place in mixed polymer systems. Chaisawang and Suphantharika (2006) found that adding xanthan gum and guar gum improved native cassava starch and anionic cassava starch and Choi and Yoo (2009) found that potato starch was improved by adding xanthan gum. Chaisawang and Suphantharika (2006) reported that native tapioca starch contains a small quantity of phosphate groups but the mechanism of association is different to that of anionic modified starches or native potato starch, as owing to their high phosphate content, the latter repel hydrocolloids with a negative charge. A smaller quantity of phosphates is present in tapioca starch and they do not play the same role in gelation (Moorthy y Ramanujam,1986).

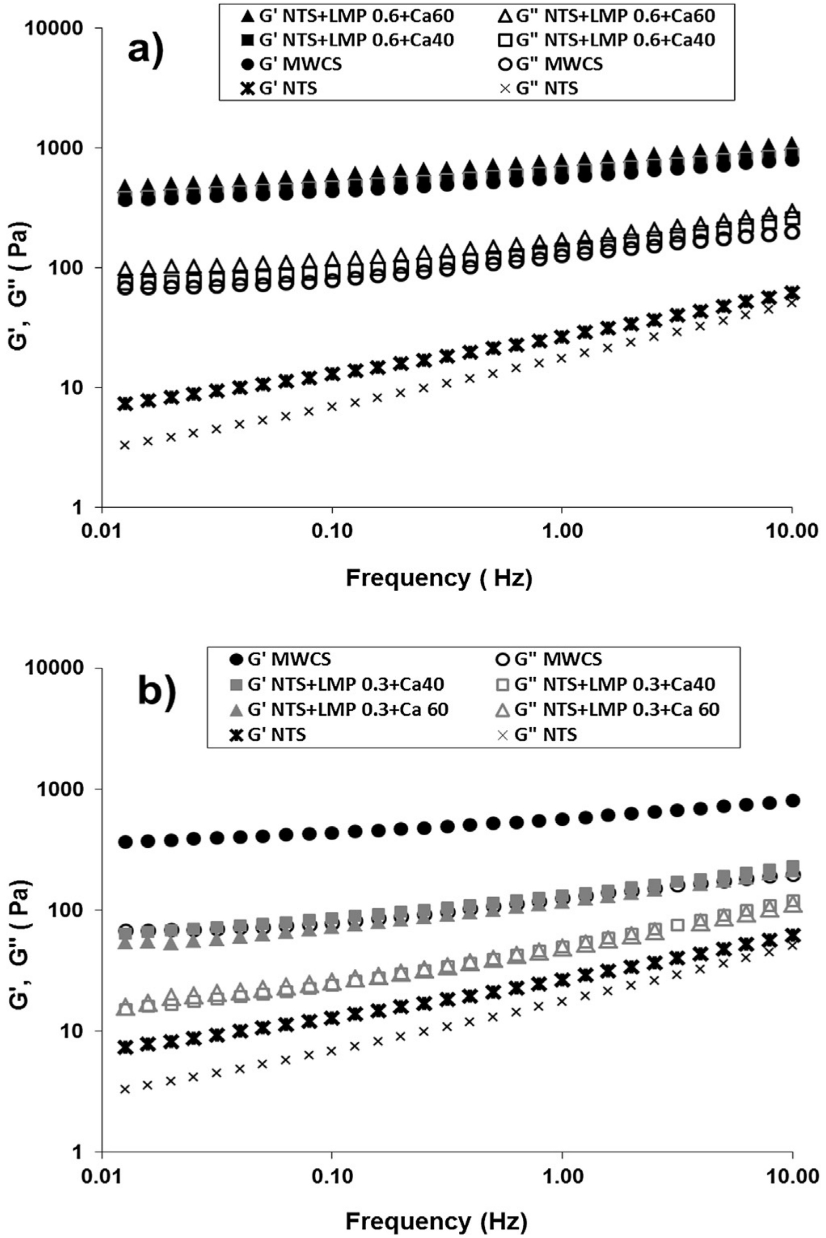

Figure1. Mechanical spectra of NTS, mixed systems with NTS plus pectin and calcium, and MWCS (pH ¼ 3, sugar level ¼ 35%) (a) 0.6% LMP, (b) 0.3% LMP.

Table 6. Mean viscoelasticity parameter values in the different model system formulations

Sample	G' (Pa)	G" (Pa)	tanδ
NTS	25.9^{a} (3.1)	16.9^{a} (0.1)	0.66^{c} (0.09)
NTS+LMP 0.3+Ca40	132.9^{b} (6.1)	50.7^{b} (4.2)	0.38^{b} (0.01)
NTS+LMP 0.3+Ca60	120.7^{b} (14.9)	47.9^{b} (4.8)	0.40^{b} (0.09)
NTS+LMP 0.6+Ca40	615.3^{c} (6.5)	139.3^{d} (0.8)	0.23^{a} (0.00)
NTS+LMP 0.6+Ca60	786.7^{d} (35.9)	171.8^{e} (1.2)	0.22^{a} (0.01)
MWCS	566.0^{c} (26.6)	125.2^{c} (1.6)	0.22^{a} (0.02)

Figures in brackets are standard deviations
Different letters indicate significant differences ($p<0.05$) between values with the same letter within the same column according to Tukey's multiple comparison test
G'=storage modulus, G''=loss modulus, tanδ=loss tangent
NTS=Native Tapioca Starch, MWCS=Modified Waxy Corn Starch, LMP=Low Methoxyl Pectin, Ca=Calcium ion

3.4 Extrusion properties

The data that were taken as representative of the extrusion force profiles in relation to time (Fig. 2) were the maximum force, as a measure of initial resistance to extrusion, and the area under the curve or extrusion work, as a measure of system consistency (Angioloni y Collar, 2009). The results (Table 7) showed that the addition of LMP led to considerable variation in extrusion properties. The NTS mixtures with LMP displayed the greatest firmness and consistency, followed by MWCS then NTS alone, which presented the least resistance to extrusion. Both the maximum force and the area under the curve increased significantly at the higher LMP concentration.

Table 7. Mean extrusion parameter values in the different model system formulations

Sample	AUC (N.s)	Maximum force (N)
NTS	11.0^{a} (0.3)	0.9^{a} (0.0)
NTS+LMP 0.3+Ca40	30.4^{c} (0.5)	2.6^{b} (0.2)
NTS+LMP 0.3+Ca60	28.0^{c} (1.4)	2.6^{b} (0.1)
NTS+LMP 0.6+Ca40	45.6^{d} (1.9)	3.9^{c} (0.1)
NTS+LMP 0.6+Ca60	44.3^{d} (2.3)	4.1^{c} (0.2)
MWCS	19.9^{b} (0.9)	1.7^{a} (0.0)

Figures in brackets are standard deviations
Different letters indicate that there are significant differences ($p<0.05$) between values with the same letter within the same column according to Tukey's multiple comparison test
AUC= Area under curve
NTS=Native Tapioca Starch, MWCS=Modified Waxy Corn Starch, LMP=Low Methoxyl Pectin, Ca=Calcium ion

The higher calcium concentration did not alter the results significantly for either of the LMP concentrations. Because instrumental measurements of extrusion provide indications of the mechanical behaviour of the system under high deformation loads, they are considered to be more closely related to oral texture (Lu y Abbott, 2004). Moreover, these properties are also important for process design, as pumping, dosing, filling, etc. are basic processes in the industrial production of fruit fillings.

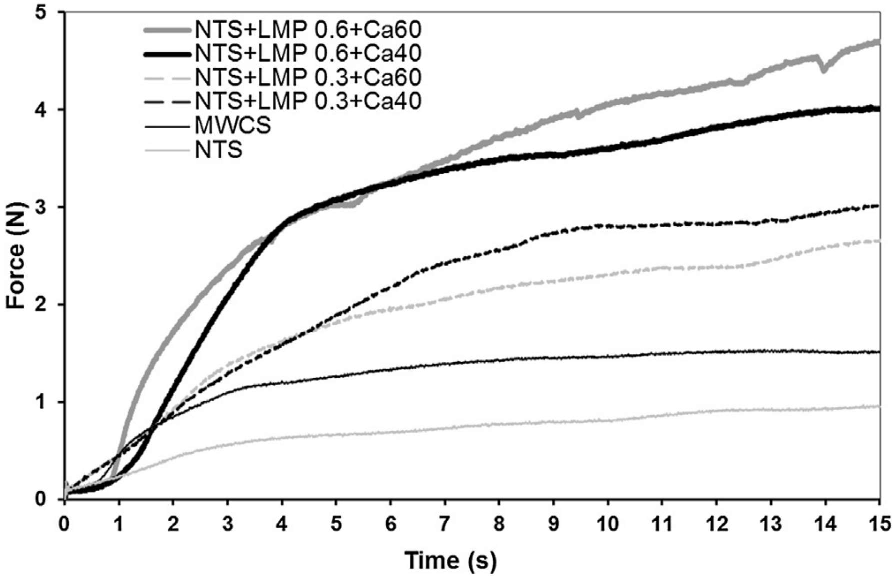

Figure 2. Extrusion profile of NTS, mixed systems with NTS plus pectin and calcium, and MWCS (pH ¼ 3, sugar level ¼ 35%).

3.5 Syneresis

For fruit fillings (and food systems in general), syneresis is a negative factor that reflects low quality. It is normally remedied by using gums that retain liquids. It is frequently encountered after technological processes such as stirring, pumping, heating, freezing and thawing. The gels formed by the NTS,MWCS and NTS/pectin mixtures did not present syneresis with any of the methods employed. Young, Kappel, and Bladt (2003) found syneresis in fruit fillings prepared with low-methoxyl pectin with a high soluble solid content at pH levels of between 3.4 and 3.7. The absence of syneresis in the fillings under study indicates that NTS mixed with pectin is a suitable system for this application.

4. CONCLUSIONS

The design of hydrocolloid system formulations that add value to the end product is a priority goal in the constantly changing world of processed foods. The present study proposed model formulations which were designed to act as thickeners in fruit fillings for pastries or in other systems that require low pH values: a system composed of native tapioca starch with the addition of small quantities of low-methoxyl pectin and calcium has proved an interesting alternative with similar properties to modified starches.

Fruit applications present additional important challenges, as they demand stability against thermal processes and against freeze/thaw cycles. The proposed system will need to be studied further to assess its stability during baking, whether the filling holds its shape during cooking and its behaviour during frozen storage and subsequent thawing.

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CAPÍTULO 2

Formulating fruit fillings. Freezing and baking stability of a tapioca
Starch-pectin mixture model

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Food Hydrocolloids, 40, 203-213

ABSTRACT

Fruit fillings are a little-studied product. Their design and formulation must take a number of factors which are inherent to their applications into account, including stability during heat treatments such as baking and freezing, during which their quality must remain intact. The present study investigated systems containing native tapioca starch (TS), low methoxyl pectin (P, at two concentrations: 0.3% and 0.6%) and calcium, compared with TS alone and with a modified waxy corn starch (C), normally used in the industry, as control. All the systems were prepared with and without the addition of fruit. A method to measure the instrumental texture of filled pastries was developed and applied to study the effect of the baking process on two types of bakery products. The rheological results indicated that in the mixed TS-P systems pectin had the dominant role. The presence of fruit caused a significant rise in the G' and G" module values for all the thickener system formulations, but the effect was greater with the mixtures that contained pectin. This would indicate that the addition of solids and/or the extra pectin contributed by the fruit led to greater structuring. During freezing, the pectin gave rise to a different gel structure to that of TS alone and acted as a retrogradation and syneresis inhibitor. The extent of this effect depended on the added pectin concentration. Pectin also imparts the stability at high temperatures and conferred similar viscoelastic behaviour to that of the modified starch control (C). The TS-pectin system also proved bake stable.

Keywords: Tapioca starch, Pectin, Fruit fillings, Freezing/thawing, Bake stable.

1. INTRODUCTION

Fruit fillings are a little-studied product and very few papers deal with this subject. Native starches are widely used in industry in order to impart viscosity, texture, and stability to food products. Their use gives a ‘clean’ label and it has been shown that consumers perceive them as being familiar ingredients and as healthier than their modified equivalents or other thickeners (Varela y Fiszman, 2013). However, native starches are of limited use in a number of food applications because the pastes and gels prepared with them tend to break down with prolonged heating or under high shear or acidic conditions. Moreover, they have a strong tendency to retrograde and undergo syneresis on cooling (Galkowska, Dlugosz, y Juszczak, 2013). Therefore, native starches are physically or chemically modified in order to improve their performance. Another strategy for improving their techno-functional properties is to add a gum or hydrocolloid, as reported by numerous authors (Alloncle, Lefebvre, Llamas, y Doublier, 1989; Biliaderis, 2009; Breuninger, Piyachomkwan, y Sriroth, 2009; Chaisawang y Suphantharika, 2006; Chantaro, Pongsawatmanit, y Nishinari, 2013; Pongsawatmanit, Temsiripong, y Suwonsichon, 2007; Sikora, Kowalski, y Tomasik, 2008). In particular, to maintain or improve desirable textural properties and the stability of native tapioca starch-based products during long storage periods, hydrocolloids have been added to control the viscosity of the continuous phase and the textural properties of the final products (Pongsawatmanit y Srijunthongsiri, 2008). In a previous paper, the authors proposed a new model system for fruit fillings (pH 3, 35% sugar) which contained native tapioca starch, low-methoxyl pectin and calcium ions and improved their viscoelastic and texture properties (Agudelo, Varela, Sanz, y Fiszman, 2014). Since fruit fillings need to be stable during all kind of technological process conditions, in that paper a comparison with a control starch (highly cross-linked waxy corn starch, hydroxypropylated and phosphated) was performed; modification by etherification provides stability against retrogradation during refrigeration/freezing and modification by cross-linking provides stability against acid, thermal and mechanical degradation (Singh, Kaur, y McCarthy, 2007). Hydrocolloid addition may decrease or increase the gel-like character of starch pastes, depending on the starch type as well as on the gum type and concentration. The most common observation is the increase in both viscosity and elasticity, with more pronounced effects on viscosity. The addition of a hydrocolloid can also accelerate gelation and reduce retrogradation (Rosell, Yokoyama, y Shoemaker, 2011).

According to Mandala (2012), retrogradation takes place in two stages. The first phase (short-term retrogradation) begins as the paste cools and a structure of entanglements and/or junction zones is created between amylose molecules, resulting in an elastic gel. This phase may last up to 48 h. The second phase (long-term retrogradation) involves amylopectin changes. It is a much slower process that may take place over several weeks, depending on the storage temperature. Both G’ and G” increase upon cooling and during short-term storage, indicating that the gels are becoming firmer. Funami et al. (2005b) studied the effect of adding guar gum on corn starch retrogradation and found that the interactions between guar and amylose (or an ‘amylose-like’ component) should be considered a factor inhibiting short-term retrogradation of starch, because the interactions may reduce the amount of the starch components that participate in gelation. They hypothesized that interactions between guar and leached amylopectin may be a main cause of increased viscosity in a starch/guar system, and are probably also responsible for the decrease in the amount of leached amylose. Galkowska et al. (2013) studied how high-methoxyl pectin and sucrose affected the rheological and textural properties of chemically-modified potato starch-pectin-sucrose systems and found that starch-pectin-sucrose gels exhibited better structuring ability and higher textural parameter values than the gels developed with modified potato starch alone. This effect was greater in at higher concentrations of starch. Two heating steps should be considered when fruit fillings are formulated: heating during the fruit filling preparation (an intermediate step in industrial manufacture) and oven heating during the baking of the pastries. Heating affects the quality of the native starch-based fruit fillings, due to gelatinization and degradation of the starch upon heating at low pH values. The viscosity of the native tapioca starch paste decreases after heating; this fact will affect fruit filling applications, leading to textural instability during storage (Biliaderis, 2009; Temsiripong, Pongsawatmanit, Ikedab, y Nishinarib, 2005). In fruit fillings in particular, Wei, Wang, and Wu (2001) studied the effect of adding guar gum, locust bean gum, carboxymethylellulose, xanthan gum or kappa-carrageenan on the flow properties of model fillings formulated with waxy corn starch and commercial fruit fillings and found that the apparent viscosity varied with the gum type and concentration and with the shear rate. Another key step for fruit filling formulations is refrigeration/freezing during storage, before or after baking: starch pastes may undergo changes in the starch biopolymer molecules, namely chain aggregation and crystallization. Moreover, it is difficult to maintain refrigerated/frozen food products at a constant optimum low temperature, and undergoing repeated freeze-thaw cycles during the supply chain leads to syneresis and to changes in rheological properties (Pongsawatmanit y Srijunthongsiri, 2008).

The effect of heating and freeze-thaw treatments on the pasting properties of tapioca starch (TS) with and without xanthan gum (Xan) has been investigated using a rapid viscoanalyzer (RVA). The breakdown values of both the TS and the TS/Xan mixtures increased with heating but the mixtures with Xan were more viscous due to the contribution of the Xan in the continuous phase of the mixtures. In repeated freeze-thaw treatments of the pastes analysed with the RVA, the TS/Xan mixtures exhibited lower water separation compared with TS alone (Chantaro y Pongsawatmanit, 2010).

Very little information is available on the effect of adding fruit to starch/hydrocolloid-based systems. The results reported by some authors indicate that adding fruit pulp modifies the rheological properties of the final products and changes their texture, and that these effects depend on a number of factors: pH, quantity of fruit added, type of fruit, fruit puree particle size, solid (sugar) content, hydrocolloid type and concentration, and the interactions between these factors (Baiano, Mastromatteo, y Del Nobile, 2012; Basu y Shivhare, 2010; Carbonell, Costell, y Duran, 1990a; 1990b; Fiszman y Duran, 1992; Wei et al., 2001). In particular, in systems that contain pectin the calcium available in the fruit is an important factor (Young, Kappel, y Bladt, 2003).

The objectives of the present study were to investigate the effect of heating and freeze/thaw treatments on the rheological properties of model systems for preparing fruit fillings containing tapioca starch-low-methoxyl pectin-calcium blends (35% sugar, pH 3) compared with a control (modified waxy corn starch system normally used in the fruit filling industry). In addition, the effects on the texture of adding fruit and of baking were investigated in two bakery products (open and closed systems).

2. MATERIAL AND METHODS

2.1. Ingredients

The ingredients employed were native tapioca starch (TS) (moisture content 13.7%, Sucroal S.A., Colombia), citric acid and sodium citrate (Sucroal S.A., Colombia), highly cross-linked waxy corn starch, hydroxypropylated and phosphated (C) (moisture content 12.3%, it contains virtually no amylose, Polartex 6716, Cargill, Spain), non-amidated low methoxyl apple pectin (P) (33-37% esterified, moisture content 12%, pH of 1% dissolution 4.5 to 5, kindly provided by Cargill, Spain) Unipectine

OB700, Cargill, España, anhydrous calcium chloride (Panreac, Spain) and white sugar (S) (Hacendado, Spain). Fruit purée (F) was obtained from canned peach halves in light syrup (ºBrix 17.7 and pH 3.7, Hacendado, Spain); the final moisture content of the fruit purée was 80.5%. Frozen pastry dough and pre-baked tartlet cases were used for preparing bakery specialities (see Section 2.6).

2.2. Model system and fruit filling preparation

The samples were prepared in a food processor-cooker (Thermomix TM 31, Wuppertal, Germany) equipped with temperature and stirring speed controls. All the samples were prepared at pH 3 and contained 35% sugar and 6% of the thickener system. Four thickener systems were employed as models: a control starch (C), native tapioca starch (TS) and TS with two levels of pectin e 0.3% (P 0.3) and 0.6% (P 0.6) of the total hydrocolloid system (dry weight basis) e and calcium ions (40 mg of calcium ion per gram of pectin). Fruit fillings were prepared with a mixture of 6% of each of the four model systems (wet basis) and 20% of the fruit purée. This fruit purée contained 17.7% soluble solids. The formulations and sample codes are shown in Table 1.The first step in preparing the samples was to add the sugar to part of the water and, in the fruit-filling samples, the fruit purée. This mixture was heated to 60ºC and stirred at 62.82 rad s-^{1} for 5 min. In the formulations with pectin, the pectin was first dispersed in water with a magnetic stirrer at 80ºC until it was totally dissolved, then allowed to cool to 60ºC before adding it to the sugar-water or fruit-sugar-water mixture. The starch was dispersed in another part of cold water and added to the sugar-water (or fruit-sugar-water) mixture, continuing the stirring and heating for another 2 min. Once the mixtures had been prepared with these ingredients, the temperature was increased to 90ºC and heating and stirring continued for a further 30 min. Calcium chloride, dissolved in a small amount of water reserved for this step, was added to the mixtures containing pectin. The pH was adjusted to 3 (+/-0.2), using citric acid and sodium citrate buffer solutions, and stirring and heating continued for a further 5 min.

Table 1. Composition of the different model system and fruit filling formulations at pH3

Sample Code	Ingredient					
	TS %	Pectin (P) %	$CaCl_2$ %*	MWCS %	Fruit (F) %	Sugar %
C	0	0	0	6	0	35
F C	0	0	0	6	20	35
TS	6	0	0	0	0	35
F TS	6	0	0	0	20	35
P 0.3	5.67	0.30	0.033	0	0	35
F P 0.3	5.67	0.30	0.033	0	20	35
P 0.6	5.33	0.60	0.067	0	0	35
F P 0.6	5.33	0.60	0.067	0	20	35

TS=Tapioca Starch, $CaCl_2$=Calcium chloride, MWCS=Modified Waxy Corn Starch, C=Control, P 0.3=Pectin at 0.3%, P 0.6=Pectin at 0.6%
* The calcium salt dosages correspond to 40 mg of calcium ion per g of pectin.

The samples were transferred to plastic containers and held in refrigeration (8ºC) for 24 h (freshly prepared samples) or in a freezer (Zanussi, Madrid, Spain) for 5 days at -18ºC (frozen samples). Before testing, the freshly prepared samples were stabilized for 1h at ambient temperature and the frozen samples were stabilized for 3h at ambient temperature. In order to study the systems after a period of heating in a real cooking process, each sample (250 g) was put in a baking tin lined with short crust pastry (thawed for 1 hat ambient temperature), covered with a pastry lid to form a closed filled pie, and baked in an oven (Fagor, Mondragon, Spain) at 180ºC for 20 min. After cooling at room temperature for 1 h the fillings were removed from the cooked dough for the rheological and instrumental texture measurements.

2.3. Linear viscoelastic properties

The linear viscoelastic properties of the different filling samples were studied with a controlled stress rheometer (AR-G2, TA Instruments, Crawley, England) using serrated plate-plate geometry (60 mm diameter). A gap of 1 mm was employed. Before measurements were taken, the samples remained between the plates for a 10 min equilibration time. The exposed edges of the samples were covered with silicon oil to avoid sample drying during measurements. The measurements were carried out at 20ºC. Strain sweeps were carried out to determine the linear viscoelastic region, followed by frequency sweeps from 10 to 0.01 Hz at a strain amplitude value inside the linear region. The storage modulus (G'), loss modulus (G") and loss tangent (tanδ= tan G"/G') were recorded with TA data analysis software (TA Instruments, Crawley, England). To simulate the effect of heating during baking on the gel structure temperature, sweeps were performed from 20 to 80ºC at a heating rate of 1.5ºC/min and a strain amplitude of 0.005. The strain applied was selected to guarantee the existence of linear viscoelastic response according to the previous strain sweeps. The temperature sweep was stopped at 80ºC and after a 10 min temperature equilibration time the storage modulus (G'), loss modulus (G"), and loss tangent (tanδ= tan G"/G') values were recorded.

2.4. Extrusion test

The extrusion properties were measured with a texture analyser (TA-XT Plus, Godalming, England) equipped with a 50-mm diameter back extrusion cell (A/BE Back Extrusion Rig) with a 10mm gap between the sample container and the disc plunger. The compression speed was 10 mm/s and the trigger point was 10 g. The duration of the test was set at 15 s (Arocas, Sanz, y Fiszman, 2009). The samples were placed in the extrusion cylinder and stabilized in a water bath at 25ºC for 10 min before making the measurements. The force-displacement profiles were recorded and the maximum extrusion force (Fmax, in N) as an index of firmness, and the area under the curve (AUC, in N/s) as an index of consistency were obtained (Cevoli, Balestra, Ragni, y Fabbri. 2013).

2.5. Syneresis

The method used was adapted from Arocas et al. (2009). Syneresis was quantified 2 min after the extrusion test. The samplewas weighed and transferred to a funnel lined with filter paper (Whatman 42) and the liquid released was collected for 15 min. This method is intended to reduce the degree of gel structure destruction that occurs with methods that use centrifugation. Syneresis was expressed as the amount of liquid released per 100 g of sample:

% Syneresis = (Weight of liquid released / Total initial weight of sample)*100

2.6. Pie and tartlet preparation

To study the effect of real baking on the final texture of the fruit fillings (FC, FTS, FP 0.3 and FP 0.6), two different products were prepared: filled pies (closed system, Fig.1A) and filled tartlets (open system, Fig. 1B) in order to know the fruit filling behaviour when submitted to different baking conditions.

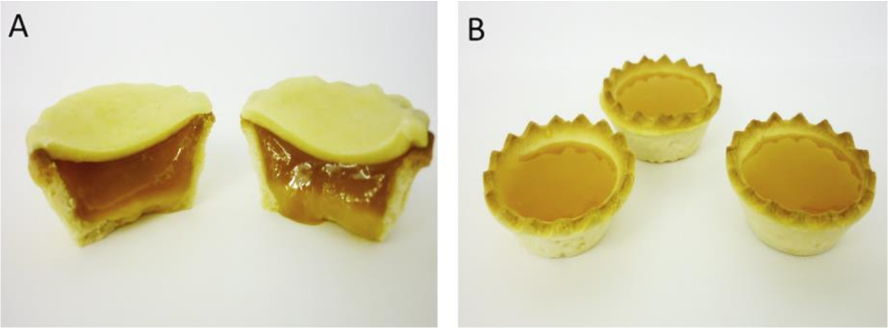

Figure 1. Photographs of the baked products. A: filled pies (closed system), and B: filled tartlets (open system).

2.6.1. Closed system

Frozen short crust pastry (Hacendado, bought from a local supermarket) was used. The pastry was thawed for 60 min before preparing the pies. The metal mould (6 cm in diameter and 1.2 cm high) was lined with pastry. The 8 g sample was placed on the pastry base and covered with a pastry lid to form a closed filled pie. The baking temperature and time were 220ºC for 10 min (to reach a golden colour (in the web version)). Six pies at a time were baked in a fan-assisted domestic oven (Fagor, Mondragon; Spain) (Fig.1A). They were then left to cool to room temperature (1 h).

2.6.2. Closed system

Pre-baked tartlet cases (Confiletas, bought from a local supermarket) were filled with 8 g of sample. They were baked at 220ºC for 10 min. Six tartlets at a time were baked in a fan-assisted domestic oven (Fagor, Mondragon; Spain) (Fig. 1B). They were then left to cool to room temperature (1 h).

2.7. Instrumental texture measurements of the pies and tartlets

The texture measurements were made with a texturometer (TAXT Plus, Godalming, England) coupled with Texture Exponent software (version 4.0.12.0). Six pies and six tartlets were measured for each type of fruit filling (FC, FTS, FP 0.3, and FP 0.6). Two replicates with each type of filling were prepared on different days. The probe descent speed was set at 1 mm/s and the data acquisition rate at 200 pps (points per second).

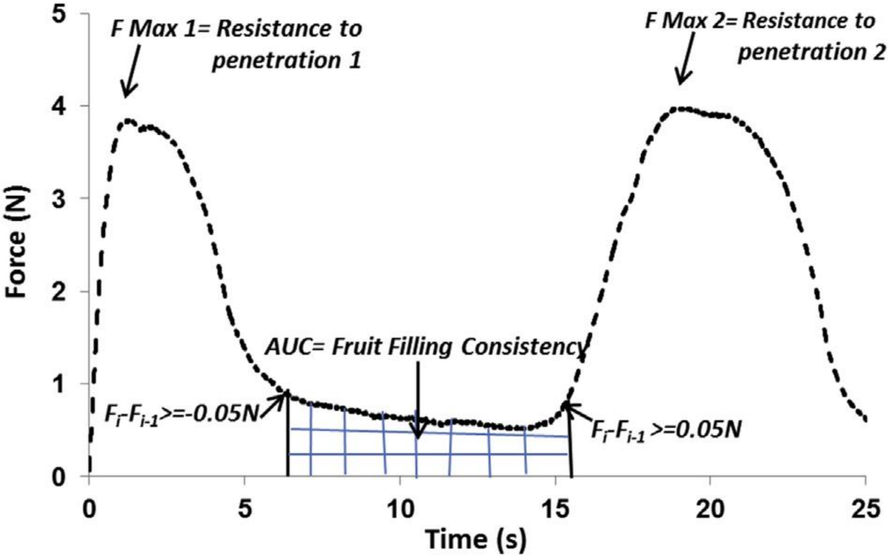

Figure 2. Example of a penetration resistance force profile curve for the filled pies (closed system), showing the details for calculating the parameters

All the penetration resistance curves (N) were plotted over time (s). For these tests, both types of filled pastry were placed in the centre of a platform with a 1 cm diameter hole so the probe went right through the filled pastry case. For the test on the pies, a ¼“ diameter cylinder probe (P/0.25R) was used and the penetration distance was 25 mm. The measurements recorded were the maximum force at peak 1 and peak 2, taken as the penetration resistance of the upper and lower pastry layer respectively, and the area under the curve (AUC), taken as the penetration resistance of the filling (Fig. 2). The latter measurement was made between the first point at which the force was 0.05 N lower than the previous point and the first point at which the force was 0.05 N higher than the previous point. For the test on the tartlets, the ½" diameter cylinder (P/0.5R) was used and the penetration distance was 10 mm.

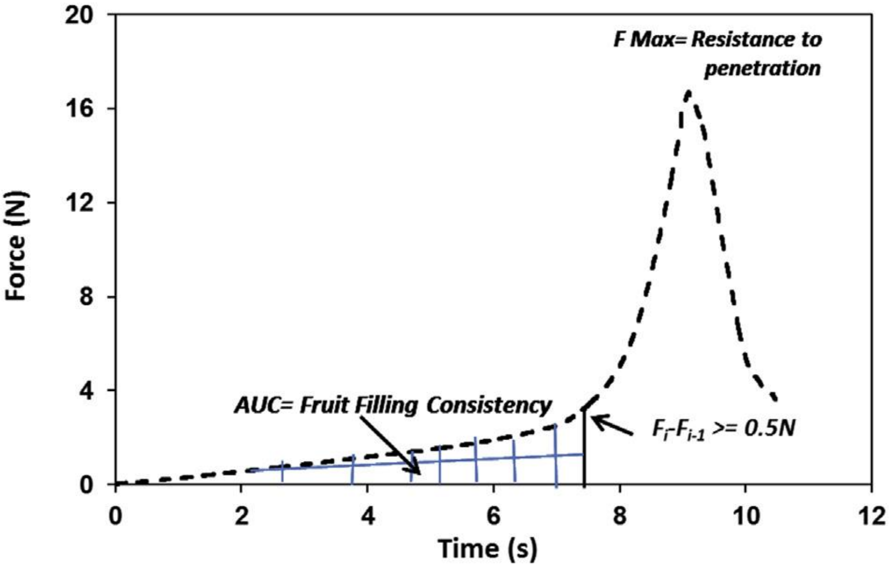

Figure 3. Example of a penetration resistance force profile curve for the filled tartlets (open system), showing the details for calculating the parameters

The measurements made with the tartlets were the maximum force at the peak, taken as the penetration resistance of the pastry, and the area under the curve (AUC), measured from time=0 to the first point at which the force was 0.5 N higher than the previous point (Fig. 3). The parameters for both products were selected following preliminary studies with different probes and test conditions, with the aim of maximising the sensitivity of the tests and their discrimination between the samples.

2.8. Statistical processing of the data

All the tests were carried out in duplicate with samples prepared on different days. Analyses of variance (ANOVA) were performed to compare the effect of different treatments (freshly prepared, freezing/thawing or baking) on the viscoelastic properties of samples C, TS, P 0.3 and P 0.6, with and without fruit (Table 1). Tukey’s multiple comparison test was used to analyse inter-group differences with a 95% confidence interval. These analyses were performed with the XLSTAT statistics software package (Addinsoft-Barcelona, Spain, version 2009, 4.03).

3. RESULTS AND DISCUSSION

3.1. Viscoelastic properties

Fig. 4 shows the mechanical spectra of the samples prepared with different thickeners and no fruit (model system) for each of the treatments e freshly prepared (Fig. 4A1), after a freeze/thaw cycle (Fig. 4A2) and after baking (Fig. 4A3) e and of the samples prepared with these thickener systems and fruit (fruit fillings) for each of the same treatments (Fig. 4B1, B2 and B3 respectively). Table 2 shows the viscoelastic parameter values for the different thickening systems and treatments.

3.1.1. Freshly prepared model systems and freshly prepared fruit Filling

As may be seen in Fig. 4A1 and Table 2, in the model systems without fruit all the samples with the different thickeners showed gel behaviour, with G’ greater than G”. As expected, a considerable difference in structure was observed between TS and C. The mechanical spectrum of TS, with G’ values only slightly higher than those of G” and quite frequency dependent, reflected a weak gel structure with low viscoelasticity; C starch was more viscoelastic, as it had significantly higher modulus values than the native starch and the two moduli were further apart; these results coincide with the results previously obtained by the authors (Agudelo et al., 2014). When a non waxy native starch (as tapioca) is heated above the gelatinization temperature in the presence of excess water, the starch granules lose their internal order and absorb the water. This causes a swelling of the granules and a rise of the viscosity (Heyman, De Vos, Van der Meeren, y Dewettinck, 2014) prior to their physical breakdown. On the other hand, chemically cross-linked starches, as C, are commercially very popular, because their strengthened granules can much better withstand the elevated temperatures and high shear forces encountered in production processes (Singh et al., 2007); the cross-linking treatment is intended to add intra- and inter-molecular bonds at random locations in the starch granule that stabilize and strengthen the granule.

A big improvement of the viscoelastic properties was obtained with the system formed by TS and pectin (samples P 0.3 and P 0.6). Moreover, when the concentration of pectin was increased the G’ and G” module values rose and G” values less dependent of the frequency; G’ values drew further away from G”, showing a firmer gel structure with greater elasticity. This behaviour could be attributed to the pectin, which happened to have the dominant role of the system, whereas the effect of the starch molecules appeared to be additive; in addition, some ionic interaction between the starch molecules and charged positions in the pectin molecules could not be discarded. In other study (Galkowska et al., 2013), high-methoxyl pectin and sucrose was added to modified starches in a concentration of 0.5 (wt%); these authors assumed that the rheology of the mixed systems was mainly dominated by the behaviour of starch, since the results of the dynamic rheological measurements indicated that pectin did not affect the proportion of the elastic and viscous properties of the gels. However, in the present case tanδ values were significantly lower in the systems containing pectin, suggesting a potential change in the type and/or strength/number of the interactions in gel network.

Table 2. Mean values of G', G" and tanδ at 1Hz and 20 °C for the samples, by treatment

Sample	Freshly prepared			Freeze/ thaw			Baked		
	G'(Pa)	**G"(Pa)**	**tan(δ)**	**G'(Pa)**	**G"(Pa)**	**tan(δ)**	**G'(Pa)**	**G"(Pa)**	**tan(δ)**
C	566.0^{Ce}(26.7)	125.2^{Cde} (1.6)	0.22^{Dij} (0.01)	577.4^{Ce}(17.25)	122.3^{Cd}(4.0)	0.21^{Ej}(0.01)	584.4^{Ce} (39.9)	124.2^{Cd}(1.8)	0.20^{Ej}(0.01)
TS	25.9^{Fk}(3.1)	16.9^{Fh}(0.1)	0.66^{Ab}(0.09)	36.3^{Fk}(2.02)	20.0^{F}(1.1)	0.55^{Ac}(0.01)	20.9^{Dh}(2.5)	23.1^{Eh}(0.9)	1.11^{Aa}(0.09)
P 0.3	132.9^{Eij}(6.1)	50.9^{Eg}(4.2)	0.38^{BCd}(0.01)	203.8^{Ehi}(21.3)	47.9^{Eg}(7.4)	0.23^{CDEh}(0.01)	139.1^{Cij}(2.7)	53.4^{Dg}(0.6)	0.38^{Cd}(0.01)
P 0.6	615.3^{Cde}(6.5)	139.3^{Bcd}(0.9)	0.22^{Dij}(0.01)	728.7^{Bbc}(28.6)	164.0^{Bb}(4.1)	0.22^{DEi}(0.01)	749.2^{Aab}(16.5)	188.8^{Aa}(10.9)	0.25^{CDg}(0.01)
F TS	114.0^{Ej}(7.5)	55.4^{Eg}(1.6)	0.48^{Bc}(0.02)	226.0^{DEgh}(10.6)	59.6^{Eg}(4.0)	0.26^{Cf}(0.01)	101.1^{CDjk}(9.5)	56.1^{Dg}(2.0)	0.55^{Bc}(0.03)
F P 0.3	322.9^{Df}(17.4)	110.3^{Def}(6.1)	0.34^{CDe}(0.01)	383.5^{Dfg}(1.3)	100.3^{Df}(4.0)	0.35^{Be}(0.01)	324.0^{Df}(23.1)	120.4^{Cde}(4.9)	0.37^{CDe}(0.01)
F P 0.6	792.6^{Aab}(8.5)	193.5^{Aa}(0.7)	0.24^{Dgh}(0.01)	810.6^{Aa}(2.12)	198.7^{Aa}(8.5)	0.24^{CDg}(0.01)	726.5^{Abc}(32.4)	201.4^{Aa}(6.1)	0.27^{CDf}(0.01)

Figures in brackets are standard deviations.^{ABC} For the same row and for the same treatment and parameter means, different letters indicate that there are significant differences ($p<0.05$) according to Tukey's multiple comparison test.
^{abc} For the same column means, different letters indicate that there are significant differences ($p<0.05$) according to Tukey's multiple comparison test. For sample codes see Table 1.

Low methoxyl pectin gelation is due to the formation of intermolecular junction zones between homogalacturonic smooth regions of different chains; the structure of such a junction zone is generally ascribed to the so called ‘egg box’ binding process. Initial strong association of two polymers into a dimer is followed by the formation of weak inter-dimer aggregation, mainly governed by electrostatic interactions. As expected, the sample P 0.6 presented higher viscoelastic properties, approaching the viscoelastic behaviour of the modified waxy corn starch used as a control. The G’ and G” modules were frequency-dependent for the frequency range under study (0.01-10 Hz). The tanδ values (closer to 0) reflected increased viscoelasticity when pectin plus calcium was present.

The mechanical spectra for the systems with fruit (Fig. 4B1) showed a similar frequency-dependent behaviour pattern for G’ and G” but the addition of fruit significantly increased the values of these modules in all the thickener systems. These results may be attributed to the greater concentration of solids in the system (from 35% to 50%) and also to some increase in the pectin content due to the fruit, thus increasing the viscosity of the aqueous phase and, consequently, the viscoelasticity of the gels. They are in line with those reported by other authors. Carbonell et al. (1990a) reported that the effects of adding pectin and of adding solids on certain rheological properties of strawberry and peach jams depended on the fruit content and its interaction with other formulation-related factors (pectin and sugar concentration). These same authors (Carbonell et al., 1990b) found that the fruit content of jams could be related to certain rheological measurements of the samples. Using the HerscheleBulkley model, they found that the jams prepared with a high concentration of fruit were firmer - with higher K (consistency index) values -and more pseudoplastic - shown by their low n (flow index) values.

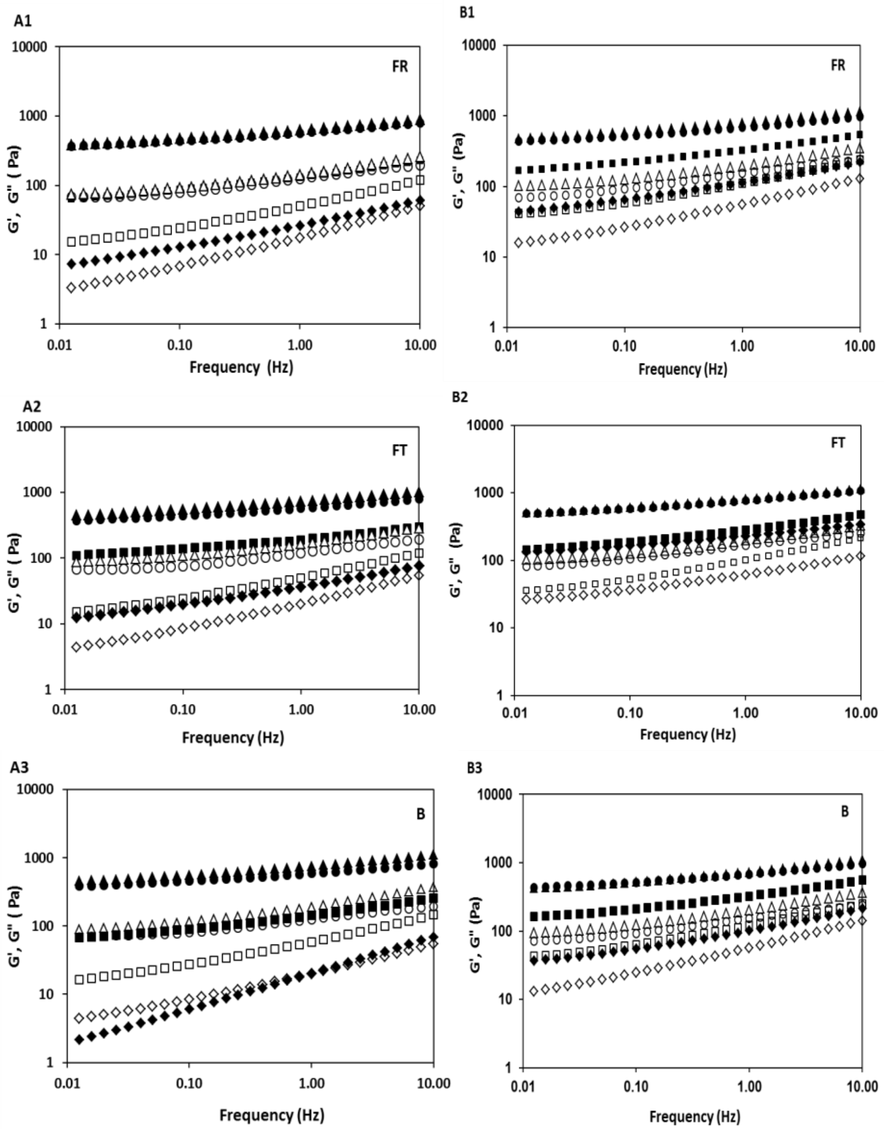

Figure 4. Mechanical spectra of the different samples submitted to different treatments. FR: Freshly prepared samples, FT: Freeze/thaw samples, and BK: Baked samples. A (left column): Fillings without fruit. B (right column): Fillings with fruit. Diamonds (TS), Circles (C), Squares (P 0.3), and Triangles (P 0.6). Closed symbols: G’ and open symbols: G” values. For formulation code see Table 1.

Baiano et al. (2012) reported that the inclusion of ground grape seeds in grape-based smoothies led to significant increases in both the moduli, G’ y G”, compared to smoothies made without the ground seeds; this behaviour is related to a more structured and elastic sample owing to the addition of solids. Pectin-calcium interactions are important for the texture of fruits and vegetables, since cross-linked pectin in the cell wall provides cellecell adhesion and gives the tissues mechanical strength (Fraeye et al, 2010). Although adding pectin and calcium to systems containing fruit improved the structure of the prepared gels, it would be rash to assume that interactions as complex as those at cellular level could be established.

3.1.2. Model systems and fruit fillings after a freeze/thaw cycle

Fig. 4A2 and B2 show the mechanical spectra of the model system samples, without and with fruit respectively, when thawed after a 5 day freezing period. The control gels with modified starch (C), both with and without fruit, retained their viscoelasticity since it paste would be considered as swollen, intact granules without significant changes due to freezing ($p > 0.05$), showing the suitability of this starch for a fruit filling application. Modification provides good retrogradation control by reducing the amylose available for aggregation during cold storage. After a freeze/thaw cycle, the sample TS, with and without fruit, showed a significant rise in G’ and G” values and decreased. While the viscoelastic parameter values indicated a very weak gel when no fruit was present, adding fruit increased the elasticity of the gel and reduced the tanδ values compared to the freshly-prepared gels (Table 2).

The TS/P/calcium mixture model system gels showed significantly higher G’ and G” values following a period of freezing than those of the TS alone system. Again, this behaviour would indicate that the pectin gel was responsible for the rheological behaviour of the complete system, showing good stability after a freeze/thaw cycle. After freezing, the tanδ of the mixtures with pectin fell, indicating that the presence of starch molecules in the continuous phase of the system induced a structural change which could be interpreted as a certain degree of retrogradation during their short cool storage period.

On comparing the tanδ values of the freshly prepared gels with those after five days' freezing, it was found that the tanδ of the mixture with the lowest proportion of pectin (P 0.3) was lower while that of the mixture with the higher proportion of pectin (P 0.6) was unchanged. This would indicate the greater structure stability of the more concentrated gel of pectin during freeze/thaw. Babic et al. (2006) found that adding pectin or carrageenan changed the viscosity of the gel and reduced tapioca starch retrogradation during storage at 4ºC for 7 and 14 days, as reflected in the lower percentage retrogradation values calculated by DSC; however these authors did not put calcium in the medium, so formation of a lowmethoxyl pectin gel was not favoured. A number of papers described the interactions between hydrocolloids and starch; Krystyjan, Adamczyk, Sikora, and Tomasik (2013) reported that different hydrocolloids added plasticity to the starch gels, resulting in gels that were fairly rheologically and texturally stable during storage. The hydrocolloids also stabilized starch gel in long-time storage, though the extent dependent on the gel concentration. A significant decrease in the G"/G' ratio within the first day of the experiment could be associated with a short-term retrogradation involving formation of a network by entanglements and/or formation of junction zones between the amylose molecules, leading to an elastic gel. Short- term retrogradation might take up to 48 h (BeMiller, 2011). A further slow decrease in the ratio (G"/G') should be related to long-term retrogradation, which also involves amylopectin (Funami et al., 2005a). However, looking at the values obtained for the viscoelastic parameters in the present work, which were at least five times the values corresponding to the tapioca starch alone, it seemed logical to hypothesize that a pectin gel was formed in the presence of calcium ions and the tapioca starch molecules reinforced the pectin network acting as a filler or establishing junction points via ionic interactions. Scarce references to starch/pectin systems could be found. The effect of oxidized starch on the networks formed by low-methoxy pectin (2.0 wt %), on cooling has been explored by rheological measurements. At low concentrations of Ca2+, incorporation of increasing concentrations of starch (across the range 0-30 wt%) causes a progressive increase in modulus G', attributed to segregative interactions between the two polymers promoting conversion of pectin from the expanded coil conformation to a more compact associated form (Picout, Richardson, Rolin, Abeysekera, y Morris, 2000). Some other papers studied the effect of pectin addition to the properties of starch pastes (Babic et al., 2006; Witczak, Witczak, y Ziobro, 2013); however, in these papers the pectin did not meet the requirements to form a gel per se. It is also important to note that the gels used in the present study contained sugar, as several authors have shown that sugars have an anti-ageing effect, inhibit retrogradation and are also cryoprotective of systems containing starch. Aee, Hiea, and Nishinari (1998) found that the retrogradation ratio (retrogradation enthalpy after 14 days' storage compared to the initial gelatinization enthalpy) of corn starch systems to which different concentrations of sugar had been added increased with time, and was smaller for gels with a higher sucrose content. In a short storage time, the effect of sucrose on the retrogradation ratio is not so dependent on sucrose concentration. It has been reported that retrogradation consists of two separable processes. The first stage is governed by the gelation of amylose solubilized during gelatinization and the second stage is induced by the recrystallization of amylopectin within the gelatinized granules. Since the retrogradation enthalpy is not so dependent on the concentration of sucrose in samples stored for one day, and is strongly dependent on the concentration of sucrose in samples stored for 14 days, the antistaling effect of sucrose should be more important for the interaction of sucrose with amylopectin than for its interaction with amylose. When the fruit was added, the viscoelasticity of all the systems increased. Specifically in the systems containing pectin, greater structural stability was observed after the freezing period (tanδ values unchanged). This may be attributed to the solids added to the system, as discussed above. The structure development rate (poise/min) of pectin gels increased at a lower temperature and higher pectin concentration, as also reported by Thakur, Singh, Handa, and Rao (1997).

3.1.3. Model system and fruit fillings after baking

Of the 250 g gel samples baked in pastry cases (see Section 2.2), those prepared with TS alone, with or without fruit, could immediately be seen to have quite a liquid consistency, making the pastries difficult to handle before and after baking, as some opened and their filling ran out. The behaviour of the fillings made with modified starch (C) and the TS/P/calcium mixtures was better, as after baking they were found to have gelled well. The gels prepared with TS, the worst-affected by baking, presented fluid behaviour with G” values higher than G’ and a tanδ of 1.11 (Fig. 4A3, without fruit, and B3, with fruit), indicating a structure with predominantly viscous behaviour. Adding fruit improved the structure, achieving gels with similar characteristics to those of the TS gels when freshly prepared or after one freezing cycle, so TS might work in fruit filling applications at certain fruit concentrations. The gels made with modified starch (C), with and without fruit, showed no significant changes in the G’ and G” module values after baking: as expected, this starch displayed the greatest resistance (fewest changes) during baking. The TS and pectin mixtures without fruit showed a slight but significant rise in tanδ after baking, sowing some higher contribution of the viscous component. When fruit was added, the structure of the system remained stable. There were no significant changes in the viscoelasticity parameters of these mixtures, which could indicate that combinations of native tapioca starch and pectin are a good option for formulating fruit fillings which are stable at baking temperatures.

3.2. Effect of heating ramps on the rheological properties of freshly prepared or frozen/thawed samples

Fig. 5 shows the changes in G’ and G” as the temperature rose from 20ºC to 80ºC at a frequency of 1 Hz (Fig. 5A, without fruit, and B, with fruit). The modified starch (C) behaved differently from the other gels made with native tapioca starch alone or the mixed system with pectin, as the G’ and G” values of C were not affected by temperatures in the 20ºC-80ºC temperature range, either when freshly prepared (Fig. 5A1 and B1) or after freezing/thawing (Fig. 5A2 and B2), and it presented very constant values in all the treatments. In the case of native TS, the G’ and G” modules decreased as the temperature rose and their values drew closer from 50ºC onwards, indicating that the gel became increasingly liquid as the temperature rose. In the mixed system with pectin, only a slight fall in the viscoelasticity modules, G’ and G”, was observed as the temperature rose. The effect was smaller in the system containing 0.6% pectin and tapioca starch. These results show the good thickening and heat-resistance properties of the C starch and the P 0.6 which is a mixture of pectin and tapioca starch. They are in accordance with those reported by Arocas et al. (2009), who found different behaviour between modified and native starch-based sauces: in the modified starch sauces, whether freshly prepared or frozen/thawed, increasing the temperature from 20 to 80ºC did not affect the values of either G’ or G” . However, in the freshly prepared native starch sauces a slight decrease in the values of the viscoelastic moduli was observed. In the native starch a predominance of G” versus G’ occurred from 40ºC onwards. The behaviour of the gels examined in the present study also showed a tendency to Arrhenius behaviour for TS and TS/pectin mixtures and it was found that their temperature dependence fell both when pectin is present and when its concentration was increased. As in the fresh and frozen systems, adding fruit increased the G’ and G” module values but the viscoelastic behaviour tendencies of each system remained unchanged. The most stable system was modified starch (C), followed by the TS/pectin mixtures.

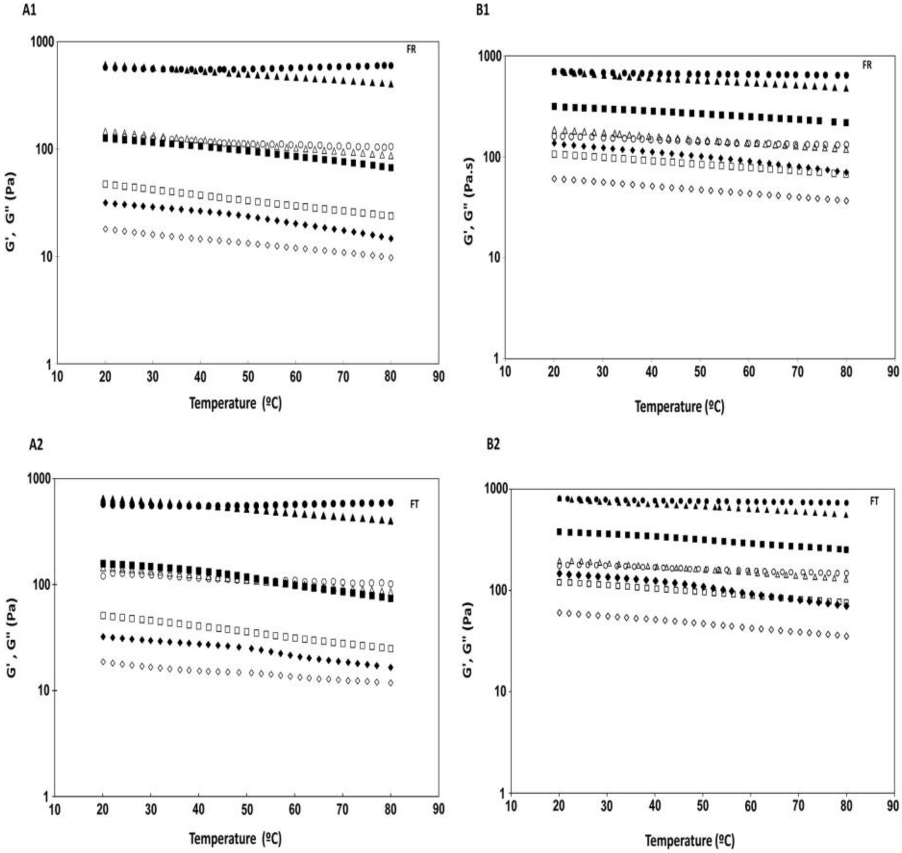

Figure. 5. Temperature ramp (20-80ºC) of the different samples submitted to different treatments. FR: Freshly prepared samples, and FT: Freeze/thaw samples. A (left column): Fillings without fruit. B (right column): Fillings with fruit. Diamonds (TS), Circles (C), Squares (P 0.3), and Triangles (P 0.6). Closed symbols: G’ and open symbols: G” values. For formulation code see Table 1.

3.3. Extrusion properties of the model systems and fruit fillings subjected to the different treatments

Extrusion tests have demonstrated to be a good tool to evaluate the consistency of semisolid systems. The values that were taken as representative from the extrusion force profiles with time, were the maximum force (Fmax), as an index of initial resistance to extrusion, and the area under the curve (AUC) or extrusion work as an index of system consistency (Angioloni y Collar, 2009; Cevoli, Balestra, Ragni, y Fabbri. 2013). They were measured for all the filling formulations, without fruit (Fig. 6A) and with fruit (Fig. 6B), with all the treatments: freshly prepared, frozen/thawed and baked (Table 3). The pectin/tapioca starch blend displayed the greatest firmness and consistency in all the treatments e freshly-prepared, frozen and baked, followed by C then TS alone, which presented the least resistance to extrusion. Both Fmax and AUC increased significantly with the higher P concentration (Fig. 6A).

The same trend was found on comparing the systems with fruit (Fig. 6B), which all had significantly higher parameter values than the same systems without fruit. Adding fruit increased the consistency and resistance to extrusion of the samples because of the solids added by the fruit and possible interactions with the pectin, as commented earlier.

Duran, Costell, Izquierdo, and Duran (1994) studied the influence of formulation on the texture of low-sugar bakery jams gelled with gellan gume guar gum mixtures and found significant effects depending on the gum type and concentration, the fruit, and their interaction. Adding gellan gum and peach pulp increased the hardness (measured as the load required for gel rupture) and rigidity (measured as the ratio of load required for gel rupture to distance penetrated at rupture) in a single cycle puncture test.

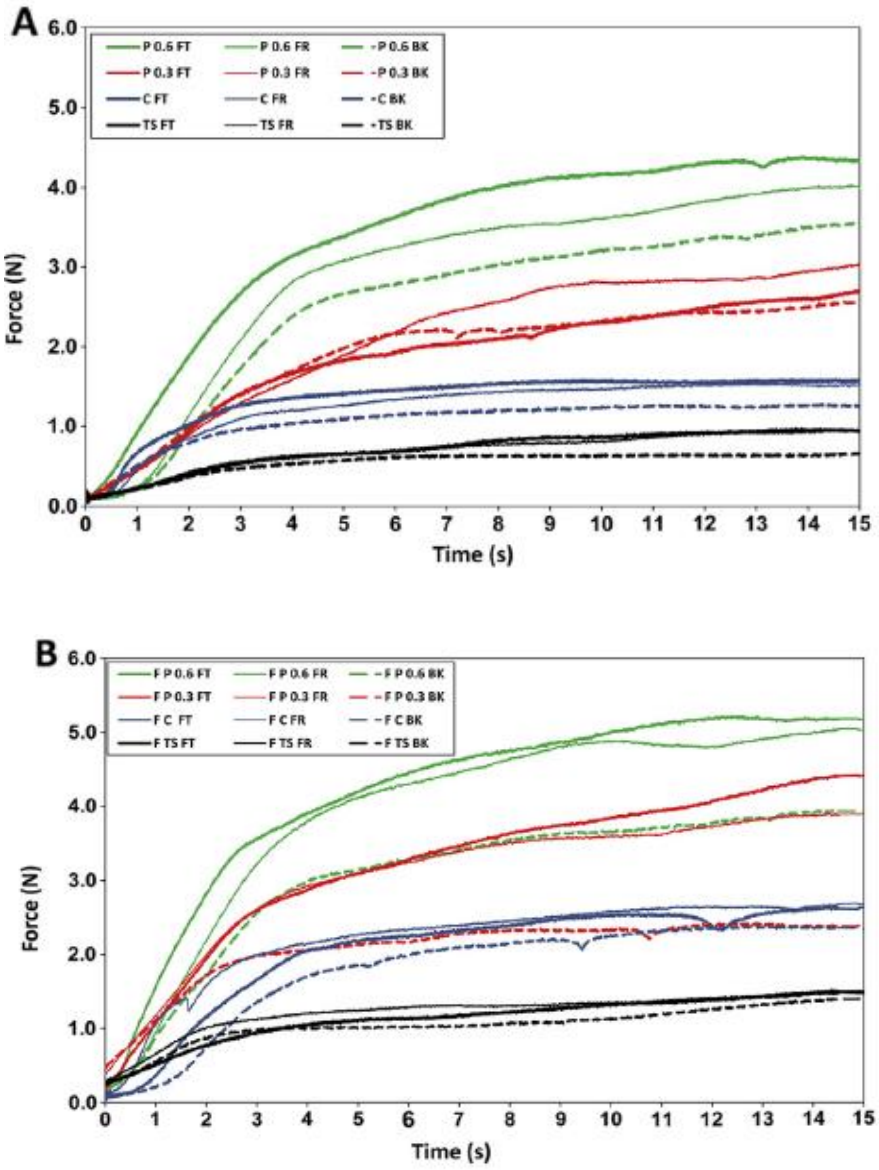

Figure 6. Extrusion profile of the different formulations. A) Fillings without fruit. B) Fillings with fruit. Freshly prepared (FR after sample code), Freeze/thaw (FT after sample code), Baked (BK after sample code). For formulation code see Table 1.

Table 3. Mean values of extrusion parameters for the different formulations and treatments

Sample	Freshly prepared		Freeze/ thaw		Baked	
	Maximum Force (N)	**AUC (N.s)**	**Maximum Force (N)**	**AUC (N.s)**	**Maximum Force(N)**	**AUC (N.s)**
C	1.55$^{\mathrm{DEf}}$(0.05)	19.18$^{\mathrm{Ef}}$(0.62)	1.58$^{\mathrm{DEef}}$(0.01)	20.04$^{\mathrm{Df}}$(0.39)	1.41$^{\mathrm{Dfg}}$(0.03)	18.09$^{\mathrm{Degh}}$(1.27)
TS	0.94$^{\mathrm{Ehg}}$(0.03)	11.03$^{\mathrm{Fi}}$(0.31)	0.94$^{\mathrm{Ehg}}$(0.02)	10.84$^{\mathrm{Ei}}$(0.33)	0.87$^{\mathrm{Eh}}$(0.04)	9.97$^{\mathrm{Fi}}$(0.30)
P 0.3	2.62$^{\mathrm{Cc}}$(0.20)	30.42$^{\mathrm{Cc}}$(0.54)	2.69$^{\mathrm{Cc}}$(0.01)	28.31$^{\mathrm{Cc}}$(0.06)	2.51$^{\mathrm{Bc}}$(0.06)	27.86B$^{\mathrm{Cc}}$(1.29)
P 0.6	3.93$^{\mathrm{Bb}}$(0.14)	45.65$^{\mathrm{Bb}}$(1.89)	4.40$^{\mathrm{Bb}}$(0.51)	47.15$^{\mathrm{Bb}}$(0.71)	3.88$^{\mathrm{Ab}}$(0.15)	40.89$^{\mathrm{Ab}}$(1.84)
F C	1.98$^{\mathrm{Dd}}$(0.05)	24.96$^{\mathrm{Dc}}$(0.05)	2.39$^{\mathrm{CDc}}$(0.02)	27.97$^{\mathrm{Cc}}$(0.29)	1.88$^{\mathrm{Ce}}$(0.12)	22.86$^{\mathrm{Cd}}$(0.48)
F TS	1.57$^{\mathrm{DEf}}$(0.07)	18.29$^{\mathrm{Egh}}$(0.63)	1.58$^{\mathrm{DEef}}$(0.14)	18.98$^{\mathrm{Df}}$(3.62)	1.41$^{\mathrm{Efg}}$(0.02)	15.37$^{\mathrm{EFhi}}$(0.27)
F P 0.3	3.87$^{\mathrm{Bb}}$(0.04)	42.73$^{\mathrm{Bb}}$(2.73)	4.28$^{\mathrm{Bb}}$(0.18)	44.96$^{\mathrm{Bb}}$(2.20)	2.48B(0.14)	33.20$^{\mathrm{Bc}}$(3.93)
F P 0.6	5.27$^{\mathrm{Aa}}$(0.34)	58.37$^{\mathrm{Aa}}$(1.62)	5.37$^{\mathrm{Aa}}$(0.28)	61.23$^{\mathrm{Aa}}$(0.71)	3.93$^{\mathrm{Ab}}$(0.02)	44.89$^{\mathrm{Ab}}$(0.79)

Figures in brackets are standard deviations.

$^{\mathrm{ABC}}$ For the same row and for the same treatment and parameter means, different letters indicate that there are significant differences ($p<0.05$) according to Tukey's multiple comparison test.

$^{\mathrm{abc}}$ For the same column means, different letters indicate that there are significant differences ($p<0.05$) according to Tukey's multiple comparison test. For sample codes see Table 1.

There were no significant differences in the hardness and stiffness of the fillings at low gellan gum concentrations with different fruit pulp contents (40%, 50% and 60%), an effect they also observed in the control system (traditional jams with high methoxyl pectin). Fiszman and Durán (1992) encountered a different effect: that adding fruit to different polysaccharide gel systems (kappa-carrageenan and kappa-carrageenan plus alginate, with or without sugar) led to a weakening of the system's structure as measured by a lower peak rupture force and deformability. They attributed the weakening to possible mechanical interference of the fruit tissue particles with hydrocolloid molecules in the formation of the basic carrageenan network. Measurements of extrusion leading to gel rupture contribute information on behaviour under high deformation forces. They confirmed the results obtained at low deformation forces (see Section 3.1), showing that the consistency and strength of the gel rose slightly with the freezing/thawing process and fell with the baking process. They also confirmed that adding fruit strengthened the structure of the gels.

3.4. Syneresis

Freeze/thaw stability is also important in the frozen pastry industry, as it represents the ability of a product to maintain its composition and integrity during storage and distribution. The liquid released within the product causes larger ice crystals to form after freezing, leading to the breakdown of the structure (Chantaro y Pongsawatmanit, 2010). The samples prepared and analysed in the present study (35% sugar) showed no syneresis either when fresh or after the freezing/thawing or baking treatments. In preliminary tests the gels prepared with 6% tapioca starch and no sugar or pectin did display syneresis (results not shown). Chantaro and Pongsawatmanit (2010), also working with tapioca starch, found that water separation (syneresis) of TS and TS/xanthan pastes increased with the number of freeze-thaw cycles and the heating time before freezing, confirming the higher breakdown of starch molecules. However, the TS pastes containing xanthan gum exhibited lower water separation ($p < 0.05$) compared with those made with TS alone.

The absence of syneresis in the present study confirms that sugars act as cryoprotectants. In Kim, Yoo, Cornillon, and Lim (2004), low molecular weight sugars or sugar alcohols acted as cryoprotectants by depressing the ice melting temperature and by increasing the solid glass content. The unfrozen liquid level depended on the sugar structure. The availability of the hydroxyl groups and structural flexibility in the sugar molecules appeared to be among the attributes determining the unfrozen liquid level. The absence of syneresis in the TS/pectin mixtures is an improvement on the behaviour of the gels with pectin alone, for which syneresis problems have been reported. Young et al. (2003) found syneresis in fruit fillings prepared with low methoxyl pectin with a high solids content (65%) at pH levels of between 3.4 and 3.7. Grujic, Grujic, and Poljasevic (2010) studied the effects of different gelling agents in heat-stable jams for doughnut fillings and encountered syneresis in some of the formulae that contained low methoxyl pectin and CaCl2. They associated this phenomenon with the type of fruit, calcium concentration and final pH, which are important factors for appropriate gel stability.

3.5. Application to fruit fillings in closed systems (pies) and open systems (tartlets)

In view of the scanty information on methods for analysing this type of filled product, preliminary instrumental texture measurement tests were carried out, the methodology was developed and the experimental conditions that best discriminated between the samples of the two types of filled pastry case (open system and close system) were chosen. The preliminary tests included penetration with an incisor-shaped probe (upper part of the Volodkevich Bite Jaws), penetration with a conical probe (60º) and penetration with a cylinder probes (P/0.25R y P/0.5R). The tests that showed the best discrimination and reproducibility were those with the cylinder (see Sections 2.6 and 2.7). During baking it was observed that in both types of filled pastry case, the samples prepared with TS alone boiled during cooking and in some cases the filling spilled out (these samples were discarded), showing that TS alone is not suitable for these applications. The instrumental texture test consisted in slowly penetrating both types of filled pastry, making it possible to record the force profile (resistance to penetration) over time.

3.5.1. Closed systems (pies)

The force-over-time curves for the pies prepared with the different filling formulations exhibited two peaks, corresponding to the penetration of each of the pastry layers (lid and base), with a plateau between them that corresponded to penetration of the filling after the probe had passed through the pastry lid (Fig. 2). The maximum force at the first and second peak was taken as indicating the hardness of the upper and lower pastry layers respectively and the area under the curve (AUC) was taken as measuring the consistency of the filling. The AUC of the pie fillings showed the same tendency as during the extrusion test (see Section 3.3): the firmest was the one prepared with TS and 0.6% pectin while the least firm was the one with TS alone. The measurements of resistance to penetration of the upper and lower pastry layers were similar (Table 4), ranging from 3.6 to 4.0 N, except with a TS alone filling, where resistance to penetration 1 (lid) was significantly lower, falling to 3.14 N. This may be attributed to the pastry's being softened by steam from the boiling filling.

3.5.2. Open system (tartlets)

The force-over-time curves for the tartlets with the different filling formulations showed a gently rising slope for the filling penetration stage and a sharper rise from the moment the probe began to penetrate the pastry case (Fig. 3). The area under the curve (AUC) from 0 time to the moment when the force suddenly increased was taken as the consistency index of the filling and the maximum or peak force as the penetration resistance of the pastry case. The AUC of the tartlet fillings showed the same tendency as during the extrusion test (see Section 3.3): the firmest was the one prepared with TS and 0.6% pectin while the least firm was the one with TS alone.

The force peak (resistance of the pastry to penetration) showed similar values, ranging from 15.9 to 16.35 N. These results indicate that despite their different consistencies, the differences in the filling formulations did not affect the texture of the pastry from the point of view of baking. As already mentioned, little information on fruit filling applications is available. Young et al. (2003) assessed bake-stable fruit fillings containing different hydrocolloids (low-methoxyl pectin, high-methoxyl pectin, alginate and mixtures of these) using Marie biscuits as a base on which to bake the filling (open system). After baking, they assessed measurements of filling deformation (spread of the filling diameter on the biscuit) and of liquid run-off onto the biscuits. The found that the mixture of alginate and low-methoxyl pectin with CaCl2 and a high solids content was the most stable. They proposed an antagonistic competition between the alginate and pectin for the available calcium, giving an overall positive, beneficial functionality to the final product. Grujic et al. (2010) used doughnuts (closed system) as a vehicle for studying the effect of different gelling agents (high-methoxyl pectin, low-methoxyl pectin, sodium alginate) on the heat-stability of fruit jams used as fillings. They found that a formulation with a gelling additive mixture (pectin and sodium alginate) and optimal calcium chloride content was effective in the filling structure, and achieved stabilization of the textural properties (sensory measurements) after reheating the product during baking. Sensory analysis of the samples was conducted before and after baking.

Table 4. Resistance to penetration values in bakery products, in a closed system (pies) and in an open system (tartlets)

Sample	Pies (closed system)			Tartlets (open system)	
	Fmax1 (N)	AUC (N.s)	Fmax2 (N)	AUC (N.s)	Fmax (N)
F C	3.69^{bc} (0.04)	3.55^{b} (0.01)	3.67^{b} (0.06)	2.15^{c} (0.06)	16.35^{a} 0.75
F TS	3.11^{c} (0.01)	2.24^{c} (0.24)	3.78^{ab} (0.04)	1.77^{d} (0.01)	15.90^{a} (0.69)
F P 0.3	3.97^{a} (0.11)	3.96^{b} (0.12)	3.49^{b} (0.13)	4.95^{b} (0.04)	16.31^{a} (0.98)
F P 0.6	4.00^{a} (0.22)	5.17^{a} (0.30)	3.98^{a} (0.01)	6.71^{a} (0.08)	16.09^{a} (1.18)

Figures in brackets are standard deviations.^{abc} Different letters indicate that there are significant differences ($p<0.05$) between values with the same letter within the same column according to Tukey's multiple comparison test. For sample codes see Table 1.

4. CONCLUSIONS

The suitability of hydrocolloid systems for fruit fillings is a little studied subject. Fruit fillings demand stability against thermal processing and against freeze/thaw cycles, among others. The development of native starch containing fruit filling demands some modifications to achieve freezing and heating stability during processing. The present study has found that fruit fillings prepared with a mixture of native tapioca starch, low-methoxyl pectin and calcium present no syneresis, good freeze/thaw and bake stability, displaying considerable advantages compared to the use of tapioca starch alone. The fruit purée (peach) improved the structure of the fillings and the baking tests with two real applications (open and closed filled pastry cases) confirmed the viability of the proposed system, which even presented advantages compared to the control.

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CAPÍTULO 3

Fruit fillings development: a multiparametric approach

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ABSTRACT

Fruit fillings were formulated with three composition variables: thickeners (native tapioca starch, modified waxy corn starch and a mixed system of native tapioca starch plus low-methoxyl pectin), quantity of fruit (25 g/100g and 50 g/100g) and replacement of sucrose with polydextrose and intense sweeteners (stevia:sucralose 50:50).

The 12 formulations were evaluated to discover their rheological behaviour and instrumental texture. Sensory evaluation by quantitative descriptive analysis was performed by a trained panel. Liking and, more importantly, the adequacy of some sensory attributes were evaluated with a panel of 100 consumers using just-about-right (JAR) scales.

Hierarchical cluster analysis was applied to the results to detect consumer groups with different preference profiles. Three groups were found, suggesting that formulations should be adapted to each scenario. One group did not like intense sweeteners at all. Another, remarkably, preferred the characteristics of the tapioca starch samples. The third group (the most numerous) did not show these marked tendencies. The results demonstrate that this kind of analysis with consumers is necessary to interpret the liking values of a population sample correctly and give the industry the necessary tools for adequate target-driven diversification of the fruit filling market.

Key words: Fruit fillings; sugar-free; adequacy of sensory attributes; consumer perception.

1. INTRODUCTION

New product development is a suitable strategy for building competitive advantage and long-term financial success in today’s global food markets. Nowadays, the food market is increasingly segmented. Consumers look for products that are not only of good quality but also meet personal needs and tastes. In the phase in which the new product starts to take shape, a careful analysis needs to be made of the relationships between consumer perceptions, preferences and choices, on one hand, and the product’s technical features, on the other, (Costa y Jongen, 2006). Incorporating the ‘voice of the consumer’ at early stages of the process has been identified as a critical success factor. However, it is often ignored or poorly executed (Van Kleef, Van Trijp, y Luning, 2005).

This approach would make it possible to design a new product that could potentially fulfil consumer needs. Among other things, this requires studies to discover whether the population’s perception of the target product is segmented and which versions of a product need to be developed. Consumer preferences differ and there are indications that they have become more diverse over time. In addition, consumers differ in the kind of qualities they expect from food products. Nevertheless, much product innovation in the food sector is still not geared towards specific consumer segments (Grunert y Valli, 2001).

In the present study, two factors were varied in the selected fruit filling: 1) the gelling agent, and consequently the final texture (one of the main factors for quality and acceptance in this type of product), and 2) sucrose or its replacement by alternative sweeteners, with the resulting benefit of a lower calorie content.

Sucrose in fruit fillings contributes to total soluble solids, an effect that is essential for their physical, chemical, and microbiological stability;

provides sweetness, body and mouthfeel; improves appearance (colour and shine); and makes gelation of pectin possible (Hyvonen y Torma, 1983; Basu, Shivhare y Singh, 2013). Sucrose also acts as a dehydrating agent for the pectin molecules (the naturally-occurring gelling agent in fruit fillings), permitting closer contact between the pectin chain molecules during filling manufacture (Suutarinen, 2002). One gram of sucrose contributes 4 calories. Nowadays, due to the growth of the health food industry, reducing the sucrose content of food products through full or partial replacement by alternative sweeteners has become a viable option for producing low or zero calorie foods. Substituting other sweeteners for sucrose is a challenge for researchers and industry alike, since in addition to the sweet taste, other sensory attributes may be modified (Cadena, Cruz, Netto, Castro, Faria, y Bolini, 2013). High intensity sweeteners are increasingly being used by consumers, either for their reduced energy content or due to the demands of diabetes mellitus sufferers (Cadena y Bolini, 2011).

The food industry frequently uses sweetener blends to overcome the sensory limitations of individual sweeteners (Zhao y Tepper, 2007). Blending takes advantage of the phenomenon of synergy among sweeteners which is typically observed for sweeteners that exhibit different flavour profiles, particularly if one of them is bitter. Blending tends to create an improved flavour profile. Stevioside and sucralose are non- nutritive high intensity sweeteners, acid- and heat-stable, that can be used in combination to prepare jam-like products without compromising taste (Basu, Shivhare, y Singh, 2013). Residual bitterness from the stevia has been reported in a number of studies (Melo, Bolini, y Efraim, 2009; Prakash, DuBois, Clos, Wilkens, y Fosdick, 2008). It has been suggested that to reduce the bitter taste, common to many Stevia species, it is important to obtain Stevia with more rebaudioside (Cadena, Cruz, Netto, Castro, Faria, y Bolini, 2013)). Sucralose is reported to have a relatively clean and lingering sweet taste with little persistence of bitterness (Nabors, 2002; Zhao, y Tepper, 2007).

However, high-potency sweeteners do not contribute texture. To maintain the structural characteristics supplied by sucrose, other substances such as polydextrose are used as bulking agent replacements for sucrose. Polydextrose has similar technical properties to sucrose, except for sweetness. It lacks a sweet taste, but provides 1 kcal/g in comparison to the 4 cal/g of sucrose (Schirmer, Jekle, Arendt y Becker, 2012). Polydextrose has been successfully incorporated into a wide range of foods, including baked goods, beverages, confectionery and frozen desserts, and is known to provide the bulk, appropriate texture and mouthfeel qualities (Aidoo, Afoakwa, y Dewettinck, 2014), no aftertaste, contribution to colour and interaction with starch and protein, in a similar manner to that of sucrose (Pereira, Rios de Souza, Teixeira, Queiroz, Borges y Souza, 2013).

The sensory quality of fruit fillings includes a number of attributes like balance of sweetness and sourness, colour, fruit flavour, medium firmness and a homogeneous gel-like texture, among others. Gel texture depends, of course, on the gelling agent selected. Different pectin preparations or some other substance such as a gelling agent can be used. For the present study, three different gelling systems (tapioca starch alone, a combination of tapioca starch and pectin and a modified waxy corn starch (MWCS)) were selected based on two previous studies that assessed certain rheological and technical characteristics (Agudelo, Varela, Sanz, y Fiszman, 2014a; Agudelo, Varela, Sanz y Fiszman, 2014b). Pectin is primarily used in the jam and bakery filling industry, since it is a gelling agent that occurs naturally in fruit (Young, Kappel, y Bladt, 2003; Grujic, Grujić, y Poljašević, 2010), and MWCS is also used to obtain syneresis-free and freeze-stable products (Gisslen, 2012).

A number of tools are available to help product developers to create or revise products to please consumers. Quantitative consumer research typically involves obtaining consumer responses through appropriate data collection methods for the products of interest. Hedonic responses are generally obtained through product liking scales or behaviour choices (preference). These methods are relevant at the development (product design) and optimization stages (testing), previous to the launch (Van Kleef van Trijp, y Luning, 2005; Costa, y Jongen, 2006). However, merely ascertaining acceptability (in the form of overall liking or preference ratings) does not open the door to further product development. Liking scales and preference ratings alone do not assist developers to understand how product attributes need be altered to improve product acceptability or relative preference. Just-about-right (JAR) scales are a technique that has been incorporated into quantitative consumer testing for this purpose (Rhotman, 2007). JAR scales are used in consumer science to identify whether an attribute is too high or too low in a product, or whether it is “just about right.” The consumer ratings provide an indication of the potential for improving the prototype and the direction of formulation change. JAR scales are frequently used in non-experimental product optimization studies, which include prototypes and/or commercial products (Popper, 2014).

The aims of the present study were to approach fruit filling development from a multiparametric perspective, studying how consumer and sensory techniques can guide the final characteristics of products that have good acceptability, and to evaluate how this is reflected in the intrinsic characteristics of the products (sensory and instrumental parameters) as defined by compositional changes (amount of fruit and sucrose replacement).

2. MATERIALS AND METHODS

2.1. Ingredients

The ingredients employed were native tapioca starch (TS) (moisture content 13.7 g/100g, Sucroal S.A., Cali, Colombia), citric acid and sodium citrate (Sucroal S.A., Cali, Colombia), highly cross-linked waxy corn starch, hydroxypropylated and phosphated (C) (moisture content 12.3 g/100g, Polartex 6716, Cargill, Martorell, Spain), low methoxyl pectin (P) (33-37% esterified), moisture content 12 g/100g, Unipectine OB700, Cargill, Martorell, Spain), anhydrous calcium chloride (Panreac, Barcelona, Spain), polydextrose (PD) (moisture content 3.2 g/100g, Stalite III, Tate y Lyle, Decatur IL, US), rebaudioside B (stevioside, purity greater than 95%, Sucroal S.A., Cali, Colombia), sucralose (Tate y Lyle, Jurong Island, Singapore) and sucrose (S) (all-purpose table sugar, Hacendado, Valencia, Spain). Fruit purée (F) was obtained from canned peach halves in light syrup (6.5 degrees Brix, pH 3.8, Hacendado, Valencia, Spain). The final moisture content of the fruit purée was 92 g/100g.

2.2. Model system and fruit filling preparation

The samples were prepared in a food processor-cooker (Thermomix TM 31, Wuppertal, Germany) equipped with temperature and stirring speed controls. All the samples were prepared at pH 3 and contained 35 g/100g total soluble solids (sucrose or polydextrose) and 6 g/100g of the thickener system. Three thickener systems were employed: a modified waxy corn starch as control (C), native tapioca starch (TS), and TS with pectin (0.6 g/100g of the total hydrocolloid system on a dry weight basis) and calcium ions (60 mg of calcium ion per gram of pectin) (P).

The first step in preparing the samples was to add the sucrose or polydextrose to part of the water. In the samples that contained fruit, the fruit purée was also added (25 g/100g or 50 g/100g). The mixture was heated to 60°C and stirred at 600 rpm for 5 minutes. In the formulations containing pectin, the pectin was first dispersed in water with a magnetic stirrer at 80°C until it was totally dissolved, then allowed to cool to 60°C before adding it to the sucrose-fruit-water or polydextrose-fruit-water mixture. The starch was dispersed in another part of cold water and added to the sucrose-water, polydextrose-water, sucrose-water-fruit mixture or polydextrose-water-fruit mixture, continuing to stir while heating for another 2 minutes. The sweetener mixture was then added to the samples that contained polydextrose. Once the mixtures had been prepared with these ingredients, the temperature was increased to 90°C and heating and stirring continued for a further 30 minutes. Calcium chloride, dissolved in a small amount of water reserved for this step, was added to the mixtures containing pectin. The pH was adjusted to 3.0 (±0.2), using citric acid and sodium citrate buffer solutions, and stirring and heating continued for a further 5 minutes. The samples were transferred to plastic containers and held in refrigeration (8°C) for 24 hours (Table 1).

2.3. Linear viscoelastic properties

The linear viscoelastic properties of the different samples were studied with a controlled stress rheometer (AR-G2, TA Instruments, Crawley, England), using serrated plate-plate geometry (40mm diameter). A gap of 1 mm was employed. Before the measurements were taken, the samples remained between the plates for 10 min equilibration time. The exposed edges of the samples were covered with silicone oil to prevent the sample from drying out during the measurements.

Table 1. Composition of the different fruit filling formulations (pH 3, 35 degrees Brix)

Sample code	Ingredient							
	Tapioca starch (TS) g/100g	Pectin (P) g/100g	$CaCl_2$* g/100g	MWCS (C) g/100g	Fruit (F) g/100g	Sucrose (S) g/100g	Polydextrose (PD) g/100g	Sweetener mix** g/100g
C25FS	0	0	0	6	25	26	0	0
C25FPD	0	0	0	6	25	0	26	0.052
TS25FS	6	0	0	0	25	26	0	0
TS25FPD	6	0	0	0	25	0	26	0.052
P25FS	5.33	0.60	0.067	0	25	26	0	0
P25FPD	5.33	0.60	0.067	0	25	0	26	0.052
C50FS	0	0	0	6	50	20	0	0
C50FPD	0	0	0	6	50	0	20	0.04
TS50FS	6	0	0	0	50	20	0	0
TS50FPD	6	0	0	0	50	0	20	0.04
P50FS	5.33	0.60	0.067	0	50	20	0	0
P50FPD	5.33	0.60	0.067	0	50	0	20	0.04

$CaCl_2$=Calcium chloride, MWCS=Modified Waxy Corn Starch, C=Control
* The calcium salt dosages correspond to 60 mg of calcium ion per g of pectin.
** The sweetener mix is a 50:50 blend of stevia and sucralose

The measurements were performed at 20ºC. Strain sweeps were carried out to determine the linear viscoelastic region, followed by frequency sweeps from 10 to 0.01 Hz at a strain amplitude value inside the linear region. The storage modulus (G‘), loss modulus (G”) and loss tangent (tanδ = tan G”/G’) were recorded with TA Data analysis software (TA Instruments, Crawley, England).

2.4. Extrusion test

The extrusion properties were measured with a texture analyser (TA-XT Plus, Godalming, England) equipped with a 50-mm diameter back extrusion cell (A/BE Back Extrusion Rig), with a 10 mm gap between the extrusion cylinder and the compression disk. The compression speed was 10 mm/s and the trigger point was 10 g. The duration of the test was set at 15 s (Arocas, Sanz, y Fiszman, 2009).

The samples were placed in the extrusion cylinder and stabilized in a water bath at 25°C for 10 minutes before making the measurements. The force-displacement profiles were recorded and the maximum extrusion force (Fmax, in N) and the area under the curve (AUC, in N/s) were obtained, as indices of firmness and consistency, respectively (Cevoli, Balestra, Ragni, y Fabbri. 2013).

2.5 Sensory and Consumer tests

All the sensory tests were carried out in a sensory laboratory equipped with individual booths (ISO, 2007). Data acquisition was performed using Compusense five release 5.0 software (Compusense Inc., Guelph, Ontario, Canada).

2.5.1 Quantitative descriptive analysis (QDA)

The twelve samples (Table 1) employed in the instrumental tests (see sections 2.2, 2.3 and 2.4) were assessed through QDA.

Selection of Terms. A panel of eight assessors (seven woman and one man, aged between 20 and 45 years), with previous experience in descriptive analysis, selected the descriptors using the Checklist Method (Lawless y Heymann, 1998). The terms were selected and discussed in four 1-hour open sessions with the panel leader. The assessors were first given a brief outline of the procedures and a list of attributes and representative samples. They were then asked to choose and write down the most appropriate attributes to describe all the sensory properties of the fruit filling or to suggest new ones. The panel leader collected and wrote down all the attributes on a new list. The panel discussed the appropriateness and definitions of the selected attributes and held preliminary discussions on how to assess the products. At the end of these sessions, a consensus on the list of attributes was reached (table

2). This procedure was proposed by Stone and Sidel (2004) in order to obtain a complete description of a product's sensory properties.

Table 2. Attributes, scale extremes and definitions used in the descriptive sensory analysis of the fruit fillings (FF) by a trained panel

Attribute	Scale extremes	Definition
Elasticity	Low/High	Recovery of the initial state and the speed of this recovery after squashing the sample against the side of the cup with a spoon
Fluidity	Weak/strong	Speed with which the FF sample falls from a spoon at a 90-degree angle
Consistency	Weak/strong	Resistance of the FF sample when rolled around the mouth with the tongue
Pulpiness	Little/much	Detection of fruit particles or pulp when rolled around the mouth with the tongue
Residence time in the mouth	Weak/strong	Speed at which the FF dissolves in the mouth or disappears
Stickiness	Weak/strong	Effort required to detach the surface of the FF sample from another surface (tongue, teeth)
Mouthcoating	Weak/strong	Feeling of having a viscous film covering the tongue and palate after swallowing the FF sample
Sweetness	Weak/strong	Sweetness perceived while chewing the FF
Acidity	Weak/strong	Acidity perceived while chewing the FF
Fruitiness	Weak/strong	Fruitiness perceived while chewing the FF
Strange taste	Weak/strong	Strange flavour perceived while chewing the FF
Aftertaste	Weak/strong	Aftertaste perceived after swallowing the FF

Panel Training. The panellists attended eight 1-hour training sessions. Training involved two stages. During the first stage, different samples were tasted by the panellists to attain a better understanding and final agreement on how to measure all the descriptors. Different tasting sessions were conducted until the panel was homogeneous in its assessments and its comprehension of the extremes of the scales. During the second stage, the panellists used a 10-cm unstructured scale to score the selected attributes of the fruit filling samples (Table 2).

Sample assessment. A complete block experimental design was carried out in duplicate (12 samples, 6 sessions, 4 samples per session). The intensities of the sensory attributes were scored on a 10-cm unstructured line scale. In each session, the samples were served in random order, each in a separate plastic cup identified with a random three-digit code. The panellists were instructed to rinse their mouths with water and eat a neutral-tasting biscuit between each sample evaluation.

2.5.2 Consumer test

This test assessed six samples prepared with the three thickeners (tapioca starch alone, TS; modified waxy corn starch, C; and the mixed system with tapioca starch and pectin, P), each with either sucrose (S samples) or a combination of polydextrose and sweeteners (PD samples). All these samples contained the highest level of fruit (50g/100g) and their final total soluble solids level was 35 g/100g. Consequently, the sample codes for the samples evaluated were C50FS, C50FPD, TS50FS, TS50FPD, P50FS, and P50FPD.

The test was conducted with 100 consumers (35 men and 65 women, with ages ranging from 18 to 62 years). All the consumers stated that they knew what fruit filling products were and that they consumed them. They assessed six fruit filling samples in a single session. The samples were coded with randomized 3-digit numbers in a balanced complete blocks experimental design.

Liking Scales

The consumers rated their liking for the fruit fillings on a 9-point hedonic scale 9 (1 = I don’t like it at all, 9 = I like it very much). The consumers rated their overall liking, consistency liking and flavour liking for each sample by choosing the point on the scale that best expressed their tastes.

Adequacy of consistency, sweetness, acidity, and fruit flavour attributes (JAR scales)

The adequacy of the consistency, sweetness, acidity, and fruit flavour of each sample was evaluated with “just-about right” (JAR) five-point bipolar scales. In this kind of test, the end-points are anchored with labels that represent the levels of the attribute that deviate from a respondent’s theoretical ideal point in opposite directions, while the central point is the ideal (Rothman, 2007). In the JAR test the consumers were asked “in your opinion this product should be ...”, rated on the following scale: 1 = much more …, 2 = more …, 3 = about right, 4 = less …, 5 = much less … (Lawless y Heymann, 1998).

2.6. Statistical processing of the data

Instrumental analysis

All the tests were carried out in duplicate with samples prepared on different days. Analyses of variance (ANOVA) were performed to compare the effect of different concentrations of polydextrose and sucrose and of two concentrations of fruit (25 g/100g and 50 g/100g), with and without added sucrose, on the viscoelastic and extrusion properties of the samples (Table 1). Tukey's multiple comparison test was used to analyse inter-group differences with a 95% confidence interval.

Quantitative descriptive analysis

Two-way analysis of variance (ANOVA) was applied to each descriptor to check panel performance and differences between products, considering the assessors, the samples and their interaction as factors. Least significant differences were calculated by Tukey’s test and the significance at $P < 0.05$ was determined. One-way ANOVA was applied to the consumer liking scores to study the differences between the samples. The least significant differences were calculated by Tukey's test ($p<0.05$). Hierarchical cluster analysis (Euclidean distance, Ward’s method) was applied to the overall liking scores in order to identify segments of consumers with similar preference patterns. The JAR results were analysed by penalty analysis (PA) to identify potential directions for reformulation on the basis of consumer liking by highlighting the most penalizing attributes. This technique is used to relate JAR scales to liking data, particularly in order to understand which side of the JAR scale is linked to lower hedonic ratings. The respondent percentages (x-axis) were plotted against the penalties (drop in liking, y-axis). Penalty analysis was used in order to gain an understanding of the attributes that most affected liking ratings (Plaehn y Horne, 2008). The usefulness of the method is that it provides guidance for product reformulation or a better understanding of attribute adequacy in relation to liking in terms of direction, with the assumption that the maximum hedonic score will occur at the “just about right” point (Rothman, 2007).

All the statistical analyses were performed with the XLSTAT statistics software package (Addinsoft, Barcelona, Spain, version 2009, 4.03).

3. RESULTS AND DISCUSSION

3.1.1 Effect of sucrose replacement on the different thickener systems without fruit

Table 3 shows the viscoelasticity parameters of the systems with the three thickeners –native tapioca starch (TS), modified waxy corn starch (MWCS) as the control (C), or the pectin-tapioca starch mixture (P) – and increasing replacement of sucrose (S) by polydextrose (PD). Adding polydextrose as a bulking agent for partial or total replacement of the sucrose led to a significant fall in the storage modulus (G’) of the three systems under study and to significantly lower G’’ values in most cases.

In the tapioca starch alone system (TS) the G’ values were slightly higher than those of G” and both were quite frequency-dependent, reflecting a weak gel structure with low viscoelasticity which fell lower as the sucrose was increasingly replaced by polydextrose.

The MWCS system had significantly higher modulus values than the TS system and the two moduli were further apart. In addition, these values were much less frequency-dependent than those of TS, reflecting the stronger gel structure of MWCS. The MWCS samples showed the same behaviour pattern as TS with increasing replacement of sucrose by polydextrose, as the G’ and G’’ values fell significantly and tanδ rose in comparison with the sucrose-only sample, indicating a weakening of the gel as the sucrose level fell.

The TS with pectin and calcium ions system (P) was also more viscoelastic than the TS alone, presenting higher G’ and G’’ and lower tanδ values, showing a sizeable increase in viscoelastic behaviour and behaving more like the modified starch system. In general, the G’ and G’’ values fell significantly as the proportion of polydextrose rose but the tanδ values remained unchanged, indicating that replacement by

polydextrose did not cause major changes in the gel structure. The lower viscoelastic moduli values in the presence of polydextrose indicated a slight but significant loss in elasticity as the sucrose was replaced.
Despite this, the structural alteration was not very great because the physico-chemical properties of polydextrose are very similar to those of sucrose (Schirmer et al., 2012). According to Pereira et al. (2013), the bulking agent must have similar characteristics to those of sucrose, including replacement of solid stability at different pH and temperature conditions. The low methoxyl pectin does not require the addition of solids in order to gel, it only needs divalent calcium ions. However, the addition of soluble solids such as sucrose to the pectin-calcium gels can enhance gel strength. The extent to which gel strength is increased depends not only on the sugar concentration, but also on the type of sugar and the pH value (Fraeye et al., 2010).

3.1.2 Effect of the amount of fruit on the viscoelastic properties of fruit fillings

The effect of adding fruit at two content levels (25 g/100g and 50 g/100g) to the three thickener systems was analysed (Table 4). Two series of samples were studied, one with sucrose and the other with complete replacement of sucrose by polydextrose. All these systems were adjusted to 35 g/100g of total soluble solids. Increasing the percentage of fruit from 25 g/100g to 50 g/100g significantly increased the G’ and G’’ values of all the samples, showing some reinforcement of the systems. The mean viscoelasticity parameter values (Table 4) show that increasing the fruit content of the TS filling from 25 g/100g to 50 g/100 g led to slight but not significant differences, and no differences were found on increasing the percentage of fruit in the samples prepared with polydextrose.

Table 3. Effect of increasing replacement of sucrose (S) by polydextrose (PD) in samples formulated with three different gelling systems, without fruit. Mean values of three replicates

S:PD Ratio	**TS**			**MWCS (C)**			**P**		
	G' (Pa)	G'' (Pa)	tan δ	G' (Pa)	G'' (Pa)	tan δ	G' (Pa)	G'' (Pa)	tan δ
35:0	25.9^{aE} (3.15)	16.9^{aD} (0.14)	0.70^{aAB} (0.09)	591.4^{aB} (19.19)	124.8^{aA} (4.81)	0.21^{aD} (0.01)	658.9^{aA} (9.40)	130.1^{aA} (7.07)	0.20^{aD} (0.01)
28:7	18.9^{abE} (1.73)	9.7^{bcD} (0.63)	0.70^{aAB} (0.04)	535.0^{abC} (7.11)	117.3^{aABC} (3.34)	0.22^{bD} (0.01)	609.1^{abAB} (13.44)	113.7^{abBC} (0.92)	0.19^{aD} (0.01)
14:21	21.1^{abE} (2.83)	10.9^{bD} (0.58)	0.50^{aBC} (0.04)	473.2^{bcD} (23.45)	110.4^{aC} (5.16)	0.23^{cCD} (0.01)	616.2^{abAB} (9.05)	108.3^{bC} (0.35)	0.18^{aD} (0.01)
0:35	8.8^{cE} (3.04)	8.1^{cD} (0.88)	0.56^{aA} (0.23)	435.5^{cD} (14.69)	115.6^{aBC} (4.52)	0.27^{dCD} (0.01)	585.7^{bBC} (26.94)	107.4^{bC} (4.45)	0.18^{aD} (0.01)

S = sucrose, PD = polydextrose, TS = native tapioca starch; MWCS = modified waxy corn starch, C = control; P = pectin-tapioca starch blend; G’ = storage modulus, G’’ = loss modulus, tanδ = loss tangent

Figures in brackets are standard deviations

Different lower case letters within the same column or different capital letters within the same row indicate significant differences ($p>0.05$) according to Tukey's multiple comparison test

Sample C showed a large, significant rise in modules G’ and G’’ when the fruit content was increased from 25 g to 50 g / 100 g, indicating a strengthening of the system’s structure, and higher values than those of the system prepared without fruit, where the solids were provided only by the sucrose or by the polydextrose (Table 3).

As in the systems without fruit, adding polydextrose lowered the G’ and G’’ values compared with the systems containing fruit and sucrose. This effect can be attributed to the difference in molecular weight and to the greater viscosity of polydextrose at the same temperature and concentration as sucrose. These characteristics enable polydextrose to provide the desirable mouth-feel and texture qualities that are so important when replacing sucrose (Amerbach y Craig, 2008). It is also known that full replacement of sucrose with polydextrose leads to a higher starch gelatinization temperature in comparison with sucrose (Hicsasmaz, Yazgan, Bozoglua, y Katnas, 2003).

The pectin-tapioca starch (P) systems exhibited different behaviour. Although increasing the quantity of fruit again improved the gel structure (higher G’ and G’’ values), as in the other thickener systems, the differences compared to samples prepared without fruit were not significant in this system (Table 3). In addition, the G’ and G’’ values were much lower than in the control. In the pectin-tapioca starch system, the polydextrose appeared not to affect gel formation when fruit was present.

In a previous study, pectin was found to be responsible for the viscoelastic properties of the mixed system, giving the gel greater strength than the system with starch alone (higher G’ and G” values), whereas the starch molecules appeared to have an additive effect. In addition, some ion interaction between the starch molecules and charged positions in the pectin molecules could not be discarded (Agudelo et al., 2014b).

Table 4. Effect of the fruit content on the mean values (three replicates) of the viscoelastic parameters G’, G” and tanδ at 1Hz and on the extrusion parameter values at 20°C

Sample*	Mean values of instrumental parameters				
	Viscoelastic parameters			Extrusion parameters	
	G' (Pa)	G" (Pa)	tanδ	AUC (N.s)	Fmax (N)
C25FS	758^{c} (38)	143.0^{b} (4.7)	0.19^{b} (0.01)	34.0^{a} (2.5)	3.14^{ab} (0.38)
C25FPD	494^{d} (47)	111.4^{bc} (12.7)	0.23^{b} (0.01)	23.1^{c} (1.3)	2.01^{c} (0.28)
TS25FS	31^{g} (5)	18.8^{ef} (0.2)	0.61^{a} (0.09)	5.2^{d} (0.1)	0.36^{d} (0.03)
TS25FPD	18^{g} (1)	11.6^{f} (0.2)	0.66^{a} (0.05)	5.01^{d} (0.3)	0.35^{d} (0.02)
P25FS	171^{f} (18)	52.5^{de} (3.3)	0.31^{b} (0.01)	25.8^{bc} (2.8)	2.43^{bc} (0.35)
P25FPD	173^{f} (7)	48.5^{de} (1.9)	0.28^{b} (0.01)	25.5^{bc} (0.6)	2.29^{bc} (0.05)
C50FS	1125^{a} (50)	225.8^{a} (0.6)	0.20^{b} (0.01)	39.1^{a} (1.6)	3.93^{a} (0.12)
C50FPD	972^{b} (36)	226.4^{a} (26.4)	0.23^{b} (0.04)	32.5^{ab} (3.4)	2.77^{abc} (0.02)
TS50FS	43^{g} (1)	32.1^{ef} (0.9)	0.74^{a} (0.02)	6.4^{d} (0.4)	0.52^{d} (0.06)
TS50FPD	34^{g} (3)	25.1^{ef} (2.0)	0.74^{a} (0.01)	5.6^{d} (0.2)	0.40^{d} (0.03)
P50FS	280^{e} (7)	82.3^{cd} (9.6)	0.29^{b} (0.04)	36.4^{a} (1.0)	3.40^{ab} (0.39)
P50FPD	298^{e} (16)	80.6^{cd} (1.1)	0.27^{b} (0.01)	38.0^{a} (3.0)	3.42^{ab} (0.48)

*All samples contain 35 g/100g total soluble solids
AUC= Area under curve, Fmax= maximum extrusion force
Figures in brackets are standard deviations. See Table 1 for sample codes.
Different letters within the same column indicate significant differences ($p>0.05$) according to Tukey's multiple comparison test

On the other hand, Galkowska, Dlugosz, and Juszczak (2013) found that when high-methoxyl pectin and sucrose were added to modified starches at a 0.5 g/100g concentration, the rheology of the mixed systems was mainly dominated by the behaviour of the starch, since the results of the dynamic rheological measurements indicated that pectin did not affect the proportion of the elastic and viscous properties of the gels. However, this was not the case in the present study.

The gel strength of pectin-calcium gels depends not only on the sugar content, but also on the type of sugar: adding sucrose increases the gel strength more than adding glucose, which in turn has a greater effect than fructose (Grosso y Rao, 1998). The mechanism by which sucrose increases the gel strength is not entirely clear. Sugars reduce the water activity, promoting pectin-pectin interactions rather than pectin-water interactions. In contrast, depending on the stereochemistry of the hydroxyl groups, some polyols may compete with pectin to bind calcium ions, which may reduce the gel promoting effect (Fraeye et al., 2010). In the present study, it was found that the solids provided by the fruit did not increase the gel strength to the same extent as those contributed by the sucrose.

3.2. Extrusion properties of fruit fillings

The extrusion properties were measured in samples of fruit fillings with 25 g or 50 g / 100 g of fruit, prepared with the highest level of sucrose or with total replacement of the sucrose by polydextrose, for each of the three thickeners (see Table 1 for sample codes). The extrusion profile values that were taken as representative were the maximum force (Fmax), as an index of initial resistance to extrusion, and the area under the curve (AUC), or extrusion work, as an index of the system consistency (Angioloni y Collar, 2009; Cevoli et al., 2013).

Measurements of extrusion leading to gel rupture contributed information on behaviour under high deformation forces; in general, the results confirmed those obtained at low deformation forces (see section 3.1.2).

System C had the highest firmness and consistency values for each fruit content level (Table 4), followed by the pectin-tapioca starch mixture samples and, lastly, by those with tapioca starch alone. These values followed the same behaviour patterns as for the viscoelastic properties of the different systems (see section 3.1), confirming that adding more fruit strengthened the gel structure in the systems studied and that the gel structure formed by the pectin-native TS system was stronger than with the TS-alone system and nearer to that of the system prepared with the control starch. Substituting polydextrose for sucrose had very little effect on the structure of the systems studied, though the C starch system was the one that showed the greatest differences.

3.3 Sensory Analysis- *Quantitative Descriptive Analysis (QDA)*

The QDA approach (Stone y Sidel, 1998) was chosen to identify and quantify the sensory properties of the samples. The composition of the twelve samples analysed is shown in Table 1 and the attributes assessed by the trained panel are described in Table 2.

ANOVA of the trained panel sensory scores indicated that the effect of the sample was significant for all the attributes ($P < 0.05$). The mean intensity values for each sensory attribute of the fruit filling samples were mapped on a spider web plot. Since the general pattern of the set of samples containing 25 g of fruit/100g (data not shown) was similar to that of the sample set with 50g of fruit/100g results, only the latter is shown (Figure 1). The only significant differences between the two sets (25g and 50g fruit) were that the samples with the higher fruit content were rated as more acid and fruitier.

Considering the texture-related attributes, as expected, the thickener systems had the greatest effect on the scores. The pectin-TS (P) and C samples showed quite similar profiles whereas the TS samples behaved differently, exhibiting greater consistency, stickiness, residence time in the mouth and mouthcoating and less fluidity and elasticity.

Regarding the flavour attributes, the greatest difference was between the samples prepared with sucrose and those prepared with sweeteners, in which aftertastes and strange flavours appeared, with significantly higher values in the case of C25FPD (data not shown), the control starch sample with the lower fruit content (25g/100g). In contrast, significantly the lowest score for strange flavours was that of the sample prepared with the pectin-TS mixture and the higher fruit content (P50FPD). None of the samples with sucrose differed from each other in sweetness. Other attributes, like acidity and pulpiness, varied moderately between the different thickeners. The three samples with sucrose (TS50FS, P50FS and C50FS) scored significantly higher for fruitiness than the samples containing polydextrose.

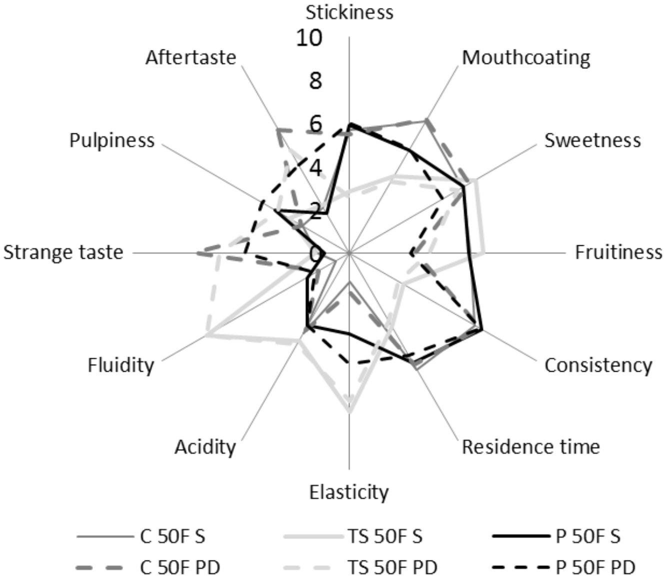

Figure 1. Spider web plot of the mean descriptive sensory scores (n=2) in for fruit filling samples containing 50g fruit/ 100g.

Previous results have also shown that increasing the sucrose level increases retronasal fruitiness (Hort y Hollowood, 2004; King, Duineveld, Arents, Meyners, Schroff y Soekhai , 2007). According to Boland, Buhr, Giannouli, and van Ruth, 2004), the effects of hydrocolloids on flavour release may be due to two mechanisms: one is the physical entrapment of flavour molecules within the food matrix and the second involves interactions between the flavour molecules and the gel components. On comparing several types of gels, these authors found that ten flavour compounds had higher partition coefficients in pectin gel than in starch gel.

The samples with the lower fruit content (25g/100g), particularly the one prepared with the control starch (C25FS), scored slightly but significantly higher for sweetness.

3.4 Sensory-instrumental correlations. Principal Component Analysis (PCA)

A PCA was calculated from the instrumental analysis and descriptive analysis data (Figure 2). The three first components accounted for 87.62% of the variability in the results. The first component (PC1) explained 53.41% of the variance. It was mainly defined by texture-related parameters, measured both sensorially and instrumentally (G', G", mouthcoating, consistency, residence time in the mouth, AUC, FMax, stickiness, fluency, elasticity).

The second component (PC2) explained 18.70% of the variance and was mainly defined by taste attributes (strange taste, aftertaste, fruitiness).

The third component (PC3) contributed a further 15.51% of the variance, mainly explained by the attributes of pulpiness, acidity and sweetness, which were not very well represented in the space defined by the two first components. Figure 2 shows two-dimensional maps of the attributes and samples in the space defined by the first three PCA components. (1 vs 2 in figures 2a and 2b and 1 vs 3 in figures 2c and 2d). The PCA results confirmed several of the results obtained by other methods and discussed in previous sections. The trained panel considered the samples made with the control starch (C) – and, to a lesser extent, those with the pectin-TS mixture (P) – to be consistent, sticky, with longer residence times in the mouth and more mouthcoating. These parameters were closely related to the instrumental measurements of G', G", AUC and F Max. A high positive correlation was found between various sensory parameters. Consistency and residence time were related to stickiness, which in turn was positively correlated with the extrusion parameters of area under the curve (AUC), taken as an index of consistency, and maximum force (FMax), indicative of the product firmness index. Another high positive correlation was found between mouthcoating and the instrumental measurements of the viscoelasticity parameters G' and G'', indicating that as the gel structure became stronger (higher G' and G'' values), the trained panel perceived greater mouthcoating (correlation coefficient values not shown). Conversely, the TS samples, which had a weaker gel structure, were perceived as fluid and elastic and were placed in the opposite quadrant to samples C and P. The samples with the higher fruit content (50 g/100 g) were placed further left along the component 1 axis than those which contained 25 g/100 g, confirming that the fruit strengthened the gel structure. In the same way, logically, a negative correlation was found between fluidity and consistency, stickiness, residence time in the mouth and the instrumental extrusion parameters of AUC and F Max: as expected, the greater the fluidity the lower the consistency indicator values, and because the filling was more fluid (so dissolved and disappeared more rapidly from the mouth) the residence time was perceived as being lower. A negative correlation was found between elasticity, mouthcoating and the viscoelastic loss modulus G', indicating that consumers perceived more elasticity and less mouthcoating for the samples with a smaller loss modulus (a less structured gel).

The flavour parameters were affected by replacing sucrose with polydextrose and sweeteners and by adding fruit. A positive correlation was found between strange taste and aftertaste, both generated by adding sweeteners (a mixture of sucralose and stevioside), and the stranger the taste the greater the aftertaste perceived.

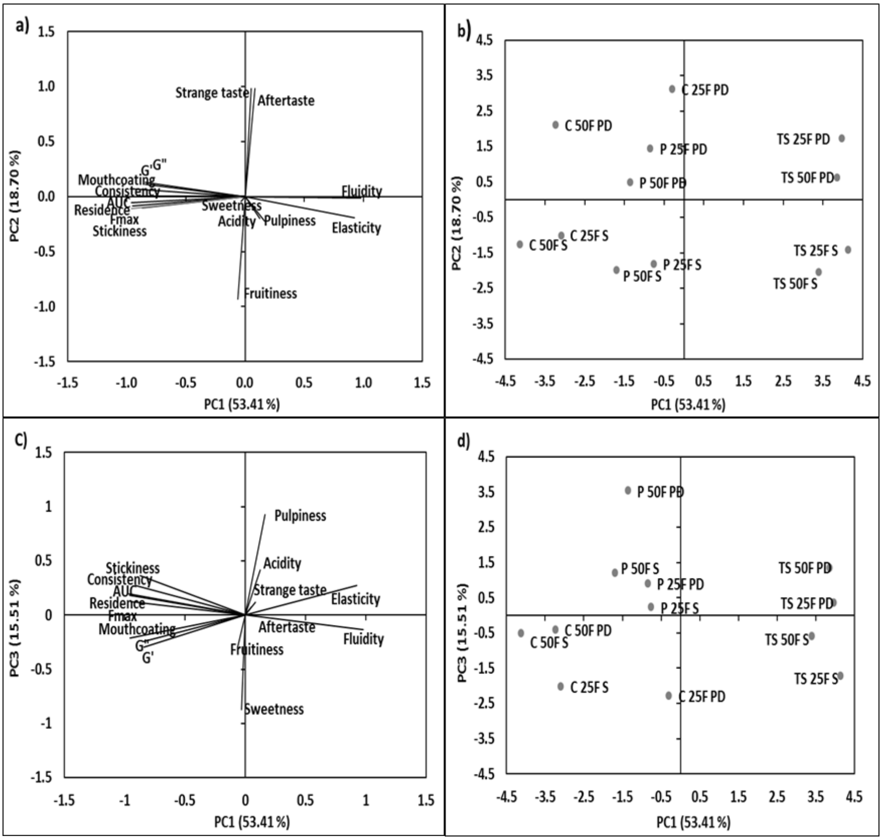

Figure 2. PCA of sensory and instrumental parameters. Spaces determined by components 1-2 and 1-3 are displayed.

A negative correlation was found between fruit content, aftertaste and strange taste: at the higher fruit content, the panel encountered less strange taste and less aftertaste. This correlation could indicate that these perceptions generated by the sweeteners could be mitigated by using a higher fruit content. The panellists perceived the highest levels of strange taste and aftertaste in the polydextrose and sweetener samples, especially those prepared with the control starch and the lower fruit content (C25FPD). The samples prepared with the higher fruit content (50g/100g) were perceived as pulpier. This perception was greatest for the sample prepared with pectin/TS and polydextrose (P50FPD). The samples with more fruit were also perceived as being more sour, with the highest acidity scores being given to those prepared with the pectin/TS mixture and polydextrose (P50FPD) and with TS alone and polydextrose (TS50FPD). The samples perceived as having the sweetest taste were those prepared with sucrose and the lower fruit content (25 g/100g). The sweetest was C25FS. A study by Broomes and Badrie (2010) of reduced-sucrose jams with a low solid content, using low methoxyl pectin as a thickener and Splenda (sucralose and maltodextrin) as a sweetener, found very high acceptability and no significant differences in sweetness compared with jams made with sucrose. They found a clean sweet taste similar to that of sucrose but low acceptability for the texture, as the solid content was very low and (unlike in the present study) no bulking agent was used to provide the solids removed through replacing the sucrose with the sweetener.

3.5 Consumer tests

3.5.1 Overall liking, consistency liking and flavour liking.

Due to the mostly similar behaviour of the high/low fruit systems, the samples with the highest fruit content (50g/100g) were selected for consumer testing as they had a fruitier flavour. The samples assessed were C50FS, C50FPD, TS50FS, TS50FPD, P50FS and P50FPD. The consumers assessed overall liking, consistency liking, and flavour liking. The overall liking values for the samples ranged between 4.2 and 6.8 (on a 9-point scale) (Table 5).

Table 5: Overall liking, consistency liking and flavour liking scores for the total sample population and for the different population clusters

Consumer population	Sample	Overall liking	Consistency Liking	Flavour liking
Total	TS50FS	6.7^{a}	5.6^{a}	6.83^{a}
	C50FS	6.1^{ab}	5.3^{ab}	6.50^{a}
	P50FS	5.8^{bc}	4.9^{ab}	6.35^{a}
	TS50FPD	4.9^{cd}	4.8^{ab}	4.81^{b}
	P50FPD	4.8^{d}	4.7^{ab}	4.72^{b}
	C50FPD	4.3^{d}	4.5^{b}	4.26^{b}
Cluster 1 (n=29)	TS50FS	6.8^{a}	4.9^{ab}	6.9^{a}
	C50FS	7.0^{a}	5.7^{a}	7.3^{a}
	P50FS	6.0^{a}	5.2^{a}	6.6^{a}
	TS50FPD	4.8^{b}	4.2^{ab}	4.8^{b}
	P50FPD	4.4^{b}	4.7^{ab}	4.7^{b}
	C50FPD	2.4^{c}	3.6^{c}	2.5^{c}
Cluster 2 (n=55)	TS50FS	6.8^{a}	6.2^{a}	7.0^{a}
	C50FS	6.6^{ab}	5.8^{a}	6.8^{a}
	P50FS	6.2^{abc}	5.2^{a}	6.6^{ab}
	TS50FPD	5.5^{c}	5.5^{a}	5.4^{c}
	P50FPD	5.7^{bc}	5.4^{a}	5.4^{c}
	C50FPD	5.9^{abc}	5.3^{a}	5.7^{bc}
Cluster 3 (n=16)	TS50FS	6.1^{a}	4.9^{a}	6.1^{a}
	C50FS	2.9^{bc}	2.5^{b}	3.8^{bc}
	P50FS	3.8^{b}	3.0^{ab}	4.9^{ab}
	TS50FPD	3.2^{bc}	3.6^{ab}	2.8^{bc}
	P50FPD	2.2^{bc}	2.5^{b}	2.4^{c}
	C50FPD	2.0^{c}	3.1^{ab}	2.4^{c}

See Table 1 for sample codes.
Figures in brackets are standard deviations
Different letters within the same column indicate significant differences ($p>0.05$) according to Tukey's multiple comparison test

Significantly the highest overall liking score was obtained by the TS-alone fruit filling with sucrose. Flavour liking values did not presented differences due to the thickener system but they did due to the presence of the intense sweeteners. Liking for the flavour fell into two groups: the samples containing sucrose and those containing sweeteners and polydextrose. In both groups, the TS-alone fruit filling samples were the most liked.

In all three liking modalities, the least-liked sample was the one made with the control starch and no sucrose. The QDA (section 3.3) showed that this sample had a more intense strange flavour and aftertaste and greater mouthcoating, which were deduced to be the reasons for its being the least liked, whereas its pulpiness, acidity, sweetness and fruitiness attributes were intermediate compared to the samples with other thickeners. Conversely, the flavour profile of the TS-alone samples presented greater acidity and fruitiness. Additionally, they were described as being less consistent and more fluid even though their consistency liking values were not significantly different to those of other samples. Tapioca starch is said to be very clean in flavour and does not mask the flavours (International Starch Institute, 2014).

3.5.2 Attribute adequacy and its relation to liking – Penalty Analysis (PA)

The samples assessed on the JAR scales were the six with the higher fruit content, with each of the three thickener systems being prepared with and without sucrose (C50FS, C50FPD, TS50FS, TS50FPD, P50FS and P50FPD).

Penalty analysis (PA) helps to identify potential product improvements that may bring a product closer to the “ideal” and so increase its overall liking. Being an attribute-by-attribute analysis, various potential product improvements can be prioritized by focusing the greatest attention on the attributes in the upper right-hand corner of the PA plots (Popper, 2014). The JAR scales were used to identify to what degree the products fails to deliver its optimum and to gain a better understanding of the attributes that most affected liking ratings (Plaehn y Horne, 2008).

An attribute was considered susceptible of modification when the respondent percentage was higher than 20% (Xiong y Meullenet, 2006) and the penalty score (drop in overall liking) was higher than 1 (Figure 3). An attribute in the upper right-hand corner of the PA plot (a high number of consumers saying the attribute level was not right, with a big impact on overall liking) is more penalising than an attribute placed in the lower left-hand corner (a few consumers saying the attribute level was not right with a small impact on overall liking).

In general, the PA of the JAR data found that the most balanced sample was TS50S (tapioca starch and sucrose), which had the least drop in liking compared to the rest of the products assessed: less than 1.8 and among fewer than 45% of the subjects (Figure 3). In principle there would be no need to make major adjustments to this sample, particularly since the attribute that seems to be most penalizing is consistency, on which the consumers' opinions were divided (more than 20% stating "too much" and more than 30% "not enough"), suggesting some segmentation in their opinion regarding the optimal consistency. Furthermore, some consumers considered it had little fruit flavour, although that did not lead to a big drop in liking (less than 1). The good adequacy of the attributes in general was in line with the fact that TS50S was the sample that scored highest for overall liking (section 3.5.1, Table 5).

The samples with sweeteners were the most unbalanced, obtaining the highest drops in liking in a number of attributes; the consumers were generally of the opinion that all of them had little fruit flavour, with 55% of consumers finding this fault with the control starch sample with polydextrose and sweetener (C50FPD, with a 2-point drop in liking) and

70% penalising this lack of fruit flavour in a further two samples (TS50FPD and P50FPD, with a 1.5-point drop in liking in both cases).

Sweetness and acidity also attracted penalties although the consumers were divided on these: some considered the samples with sweeteners insufficiently sweet or lacking in acidity, while others considered them much too sweet or much too sour. In the case of C50FPD, over 50% of the consumers considered it not sweet enough, with a drop in liking of more than 2 points, but nearly 25% found it too sweet and over 40% too sour, with a drop in liking of 1.5 points. Nearly 50% of the consumers believed that sample P50FPD was not sweet enough, with a 1-point drop in acceptability.

The consumers were also divided regarding acidity (Figure 3). The samples with sweeteners scored the lowest on overall liking, particularly C50FPD, which was rated highest for strange taste, aftertaste and sweetness in the QDA (Table 5 and section 3.3).

In general, a lack of fruit flavour was a penalising attribute for almost all the samples, not just for those made with polydextrose and sweeteners. The least penalised was T50FS: though 60% consumers considered it had insufficient fruit flavour, this did not cause a major drop in liking. The fact that the fruit flavour was considered “not enough” in most cases could in a way be an example of how consumer perceptions of the intrinsic desirability of certain attributes may influence a JAR response, as attributes that have a positive halo have a tendency to be rated always as “not enough” (Popper, 2014).

The consistency of the fruit filling attracted penalties in almost all the control starch and pectin-TS mixture samples. The control starch samples (C50FS and C50FPD) were considered too consistent by almost 65% and 55% of the consumers respectively with a 2-point drop in liking for both.

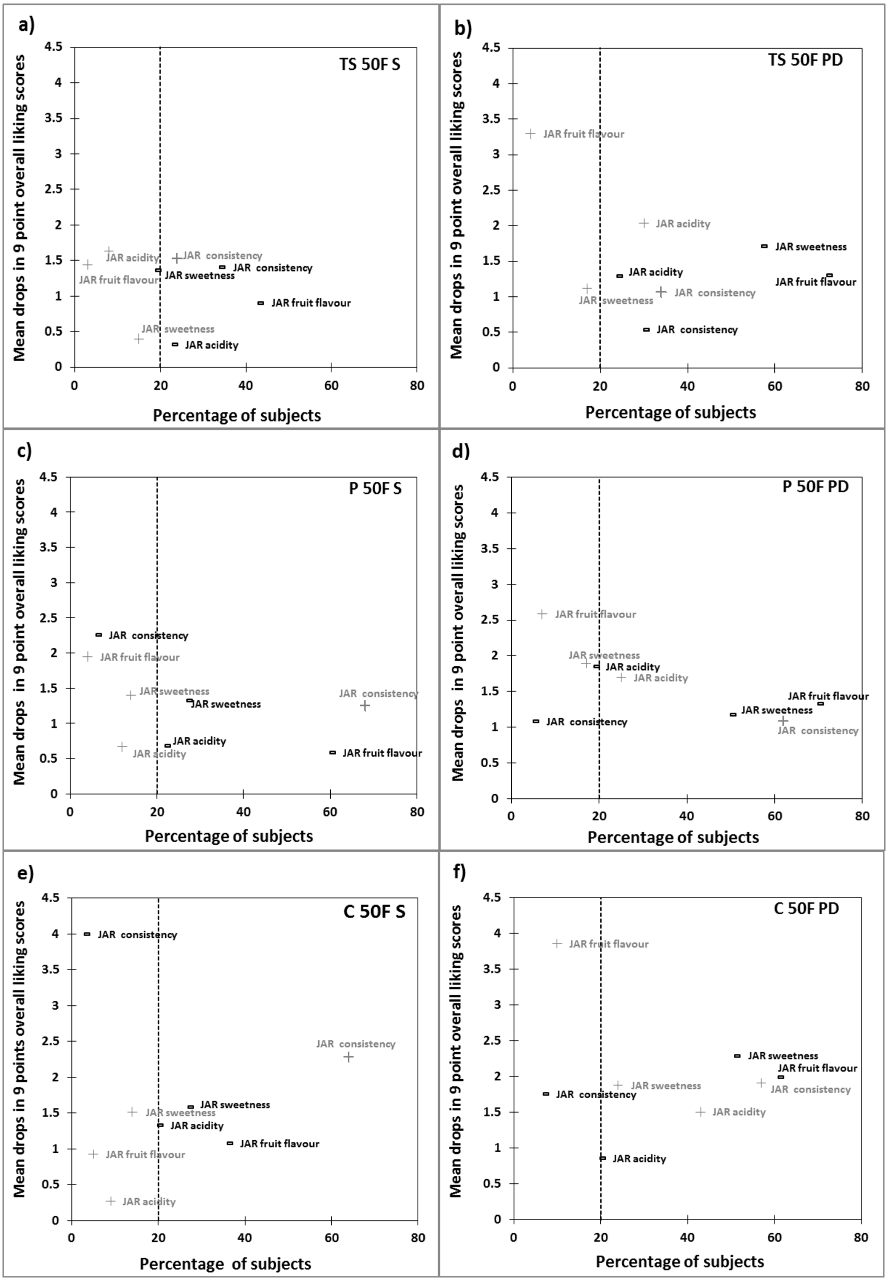

Figure 3. Penalty analysis of the samples containing 50% fruit. Representation of significant penalties (mean drops in liking) vs. the percentage of consumers. The cut-off point was 20% of consumers stating that an attribute was “not enough” (-) or “too much” (+).

“Too consistent” was the main penalising attribute for the pectin-TS mixture, where it was noted by 70% of the consumers and caused a 1.5-point drop in overall liking in the case of P50FS, and by 60% of consumers with a 1-point drop in acceptability for the P50FPD sample. For an untrained consumer, consistency can be a somewhat complex attribute to measure. The trained panel was able to assess a number of texture parameters separately (consistency, fluidity, elasticity, stickiness, mouthcoating and residence time in the mouth). These attributes are easily rated by a trained person but there is usually less consensus among untrained consumers, who may not all be paying attention to the same characteristics or in-mouth sensations. The trained panel rated the samples with tapioca starch alone as having little consistency and considerable fluidity but the consumers’ tastes were divided between those that preferred the harder samples (more viscous and consistent) and those who preferred the softer ones (less viscous, less consistent or more fluid). According to Popper (2014), polarization may also be the result of a problem with the quality of an attribute, rather than its quantity.

From the instrumental measurements (Table 4) and QDA (section 3.3) it is clear that the samples prepared with the control starch and the pectin-TS mixture presented greater indications of high consistency, as reflected in the higher G’, G’’, AUC and F max values, while the TS-alone samples had the lowest values for these parameters. It would appear that the consumers liked a less consistent product (Table 5).

As expected, the sweetness liking scores were not the same in the sucrose samples as in those prepared with the sweetener mixture, which generally did not manage to reproduce the sweetness profile of sucrose. Some consumers found the samples insufficiently sweet and others found them too sweet. The present study used a 1:1 ratio of stevioside and sucralose, with different sweetness profiles which could be affected in turn by the fruit filling matrix formed with the different thickeners. Some studies have described bitter characteristics of stevioside. Cardoso and Bolini (2007) found that the sweetness ratio of a peach nectar was lower with stevia than with other sweeteners. A possible explanation for this fact is that stevia has a characteristic bitter taste, especially at high concentrations. In a study with yogurt, it had a high-quality time-intensity profile, quite similar to that of sucrose, and its perceived sweetness was fast, persisted for slightly longer than that of sucrose and did not present any metallic aftertaste (Pinheiro, Oliveira, Penna, y Tamine, 2005). Cadena et al. (2013) found that mango nectar samples with stevia presented the greatest intensity of residual bitterness and a decrease in mango flavor. Cadena and Bolini (2011) encountered a different time of maximum intensity and longer duration of the sweetness in ice cream with sucralose, suggesting that the residual sweetness of this ice cream was lower. Sucralose is reported to have a relatively clean, sweet taste with little persistence of bitterness (Zhao y Tepper, 2007).

The above results show that sucrose replacement is not an easy task. From the results of the present study it may be concluded that the stevioside was the main cause of strange tastes and aftertastes in the fruit filling samples prepared with the sweetener mixture. Texture is an important factor for the perception of flavour. Boland, Delahunty, and Van Ruth (2006), analysing pectin and gelatine gels, found that increased gel rigidity resulted in lower air/gel partition coefficients, higher maximum concentrations of volatiles and lower release rates during in-nose analysis, decreased perception of odour, strawberry flavour and sweetness, and higher intensity ratings for thickness in sensory analysis. Consequently, both the type of hydrocolloid and the rigidity of the sample greatly affected flavour release and perception.

The possibility of finding populations with different preferences was studied in greater detail through cluster analysis (see section 3.5.3).

3.5.3 Liking segmentation - Cluster Analysis

The above mentioned high proportion of responses on both sides of “just right” for the same attribute may suggest the presence of various segments within the consumer population being tested. Consumers might have different ideal attribute levels. For example, one group of consumers (segment) could prefer a lower level of sweetness while another could prefer a sweeter sample. In this case it could be difficult to achieve a level that is ideal for everyone and the solution could sometimes be to develop two products that target the different groups (Rothman, 2007). Based on these observations, a hierarchical cluster analysis was run on the overall liking data. Agglomerative Hierarchical Clustering (AHC) is an iterative classification method that supplies (among other results) a dendrogram that shows the progressive grouping of the data graphically, which is then used to decide how many clusters or groups of consumers with different liking patterns to consider. In order to be actionable for guidance in the product development process, the clusters obtained in this way have to be both consistent, in terms of having really distinct liking patterns, and understandable when looking at the other available information on the products (sensory data for example) (Varela, 2013).

AHC clearly showed a division into three groups (Table 5): one that rejected the samples without sucrose (cluster 1, n=29), another that rather liked all the samples (cluster 2, n=55) and a third that only liked the TS-alone sample with sucrose and strongly rejected all the others (cluster 3, n=16). Those liked by cluster 1 presented a taste profile that the QDA identified as the samples with sucrose (TS50FS, C50FS and P50FS), which had slightly more acidity, sweetness and fruit flavour than the samples prepared without sugar and also presented less strange taste and aftertaste than those prepared with sweeteners. Texture was a less important factor. When looking at the flavour liking and consistency liking, cluster 1 consumers distinguished the samples more on their taste than their texture. It is clear that this subpopulation did not like the flavour of the sweeteners in the PD samples at all.

For cluster 2 consumers, consistency again seems not to have been a very important factor (there were no significant differences in liking) and the flavour liking scores were significantly higher for the samples prepared with sucrose, but all the samples rated highly on overall liking.

Cluster 3 consumers attached most importance to flavour. In particular, they liked the samples with tapioca starch alone the most, both on flavour and on texture, and gave the other samples significantly lower scores. The QDA found that the TS samples had the most balanced flavour. Even the TS sample without sugar (TS50FPD) exhibited a good acidity, sweetness and fruit flavour profile and had little strange taste or aftertaste compared to the other samples with sweeteners. The different responses to flavour and consistency among the clusters would explain the PA results.

4. CONCLUSIONS

From the results obtained it is evident that the consumers' preferences were segmented. There was a consumer niche for fruit fillings with a bland, soft texture and a sweet, acid, and highly fruity taste, corresponding to the sensory profile of the sample prepared with native tapioca starch and sucrose. This group could be described as preferring a "home-made style" and a natural, clean label product. Another group clearly rejected the flavour with the intense sweeteners, so if the goal is to launch a fruit filling without sugar (sucrose), in-depth studies should be made to formulate a new sweetness profile for this population or to make a greater effort to discover how to inform the consumers of the benefits of calorie saving and diabetes/weight control, in fitting with a healthier diet and lifestyle pattern. Finally, a big consumer group liked both the sucrose and non-sucrose samples, so all the formulations proposed would fit its preferences. This study has demonstrated the relevance of taking consumer preference segmentation into account and the adequacy of the sensory methods and techniques used in food product design.

ACKNOWLEDGEMENTS

The authors are grateful to Sucroal S.A. (Colombia) and SENA (Servicio Nacional de Aprendizaje de Colombia) for funding the PhD studies of Maria Alejandra Agudelo (Sucroal S.A.) at the Polytechnic University of Valencia and to the Spanish Ministry of Science and Innovation for financial support (AGL2012-36753-C02-01). They would also like to thank Mary Georgina Hardinge for translating this paper into English.

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CAPÍTULO 4

Methods for a deeper understanding of the sensory perception of fruit fillings

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ABSTRACT

Variations in ingredients essentially affect the quality of soft gelled systems in terms of texture. In two previous papers the authors studied instrumental (rheometer, texture analyser) parameters in gelled fruit systems with three different thickeners. The sensory perception of soft gelled systems is a rather subtle issue. Their oral processing is quite limited in terms of chewing, as almost no mastication or bolus formation is required. However, a number of textural features assessed during their consumption can modulate their perceived flavour and several relatively new sensory evaluation techniques can provide a deeper understanding of the perception of soft gelled systems.

In the present work, six fruit gels were prepared with three different gelling systems: tapioca starch alone (TS), modified waxy corn starch (C), and a mixed system with tapioca starch plus pectin (P). Each of these was prepared with sucrose or with polydextrose and intense sweeteners. The samples were subjected to two sensory techniques: Temporal Dominance of Sensations (TDS) with trained assessors (evaluating the texture and flavour modalities separately) and a check-all-that-apply questionnaire with consumers, including the evaluation of an “ideal fruit filling”. Finally, the results were correlated with the consumers’ liking for the samples. The results indicated that flavour TDS curves mainly depended on the type of sweetener (sugar or intense sweetener) while, as expected, the texture TDS curve patterns were dependent on the type of thickener system. The best-liked set of samples was that with sugar (demonstrating that flavour dominated over texture) and, among these, TS was the preferred hydrocolloid system, for its creamy, fondant texture.

1. INTRODUCTION

Product reformulation to fit consumer demands and segmentation is an immensely important activity when designing food. It is said that product quality is a major determinant of consumer choice. However, “quality” is a somewhat vague concept. In the case of soft gelled products (fruit fillings, jams, etc.), it is evident that the ingredients, particularly hydrocolloids, affect their quality in terms of both physical properties (instrumental texture and rheological) (Basu, Shivhare, y Singh, 2013) and sensory properties, which are not always taken into account sufficiently in the product design phase. In particular, it is important to understand the relationships between the perception of the gel texture and its structure (Renard, van de Velde y Visschers, 2006) and how it, in turn, can modulate the perception of the flavour attributes. People like to be in full control of the food placed in their mouth. In the case of gels, gummy or slimy products or those containing unexpected lumps or hard particles are rejected (Grujić, Grujić, y Poljasević, 2010). In the world of food hydrocolloid applications, rheological properties are very widely studied to assess all the components’ technical functionality in product development and quality control and to correlate them with sensory attributes (Dervisi, Lamb y Zabetakis, 2001). However, perceived texture is a very complex sensory issue that comprises numerous different channels. Texture perception can involve one or many stimuli, including visual, auditory, tactile and kinaesthetic factors, working in combination. While seeing and touching can provide useful information, oral processing is the most important stage of textural perception and appreciation. Oral processing of food involves a series of complex operations, including grip and first bite, first stage transportation, chewing, second stage transportation, bolus formation, and swallowing. Texture perception and appreciation is a dynamic process, based on the perception obtained from continuous oral destruction (and breakdown) of food material

(Chen, 2009). In the case of soft gels these steps are simplified slightly since almost no particle reduction is necessary and insalivation and bolus formation are much milder operations, but other sensations such as creaminess or fondant become important. A study with consumers that explored the vocabulary of texture highlighted the importance of creaminess, since it was the most frequently cited texture term, mentioned by more than 50% of the participants (Antmann, Ares, Varela, Salvador, Coste, y Fiszman, 2011). Variations in ingredients or their concentration usually lead to changes in gel structures being perceived by the consumers through what is called mouth-feel. Mouth-feel has been defined as the sensory experience derived from the sensation in the mouth or on the tongue during and after ingestion of a food material (Basu y Shivhare, 2010). It is especially important in semi-solid foods. In gelled materials, different thickener systems give the final product different consistencies and are responsible for its main texture features. In fruit fillings (FF), the fruit pulp interacts with the hydrocolloid matrix in many different ways, depending on the nature of the matrix (and a number of factors such as pH, quantity of fruit, type of fruit, fruit puree particle size and solid content). It provides an acidic and fruity flavour, which in turn is perceived with differing intensity depending on the solid matrix, and also gives graininess, depending on the size and distribution of its particles and their integration into the matrix (Baiano, Mastromatteo, y Del Nobile, 2012; Basu y Shivhare, 2010; Wei, Wang, y Wu, 2001). Sugar also plays an important function in giving the FF mass body and a sweet flavour. When sugar is removed to produce a sugar-free FF, alternative components come to have a role: bulking agents such as polydextrose contribute body while intense sweeteners contribute a sweet flavour. However, reformulation is not easy since the acid/sweetness balance alters the global flavour perception.

In two previous papers (Agudelo, Varela, Sanz y Fiszman 2014 a, b), the rheological performance and stability of a mixture of native tapioca starch plus low-methoxyl pectin were studied and compared with a modified starch control sample. In an acid medium, an improvement in native starch performance during processing (freezing or baking) and during long storage periods was demonstrated. However, one of the most important steps in the new product development process is identifying the consumers' ideal products and directions for product reformulation (Ares, Dauber, Fernández, Giménez, y Varela, 2014). In product design, one key step is the selection of a product formulation that is aligned as much as possible with their sensory preferences (van Kleef, van Trijp, y Luning, 2006). In this regard, one of the main challenges for Sensory and Consumer Science is to provide actionable information for making specific changes in product formulation, not just product descriptions (Moskowitz y Hartmann, 2008; Ares *et al*., 2014).

CATA (check-all-that-apply) questionnaires are a consumer-friendly method that is increasingly being used due to their simplicity and ease of use (Varela y Ares, 2012). In this approach, consumers are presented with a list of terms and are asked to select those that in their opinion fit the product. The relevance of each term is determined by calculating its frequency of selection. The attributes are not limited to sensory aspects but can also be related to hedonic and emotional aspects, product use and concept fit (Dooley, Lee, y Meullenet, 2010). The method has been applied to salty snacks (Adams, Williams, Lancaster, y Foley, 2007), strawberries (Lado, Vicente, Manzzioni, y Ares, 2010), ice cream (Dooley *et al*., 2010; Varela, Pintor, y Fiszman, 2014), chocolate milk desserts (Ares´Deliza, Barreiro, Giménez, y Gámbaro, 2010), orange-flavoured powdered drinks (Ares, Varela, Rado, y Giménez 2011a,b) and the texture of milk desserts (Bruzzone, Ares, y Giménez, 2011). Some of these authors have used it in addition to hedonic ratings to provide an alternative to classical external preference maps generated from sensory profiles. Valentin, Chollet, Lelievre, and Abdi (2012) have recently reviewed the new descriptive methods in food science and concluded that CATA is powerful enough to discriminate between samples. Compared with descriptive analysis, the main advantage of CATA from both the assessors' and the experimenter's points of view is its great simplicity.

Another aspect which is often overlooked is examining flavour and textural changes during a masticatory/ consumption sequence. When a food product is put in the mouth a first impact suddenly appears, producing a sensation that dominates over others and probably leading to like or dislike at a certain point. This first sensation is followed by a cascade or sequence of sensations. To record the emergence of each salient sensation – both texture- and flavour-related – during the consumption of a food product, sensory techniques involving the additional dimension of time are required. The Temporal Dominance of Sensations (TDS) method developed in recent years makes it possible to record the evolution of sensory perceptions in the mouth during product tasting (Pineau *et al*., 2009). This method has already been used for a number of products with different texture properties: cereals (Lenfant, Loret, Pineau, Hartmann, y Martin, 2009), dairy products (Pineau *et al*., 2009), yoghurt (Bruzzone *et al*., 2009) and ice cream (Varela, Pintor, y Fiszman, 2014).

The objectives of the present work were 1) to assess three thickener systems in fruit preparations, using two novel sensory techniques with consumers (temporal dominance of sensations and check-all-that-apply) and 2) to link these consumer results with product liking. The three thickener systems were tapioca starch, modified waxy corn starch and a tapioca starch-pectin blend, each with sugar or without sugar but with an intense sweetener plus polydextrose as a bulking agent.

2. MATERIALS AND METHODS

2.1. Ingredients

The ingredients employed were native tapioca starch (TS) (moisture content 13.7 g/100g, Sucroal S.A., Colombia), citric acid and sodium citrate

(Sucroal S.A., Colombia), highly cross-linked waxy corn starch, hydroxypropylated and phosphated (C) (moisture content 12.3 g/100g, Polartex 6716, Cargill, Martorell, Spain), low methoxyl pectin (P) (33-37% esterified, moisture content 12 g/100g, Unipectine OB700, Cargill, Martorell, Spain), anhydrous calcium chloride (Panreac, Spain), polydextrose (PD), (moisture content 3.2 g/100g, Stalite III, Tate y Lyle, Decatur IL, US), Rebaudioside B (stevioside, 95% purity, Sucroal S.A. Colombia), Sucralose (Tate y Lyle, Jurong Island, Singapore) and sugar (S) (Hacendado, Spain). Fruit purée (F) was obtained from canned peach halves in light syrup (6.5 degrees Brix, pH 3.8, Hacendado, Spain). The final moisture content of the fruit purée was 92 g/100g.

2.2. Sample preparation

The samples (Table 1) were prepared in a food processor-cooker (Thermomix TM 31, Wuppertal, Germany) equipped with temperature and stirring speed controls. All the samples were prepared at pH 3 and contained 35g/100g total soluble solids (sucrose or polydextrose and fruit) and 6 g/100g of the thickener system. Three thickener systems were employed: a control starch (C), native tapioca starch (TS) and TS with pectin – 0.6g/100g (P) of the total hydrocolloid system (dry weight basis) – and calcium ions – 60 mg of calcium ion per gram of pectin.

The first step in preparing the samples was to add the sugar or polydextrose to part of the water, then the fruit purée (50 g/100g), heat the mixture to 60°C and stir it at 600 rpm for 5 minutes. In the formulations with pectin, this was first dispersed in water with a magnetic stirrer at 80°C until totally dissolved, then allowed to cool to 60°C before adding it to the sugar-fruit-water or polydextrose-water-fruit mixture. The starch was dispersed in another part of cold water and added to the sugar- or polydextrose-water-fruit mixture, continuing to stir and heat the mixture for another 2 minutes. The intense sweeteners were then added to the samples containing polydextrose. Once the mixtures had been prepared with these ingredients, the temperature was increased to 90°C and heating and stirring continued for a further 30 minutes. Calcium chloride dissolved in a small amount of water reserved for this step was added to the mixtures containing pectin. The pH was adjusted to 3.0 (±0.2), using citric acid and sodium citrate buffer solutions, and stirring and heating continued for a further 5 minutes. The samples were transferred to plastic containers and held in refrigeration (8°C) for 24 hours (Table 1).

Table 1. Composition of the different fruit filling formulations (pH 3, 50 g of fruit/100 g, 35 degrees Brix).

	Ingredient						
Sample code	Tapioca Starch (TS) g/100g	Pectin (P) g/100g	$CaCl_2$* g/100g	MWCS (C) g/100g	Sucrose (S) g/100g	Polydextrose (PD) g/100g	Sweetener ** g/100g
CS	0	0	0	6	20	0	0
CPD	0	0	0	6	0	20	0.04
TSS	6	0	0	0	20	0	0
TSPD	6	0	0	0	0	20	0.04
PS	5.33	0.60	0.067	0	20	0	0
PPD	5.33	0.60	0.067	0	0	20	0.04

$CaCl_2$=Calcium chloride; MWCS=Modified Waxy Corn Starch; C=Control
* The calcium salt dosages correspond to 60 mg of calcium ion per g of pectin.
** The sweetener is a blend of Stevia:Sucralose (50:50)

2.3 TDS with the trained panel

Selection of terms and panel instruction. Fourteen assessors with previous experience of quantitative descriptive analysis of fruit gelled systems took part in this study. Two preliminary sessions were conducted. In the first, the panellists were introduced to the concept of the dominance of a sensation at a given time during the consumption of the food product and to the TDS technique, and had to list all the in-mouth sensations they felt while tasting all 6 samples, focusing on the changes in dominance over the other sensations during the consumption period; the descriptors were both texture- and flavour-related. In the second session, the most frequently cited attributes were selected and their definitions and the protocol for measuring them were developed (Table 2) until consensus was reached. These attributes numbered six for texture – creamy, cohesive, fondant, adhesive, pulpy and mouth-coating – and four for flavour – sweet, acid, fruity and bitter. During the third and fourth sessions, the panellists were able to understand the sequential attribute appearance concept and participated in a simulated TDS session with several fruit filling samples in order to answer questions and get used to the computer program and methodology.

Formal assessment. The TDS evaluation took place over six sessions, held on different days, in order to conduct three replicated evaluations of the six samples (Table 1). Three samples were evaluated per session. The panellists were given half a spoonful of one of the samples (always the same amount) and had to check its texture attributes (creamy, cohesive, fondant, adhesive, pulpy, and mouth coating) on the first screen. After this they rinsed their mouths (still mineral water and unsalted crackers were available) and rested for some seconds, then they were given another half spoonful of the same sample and checked its flavour attributes on a second screen (sweet, acid, fruity and bitter). After mouth rinsing, a new sample was assessed, then the procedure was repeated for the third sample. The samples were presented according to a complete balanced experimental design. The panellists were presented with the list of texture (or flavour) attributes on the computer screen. At the same time they put the sample spoon in their mouth they clicked the Start button (starting the chronometer software) to begin the test. The panellists were free to choose the same attribute for the same sample as often as they considered necessary or never to select any particular attribute as dominant.

Table 2. Attribute definitions generated by the trained panel for the TDS task

Attribute	Description
Cohesive	Tendency of the product mass to remain in one piece. Degree to which the sample deforms or compresses before spreading
Fondant	Speed and degree of sample spreading down due to mechanical action by the tongue. Speed at which sample disappears during consumption
Pulpy	Presence of particles or lumps (heterogeneous texture)
Creamy	Soft, homogeneous texture
Adhesive	Force required for tongue to remove sample adhered to the mouth during consumption
Mouth coating	Viscous film covering the tongue and palate during consumption or after swallowing
Acid	Acid flavour perceived during consumption
Sweet	Sweet flavour perceived during consumption
Bitter	Bitter flavour perceived during consumption
Fruity	Fruity flavour perceived during consumption

The evaluation ended when the panellists no longer perceived sensations after swallowing the sample and clicked the Stop button (stopping the chronometer). The order of the descriptors was different for each panellist in order to guard against list order bias. The data were collected with Fizz Software version 2.45 (Biosystems, Counternon, France).

2.4 Consumer tests

The tests were conducted in the standard sensory rooms of IATA and the Universitat Politècnica de València, using 100 untrained consumers (35 men, 65 women) aged between 18- 62. All the consumers declared that they knew about or consumed fruit fillings. The six samples were evaluated at a single session, in sensory booths with artificial daylight-type illumination, temperature control and air circulation. The six samples (Table 1) were presented at room temperature in small plastic cups labelled with random three-digit numbers. Twenty grams of each sample were served to the assessors. The samples were presented in a sequential monadic series, following a complete block design balanced for carry-over position effects.

2.4.1. Overall liking rating

The consumers’ overall liking rating for the fruit fillings was obtained on a 9-point hedonic scale (1=do not like it at all; 9= like it a lot).

2.4.2. Check-all-that-apply (CATA) task

After rating their overall liking, the consumers answered a check-all-that-apply (CATA) question. The consumers selected all the words or expressions from a given list that (in their opinion) fitted a description of the sample they were tasting. In this study, the consumers described the six samples (Table 1) by selecting the attributes/ expressions they considered applicable from a 38-attribute list that included texture, flavour and use and attitude attributes. These attributes were selected based on the literature and on previous sensory studies. The 38 terms were: Very consistent, Consistent, Low consistency, Mouth-coating, Mucous-like, Very fluid, Fluid, Pulpy, Fibrous, Sticky, Elastic, Homogeneous, Grainy, Melts quickly in the mouth, Soft, Cohesive (texture attributes); Bitter, Very sweet, Sweet, Low sweetness, Slightly fruity, Fruity, Very fruity, Very acid, Acid, Slightly acid, Off-flavour, Metallic taste, Aftertaste (flavour attributes), and Very calorific, It is a light product, I would use it as a pastry filling, I would use it as a jam, Delicious, I would buy it if available, Unpleasant, I would use it as a pie filling, and I would use it as tartlet filling (use and attitude attributes). The attributes were randomized between products and across consumers within each of the groups (texture, flavour, use and attitude). The instruction given to the participants was: “Please check all the answers that apply to the sample you have tasted”. After finishing their descriptions of all the samples, the consumers were asked to select the words/expressions that applied to their ideal fruit filling.

2.5 Data analysis

For the TDS data analysis, the attribute chosen as dominant and the times when the dominance begun and finished were collected for each panellist run. As the duration of the period up to complete swallowing and no more sensations perceived differed from one panellist to another, the data were normalized, adjusting them according to the individual duration of each panellist’s test (Albert, Salvador, Schlich y Fiszman, 2012). Finally, to build the TDS curves, the period when a sensation was dominant for a product at panel level (dominance rate) was computed at each point of time (Lenfant *et al.*, 2009). The data were collected with Fizz Software version 2.45 (Biosystems, Counternon, France).

One-way ANOVA was applied to the consumer liking scores to study the differences between the samples. The least significant differences were calculated by Tukey's test ($p<0.05$). XLStat 2009 software (Addinsoft, Paris, France).

Cochran's Q test (Manoukian, 1986) was carried out on the CATA data in order to identify significant differences between samples for each of the attributes. The CATA results were analysed by Multiple Factor Analysis (MFA) of the frequency counts of the attributes selected for each sample in order to obtain a two-dimensional representation of the attributes and samples. The Ideal sample data was used as supplementary observation in the MFA. The overall liking data were used as supplementary variables in the MFA analysis. All the statistical analyses were performed with XLStat 2009 software (Addinsoft, Paris, France).

3. RESULTS

3.1. TDS test

3.1.1 TDS Curves

In TDS studies, it is recommended that panellists use a reduced list of attributes (normally no more than 8 per screen). The attributes, which were generated by the panellists, were related to the main sensory characteristics of the product. A number of TDS studies have already investigated the temporality of texture attributes alone (Lenfant *et al*, 2009; Bruzzone *et al*., 2012; Varela, *et al*., 2014). However, those studies were only designed to focus on texture attributes, not with the purpose of also performing a separate flavour TDS. In other studies, a very few texture and flavour attributes were evaluated in the same TDS session, as in Pineaut *et al*. (2009), working with dairy products.

In the present case of gelled fruit products, both texture and flavour were considered important features for product acceptance (Saint-Eve *et al.*, 2011; Foster *et al*., 2011), so each were focused on separately. In a previous work, gelatin- and pectin-based gummy confections were evaluated by free choice profiling (another type of sensory test): the panellists were asked to generate their own list of both texture and flavour attributes and the results were analysed separately (De Mars y Ziegler, 2001). Following this idea, and also in view of the trained panel feedback, it was hypothesised that by concentrating on just in one modality at a time (flavour or texture), the test would give better results and the panellists' task would be easier. As a result, the TDS evaluation was split in two to assess the dominance of texture and flavour sensations separately and consecutively (on consecutive screens).

The TDS curves were obtained by plotting the dominance rate of each of the sensations at different points of the eating period, for each sample, across the panel (Pineau *et al*., 2009). Since the duration of consumption of the food item up to swallowing differed from one subject to another, the sensory perception time scales differed as well (Lenfant *et al*., 2009). In order to take this point into account in the computation of the TDS curves, the data from each subject were normalized according to individual mastication durations, so the x-axis shows values from x = 0 (first scoring) to x = 100 (swallowing); in the present study, the x-axis of the TDS curves corresponds to the normalized time (% of consumption time) and the y-axis to the dominance rate (%).

The TDS responses are then linked to the liking scores and to the other consumers' sensory evaluations in order to capture the consumer perceptions, gaining a better understanding of consumer response and how to apply it to product reformulation. Better identification and control of the sensory contrasts that potentially drive liking is key to developing innovations for food (Lenfant *et al*., 2009).

On the TDS plots (Figures 1 and 2), two lines were drawn for the chance (CL) and significance levels (LS). The CL refers to the dominance rate that an attribute could obtain by chance. Its value is inversely proportional to the number of attributes (P0 = 1/p, where p is the number of attributes).

The LS is the minimum value this proportion should equal if it is to be considered significantly ($p<0.05$) higher than P_0. It is calculated as follows:

$$Ps = P_0 + 1.645\sqrt{\frac{P_0(1-P_0)}{n}}$$

where Ps is the lowest significant proportion value ($\alpha = 0.05$) at any point in time for a TDS curve and n is the number of panellists x number of replications (Pineau *et al*. 2009; Laguna, Varela, Salvador y Fiszman, 2012). Rosner (1995) recommended that $n*p*(1-p)>5$ (where n=number of trials and p=probability of success). In the present study 14, panellists assessed 3 replications of each product.

The two modalities – six texture attributes and four flavour attributes – were recorded on two consecutive screens (see section 2.3.). In general, when the TDS curves rise from between the chance and significance levels to above the latter they are considered consistent at panel level. For each product evaluated and each point in time, the dominance rates by attribute were calculated (Labbe, Schlich, Pineau, Gilbert, y Martin, 2009). These rates were obtained by dividing the number of citations of an attribute (all replications) by the number of panellists and the number of replications. Since a panellist can only have one dominant attribute at a time, the sum of the dominance rates of all the attributes at each point in time for that panellist is 1. The higher the dominance rate for an attribute, the better the agreement among panellists.

3.1.2. TDS texture curves

From the TDS texture curves (Figure 1), it is evident that texture attribute dominance rates were strongly dependent on the thickener system. As a rule of thumb, the tapioca starch samples (TS) were perceived as pulpy, cohesive and creamy during the first half of consumption time, and both the sugar (TSS) and sugar-free versions (TSPD), presented dominance rates not exceeding the significance level.

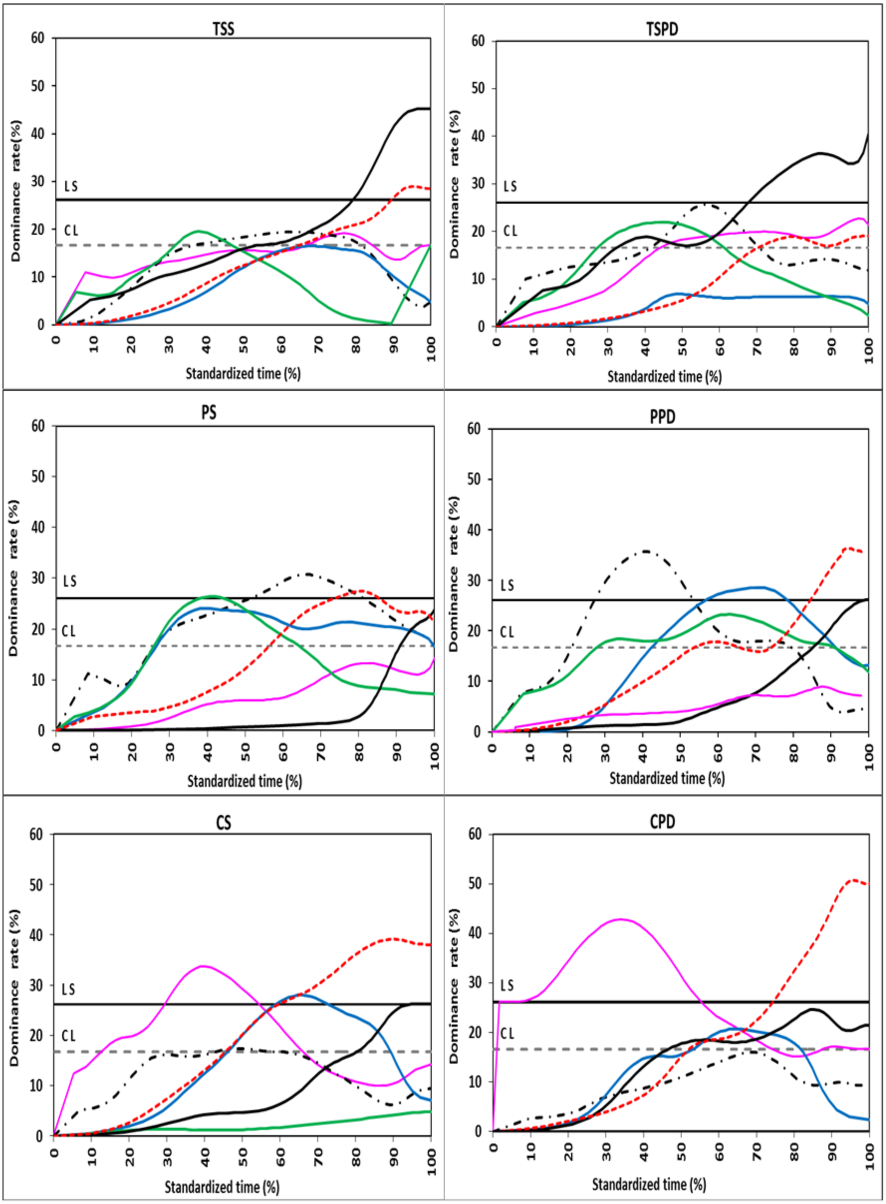

Figure 1. Texture TDS curves: — Creamy, — Adhesive, — Fondant, — Pulpy, – · – Cohesive, – – Mouth coating. LS: Level of Significance (5%), CL: Chance Level. See Table 1 for sample codes

A high, significant dominance rate of fondant perception was found in the last stage of consumption, meaning that the sample melted quickly and did not remain for long in the mouth. The samples containing pectin (P) (prepared with pectin and tapioca starch) presented a high dominance rate for cohesiveness, both for the samples with and without sugar (PS and PPD, respectively), and adhesive and pulpy also appeared as dominant sensations for these systems, generally without exceeding the significance level. Comparison of these two samples (TS alone and TS with pectin) showed that the main difference between them was the highly fondant sensation of the tapioca starch sample and the cohesiveness when tapioca starch was combined with pectin. This is in agreement with previous studies on the instrumental mechanical properties of these systems, where the TS gelling system presented a mechanical spectrum with G’ values only slightly higher than those of G” and quite strong frequency dependency, reflecting a weak gel structure with low viscoelasticity (a fluid, viscous gel), whereas the P gelling system (mixture of TS with pectin and calcium ions) showed considerably higher G‘ and G” values, a greater distance between the two, and lower $\tan\delta$ values (closer to 0), reflecting increased viscoelasticity. In addition, an extrusion test showed that the P mixture displayed greater firmness than TS alone, which presented low resistance to extrusion. P samples have a firmer and more compact and solid structure (Agudelo *et al*., 2014a).

It is worth noting that the P samples were not perceived as predominantly creamy at any moment of consumption. The reason can be attributed to the absence of perception of mouth-coating at the moment of putting the sample on the tongue, as it remained in one piece and was described as cohesive. Mouth-coating only began to be perceived at 25% of the consumption time for both the sugar and sugar-free samples, and then lasted up to the final stage. A possible explanation is that a pulpy (heterogeneous) sensation was probably found somewhat opposite to creamy and fondant. In previous studies, P was shown to be responsible for the gel structure of the fruit filling (Agudelo *et al*., 2014b), having a firmer gel structure with greater elasticity and consistency than the TS alone system.

Samples with native starch alone would additionally undergo enzymatic breakdown in the mouth that would reduce the perception of persistent cohesiveness (Pascua, Koç, y Foegeding, 2013) and produce sensations of disappearing (fondant texture).

Finally, for samples C, prepared with modified waxy maize starch, both with and without sugar, the sensation of creaminess presented a high dominance rate during the first stage of consumption and a mouth-coating sensation dominated the last stage. Creaminess is a very difficult texture attribute to define. Several authors recognise that the term “creamy” involves several aspects, principally related to texture but also to flavour, such as vanilla, sweet and dairy (Antmann *et al*., 2011). In the case of fruit fillings it would be related more to some texture features (smooth, soft, dissolving easily in the mouth) than to sweetness. The C samples were perceived as creamy earlier and with a higher dominance rate than for the other thickeners. In CPD, creaminess appeared at 5% of the consumption period and lasted up to 78%; for the CS sample, the period of perceiving creaminess as dominant was a little shorter. In comparison, the creaminess also perceived in the TS samples was not dominant over the very early stage of consumption but towards the second half, as TSPD presented creaminess as dominant from 45% up to the end of the consumption period, and it appeared even later in the samples with sugar.

The C samples were also perceived as somewhat adhesive and fondant but not exceeding the significance level, while the TS samples were perceived as fondant for a longer period of time than the C samples (TSPD from 30% to 100% and TS from 48% to 100% of consumption time).

In previous work, a decrease in the G’ and G’’ values was observed in the systems prepared with fruit pulp, TS or C and polydextrose, indicating a less solid texture compared to the fruit with sugar systems. This decrease could be attributable to the difference in molecular weight and higher viscosity (at the same temperature and concentration) of polydextrose in comparison with sucrose. On the other hand, it is this characteristic that enables polydextrose to provide the desirable mouth-feel and texture qualities that are so important when replacing sucrose (Auerbach y Craig, 2008). It is known that full replacement of sucrose with polydextrose leads to a higher starch gelatinization temperature in comparison with sucrose (Hicsasmaz, Yazgan, Bozoglua, y Katnas, 2003). These properties of the polydextrose may generate the sensation that samples CPD and TSPD are creamier. The sensation of adhesiveness was found for P and C systems, with a higher dominance and later appearance for the latter, and was probably associated with mouth coating, which was also higher for the C samples. In general it was found that the attributes proposed by the panel did not obtain very high consensus (reflected in the not very high dominance rate values). The reason is probably that the order of attribute dominance was not the same for all the participants, although another explanation could be that except for those that defined each thickener system (see above and Figure 2), certain attributes did not have a very salient impact compared to the rest.

3.1.3. TDS flavour curves

The type of sweetener (sugar or intense sweetener) used in the sample was decisive for the flavour TDS curve patterns, whereas the type of thickener was much less important.

Samples with sugar

For all the samples containing sugar, regardless of the type of thickener used, the first dominant sensation was sweetness, although the TS sample was the only one that showed a significant dominance rate value.

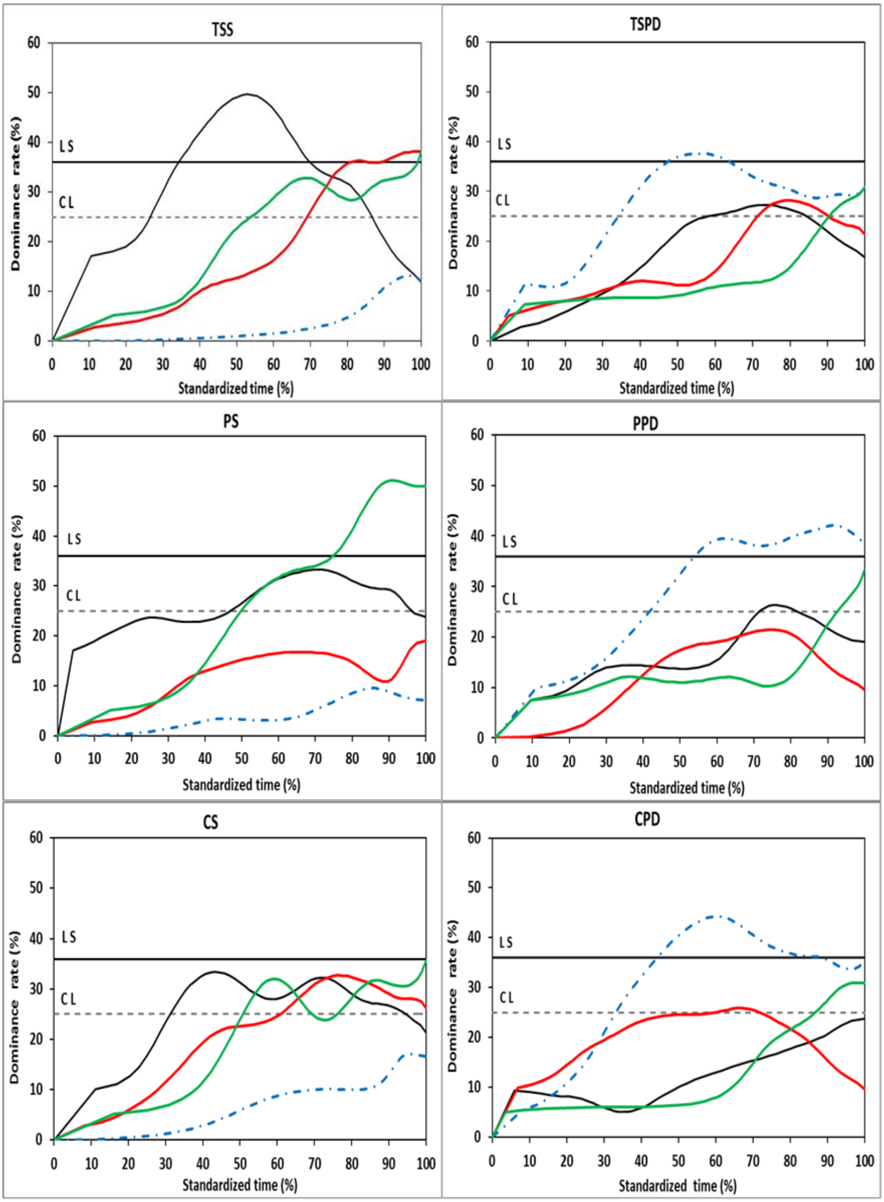

Figure 2. Flavour TDS curves: —— Sweet, —— Acid, —— Fruity, – · – Bitter. LS: Level of Significance (5%), CL: Chance Level. See Table 1 for sample codes

The second dominant sensation above the chance level for the three systems prepared with sugar was fruity, which exceeded the significance level in the P system during the second half of the consumption period. The third and last sensation perceived for the three systems with sugar was acid, which almost never exceeded the significance level.

In the TS samples, a sweet flavour was perceived earlier than in the other samples (from 25% to 85% of the consumption time), with a high dominance rate, followed by the CS samples (from 28% to 92%) and PS samples, where the perception of sweetness arrived later (from 44% to 100%).

For fruity, the second dominant sensation over the consumption time, the highest dominance rate was shown by the P samples, and for a long period (from 48% to 100%); this could be attributed to pectin’s having an inherent fruity flavour (DeMars y Zielgler, 2001). It has to be remembered that the pulpy texture sensation was found to be dominant in the P systems, so there could be a certain interaction between the two perceptions, since fruity and pulpy are sensations that go hand in hand in the fruit filling context.

The TS samples showed a dominance of fruity flavour above the chance level from 50% to 100% of the consumption period, but always below the perceptions of sweet or acid, both of which presented higher dominance rates.

The acid flavour appeared only in the TS and C samples (TSS from 60% to 100% and CS from 65% to 100%) and was not perceived as dominant in the P fruit fillings. Bitterness was not perceived as dominant in any of the samples with sugar.

Sugar-free samples

For all the samples with intense sweeteners the first dominant sensation was bitter, which surpassed the significance level at some point of the consumption period for all three systems and lasted almost throughout the consumption period. All the other sensations were highly muted, with fruity as the last one to exceed the chance level in the three systems.

The C samples presented the highest dominance rate for a bitter flavour but the duration of the bitter sensation was similar for all the samples, appearing at 30%, 35% and 40% of the consumption time for C, TS and P samples respectively, and lasting up to 100%. The second attribute that appeared as dominant was sweetness, but only in the TS (from 60% to 85% of consumption time) and P samples (for the short period: 70%-80% of consumption time). The C samples were not perceived as having any dominance of sweetness, and for these samples, acid was the second attribute that appeared as dominant.

The last attribute to appear as dominant was fruity, with a very similar pattern for all the three samples: it appeared above the chance level at around 90% of the consumption time and lasted up to 100%. Cadena *et al*. (2013) found that in mango nectar samples with different individual sweeteners, a blend of sweeteners and a control sample with sucrose, stevia presented the greatest intensity of residual bitterness and a low mango flavour when quantitative descriptive sensory analysis was performed on the samples.

3.2. Consumer Test

3.2.1. Liking test

Significant differences were found in the overall liking (OL) scores of the fruit filling samples (Table 3) (F =19.05, $p < 0.0001$), with average OL scores ranging from 4.26 (SD = 2.37) to 6.68 (SD = 1.66). The highest OL scores were for the samples with sucrose (TSS, CS and PS), with values exceeding 5. TSS obtained the highest OL score. All the sugar-free samples (TSPD, PPD and CPD) obtained scores below 5 but CPD scored the lowest. According to the TDS results, the first dominant sensation in the samples containing intense sweeteners was not a sweet but a bitter flavour, which would seem to indicate that their flavour was not well accepted, and the fruity flavour that appeared in the samples containing sucrose in the final stage of consumption did not appear in the sugar-free samples.

Table 3. Mean (n=100) overall liking score values for the samples evaluated

	Sample					
	TSS	CS	PS	TSPD	PPD	CPD
Overall liking	6.7^{a} (1.7)	6.1^{ab} (2.1)	5.8^{bc} (1.9)	4.9^{cd} (2.2)	4.8^{d} (2.2)	4.3^{d} (2.4)

Figures in brackets are standard deviations
Different superscript letters indicate significant differences ($p>0.05$) according to Tukey's multiple comparison test. See Table 1 for sample codes.

Regarding the type of gelling system, no significant differences were found between the three sugar-free samples, indicating no clear preference for any type of consistency or texture within this set of samples. Among the samples with sugar, only PS was significantly less accepted than TSS, but TSS was accepted equally to CS which was accepted equally to PS, again showing no clear distinction in preferences due to the samples' texture. According to the texture TDS curves, the PS samples were predominantly cohesive and not at all creamy, whereas the cohesiveness of samples CS and TSS did not exceed the significance level. On the other hand, sample CS elicited a significantly dominant perception of creaminess and the TSS samples a significantly dominant fondant sensation. Both of these attributes could be considered somewhat opposite to cohesive in the sense that they indicate spreading in the mouth instead of remaining "in one piece".

3.2.2. Check-all-that-apply (CATA) questionnaire

The consumers were asked to try the six FF samples in sequential monadic series and select among 38 terms to describe them, and also to describe their potential ideal FF. Of the 38 terms listed in the CATA question, 33 presented significant differences between the samples (Cochran Q test, $p<0.05$, Table 4). These differences implied that consumers perceived differences in the sensory (and some non-sensory) characteristics of the samples evaluated, since they selected them in a distinctive way.

The ideal fruit filling was described as sweet (but not “very sweet”), soft, very fruity, fruity, homogeneous, consistent, melts quickly in the mouth, and, as expected, delicious, as these attributes were very frequently mentioned (by over 20% of the consumers), indicating that they could be considered the main drivers of liking for this type of product. The ideal sample also obtained high frequencies for use terms such as I would buy it if available, I would use it as a jam and I would use it as tartlet filling; both these last uses correspond to a more direct perception than for other applications such as a pastry filling. The fruit filling with the most similar characteristics to the ideal FF was TSS, though with a lower frequency of mentions for consistent, very fruity, homogeneous, and delicious and a higher frequency of mentions for fruity and melts quickly in the mouth. TSS was also the sample with significantly the highest OL. Mucous-like is a potentially negative attribute that showed a very high frequency of mention for TSS as compared to the ideal. However, it was mentioned with the same frequency for all the real samples (Table 4), so this attribute appears to be connected with some in-mouth slimy sensation which is shared by all the samples.

MFA analysis of CATA question results makes it possible to work with different groups of variables, like appearance, texture and flavour and obtain a concise representation that considers all the information together, linking it to sample positioning (Varela y Ares, 2014).

Table 4. Frequency with which the terms of the CATA question were used by consumers to describe the six samples and their ideal product, and results of Cochran's Q test for comparison between samples.

Attributes and uses	Sample						
	Ideal	TSS	CS	PS	TSPD	PPD	CPD
Sweet***	67	49	35	47	20	21	17
Soft***	57	45	27	24	28	17	19
I would use it as a jam***	56	56	41	42	36	26	21
I would use it as tartlet	54	40	38	30	21	20	12
Very fruity***	47	11	17	6	6	5	12
Delicious***	46	21	17	12	3	4	5
Fruity***	45	49	40	45	27	25	26
I would buy it if	42	20	24	13	10	8	6
Homogeneous***	38	17	25	16	19	21	11
Consistent**	34	27	41	40	16	29	27
Melts quickly in the	32	34	11	11	32	13	7
I would use it as a pastry	27	10	14	16	10	13	9
I would use it as a pie	22	8	12	8	6	1	4
It is a light product ^{ns}	18	12	5	11	13	7	12
Acid **	18	10	6	5	14	13	20
Slightly acid ^{ns}	17	9	15	9	7	8	9
Mouth coating***	13	26	39	36	18	29	44
Heterogeneous ^{ns}	13	7	5	7	7	4	4
Elastic**	12	19	11	18	28	14	9
Cohesive***	10	7	30	25	12	19	21
Fluid***	10	16	2	2	13	4	3
Grainy**	9	7	8	22	13	10	6
Low Sweetness***	8	11	14	16	32	31	31
Very sweet ^{ns}	7	12	10	6	6	12	15
Low consistency***	7	17	2	1	13	0	4
Very consistent***	6	4	36	33	11	29	30
Aftertaste***	5	7	9	8	15	19	21
Very fluid***	5	11	0	1	9	0	2
Very calorific*	4	10	16	11	6	7	8
Sticky***	3	25	53	52	41	45	52
Mucous-like***	3	43	43	46	46	46	48
Fibrous ^{ns}	2	2	4	5	3	7	4
Very acid**	2	1	0	0	9	6	7
Slightly fruity***	1	17	13	21	35	34	24
Bitter ***	1	2	7	4	20	18	33
Off flavour***	0	8	9	12	28	26	31
Unpleasant***	0	4	10	12	13	16	39
Metallic taste***	0	3	0	4	9	10	14

Samples are arranged in descending overall liking order from left to right and attributes are arranged in descending frequency from ideal sample.
*** Indicates significant differences between samples according to Cochran's Q test at $p \leq 0.001$.
** Indicates significant differences between samples according to Cochran's Q test at $p \leq 0.01$.
* Indicates significant differences between samples according to Cochran's Q test at $p \leq 0.05$.
ns Indicates no significant differences between samples according to Cochran's Q test ($p \leq 0.05$).

It also allows overall liking to be superimposed on the resulting perceptual space. In the present work the MFA of the two first factors (Figures 3 and 4) explained 80.01 % of the variability of the data. This test provided a better understanding of which sensory and non-sensory descriptors defined the samples and which were responsible for the hedonic response of consumers, for which purpose overall liking was plotted as a supplementary variable in the MFA configuration (Figure 4).

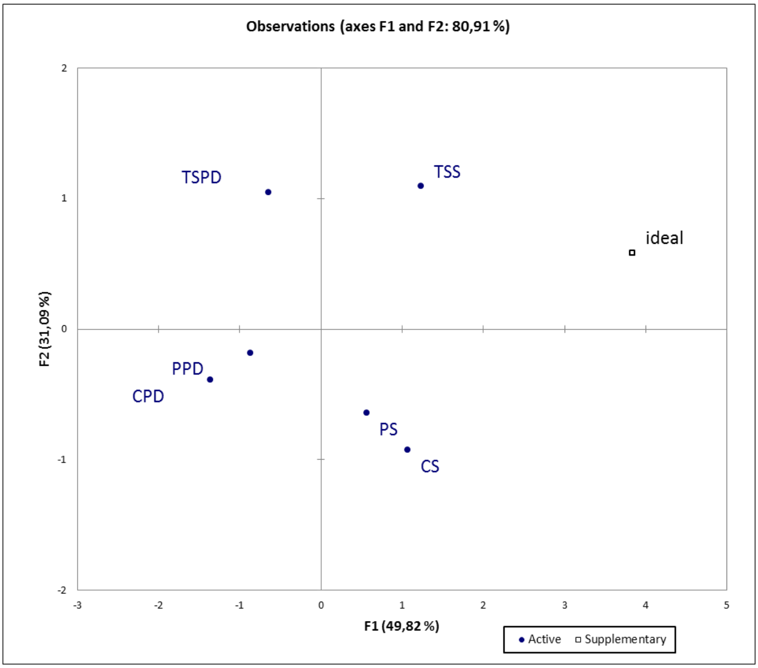

Figure 3. Multiple Factor Analysis map of samples (dimensions 1 and 2) obtained from the consumers' descriptions in the CATA questionnaire.

The first component discriminated between the flavour attributes: all the sugar-free samples (TSPD, PPD, and CPD) were placed in the left-hand part of the MFA plot (Figure 3), related to the negative values of the first factor, whereas the samples with sugar were placed towards the positive values of the first factor. The sample plot showed a good separation of both kinds of sample, with aftertaste, metallic taste, off-flavour, low sweetness, slightly fruity, bitter, acid, very acid, and unpleasant being used to describe the samples containing the intense sweetener. These flavour attributes contrasted with the attributes and uses of the half map containing the samples with sugar (sweet, fruity, very fruity and delicious, I would use it as a jam, I would use it as tartlet filling, I would buy it if available, and I would use it as a pie filling), and applied especially to the ideal sample.

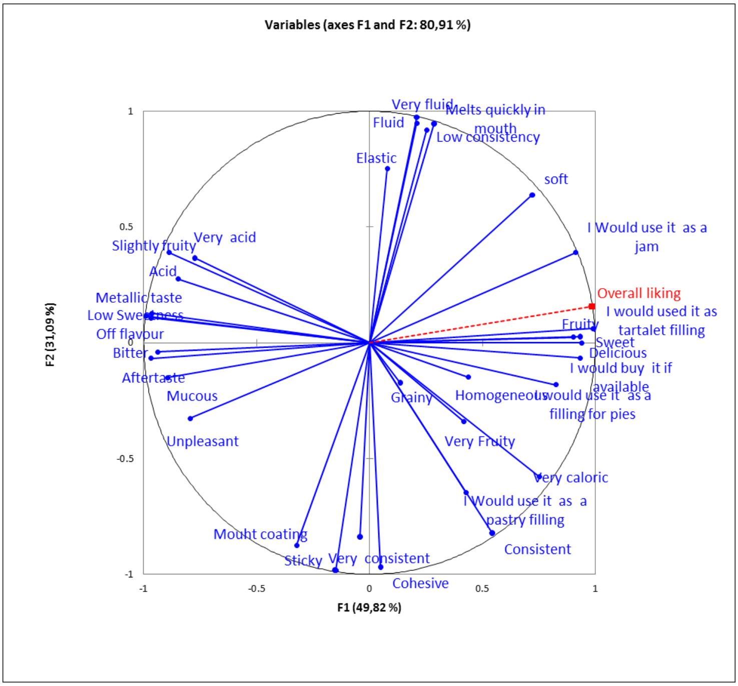

Figure 4. Multiple Factor Analysis map of attributes (dimensions 1 and 2; overall liking plotted as a supplementary variable) obtained from the consumers' descriptions in the CATA questionnaire

The second component was related to texture attributes, which again were placed on opposite halves of the map. Attributes like very consistent, consistent, mouth coating, sticky and cohesive and some use terms like "I would use it as a pastry filling" were well correlated to the negative values of the second component. The TS samples were plotted in the upper part of the map, identifying them as very fluid, fluid, with little consistency, melts quickly in mouth and soft. The P samples were placed near very consistent, cohesive, mouth coating and sticky. Finally, the CS sample, prepared with the control starch, was a little to the right of PS, related to the attributes of mouth coating, sticky, very consistent and cohesive. Mouth coating was dominant in the TDS curves from 40 % of the consumption time. The overall liking was plotted very near to the ideal fruit filling, as expected. A number of use and hedonic terms were well correlated to it: delicious, I would use it as a jam, I would use it as tartlet filling, I would buy it if available, I would use it as a pie filling. The flavour attributes of this zone of the map were sweet and fruity. They were found to be dominant in the TDS curves for the sucrose-containing samples, confirming that these attributes are drivers of liking (and of a perception of quality).

In this sample set, the main variation in consumer perception was driven by flavour more than by texture. According to Szczesniak (2002) for the most part, texture is taken for granted and consumers do not comment on it unless asked specific questions, or unless texture is definitely off or inappropriate, expectations are violated or non-food associations are triggered; this is important to remember when conducting consumer tests. Flavour attributes were correlated to the first factor of the MFA, which explained their higher contribution to discrimination amongst the samples. Flavour also appeared as the main driver of liking, particularly through rejection of the (negative) characteristics generated by the artificial sweeteners. The sweeteners had time-intensity sweetness and time-intensity bitterness profiles that differ from those of sucrose, showing that a number of factors should be taken into account (deSouza *et al.*, 2013). From these results it was evident that substitution of sucrose by other sweeteners is a challenge for researchers and the industry alike, and in addition to the sweet taste, attributes other than flavour may be modified (Cadena *et al*., 2013). The residual bitterness of stevia has been reported in a number of studies (Melo*et al.,* 2009; Prakash *et al.,* 2008). Sucralose is reported to have a relatively clean and lingering sweet taste with little persistence of bitterness (Nabors, 2002; Zhao, y Tepper, 2007). Formulating food products for targeted niches such as low-calorie consumers is a key point in new developments. Changing the sweetness profile would probably be a good option, or implementing marketing strategies to inform the consumer about the advantages of a low calorie intake or low glycaemic index in relation with health issues such as diabetes, obesity, and weight control, and also to fit the pattern of a healthier diet and lifestyle.

Regarding texture, the ideal fruit filling and OL were in an intermediate position between opposite texture attributes. This could indicate segmentation regarding texture preferences.

4. CONCLUSIONS

Conventional rheological and instrumental measurements are widely used for measuring the characteristics of soft gelled systems but are insufficient when formulating new real products. New sensory techniques with consumers are available to gather information that allows a deeper insight into consumer perceptions. These techniques contribute a very rich panorama, making it possible to position the product in the market. In the present work, the analysis of detailed information on the predominant perceptions of consumers while consuming fruit fillings showed the differences in perception elicited by the three systems studied. In addition, a quick and spontaneous description of newly formulated products clearly showed the way forward: the samples with sugar were by far the most liked and were closer to the “ideal” sample, while replacement of sugar with intense sweeteners has to be rethought to fit into the low-calorie consumer niche, as these results pointed to the intense sweetener’s flavour as being pivotal for sample rejection. In the set of samples containing sugar, the choice of hydrocolloid system pointed to a preference for the creamy, fondant textures identified in the tapioca starch sample.

ACKNOWLEDGEMENTS

The authors are grateful to Sucroal S.A. (Colombia) and SENA (Servicio Nacional de Aprendizaje de Colombia) for funding the PhD studies of Maria Alejandra Agudelo (Sucroal S.A.) at the Polytechnic University of Valencia and to the Spanish Ministry of Science and Innovation for financial support (AGL2012-36753-C02-01). They would also like to thank Mary Georgina Hardinge for language correction of this paper.

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RESUMEN Y DISCUSIÓN

En La presente tesis doctoral “La revalorización del uso de almidón de tapioca. Estrategia multienfoque en su aplicación en rellenos de fruta”, Se han desarrollado sistemas basados en almidón nativo de tapioca para aplicación en rellenos de fruta con el fin de revalorizar el uso de este almidón en la industria de alimentos. Se desarrollaron modelos y productos y se aplicaron herramientas para su desarrollo desde el punto de vista instrumental y sensorial. Todos ellos están enmarcado en los proyectos que se pueden desarrollar y aplicar en Sucroal S.A empresa en la que trabajo y con la participación del estado colombiano, programa del SENA “Apoyo a la creación y fortalecimiento de unidades de investigación aplicada y desarrollo tecnológico”. El estudio y la aplicación de algunas herramientas nuevas para el desarrollo de productos tanto desde el punto de vista instrumental como sensorial constituyen un importante aporte en la presente memoria.

Para el cumplimento de los objetivos propuestos, se evaluó la adición de un hidrocoloide como modelo principal: sistema mixto, basado en almidón nativo de tapioca (NTS) con adición de pectina de bajo metoxilo (LMP). Los rellenos de fruta para pastelería suelen tener un bajo valor de pH y normalmente deben soportar altas temperaturas de proceso y horneado sin alterar su calidad, por esta razón, el sistema propuesto se comparó con un control, elaborado con un almidón modificado altamente entrecruzado, hidroxipropilado y fosfatado – de maíz waxy (MWCS) que se utiliza normalmente en rellenos de fruta elaborados industrialmente. Se estudiaron las propiedades de formación de pasta de los almidones y las propiedades viscoelásticas, los parámetros de textura instrumental (extrusión) y sinéresis de los diferentes sistemas modelo. Los resultados indicaron que la adición de LMP reemplazando un 10 % del NTS aumentó significativamente el PV, HPV, CPV y *total relative setback* del NTS y disminuyó el *breakdowm*. Así mismo el sistema mixto proporcionó características viscoelásticas de gel más fuerte y elástico alcanzando valores similares a los del almidón control. Los valores de los parámetros viscoelásticos G', G" y tan G'/G", a frecuencia de 1Hz, no presentaron diferencias significativas entre el sistema mixto y el MWCS en condiciones ácidas (pH 3,0-3,2) y con un 35% de azúcar. La adición de pectina aumentó significativamente la firmeza y la consistencia de los geles analizados mediante pruebas de extrusión. El diseño de formulaciones de sistemas de hidrocoloides que añadan valor al producto final, es un objetivo prioritario en el cambiante mundo de constante aparición de nuevos alimentos procesados. En el presente estudio se proponen formulaciones modelo pensadas para actuar como espesantes en rellenos de frutas de pastelería, o sistemas que requieran baja acidez.

En el diseño y formulación del sistema espesante propuesto se consideraron también diversos factores inherentes a las condiciones experimentales de proceso de los rellenos de fruta como la cantidad de fruta y la estabilidad frente a los tratamientos térmicos (horneado y congelación), durante los cuales deberán conservar su calidad intacta. Para ello se investigó la influencia de los tratamientos de calentamiento y congelamiento/ descongelamiento sobre las propiedades de formación de pasta, propiedades viscoelásticas, propiedades de textura (extrusión) y la sinéresis de los rellenos con y sin fruta, elaborados con los tres sistemas espesantes (mezcla de TS y pectina, almidón control y almidón nativo de tapioca). Además se evaluó el efecto de la cocción sobre la textura en dos aplicaciones de pastelería (sistemas abiertos y cerrados). La adición de fruta causo un aumento significativo de los módulos G' y G" en todos los sistemas siendo este efecto mayor en los sistemas que tenían pectina; esto indicó mayor estructura del sistema por la adición de sólidos y pectina de la fruta. La adición de pectina modifico la estructura del gel de TS, actuando como inhibidor de la retrogradación (tanδ permaneció más estable para las mezclas con pectina durante el congelamiento) y este efecto fue dependiente de la concentración de pectina adicionada; además aumentó la estabilidad a las temperaturas de horneado presentando valores estables de tanδ, similar comportamiento viscoelástico y resistencia. Los rellenos con y sin fruta preparados con una mezcla de almidón nativo de tapioca, pectina de bajo metoxilo y calcio, fueron más resistentes a tratamientos térmicos tanto congelamiento/ descongelamiento como procesos de horneado que los rellenos preparados con almidón de tapioca solo, mostrando propiedades reológicas y texturales estables durante los diferentes procesos y similares a las del almidón de maíz modificado, usado como control. La adición de fruta (melocotón) confirió mayor estructura a los rellenos.

Teniendo en cuenta que en la actualidad, el mercado de los alimentos se encuentra cada vez más segmentado y los consumidores buscan productos no solo de buena calidad sino que sean más saludables, satisfagan necesidades y gustos personales. Por ello también se evaluaron rellenos de fruta reducidos en azúcar, elaborados con diferente cantidad de fruta y remplazando el azúcar por polidextrosa como agente de carga y una mezcla de edulcorantes de alta intensidad. La reducción de azúcares no es fácil debido a que proporcionan buenas texturas y además los productos son más apetecibles. Para cumplir este objetivo se aplicaron técnicas instrumentales (reológicas y de textura) y técnicas sensoriales (estudios de análisis sensorial descriptivo (QDA) clásico con panel entrenado y estudios con consumidores no entrenados para evaluar su aceptabilidad). La adecuación de algunos atributos sensoriales se evaluó con un panel de 100 consumidores mediante escalas JAR. Los resultados instrumentales de reología y textura y los descriptores de textura del QDA se encontraron altamente correlacionados, describiendo a los rellenos elaborados con el almidón control y la mezcla de tapioca-pectina como; consistentes, adherentes, de mayor tiempo de residencia en boca, y recubrimiento que los elaborados con almidón de tapioca. Estos últimos fueron descritos como fluidos. Las muestras con alto contenido de fruta (50 g/100 g) fueron descritas como de mayor consistencia que las elaboradas con 25 g/100 g. Estos resultados confirman los datos obtenidos instrumentalmente en los cuales los sistemas elaborados con almidón control y con la mezcla de tapioca y pectina tienen una estructura de gel más fuerte que la del almidón de tapioca solo y la adición de fruta fortalece la estructura del gel. Los parámetros de sabor se afectaron por el remplazo de azúcar por polidextrosa y edulcorante y por la adición de alto contenido de fruta; el panel entrenado encontró mayor sabor extraño y retrogusto en las muestras que contenían edulcorante siendo estos valores mayores en los rellenos elaborados con almidón control y menores en los elaborados con almidón de tapioca. También se percibió menor sabor extraño y retrogusto en los rellenos elaborados con mayor contenido de fruta; este resultado puede indicar que la percepción generada por el edulcorante puede ser mitigada usando un alto contenido de fruta.

Se aplicó un análisis de conglomerados jerárquico a los resultados obtenidos de la prueba con consumidores para detectar los grupos con diferentes perfiles de preferencias. A partir de los resultados obtenidos fue evidente que las preferencias de los consumidores estaban segmentadas. Hubo un nicho de consumidores que prefería los rellenos de frutas con una textura suave y un sabor dulce, ácido, y muy afrutado, correspondiente al perfil sensorial de la muestra preparada con almidón de tapioca nativo y azúcar. Este grupo podría ser descrito como de un "estilo casero" por preferir un producto natural o estilo casero. Otro grupo rechazó claramente el sabor de los edulcorantes intensos, por lo que para el objetivo de elaborar un relleno de frutas sin azúcar se deberán hacer estudios en profundidad para formular un nuevo perfil de dulzor para esta población o hacer un mayor esfuerzo para descubrir la manera de informar a los consumidores de los beneficios de la disminución de calorías y el control de la diabetes o del peso, en el contexto de dieta y estilo de vida más saludable. Por último, a un grupo numeroso de consumidores le gusta tanto las muestras con azúcar como las sin azúcar, por lo que todas las formulaciones propuestas encajarían en sus preferencias

Para el cumplimiento del último objetivo, dada la segmentación de los consumidores con respecto a los productos evaluados y sabiendo que una serie de características texturales se evalúan durante el consumo y la masticación del producto, que a su vez modulan la percepción del sabor, se utilizaron técnicas sensoriales relativamente nuevas para poder profundizar en la comprensión de la percepción de los rellenos de fruta. Adicionalmente estas técnicas sensoriales nos permiten que sea el consumidor quien dirija y sugiera qué aspectos de la formulación pueden ser rediseñados.

Las muestras elaboradas con los tres sistemas espesantes con y sin azúcar y con contenido de fruta 50g/100g, se sometieron a dos técnicas sensoriales: Dominio temporal de las sensaciones (TDS: *Temporal Dominance of Sensations*) evaluando textura y sabor por separado y análisis CATA (*Check-all-that-apply*) incluyendo la evaluación de un "relleno de fruta ideal". Los resultados se relacionaron con la aceptabilidad por los consumidores e indicaron, como era de esperar de acuerdo a los parámetros evaluados anteriormente, que los atributos de textura fueron muy dependientes del sistema espesante tanto en TDS como en análisis CATA, Sin embargo el producto ideal y la aceptabilidad se ubicaron alejados de estos atributos de textura, indicando que existe una segmentación en las preferencias por los consumidores dirigida por el sabor; de hecho hubo varios atributos de textura en TDS que no fueron significativos.

De acuerdo con las curvas de TDS de textura las muestras con pectina fueron predominantemente cohesivas y no cremosas, mientras que para las muestras con almidones, la cohesividad no excedió el nivel significativo. Por otra lado las muestras de almidón control se percibieron significativamente dominantes como cremosas y las muestras de almidón nativo solo significativamente dominantes como “fondant” (de fácil fusión en la boca). Estos dos atributos se consideran algo opuesto a "cohesivo" en el sentido de que indican la difusión en la boca en vez de permanecer “en una sola pieza".

Como resultado del análisis CATA, el relleno de fruta ideal fue descrito como dulce (pero no "muy dulce"), suave, con sabor a fruta, homogéneo, consistente y que se funde rápidamente en la boca, y, como se esperaba, delicioso. Estos atributos tienen una alta frecuencia de mención (más del 20% de los consumidores) lo cual indica que pueden considerarse como los principales motores de aceptabilidad para este tipo de producto. En cuanto a sabor, las muestras elaboradas con azúcar fueron las más aceptadas por los consumidores ubicándose cerca del producto ideal y los atributos de dulce y afrutado; estos dos atributos también se encontraron como dominantes en las curvas de TDS para sabor, confirmando que el azúcar tiene gran poder en la dirección de determinar la calidad.

A partir de estos resultados es evidente que la sustitución de azúcar por otros edulcorantes es un reto para los investigadores y la industria por igual, ya que pueden modificarse además del sabor dulce, otros atributos de sabor. La formulación de los productos alimenticios para nichos específicos como los consumidores de productos bajos en calorías es un punto clave en los nuevos desarrollos.

CONCLUSIONES

Las principales conclusiones de la presente tesis doctoral ”La revalorización del uso de almidón de tapioca. Estrategia multienfoque en su aplicación en rellenos de fruta”, son:

- Un sistema compuesto por almidón de tapioca nativo con adición de pectina de bajo metoxilo y calcio, ha demostrado ser una alternativa interesante que presenta propiedades reológicas y de textura similares que los almidones modificados para aplicación en rellenos de fruta.

- Los resultados reológicos indican que en el sistema elaborado con la mezcla de almidón de tapioca, pectina de bajo metoxilo y calcio, la pectina tiene un papel dominante en la estructura del sistema.

- Los rellenos de fruta preparados con la mezcla propuesta de almidón de tapioca, pectina de bajo metoxilo y calcio fueron estables a las temperaturas de horneado, mostrando ventajas considerables en comparación con la utilización de almidón de tapioca solo.

- La adición de puré de fruta (melocotón) mejoró la estructura de los rellenos; las pruebas de cocción en dos aplicaciones reales: pasteles (cerrado) y tartaletas (abierto) confirmaron la viabilidad del sistema propuesto, que incluso presentó ventajas en comparación con el control.

- El diseño de formulaciones de sistemas de hidrocoloides que añadan valor al producto final, utilizando el almidón nativo de tapioca en su formulación revaloriza el uso de este ingrediente en la industria en alimentos.

- Las nuevas técnicas sensoriales y de estudios con consumidores disponibles aportan la posibilidad de recoger información que permite profundizar en el conocimiento de las preferencias del consumidor.

- La elección de las formulaciones por parte de los consumidores depende en gran manera de sus preferencias: éstas estuvieron segmentadas por la presencia de edulcorante o azúcar, y entre texturas más consistentes o más fluidas.

- La sustitución de azúcar por otros edulcorantes es un reto. La formulación de los productos alimenticios para nichos específicos como los consumidores de productos bajos en calorías ha resultado ser un punto clave en los nuevos desarrollos.

- El estudio dinámico de la percepción sensorial durante el consumo y degustación de un alimento, además de una descripción más realista permite una mayor comprensión de la complejidad de la percepción y su relación con las preferencias del consumidor.

- Este estudio ha demostrado la importancia de tomar en cuenta la segmentación de las preferencias del consumidor y la adecuación de los métodos y técnicas sensoriales utilizadas en el diseño de nuevos productos alimenticios como rellenos de fruta bajos en calorías.