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Cellulose ether oleogels to reduce saturated fatty acids. Application in cream cheese and puff pastry

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TESIS DOCTORAL

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La tesis doctoral titulada: **"Cellulose ether oleogels to reduce saturated fatty acids. Application in cream cheese and puff pastry"** que presenta **D. Qi Wang** por la Universidad de Valencia, ha sido realizado bajo su dirección en el Departamento de Ciencias de los Alimentos del Instituto de Agroquímica y Tecnología de Alimentos (IATA-CSIC), y autorizan su presentación para optar al título de **Doctor** por la Universitat de València.

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To all my family and

everyone who has helped me

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Qi Wang

Abstract

Conventional solid fats (e.g., butter, margarine, and shortening) play an essential functional role in food products. They provide structure, texture, and flavour to foods and are widely used in foods such as bakery products, confectionery, and puff pastry. These fats provide desirable textures, such as layers in puff pastry and firmness in chocolate, and also extend the shelf life of foods and prevent moisture loss. However, conventional solid fats are high in saturated fatty acids (SFA), which have detrimental health effects at high concentration. Excessive intake of SFA and TFA can cause elevated low-density lipoprotein (LDL) cholesterol, in turn increasing the risk of heart disease, stroke, and other cardiovascular conditions. As awareness of these health risks rises, the food industry has gradually been working on the reduction or replacement of these unhealthy fats, to develop low-SFA and alternatives, which not only can maintain the functional properties of traditional solid fats, but also improve the nutritional structure of the food. Oleogels, which are made by physically gelatinizing vegetable oils with a minimal quantity of gelling factors, have been considered a novel fat material that may replace conventional plastic fats because of their low saturated fatty acid content and zero trans-fat content. Currently, the primary challenges to the commercialization of oleogels are the discovery of food-grade gelling factors that are safe, effective, nutritious, and non-toxic, as well as reducing the effects of substituting plastic fats with oleogels on product qualities and properties. Some food-grade polymers (e.g., proteins and polysaccharides) can be applied to the construction of emulsions and oleogels due to their unique interfacial properties.

Given the above context, the focus of this PhD thesis is to develop different edible oleogelators to construct stable oleogels via indirect methods, explore their physical properties as well as the gelation mechanism, and further investigate their feasibility as alternative fats to traditional plasticized fats for application in food formulations and to study the effect of addition of oleogels on the physical properties of the products, providing data for the application of oleogels in food systems.

The food-grade hydrocolloids methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC) were employed as gelators in two indirect approaches (the foam-template approach and the emulsion-template method) to prepare oleogels at three distinct oil concentrations. The microstructure, texture, rheology, and oil retention capacity of the oleogels were measured to investigate the effects of the components of the gelators, the preparation methods, and the oil content on the structural and physicochemical properties of the oleogels. The findings demonstrated that variations in the oleogels' microstructure and oil retention ability were caused by the preparation methodologies. Emulsion-based oleogels showed a distinct droplet structure, whereas foam-based oleogels exhibited a typical porous foam structure in the network. Compared to foam-based oleogel, which absorbs liquid oil through its interior porous sponge structure, the oleogel made using the emulsion template approach has a 100% oil retention capability. The rheology demonstrated that the storage modulus of all oleogels is much higher than the loss modulus, indicating the elastic behavior outweighed viscous behaviour in the oleogels made using both techniques. The storage modulus of the oleogels showed high-frequency independence as well as slight temperature dependence, revealing excellent mechanical properties and gel strength. However, the differences in HPMC and MC compositions affected the structural and mechanical properties of the two types of oleogels to varying degrees, which were also related to the oil content.

In order to further validate the feasibility of oleogels as an alternative to traditional solid fats in food formulations, the present study was carried out to compare the physicochemical properties of oleogels as well as blends of oleogels with shortening, and to simulate the physiochemical changes and oxidative stability of the different fats during the storage period via techniques such as penetration, differential scanning calorimetry (DSC), and high-performance liquid chromatography (HPLC) -mass spectrometry (MS). The results showed that the texture of the oleogels prepared by the emulsion-template method became hardened after four weeks, but their mixtures with shortening had textural properties similar to shortening, whereas the texture of the oleogels prepared by the foam-template method as well as their mixtures with shortening was softer. Melting behaviour tests showed that the melting behaviour of emulsion-based oleogels with shortening blends was not affected by time. Oxidative stability showed that both foam-based oleogels and emulsion-based oleogel shortening mixtures have excellent oxidative stability. The above results indicate the potential of oleogels as an alternative to conventional plasticized fats.

In order to validate the application of oleogel prepared from HPMC in the food industry, a healthy low-fat cream cheese was prepared using HPMC oleogel instead of butter via an emulsion template approach, and the effect of HPMC oleogel on spreadability, viscoelasticity, and sensory acceptability of cream cheese was evaluated. The HPMC emulsion was also chosen to be compared with control (shortening) and oleogel, respectively, to investigate the rheological changes of cream cheese prepared from different fats under small amplitude oscillatory shear (SAOS) and large amplitude oscillatory shear (LAOS). The results showed that all cheeses showed a predominance of G' over G'' in the linear viscoelastic region (LVR), where G' and G'' had a lower frequency dependence.

Replacement of butter with emulsion or oleogel can significantly reduce the G' and G'' values in the linear viscoelastic region, yield point, and flow point of cream cheese but increase the spreadability. However, the incorporation of emulsion or oleogel had little effect on tan δ, yield stress, yield strain, flow stress, and flow strain. The elastic and viscous developments during the transition from SAOS to LAOS were similar in all the cheeses, although their spreading properties differed. In LAOS, all samples showed strain-hardening and shear-thinning behavior. The sensory evaluation showed a similar sensory acceptability for all cream cheeses. Consumer favorability assessments showed that the willingness to purchase cream cheese with oleogel and emulsion would increase if information about the type and amount of fat was provided. These results all suggest that HPMC oleogel has the potential to be a fat substitute in cream cheese.

In addition to cream cheese, the application of oleogels in food products was further expanded in the current work, whereby oleogels were prepared via the emulsion template approach using sunflower oil and HPMC as a substitute for conventional fats in puff pastry, which enabled the production of low SFA and zero TFA puff pastry products with improved nutritional profiles. First, fat blends were prepared as fat substitutes using commercial shortening with oleogel in different ratios (SH100:OG0, SH50:OG50, SH40:OG60, or SH30:OG70, and SH100:OG0), and croissants were made. The effect of oleogel as fat on the textural and sensory properties of croissants was then evaluated. The results showed that the incorporation of the oleogel gave croissants with lower SFA content, lower bite firmness, and a texture similar to that of the selected commercial shortenings. The maximum addition of 100% oleogel did not negatively affect the firmness or resilience of the croissants. However, the

croissants became chewier and more cohesive as the level of oleogel substitution increased. In terms of sensory perception, the croissants made with the SH:OG blend were similar to those described for the control, but which were perceived to be firmer. The above results indicated that sunflower oil-cellulose-based oleogels could effectively replace shortening by up to 100% without significantly reducing the quality characteristics of the croissants. Thus, the replacement of solid conventional fats with structured vegetable oils is a promising strategy to reduce the consumption of saturated and trans fats in shortening bakery products while maintaining the functional and sensory properties of products such as traditional croissants.

To further compare the effects of HPMC oleogels prepared by the emulsion-template approach and foam-template approach as a fat source in a puff pastry dough on the mechanical properties of shortening dough, the spreadability and thermal properties of shortening, 100% emulsion-template and foam-template oleogels, as well as shortening/oleogel (50/50) blends, were first investigated, as well as the effects of different fats on the rheological and textural properties of shortening dough. Results showed that partial replacement of shortening with oleogels could significantly decrease the firmness values (from 115 to 26 N) ($P<0.05$) and increase the spreadability of shortening. The methodology to prepare the oleogel also significantly affected the texture parameters, shortening/foam-template oleogel blends had the highest spreadability with significantly lower firmness values and area under the curve. Thermal values showed that both oleogels could slightly increase the melting point of shortening from 47 to 50 °C. The replacement of shortening with oleogel decreases the viscoelasticity of puff pastry dough and increases its thermal stability but does not significantly change dough viscoelasticity in the

shortening/oleogel mixture. These results indicated that both oleogels have promising potential to replace shortening in puff pastry dough formulations, but the emulsion-template oleogel showed more similar behaviour to the control shortening than the foam-template oleogel.

After studied the effect of replacing shortening with HPMC oleogel prepared by emulsion and foam template approach on the rheological properties and texture of puff pastry dough, the effect of replacing shortening with HPMC oleogel prepared by emulsion- and foam-template approach in puff pastry on the textural and sensory properties of the product, texture profile analysis (TPA) and penetration tests, as well as temporal-dominant sensory (TDS) analyses, were examined. The results showed that the appearance of bakery pastries made with the 50/50 (shortening/oil gel) formulation was similar to that of the control (100% shortening). Conversely, the bakery pastries made with 100% oleogel had a denser and less airy crumb quality. The TPA test showed that there was no significant difference between the puff pastry made with 100% foam-based oleogel and the control, while the samples made with emulsion-based oleogel were significantly harder and chewier than the control. In terms of sensory analysis, all the puff pastry treats were predominantly "crunchy" during chewing. The denser puff pastry was produced by increasing the oleogel percentage, although samples made with a 50/50 foam-based oleogel were "easier to chew." The main sensation changed to "firmness" when the oleogel content was raised to 100%, which could be connected to the thick structure seen in the crumb form.

Overall, in the present thesis, cellulose-based oleogels enriched with unsaturated fatty acids were prepared using two indirect methods (emulsion template and foam template approaches) and applied as traditional solid fat substitutes in different food formulations. The comparison of the effects of the preparation methods on the physicochemical properties of the oleogels as well as the properties of the product formulations revealed that the oleogels had excellent potential as solid fat substitutes in different food formulations without negatively affecting the product quality. Furthermore, there are potential health benefits and consumer acceptance of replacing conventional solid fats containing high levels of saturated fatty acids and trans fats with the utilization of oleogels enriched with high levels of unsaturated fatty acids. This thesis provides the basis for the application of hydrocolloid-constructed oleogels as healthy fat substitutes in food formulations. In particular, the croissant, which is a complicated puff pastry product, was chosen as a model to provide more ideas for the development and application of oleogel-based bakery products.

Keywords: HPMC, oleogel, shortening, physicochemical properties, food application, cream cheese, puff pastry dough, croissant, texture, rheology, sensory evaluation.

Resumen

Las grasas sólidas convencionales (por ejemplo, mantequilla, margarina y manteca) juegan un papel funcional esencial en los productos alimenticios. Proporcionan estructura, textura y sabor a los alimentos, y se utilizan ampliamente en productos de panadería, confitería y hojaldre. Estas grasas aportan texturas deseables, como las láminas en el hojaldre y la firmeza en el chocolate, también prolongan la vida útil de los alimentos y evitan la pérdida de humedad. Sin embargo, las grasas sólidas convencionales son ricas en ácidos grasos saturados (AGS), que tienen posibles efectos perjudiciales para la salud. El consumo excesivo de AGS puede elevar el colesterol de lipoproteínas de baja densidad (LDL), lo que a su vez aumenta el riesgo de enfermedades cardíacas, accidentes cerebrovasculares y otras afecciones cardiovasculares. A medida que aumenta la conciencia sobre estos riesgos para la salud, la industria alimentaria ha estado trabajando gradualmente en la reducción o sustitución de estas grasas poco saludables, desarrollando alternativas bajas en AGS, que no solo puedan mantener las propiedades funcionales de las grasas sólidas tradicionales, sino también mejorar la estructura nutricional de los alimentos. Los oleogeles, que se elaboran gelificando físicamente aceites vegetales con una cantidad mínima de factores gelificantes, se han considerado un material graso novedoso que puede reemplazar las grasas plásticas convencionales debido a su bajo contenido de ácidos grasos saturados y ausencia de grasas trans. Actualmente, los principales desafíos para la comercialización de oleogeles son la identificación de factores gelificantes aptos para el consumo, seguros, efectivos, nutritivos y no tóxicos, así como reducir los efectos de la sustitución de las grasas plásticas con oleogeles sobre las cualidades y propiedades de los productos. Algunos polímeros aptos para alimentos (por ejemplo, proteínas y polisacáridos) pueden aplicarse a la construcción de emulsiones y oleogeles debido a sus propiedades interfaciales únicas.

Dado el contexto anterior, el objetivo de esta tesis doctoral es desarrollar diferentes oleogelificantes comestibles para construir oleogeles estables mediante métodos indirectos, explorar sus propiedades físicas y el mecanismo de gelificación, e investigar su viabilidad como grasas alternativas a las grasas plásticas tradicionales para su aplicación en formulaciones alimentarias. Asimismo, se estudia el efecto de la adición de oleogeles en las propiedades físicas de los productos, proporcionando datos para la aplicación de oleogeles en sistemas alimentarios.

Los hidrocoloides de grado alimentario, metilcelulosa (MC) y metilcelulosa hidroxipropílica (HPMC), se emplearon como gelificantes en dos enfoques indirectos (el método de plantilla de espuma y el método de plantilla de emulsión) para preparar oleogeles a tres concentraciones distintas de aceite. Se midieron la microestructura, textura, reología y capacidad de retención de aceite de los oleogeles para investigar los efectos de los componentes de los gelificantes, los métodos de preparación y el contenido de aceite sobre las propiedades estructurales y fisicoquímicas de los oleogeles. Los resultados demostraron que las variaciones en la microestructura y la capacidad de retención de aceite de los oleogeles fueron causadas por las metodologías de preparación. Los oleogeles basados en emulsiones mostraron una estructura de gotas distinta, mientras que los oleogeles basados en espuma exhibieron una estructura típica de espuma porosa en la red. En comparación con el oleogel basado en espuma, que absorbe aceite líquido a través de su estructura interior porosa tipo esponja, el oleogel hecho mediante el enfoque de plantilla de emulsión tiene una capacidad de retención de aceite del 100%. La reología demostró que el módulo de almacenamiento de todos los oleogeles es mucho mayor

que el módulo de pérdida, lo que indica que el comportamiento elástico prevalece sobre el comportamiento viscoso en los oleogeles elaborados con ambas técnicas. El módulo de almacenamiento de los oleogeles mostró una alta independencia de la frecuencia, así como una ligera dependencia de la temperatura, revelando excelentes propiedades mecánicas y resistencia al gel. Sin embargo, las diferencias en las composiciones de HPMC y MC afectaron las propiedades estructurales y mecánicas de los dos tipos de oleogeles en distintos grados, lo que también estaba relacionado con el contenido de aceite.

Para validar la viabilidad de los oleogeles como una alternativa a las grasas sólidas tradicionales en formulaciones alimentarias, se estudiaron las propiedades fisicoquímicas de los oleogeles, así como las mezclas de oleogeles con manteca, así como los cambios fisicoquímicos y la estabilidad oxidativa de las diferentes grasas durante el período de almacenamiento mediante técnicas como penetración, calorimetría diferencial de barrido (DSC) y cromatografía líquida de alto rendimiento (HPLC)-espectrometría de masas (MS). Los resultados mostraron que la textura de los oleogeles preparados por el método de plantilla de emulsión se endureció después de cuatro semanas, pero sus mezclas con manteca presentaron propiedades texturales similares a la manteca, mientras que la textura de los oleogeles preparados por el método de plantilla de espuma, así como sus mezclas con manteca, fueron más suave. Las pruebas de comportamiento de fusión mostraron que el comportamiento de fusión de las mezclas de oleogeles basados en emulsiones con manteca no se vio afectado por el tiempo. La estabilidad oxidativa mostró que tanto los oleogeles basados en espuma como las mezclas de oleogeles basados en emulsiones con manteca tienen una excelente estabilidad oxidativa. Estos

resultados indican el potencial de los oleogeles como una alternativa a las grasas plásticas convencionales.

Para validar la aplicación del oleogel de HPMC en la industria alimentaria, se preparó un queso crema bajo en grasa utilizando oleogel de HPMC en lugar de mantequilla, mediante el enfoque de plantilla de emulsión. Se evaluó el efecto del oleogel de HPMC en la untabilidad, viscoelasticidad y aceptabilidad sensorial del queso crema. También se eligió la emulsión de HPMC para compararla con el control (manteca) y oleogel, respectivamente, para investigar los cambios reológicos del queso crema preparado con diferentes grasas bajo cizallamiento oscilatorio de pequeña amplitud (SAOS) y cizallamiento oscilatorio de gran amplitud (LAOS). Los resultados mostraron que todos los quesos presentaban predominancia de G' sobre G'' en la región lineal viscoelástica (LVR), donde G' y G'' tenían una menor dependencia de la frecuencia. La sustitución de la mantequilla por emulsión u oleogel puede reducir significativamente los valores de G' y G'' en la región viscoelástica lineal, el punto de fluidez y el punto de ruptura del queso crema, pero aumentar la untabilidad. Sin embargo, la incorporación de emulsión u oleogel tuvo poco efecto sobre el tan δ, el esfuerzo de fluencia, la deformación de fluencia, el esfuerzo de flujo y la deformación de flujo. Los desarrollos elásticos y viscosos durante la transición de SAOS a LAOS fueron similares en todos los quesos, aunque sus propiedades de untado variaron. En LAOS, todas las muestras mostraron comportamiento de endurecimiento por deformación y adelgazamiento por cizallamiento. La evaluación sensorial mostró una aceptabilidad sensorial similar para todos los quesos crema. Las evaluaciones de intención de compra del consumidor indicaron que la disposición a comprar queso crema con oleogel y emulsión aumentaría si se proporcionara información sobre el tipo y la cantidad de

grasa. Estos resultados sugieren que el oleogel de HPMC tiene el potencial de ser un sustituto de la grasa en el queso crema.

Además del queso crema, la aplicación de oleogeles en productos alimentarios se amplió en la presente tesis, donde se prepararon oleogeles mediante el enfoque de plantilla de emulsión utilizando aceite de girasol y HPMC como sustituto de las grasas convencionales en la masa de hojaldre, lo que permitió la producción de productos de hojaldre con bajo contenido de ácidos grasos saturados (SFA) y cero ácidos grasos trans (TFA), mejorando así su perfil nutricional. Primero, se prepararon mezclas de grasas como sustitutos de la grasa utilizando manteca comercial con oleogel en diferentes proporciones (SH100, SH50, SH40, SH30 y SH100) y se elaboraron croissants. Luego se evaluó el efecto del oleogel como sustituto de grasa en las propiedades sensoriales y texturales de los croissants. Los resultados mostraron que la incorporación del oleogel dio como resultado croissants con menor contenido de SFA, menor firmeza al morder y una textura similar a la de las mantecas comerciales seleccionadas. La adición máxima del 100% de oleogel no afectó negativamente la firmeza ni la resiliencia de los croissants. Sin embargo, los croissants se volvieron más masticables y cohesivos a medida que aumentaba el nivel de sustitución por oleogel. En términos de percepción sensorial, los croissants hechos con la mezcla SH:OG fueron similares a los descritos para el control, aunque se percibieron un poco más firmes. Estos resultados indican que los oleogeles a base de aceite de girasol y celulosa pueden reemplazar eficazmente la manteca hasta en un 100% sin reducir significativamente las características de calidad de los croissants. Por lo tanto, la sustitución de grasas sólidas convencionales por aceites vegetales estructurados es una estrategia prometedora para reducir el consumo de grasas saturadas y trans en productos de panadería de manteca, manteniendo las propiedades funcionales y sensoriales de productos como los croissants tradicionales.

Para comparar los efectos de los oleogeles de HPMC preparados mediante el enfoque de plantilla de emulsión y el enfoque de plantilla de espuma como fuente de grasa en la masa de hojaldre, en el presente trabajo se investigaron las propiedades mecánicas de la masa de manteca, la untabilidad y las propiedades térmicas de la manteca, oleogeles al 100% (tanto de plantilla de emulsión como de espuma) y mezclas de manteca/oleogel (50/50). Asimismo, se evaluaron los efectos de diferentes tipos de grasas en las propiedades reológicas y texturales de la masa de manteca.

Los resultados mostraron que la sustitución parcial de la manteca con oleogeles podría reducir significativamente los valores de firmeza (de 115 a 26 N) ($P<0.05$) y aumentar la untabilidad de la manteca. Además, el método utilizado para preparar el oleogel afectó de manera significativa los parámetros de textura, siendo las mezclas de manteca/oleogel de plantilla de espuma las que presentaron la mayor untabilidad con valores de firmeza y área bajo la curva significativamente menores. En cuanto a las propiedades térmicas, se observó que ambos oleogeles aumentaron ligeramente el punto de fusión de la manteca de 47 a 50 °C. La sustitución de la manteca por oleogel disminuyó la viscoelasticidad de la masa de hojaldre y aumentó su estabilidad térmica, aunque no se observaron cambios significativos en la viscoelasticidad de la masa en las mezclas de manteca/oleogel. Estos resultados indicaron que ambos oleogeles tienen un potencial prometedor como sustitutos de la manteca en formulaciones de masa de hojaldre, aunque el oleogel de plantilla de emulsión mostró un comportamiento más similar al de la manteca control que el oleogel de plantilla de espuma.

Por último, se evaluó ael efecto de sustituir la manteca por oleogel de HPMC en la masa de hojaldre sobre las propiedades texturales y sensoriales de croisants, realizando análisis de perfil de textura (TPA) y pruebas de penetración, así como análisis sensorial llamado Dominancia Temporal de las Sensaciones (TDS). Los resultados mostraron que la apariencia de los productos de repostería elaborados con la formulación 50/50 (manteca/oleogel) fue similar a la del control (100% manteca). En cambio, los productos de repostería elaborados con 100% oleogel presentaron una calidad de miga más densa y menos aireada. La prueba de TPA indicó que no había diferencias significativas entre la masa de hojaldre hecha con 100% oleogel de espuma y el control, mientras que las muestras elaboradas con oleogel de emulsión resultaron ser significativamente más duras y masticables que el control. En cuanto al análisis sensorial, todos los productos de hojaldre fueron predominantemente "crujientes" al masticar. La masa de hojaldre más densa se producía al aumentar el porcentaje de oleogel, aunque las muestras elaboradas con 50/50 de oleogel de espuma eran "más fáciles de masticar." La sensación principal cambió a "firmeza" cuando se elevó el contenido de oleogel al 100%, lo que podría estar relacionado con la estructura más espesa observada en la miga.

En general, en el presente estudio se prepararon oleogeles a base de celulosa enriquecidos con ácidos grasos insaturados utilizando dos métodos indirectos (plantilla de emulsión y plantilla de espuma) y se aplicaron como sustitutos tradicionales de la grasa sólida en diferentes formulaciones alimentarias. La comparación de los efectos de los métodos de preparación en las propiedades fisicoquímicas de los oleogeles, así como en las propiedades de las formulaciones de los productos, reveló que los oleogeles tenían un excelente potencial como sustitutos sólidos de la

grasa en diferentes formulaciones alimentarias sin afectar negativamente a la calidad del producto. Además, la sustitución de grasas sólidas convencionales que contienen altos niveles de ácidos grasos saturados y grasas trans por la utilización de oleogeles enriquecidos con altos niveles de ácidos grasos insaturados puede resultar beneficiosa para la salud y para la aceptación de los consumidores.

Esta tesis sienta las bases para la aplicación de oleogeles construidos con hidrocoloides como sustitutos de grasas saludables en formulaciones alimentarias. En particular, se eligió el croissant, que es un producto de hojaldre complicado, como modelo para proporcionar más ideas para el desarrollo y la aplicación de productos de panadería basados en oleogeles.

Palabras clave: HPMC, oleogel, manteca, propiedades fisicoquímicas, aplicación alimentaria, queso crema, masa de hojaldre, croissant, textura, reología, evaluación sensorial.

List of abbreviations

ANOVA	Analysis of variance
AUC	Area under the curve
BW	Beeswax
BG	β-glucan
CDW	Candelilla wax
CHD	Coronary heart disease
DSC	Differential Scanning Calorimeter
EC	Ethylcellulose
ET	Emulsion template
ETOG	Emulsion template oleogel
FCP	Free Choice Profile
FDA	Food and Drug Administration
FT	Foam template
FTOG	Foam template oleogel
GPA	Generalized Procrustes Analysis
HDL	High-density lipoprotein
HMOG	High molecular weight oil gelators
HPMC	Hydroxypropyl methylcellulose
HRCs	Heat-resistant chocolates
LAOS	Large-amplitude oscillatory shear
LDL	Low-density lipoprotein
LM	Light microscopy
LMOG	Low molecular weight oil gelators
LMWGs	Low molecular weight gelators
LSAFA	Low saturated fatty acid
LVR	Linear viscoelastic region
MC	Methylcellulose

MUFAs	Monounsaturated fatty acids
OBC	Oil binding capacity
PCA	Principal Component Analysis
PS	Phytosterols
PUFAs	Polyunsaturated fatty acids
RBW	Rice bran wax
SAOS	Small-amplitude oscillatory shear
SEM	Scanning electron microscopy
SFA	Saturated fatty acid
SH	Shortening
TDS	Temporal Dominance Sensory
TFAs	Trans fatty acids
SFA	Saturated fatty acids
WHO	World Health Organization
XG	Xanthan gum

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1. INTRODUCTION

1.1 Type of fats and their properties

Fat is one of the main sources of energy in the human diet, providing twice as many calories as proteins or carbohydrates (Siri-Tarino, Chiu, Bergeron, & Krauss, 2015). The body obtains the diverse sorts of fats required from the diet, including saturated fats, unsaturated fats, and small amounts of trans fats. Healthy fat sources are beneficial for sustaining general well-being. With the rapid development of the economy and trade, consumers are able to purchase a wide range of foods from all over the world, which has caused a transformation in dietary habits from traditional diets centered on whole foods grown locally to diets that contain more processed and convenience foods. The consumption of foods with higher fat content, processed meats, and dairy products, as well as high-fat convenience foods, fast foods, and snacks, has become more widely available and consumed. A publicly accessible statistical report (Figure 1) showed that the amount of fats and oils consumed worldwide increased gradually between 2018 and 2023("Oils & Fats: market data & analysis," 2024), rising from 185 billion US dollars to 235.6 billion US dollars in 2023, and is predicted to reach 327.3 billion US dollars in 2028. Edible oils still dominated the consumption of fats and oils, and it could be easily found that of these, the overall consumption of fats and oils—which was projected to rise from 62 billion USD in 2018 to 118 billion USD in 2028—was made up of one-third butter and margarine consumption.

Fats and oils play a vital role in food cooking or food processing. The terms fat and oil refer to the consistency at room temperature: fats are solid and oils are liquid are room temperature. Fat consistency is positively related to the amount of saturated fatty acids. Solid fats rich in saturated fatty acids are required for the industrial manufacturing of many foods, as they provide the required solid texture, high stability, and excellent sensory properties in the final food. Liquid oils are in general healthier than solid fats but do not have these requirements. For instance, solid fats contribute to their crisp texture and excellent form preservation in breads, crackers, and pastries. Conversely, solid fats are simpler to handle, transport, and storage.

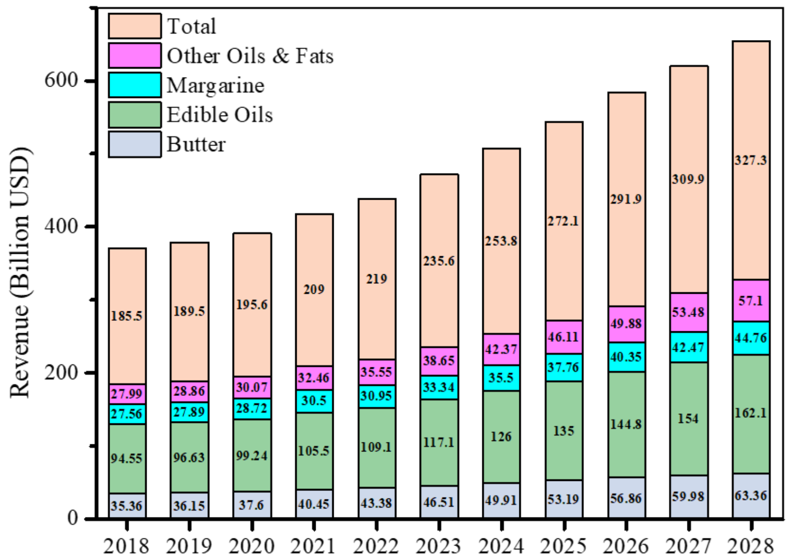

Figure 1. Consumption and Estimates of Global Oils and Fats from 2018-2028.

Fats and oils play a vital role in food cooking or food processing. The terms fat and oil refer to the consistency at room temperature: fats are solid and oils are liquid are room temperature. Fat consistency is positively related to the amount of saturated fatty acids. Solid fats rich in saturated fatty acids are required for the industrial manufacturing of many foods, as they provide the required solid texture, high stability, and excellent sensory properties in the final food. Liquid oils are in general healthier than solid fats but do not have these requirements. For instance, solid fats contribute to their crisp texture and excellent form preservation in breads, crackers, and pastries. Conversely, solid fats are simpler to handle, transport, and storage.

Apart from animal fat, the majority of solid fats used in the food industry are converted into edible solid fats by subjecting vegetable oils to chemical reactions such as hydrogenation or transesterification reactions. The process of hydrogenation modifies the fat structure by converting a portion or all of its unsaturated fatty acids into partially or fully saturated fatty acids, altering the physical and chemical characteristics of fat. The hydrogenated oils have higher oxidative stability than the original liquid oils, and they also significantly increase food products' shelf life and enhance their texture and mouthfeel, particularly for chocolates, candy, and bakery products. However, solid fats have a high concentration of saturated fatty acids, which consumed in excess increase the potential risk of diabetes, obesity, and cardiovascular disease (Mozaffarian, Aro, & Willett, 2009; Muguerza, Fista, Ansorena, Astiasarán, & Bloukas, 2002; Siri-Tarino, Chiu, Bergeron, & Krauss, 2015). In addition, partial hydrogenation produces as secondary products trans fatty acids, which are unhealthy and should not be present at any concentration in food products. In the case of total hydrogenation, all the double bonds are saturated and no trans fatty acids are formed. Also, the transesterification reactions are able to saturate the fat without producing trans fatty acids (TFAs). Several studies have demonstrated that TFA raised the perilously high levels of low-density lipoprotein (LDL) and lowered the advantageous levels of high-density lipoprotein (HDL), thus increasing the LDL/HDL ratio and raising the risk of atherosclerosis and coronary heart disease (CHD) (De Souza, Mente, Maroleanu, Cozma, Ha, Kishibe, et al., 2015; Dhaka, Gulia, Ahlawat, & Khatkar, 2011). TFA also raises the risk of allergic responses, obesity, breast cancer, and type II diabetes (Nettleton, Brouwer, Geleijnse, & Hornstra, 2017).

The World Health Organization (WHO) suggested that the amount of dietary energy derived from saturated fatty acids should not exceed 10% of total dietary energy in order to minimize the health hazards associated with the intake of SFA and TFA (Organization, 2002). Even better, their proportion of overall energy should not exceed 7%. In 2015, the U.S. Food and Drug Administration (FDA) eliminated TFA's unrestricted regulation and declared that TFA products would not be permitted in food items after 2018 (Nagpal, Sahu, Khare, Bashir, & Jan, 2021).

However, as stated before saturated fatty acids (TFA) have a very positive impact on food quality in terms of texture, shelf-life, and flavor (Li, Wu, Li, Jin, Wang, & Zhang, 2021; López-Pedrouso, Lorenzo, Gullón, Campagnol, & Franco, 2021). In order to overcome the restrictions as well as bans on the use of SFA or TFA in food processing, it has become a great challenge for food producers and related researchers to find healthy zero-TFA and low saturated fatty acid (LSAFA) novel fat, which could satisfy the requirement of the special food texture and stability while removing the TFA and reducing the SFA in the diet (Jang, Bae, Hwang, Lee, & Lee, 2015; Mert & Demirkesen, 2016b; Sun, Xia, Ni, Wang, Elam, Thakur, et al., 2021). A new research hotspot in this topic is oleogels. Oleogel is composed of liquid oil that is gelated by an oleogelator, thus a solid fat with a low percentage of saturated fatty acids is obtained. Oleogelation is a feasible technology that can structure liquid oil with highly unsaturated triglycerides for the preparation of new solid lipids (Mert & Demirkesen, 2016b).

1.2 Oleogelation

Oleogels are produced by the interaction of small amounts of gelators with vegetable oils to entrap or immobilize liquid oils in a three-dimensional network structure, resulting in a coexistence hybrid system consisting of the three-dimensional network structure and liquid oils (Adili, Roufegarinejad, Tabibiazar, Hamishehkar, & Alizadeh, 2020; Lim, Jeong, Lee, Park, Lee, & Lee, 2017; Mert & Demirkesen, 2016a). Oleogels are prepared with vegetable oils as a source of fat, thereby satisfying the diverse requirements of mankind for healthy oils. Additionally, since the preparation process is physical rather than involving chemical reactions like hydrogenation, it largely preserves the unsaturated fatty acids, sterols, vitamin E, and other healthy elements found in vegetable oils and is free of trans fatty acids (Andreea, Vlad, Carmen, & Sevastit, 2020; Gómez-Estaca, Herrero, Herranz, Álvarez, Jiménez-Colmenero, & Cofrades, 2019; Jang, Bae, Hwang, Lee, & Lee, 2015). Oleogels also have physical characteristics similar to margarine, like spreadability and extensibility, and maintain solid texture, which is suitable for specific food processing requirements and storage situations.

1.3 Formation mechanism and classification of oleogels

In order to prepare oleogel that could be an alternative to traditional solid fats and to realize the demands for functional properties and delivery of bioactive substances in processed foods, numerous researchers have dedicated great efforts to construct healthy oleogel systems with low-saturated fatty acid and zero-trans fatty acid using various structures of gelators and different vegetable oil systems. The methodologies to classify oleogels can be divided into direct and indirect methods (Figure 2).

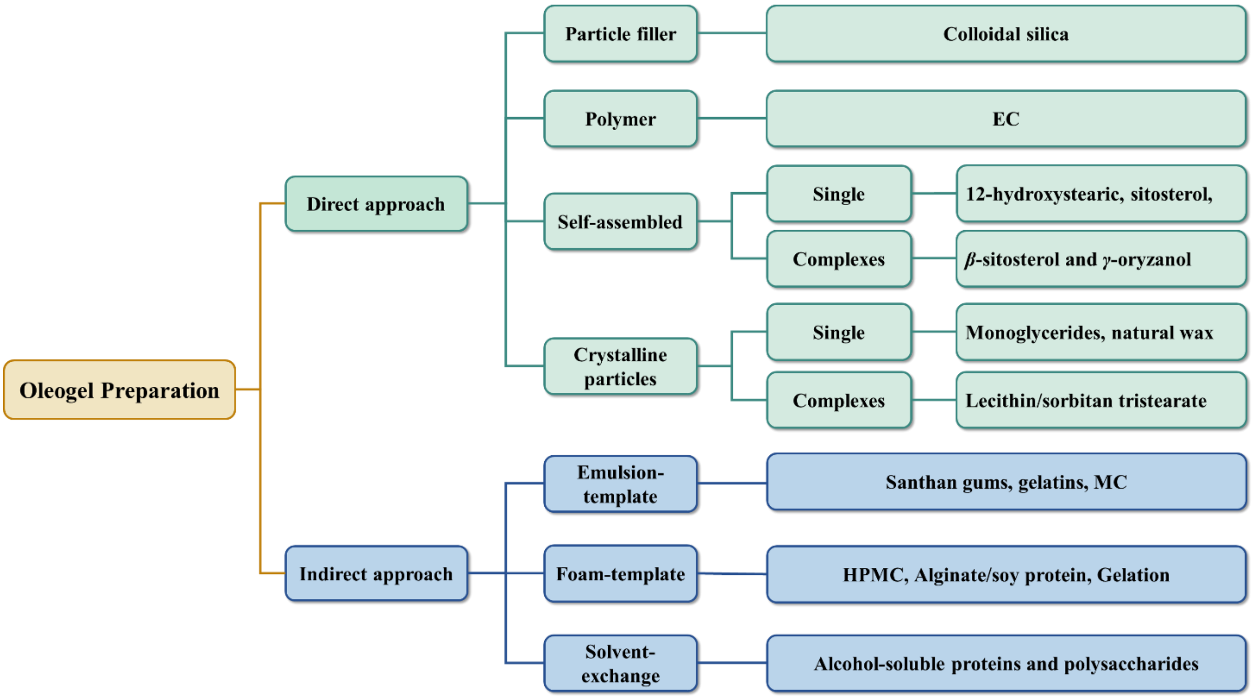

Figure 2. Methodology for the preparation of oleogels

1.3.1 Direct methods

The direct method, as the name suggests involves dispersing the gelators into the oil phase directly and cooling it to create a self-supporting gel. Initially, researchers used lipid-soluble small molecules such as botanical waxes, monoglycerides, diglycerides, long-chain fatty acids, long-chain fatty alcohols, and hydroxylated fatty acids to serve as gelators, which could be directly dispersed into the oil phase after melting at high temperatures, and the oleogels could be obtained after cooling. Later, the synergistic effect between different substances to promote the construction of oleogels was investigated, such as sterol and glutenin, lecithin, and sorbitan stearate. A detailed description of the mechanisms by which these strategies (i.e., crystalline particles, self-assembled structure, particle filler, and polymer network) form oleogel is given in Figure 3:

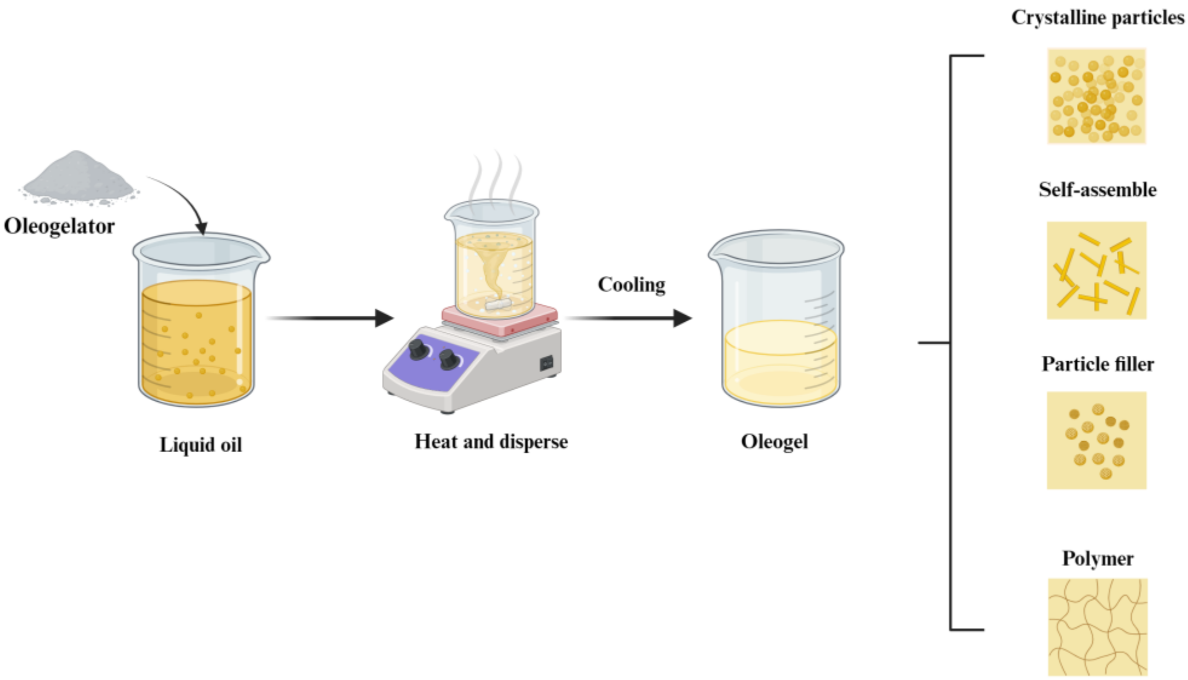

Figure 3. Methodology for the direct preparation of oleogels.

1.3.1.1 Crystalline particles based oleogels

The principle of particle crystallization for the preparation of oleogel is based on the formation of a network structure by aggregation of crystalline particles and trapping of liquid triglycerides into the network of crystalline particles (Blake & Marangoni, 2015; Ashok R Patel & Dewettinck, 2016; Valoppi, Calligaris, Barba, Šegatin, Poklar Ulrih, & Nicoli, 2017). Nucleation and crystal growth, aggregation, and network creation are the three broad steps comprising the gelation process (Pinto, Martins, Pastrana, Pereira, & Cerqueira, 2021). Briefly, the primary particles crystallize by interaction with the oil phase; subsequently, individual particles assemble into distinct crystalline particles. Hydrophobic and hydrogen bonding, π - π covalent bonding, van der Waals forces, and/or electrostatic interactions between tiny molecules are the final mechanisms that stabilize molecular clusters. Thermoreversible oleogel systems with continuous or spatially spanning networks are produced by interactions between particles that cause anisotropic diffusion and/or formation of mesoscale structures (Sivakanthan, Fawzia, Madhujith, & Karim, 2022). Thus, the macroscopic mechanical properties of such oleogels are determined by the size and shape of the crystalline particles as well as the interactions between the crystalline particles (McClements, 2007). Common gelators are monoglycerides (Palla, de Vicente, Carrín, & Ruiz, 2019), glycerides (Wojtalewicz, Erickson, Vizmeg, Shuckra, Barger, Cleveland, et al., 2023), fatty acids, wax esters, sorbitan monostearate, ceramides (Lee & Jin, 2023), and lecithin/sorbitan tristearate (Daniel & Rajasekharan, 2003; Rogers, 2009), all of which could be employed for the construction of such oleogels. Although the mechanism is comparable to conventional high-melting-point solid fats, the type, morphology, and crystallization characteristics (including nucleation, crystal growth direction, polycrystalline transformation, etc.) of the crystal structure formed by the gelator significantly differentiate from that of conventional solid fats, resulting in oleogels formed from these gelators that are commonly softer and more spreadable compared to dense conventional solid fats (Zhao, Wei, & Xue, 2021).

1.3.1.2 Self-assembled structures based oleogels

The self-assembled structures of oleogels are based on the aggregation of low molecular weight gelators in a solvent to self-assemble, whose initial structural units form hundreds of micrometer-long fibrillar networks by one-dimensional growth, helix, and twisting to bind the liquid oil migration and gel the system (Bot & Agterof, 2006). Common gelators are 12-hydroxystearic acid, glutenin/sitosterol, sorbitan monostearate, etc. It has been reported in the literature that 12-hydroxystearic acid (12-hydroxystearic acid) and ricinoleic acid can immobilize liquid oils through self-assembled structures to form oleogels with advanced mechanical properties (Rogers, Wright, & Marangoni, 2008). The combination of lecithin/sitosterol is typical of low molecular weight gelators, where the mixture forms a self-assembled fibrous network in the interior of the system, with the fiber length determined by the cooling rate and storage temperature during preparation (Bot & Agterof, 2006). Additionally, Dassanayake, Kodali, and Ueno (2011) demonstrated that *β*-sitosterol and *γ*-oryzanol units could be linked together to create thin, fibrous structural units from the molecular level. Similar results were also seen in another research that confirmed the hollow fiber-like form and method of self-assembly of mixed oleogels of *β*-sitosterol and *γ*-oryzanol using small-angle X-ray scattering (Martins, Cerqueira, Pastrana, Cunha, & Vicente, 2019). Along with 12-hydroxystearic acid as well as sitosterol, sorbitan monostearate was also capable of building edible oleogel structures through self-assembling systems, whose gel network formation was influenced by the interactions between the hydroxyl groups of sorbitan monostearate (Sagiri, Kasiviswanathan, Shaw, Singh, Anis, & Pal, 2016).

1.3.1.3 Particle filler-based oleogels

The preparation of oleogels from particle filler networks involves the dispersion of a large number of inert particles in a continuous phase of liquid oils and fats, relying on inert filler particles to achieve a structured gel. The prerequisites for the formation of such oleogel networks are that the solid or liquid particles are able to act as internal particles and the concentration present exceeds the close-packed fraction significantly (A. R. Patel, 2017). When these particles are encapsulated and beyond the close-packed fraction, mechanical contact between the particles facilitates the formation of the oleogel. Moreover, the suspension system forms when the interior particles are solid, and the emulsion forms when the interior particles are liquid (A. R. Patel, 2017). Peanut paste structured from peanut oil (1-2% dry matter) and 50% non-fat solid particles represent this type of system (Pernetti, van Malssen, Flöter, & Bot, 2007). The main drawback of this dispersion system is that a great deal of structural aids are required to enable the system to gel. Food-grade colloidal silica is used as a particle filler gelator because it forms fractal aggregates in the solution by hydrogen bonding and electrostatic interactions, forming a stable three-dimensional network structure.

1.3.1.4 Polymer-based oleogels

The only known polymer gelator that can be used to directly create an oleogel is ethylcellulose (EC). EC dispersions are heated beyond EC's glass transition temperature (about 140°C) and sheared to produce homogenous dispersions. The crystalline regions are transformed into amorphous regions during this process, resulting in the exposure of ethoxylates (Zhao, Wei, & Xue, 2021). The ethylcellulose molecules cluster together to form a hydrogen-bonded stabilized polymer network in the oil phase, and the surfactants and polymers interact to harden the polymer network and create structures like coral with tiny holes and pockets that are used to trap liquid oils forming the oleogel (M Davidovich-Pinhas, Barbut, & Marangoni, 2015; Fu, Lo, Yan, Li, & Cao, 2020). However, the network structure is actually relatively fragile, formed by physical behavior. Recent studies have reported that the mechanical properties of the oleogels prepared with EC as a gelling agent are highly associated with the EC mass fraction, the mass fraction of surface-active substances, the molecular weight of EC, the type of oil, the type of surface-active substances, and the ratio of EC and surface-active substances. The solvent-polymer interaction in oleogels is one of the most important variables influencing the structural behavior of oleogel among all the factors. Gravelle, Davidovich-Pinhas, Zetzl, Barbut, and Marangoni (2016) explored the effect of solvent on the large deformation mechanical behavior of EC oleogels and found that the gel strength was positively correlated with solvent polarity, which was attributed to the ability of polar substances in the oil phase to interact with the EC gel network. Due to variations in the polarity and fatty acid content of the liquid oils, using oils produced by distinct methods also resulted in variations in the mechanical behavior of the oleogels. Another study also indicated that the involvement of surfactants could significantly enhance the mechanical strength of EC oleogels (M Davidovich-Pinhas, Barbut, & Marangoni, 2015), but there was a critical concentration beyond which the gel strength gradually decreased as the addition ratio increased. Numerous investigations are currently being conducted to improve the properties of EC oleogel, however, one inevitable limitation is that high temperatures as well as continuous heating continuous heating during the preparation process may initiate oxidation of the oils leading to changes in the dispersant components as well as thermal degradation of the surfactants.

The other polymeric gelators, like hydrophilic polysaccharides, proteins, and their complexes, are typically employed in an indirect method (solvent exchange, emulsion template, or foam template methods) to create oleogels.

1.3.2 Indirect methods

For edible polymers, such as proteins and polysaccharides and their complexes, which cannot be obtained by direct methods for the preparation of oleogels, the construction of oleogels is generally achieved by indirect methods (Figure 4). Briefly, the gelling agent is usually dispersed into water, a polymer network is formed at the oil-water interface or the air-water interface by homogenization, and then the aqueous phase is removed from the system and the liquid oil is immobilized as droplets or adsorbed onto the porous polymer network, resulting in the formation of an oleogel.

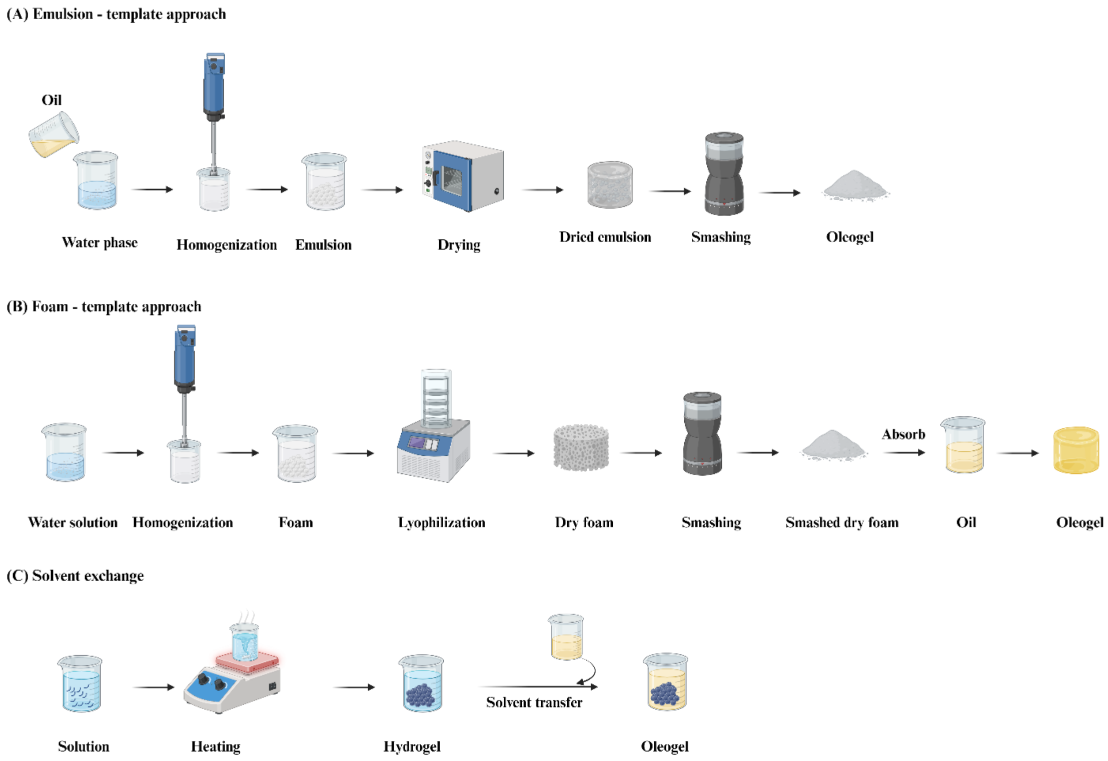

Figure 4. Methodology for the indirect preparation of oleogels.

1.3.2.1 Emulsion-template approach

Hydrocolloids or hydrophilic biopolymers, including proteins, polysaccharides, protein-polysaccharide complexes, or protein-polysaccharide-polyphenol ternary complexes, are the main gelling agents used in the emulsion template approach (Alavi & Ciftci, 2022; Silva, Barrera-Arellano, & Ribeiro, 2021; Tang & Ghosh, 2021). The hydrophilic gelling agent is initially dispersed in the aqueous phase, followed by the liquid oil being homogenized, the polymer will tightly encapsulate oil droplets that are either uniformly dispersed or clustered as isolated droplets in the continuous phase (Wijaya, Sun, Vermeir, Dewettinck, Patel, & Van der Meeren, 2019). A polymeric gel network with oil droplets being tightly encapsulated will be obtained after the removal of the aqueous phase by drying. Finally, oleogel can be obtained by shearing the polymer gel network. The emulsion template technique may be used to generate various oleogel items, including medicine vehicles and cosmetics due to a wide range of sources of gelators. The oleogel exhibits remarkable stability and ease of manipulation which can be achieved by varying the proportion of the water and oil phases, incorporating surfactants, and other techniques to control the viscosity and fluidity of oleogel (M. Espert, Salvador, & Sanz, 2020; Jiang, Liu, Wang, Sui, Zhong, Zhang, et al., 2018). Particularly for some weaker gelators like chitin, its usage as a gelling agent directly distributed in the oil phase for the manufacture of oleogels might result in an unstable system due to the low effectiveness of the components, despite its strong biocompatibility and degradability. Surprisingly, Gao, Zhang, Wu, Chen, Hu, Wang, et al. (2022) discovered that when combined with surfactants (phosphatidylcholine and sorbitan monostearate) as a composite gelling agent and used in the construction of oleogels via emulsion templates approach, the gel strength of oleogel was greatly increased. Similar deficiencies in propyl methyl cellulose, carboxymethyl cellulose, and regenerated cellulose may all be exploited to make emulsion-based oleogels by adding surfactants, which thus increases the oleogels' mechanical strength (Jiang, et al., 2018; I. K. Oh & Lee, 2018).

Emulsion-based oleogels are a well-established method for constructing gel systems with viscoelastic properties, with more reports on the utilization of proteins or polysaccharides to stabilize the water-oil interface for the formation of gel structures, and it is possible to increase the interfacial tension preventing the coalescence of oil droplets, and thus the stability of the oleogel, by adding additional polysaccharides or gelatins, xanthan gums, and other substances to the system (Qiming Wang, Rao, Chen, Lei, Zhao, Li, et al., 2022). Nevertheless, there are drawbacks to the emulsion template approach as well. For example, the emulsion may cause droplet fragmentation or aggregation during the drying process, which alters the internal structure of the gel-causing polymer network after drying.

1.3.2.2 Foam-template approach

The foam template method for the preparation of oleogels is achieved by preparing a dry oil polymer network composed of porous foam to adsorb the liquid oil. Initially, the gelator is dissolved in water, followed by homogenization to form an aqueous foam, and then drying the aqueous foam to remove the aqueous phase forming an aerogel-like dry foams with porous polymer network structures. Foam-based oleogels are finally produced by absorbing liquid oil into the dry polymer network. Initially, Manzocco, Valoppi, Calligaris, Andreatta, Spilimbergo, and Nicoli (2017) discovered that oleogels could be successfully prepared using a foam template approach formed from the edible gel factor carrageenan. The aqueous phase was utilized to dissolve the carrageenan to create a hydrogel, which was subsequently transformed into an alcohol gel and dried using supercritical carbon dioxide to create a foam gel structure. Liquid oil was then adsorbed onto the foam gel to form an oleogel. In 2020, Plazzotta, Calligaris, and Manzocco (2020) also published a study on the production of whey protein foam gels using freeze-drying or supercritical carbon dioxide drying, which absorbed liquid oil to create oleogels. Furthermore, it was discovered that supercritical carbon dioxide drying was superior to the other drying approach as the oleogels that were produced from the dried foam gels exhibited rheological characteristics that were strikingly comparable to those of ordinary fats, as well as being mechanically stronger and more malleable. Q Wang, Espert, Larrea, Quiles, Salvador, and Sanz (2023) successfully prepared HPMC oleogels with promising spreadability and rheological properties with the foam template method. Another study generated alginate/soy protein conjugates using the Maillard reaction, freeze-dried them to produce aerogel templates, and then submerged them in corn oil for six hours to promote the development of oleogels (K. Chen & Zhang, 2020). These studies have demonstrated that the foam template method has the ability to form oleogels and that the structural organization of the foam gel structure, including the number, size, and length of pores, plays a significant role in oil retention and content.

1.3.2.3 Solvent-exchange method

The solvent exchange method was developed to use gel factors that are insoluble in polar solvents (water). Food-grade polymers that are not soluble in water, like alcohol-soluble proteins and polysaccharides, require heating to expose the hydrophobic groups (de Vries, Jansen, van der Linden, & Scholten, 2018). The aggregates are dispersed in the organic solvent to weaken the polarity of the gelators once the network structure has developed in the aqueous phase. The solvent is then eliminated by centrifugation and evaporation and finally re-dispersed from the system to form the oleogel. The solvent exchange has also emerged as a promising method of oleogel fabrication due to the wide range of polarity of the intermediate solvents (Vries, Hendriks, Linden, & Scholten, 2015).

1.4 Application of oleogel in the food industry

Oleogels have received great attention in recent years because of their potential applications in the food, cosmetic, pharmaceutical, and petrochemical industries (Maya Davidovich-Pinhas, 2016). In the cosmetics industry, they can be used to prevent oil spills; in pharmaceuticals and biotechnology, they can be used for microencapsulation or release of hydrophobic natural active substances;

Figure 5. Main application of Oleogels in Food Formulation.

And in the coatings, paints, and plastics industries, they can be used to encapsulate organic solvents due to oleogelation technology. As for the food industry, it is primarily utilized to lower saturated fatty acids, prevent the migration of oils and fats from candy or sandwiches, and serve as a vehicle for the controlled release of nutrients and drug delivery. Although research interest in oleogel has been increasing over the last years, there is less research information on its application in the food industry. The main sectors in which oleogels have been applied include bakery, spreading fats, chocolate, dairy, and meat products. A review of the present state of the art of oleogels application in food is discussed below (Figure 5).

1.4.1 Bakery products

Margarine, shortening, butter, palm oil, and hydrogenated oils are some of the fat sources employed in the formulation of bakery products. In addition to giving the food a longer shelf life, rich texture, creamy flavor, and attractive appearance, these traditional solid fats also can enhance the product's texture making it crispier, crunchier, or fluffier. However, most of these benefits derive from the effects of saturated fatty acids, which should be consumed in low quantities in the human diet. Oleogels have been investigated as a healthy fat source in bakery food. Jang, Bae, Hwang, Lee, and Lee (2015) found that biscuits made with sunflower oleogel prepared with botanical waxes instead of shortening exhibited lower firmness, higher fat spoilage, and higher consumer preference. The fatty acid composition of the products indicated that the unsaturated fatty acid content of the oleogel-made biscuits was around 90%, which was almost twice as high as that of the traditional shortening biscuits. Ye, Li, Lo, Fu, and Cao (2019) used ethyl cellulose with different viscosity characteristics and 1% triglycerides of monostearic acid to prepare oleogels in search of an alternative to shortening that could make stable, soft bread. The findings demonstrated that low-saturated oleogels could completely substitute shortening in bread, with the volume of the product being comparable to that produced by shortening and providing a stable soft texture. Kim, Lim, Lee, Hwang, and Lee (2017) developed Canola oil oleogels using carnauba wax as an oleogelator instead of shortening in cakes to reduce saturated fats. The results showed that parameters such as total pore number were reduced in oleogel-prepared cakes, which showed a more compact solid structure, but the saturated fatty acid content of oleogel-prepared cakes (13.3%) was significantly lower than that of shortening-prepared cakes (74.2%). Besides, (María Espert, Wang, Sanz, & Salvador, 2023) used sunflower oil HPMC oleogel as a fat source in puff pastry, and showed that the texture, hardness, and saturated fat content of croissants made with oleogel were similar to those made with commercial shortening. The croissants' firmness and elasticity were unaffected even after attaining a 100% shortening replacement by oleogel, despite the fact that their texture became chewier and more cohesive as the percentage of oleogel rose.

1.4.2 Fat spreads

Another application of oleogels is to be used simply as spreadable fats, like margarine or butter. Studies have shown that oleogels with characteristics like solid fat structures could be an ideal substitute for conventional spreading fats, with desirable texture, color, and oxidation stability. Yılmaz and Öğütcü (2014) developed olive oil-based oleogels using beeswax and sunflower wax to structure oils. Oleogels made with either 3% (Sunflower Wax) or 7% beeswax exhibited hardness and viscosity values that were comparable to those of commercially available spreads. The potential of using beeswax (BW) and candelilla wax (CDW) as combined gelling agents to stabilize oleogels for the production of margarine was also confirmed in another investigation (Hwang & Winkler-Moser, 2020). Margarine with a CDW-BW concentration of less than 3% achieved a firmness similar to that of commercial spreads. Additionally, oleogels can modify the melting point and stiffness of margarine by adjusting the ratio of the two waxes. However, wax-based oleogels may affect the mouthfeel of margarine and the gel network could reduce fat digestibility (Limpimwong, Kumrungsee, Kato, Yanaka, & Thongngam, 2017).

1.4.3 Chocolate and chocolate spreads

Chocolate and chocolate spreads also contain a high content of saturated fatty acids, since cocoa butter, hydrogenated vegetable oil, or palm oil are all fat sources rich in saturated fatty acids. Alvarez, Cofrades, Espert, Sanz, and Salvador (2021) developed HPMC oleogels using a foam template approach to substitute cocoa butter in chocolate. The results showed that a higher oleogel concentration in the chocolate decreased the stiffness and strength of the fat crystal network of the mixed fat made up of cocoa butter and oleogel, as well as the viscoelasticity and thermal parameters. The saturated fatty acid concentration in chocolate was decreased to 55% when the amount of oleogel replacement was 50%, and the product's quality did not change noticeably from the control. María Espert, Hernández, Sanz, and Salvador (2021) prepared sunflower-HPMC oleogels by using a foam template approach, which allowed them to substitute part of the cocoa butter and greatly reduce the hardness of the chocolate. The HPMC oleogel had no negative impact on the texture and flavor of the chocolate and its characteristics were comparable to those of cocoa butter chocolate, even though the melting temperature of the chocolate was not considerably raised. Apart from the elevated level of saturated fatty acids, another difficulty in the manufacture and storage of chocolate is the low melting point of cocoa butter (34 °C), which can result in alterations to the product's appearance, flavor, and even quality if the manufacturing and storage temperatures are near or surpass this point. In order to overcome this challenge, chocolate manufacturers and researchers have worked rigorously to formulate heat-resistant chocolates (HRCs) that resist melting and deformation. Stortz and Marangoni (2013) employed oleogels based on EC in their chocolate, which significantly increased the thermal stability of the chocolate and could maintain its original shape at temperatures above 40 °C. These efforts to partially replace conventional solid fats have also advanced significantly in formulations for chocolate spreads. Bascuas, Espert, Llorca, Quiles, Salvador, and Hernando (2021) designed a low-fat chocolate spread using XG and HPMC-based oleogels. The physical properties revealed that HPMC/XG oleogels could increase the viscosity of the chocolate spread, and that oleogel substitution was restricted to 50% to maintain the chocolate spread's structural similarities to the shortening control group. Complete substitution led to a significant spreadability increase. The sensory attributes "creamy appearance," "creamy texture," and "cocoa flavor," were found in the control group as well as in the chocolate spreads containing 50% oleogel. In a related study, Roufegarinejad, Habibzadeh Khiabani, Konar, Toofighi, and Rasouli Pirouzian (2024) prepared two oleogel to replace cocoa butter substitutes in chocolate spread using 6% carnauba wax and 2% carnauba wax containing 4% adipic acid. They observed that the hardness of the product was significantly reduced when the rate of oleogel substitution for the CBS in the formulation increased, and the oxidative stability tests showed a positive correlation with the increase in the level of substitution of oleogel for CBS over the course of 90 days of storage.

1.4.4 Dairy products

The application of oleogels in dairy products such as cheese, cream cheese, and ice cream has become a hot research topic in recent years. Numerous studies have shown that the introduction of oleogels can significantly improve the texture as well as the organoleptic properties of the products. In one investigation, a rapeseed oil palm wax oleogel was shown to be an effective substitute for palm oil in producing imitation cheese with a high unsaturated fat content and a low saturated fat level. Moreover, it was discovered that the oleogel offered the cheese samples a more dense, chewy texture. The findings of the rheological characterization indicated that the oleogel cheese's elasticity had enhanced (Moon, Choi, Jeong, Kim, & Lee, 2021). Q Wang, Espert, Hernández, Salvador, and Sanz (2024) conducted a sensory assessment with almost 100 individual participants to assess cream cheese produced with HPMC oleogel. The results demonstrated that the cream cheese was mostly unaffected by the oleogel and that it improved the spreadability of the product, as well as the flavor of the cream cheese, spread cookies, and even the overall assessment ratings of the product. Jing, Chen, Tang, Tao, Huang, Wu, et al. (2022). prepared an oleogel composed of white beeswax and camellia oil, and investigated the feasibility of replacing solid fat in ice cream by comparing the physical properties of oleogel ice cream with camellia oil ice cream and butter ice cream. The results of the overflow rate and melting rate showed that the overflow rate of the oleogel ice cream was higher than the camellia oil ice cream, and the melting rate was lower than that of the butter ice cream. The hardness of the ice cream made from oleogel was moderate, and the time to first drop was significantly longer than ($P < 0.05$) that of camellia oil ice cream and close to that of butter ice cream with no significant difference ($P > 0.05$). The viscosity and fat globule stability of the ice creams were considerably decreased by oleogel, but overall, oleogel-based ice creams had the greatest qualities. Another study found that oleogel ice cream had an enhanced melting time commencement and comparable density and viscosity values to butter ice cream when it was made with sunflower seed oil-based oleogel produced with phytosterols and γ-glutamine instead of whipped cream for low-fat ice cream (Moriano & Alamprese, 2017).

1.4.5 Meat products

The major objective of processed meat products is to lower the amount of fat and cholesterol while also decreasing the amount of saturated fatty acids, which can be accomplished by the incorporation of oleogels. Zetzl, Marangoni, and Barbut (2012) prepared canola oil oleogel using ethyl cellulose instead of animal fats in order to make frankfurter sausage. The results revealed that the chewiness, hardness, and other characteristics of the frankfurter sausage made with oleogel were not significantly different than of the one made with control beef tallow. Similar findings were reported in another study (Stortz, Zetzl, Barbut, Cattaruzza, & Marangoni, 2012), which might be explained by the fact that EC gels can contribute to improving product stability and avoiding oil spills by binding liquid canola oil flow through a three-dimensional network structure. Apart from EC, animal fats of frankfurter sausages can also be replaced with oleogels made from phytosterols and γ-glutamate. Comprehensive textural and sensory evaluations revealed that there was no significant difference in any parameters between the sausages prepared with oleogel and the control group, as well as the acceptability of the product. The aforementioned findings suggest that animal saturated fats in frankfurters may be substituted with oleogels formed from phytosterols and γ-glutamine, without affecting the frankfurters' physicochemical and sensory characteristics (Panagiotopoulou, Moschakis, & Katsanidis, 2016).

The researchers discovered that soy protein oleogels prepared with the emulsion template approach may be employed to make healthier venison salchichon in place of regular pork meat (Utrilla, Ruiz, & Soriano, 2014). Consumer acceptance of all sausage samples tested was determined, with the sample containing up to 25% of the oleogel receiving the highest rating. Furthermore, the physicochemical properties (pH, water activity, and moisture losses) and instrumental color evaluation during the ripening process of the oleogel salchichon were comparable with those made with venison and pork meat. In comparison to the traditional salchichon composition, the oleic acid level of the consumer-accepted oleogel sausage was twice as high as that of the traditional salchichon sausage.

Oleogels have shown similarly encouraging progress in the manufacture of meat patties as they have in sausages. Equimolar amounts of γ-oryzanol and β-sitosterol were utilized to generate flaxseed oil oleogels for the substitution of pig patties fat. The hardness and chewiness revealed that the textures of hamburgers formulated with 25% oleogel and pork subcutaneous fat were comparable with those of commercial hamburgers (Martins, Lorenzo, Franco, Vicente, Cunha, Pastrana, et al., 2019). Similar results were shown in another research that used HPMC oleogel to partially substitute beef fat, resulting in patties with a much lower saturated fatty acid content of 15% and acceptable by consumers (I. Oh, Lee, Lee, & Lee, 2019).

In summary, the application of oleogels in the food industry is still in its early stages but has great potential, although oleogels have been attempted to be applied in different food systems, in general, the application of oleogels in aerated bakery products is still scarce, and further related studies are needed.

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2. OBJECTIVES

Although oleogel has been attempted to be applied in different food systems, overall, the application of oleogel in food products products is still scarce. Outstanding limitations of the application of oleogels in food are, first, the complex methodologies available to obtain oleogels, and second, the fact that the available oleagelators are not well-known additives to the consumer. Herin, the general objective of this PhD dissertation is to investigate the feasibility of the cellulose ethers, hydroxypropyl methylcellulose (HPMC), and methylcellulose (MC), to act as oleogelators in sunflower oil oleogels, and to investigate their application in two different food applications: 1) cream cheese, a spreadable and creamy semisolid food and 2) croissant, as example of puff pastry food.

For this purpose, the following partial objectives are proposed:

- To evaluate the effect of the obtention methodology, type of cellulose ether, and initial oil content in the oleogel texture, rheological, microstructure, and oil retention properties.
- To determine the oleogel structure and oxidative stability during storage.
- To study the suitability of HPMC oleogels and HPMC emulsions as fat sources in the manufacturing of cream cheese and to evaluate texture, rheological, and sensory properties.
- To investigate the effect of the oleogel obtention methodology and level of fat replacement on the texture and rheological properties of puff pastry dough.
- To determine the effect of the level of shortening replacement by oleogel in the croissant texture and sensory properties.
- To investigate the effect of the oleogel obtention methodology on the appearance, texture, and sensory properties of croissants.

3. RESULTS

The doctoral thesis is structured in three chapters. The first one focuses on the structure, properties and oxidative stability of cellulose ether oleogels, the second on the application of oleogels in cream cheese and the third on the application of oleogels in puff pastry. Then, published research articles on the topics of the three chapters are shown. The present doctoral thesis has resulted in 6 articles published or to be published in the following journals. This is followed by the dissertation summary and discussion section, in which the important aspects of this research are presented and summarized. Finally, the main conclusions of the dissertation are listed.

Chapter 1

- **Qi Wang**, María Espert, Virginia Larrea, Amparo Quiles, Ana Salvador & Teresa Sanz. (2023). Comparison of different indirect approaches to design edible oleogels based on cellulose ethers. *Food Hydrocolloids*, 134: 108007. https://doi.org/10.1016/j.foodhyd.2022.108007. *Impact factor: 11.0.*

- **Qi Wang**, María Espert, Mónica Flores, Teresa Sanz & Ana Salvador. (2024). Physicochemical stability of sunflower oil-based oleogels prepared by different indirect oleogelation approaches. *Food Hydrocolloids*. (Submitted). *Impact factor: 11.0.*

Chapter 2

- **Qi Wang**, María Espert, María Jesús Hernández, Ana Salvador & Teresa Sanz. (2024). Effect of cellulose ether emulsion and oleogel as healthy fat alternatives in cream cheese. Linear and nonlinear rheology, texture, and sensory properties. *Food Hydrocolloids*, 150: 109740. https://doi.org/10.1016/j.foodhyd.2024.109740. *Impact factor: 11.0.*

Chapter 3

- María Espert, **Qi Wang**, Teresa Sanz, & Ana Salvador. (2023). Sunflower oil-based oleogel as fat replacer in croissants: textural and sensory characterization. *Food Bioprocess Technology*, 16, 1943–1952. https://doi.org/10.1007/s11947-023-03029-w. *Impact factor:5.3.*

- **Qi Wang**, María Espert, Ana Salvador & Teresa Sanz. (2023). Shortening replacement by emulsion and foam template hydroxypropyl methylcellulose (HPMC)-based oleogels in puff pastry dough. Rheological and texture properties. *Current Research in Food Science,* 7, 100558. https://doi.org/10.1016/j.crfs.2023.100558. *Impact factor:6.2.*

- **Qi Wang**, Silvia Bobadilla, María Espert, Teresa Sanz, & Ana Salvador. (2024). Shortening replacement by emulsion and foam template hydroxypropyl methylcellulose (HPMC)-based oleogels in puff pastry. Texture and sensory properties. *Food Hydrocolloids*, 153, 109936. https://doi.org/10.1016/j.foodhyd.2024.109936. *Impact factor: 11.0.*

Chapter 1

Structure, properties, and oxidative stability of cellulose ether oleogels

Comparison of different indirect approaches to design edible oleogels based on cellulose ethers

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Abstract

Growing public concern about the adverse health effects of overconsumption of saturated fat has contributed to the rising research interest in the field of using healthy oils to construct edible structured oils (oloegels) as fat-based alternatives. In this study, two indirect methodologies (the emulsion template approach and the foam template approach) were investigated to prepare oleogels with hydroxypropyl methylcellulose and methylcellulose as gelling agents at three different oil concentrations. Microstructure, texture, rheology, and oil retention capacity were measured to evaluate the structural and physicochemical properties of oleogels. Results showed that the emulsion-based oleogel effectively inhibited the aggregation of droplets. The dry emulsion showed independent droplets and an oil retention capacity of 100%. In foam-type oleogels, the oil retention rate was negatively correlated with the oil content. The oleogels prepared by both methods have excellent mechanical properties and gel strength, with a predominance of elastic versus viscous behavior. Hydroxypropyl methylcellulose and methylcellulose had different degrees of influence on the structure and mechanical properties of the two oleogels. The results of this paper provide guidance for the development and application of cellulose-based oleogels as healthy alternatives to saturated fat.

Keywords

Foam-template approach; emulsion-template approach; rheology; microstructure; oleogel.

1. Introduction

Solid fats such as shortenings, butter, palm fat, cocoa butter, etc., are widely used in bakery products, chocolate, spread sauces, quick-frozen food, snacks, and other industrial foods due to their ability to endow technological and organoleptic properties (flavor, taste, texture, etc.) (Feichtinger & Scholten, 2020; Gómez-Estaca et al., 2019; Naeli, Milani, Farmani, & Zargaraan, 2022). Solid fat functional properties depend to a large extent on the crystal network structure of the high melting point components in the fat used. Without saturated fatty acid (SFA), these fats would not be able to provide the required structure and texture. However, excessive intake of saturated fat has potential risks for cardiovascular disease (Adili, Roufegarinejad, Tabibiazar, Hamishehkar, & Alizadeh, 2020), diabetes (Oh, Lee, Lee, & Lee, 2019), or metabolic syndrome (Bascuas et al., 2021), which seriously endangers human health.

An alternative to conventional solid fat is oleogelation. Oleogelation confers solid properties to liquid oil and requires the use of gelators or structurants to form a three-dimensional network polymeric structure to trap the liquid oil (Davidovich-Pinhas, Barbut, & Marangoni, 2015; Li et al., 2021). In recent years, the development of edible oleogels based on polymers has been flourishing. Initially, researchers focused on small fat-soluble molecules, e.g., waxes (Yılmaz & Öğütcü, 2015), monoglycerides, diglycerides, long-chain fatty acids (Martins, Vicente, Cunha, & Cerqueira, 2018) or long-chain fatty alcohols (Lupi et al., 2013). Later, the interests gradually shifted from small polymers to edible natural polymers being developed due to their more plentiful and economical availability (Matalanis & McClements, 2013), such as proteins (de Vries, Gomez, van der Linden, & Scholten, 2017; de Vries, Jansen, van der Linden, &

Scholten, 2018; Mohanan, Tang, Nickerson, & Ghosh, 2020), polysaccharides (Patel et al., 2014), hydroxypropyl methylcellulose (HPMC), and methylcellulose (MC) (Patel & Dewettinck, 2015; Zetzl et al., 2014).

The methodologies to prepare oleogels with polysaccharides as structure agents required indirect approaches, as the oil cannot directly interact with the polysaccharide. In the direct method, the gelling agent is directly mixed with oil to form a gel at the appropriate temperature (Shi et al., 2021). The emulsion template approach and the foam template approach are two of the indirect methodologies available. The emulsion template approach involves forming an emulsion and, subsequently water removal to form the oleogel. In the foam template approach (Patel, Schatteman, Lesaffer, and Dewettinck, 2013) the hydrocolloid is hydrated in water to develop its structure, lyophilized, and finally, the oil is incorporated in the dry foam to obtain the oleogel.

Abdollahi, Goli, and Soltanizadeh (2019) prepared oleogels by foam template method using gelatin and xanthan gum biopolymers with high gel strength, good thixotropy, and thermal stability. In contrast, Pan et al. (2021) required the addition of proanthocyanidins to stabilize the emulsion and prepare highly stable oleogels. Patel et al. (2015) compared wax crystals, hydrophilic cellulose derivatives, and gelled water droplets as structurants to prepare oleogels, exploring the impact of different structurants and preparation methods on the structural properties, functions, and limitations of oleogels. In other studies, different surfactants were also added to gelators to improve the gel strength of oleogels. However, in food development, the amount and type of gelling agents should be as little as possible to avoid health concerns from consumers. Hence, selecting appropriate gelling agents and a simple methodology to prepare oleogels is the most required.

In our previous work, oleogels with favorable mechanical properties and stable structure using MC or HPMC without additional thickeners by an emulsion template method have been successfully prepared and applied as conventional fat replacers in chocolate and baked pasta products (Espert, Hernández, Sanz, & Salvador, 2021; Espert, Salvador, & Sanz, 2020; Espert, Sanz, & Salvador, 2021). The current work aims to compare the differences in properties (microstructure, rheological properties, texture, and oil binding capacity) between the emulsion template and foam template approaches for the preparation of oleogels with the purpose of providing a basic guide for further expansion of emulsion-based and foam-based oleogels for applications in the food industry. Methylcellulose and hydroxypropyl methylcellulose ethers were used as gelators and the effect of three different oil concentrations on the oleogel structure and properties was also studied.

2. Materials and methods

Methylcellulose (A4M) (30% methoxyl content) and hydroxypropyl methylcellulose (F4M) (29% methoxyl, 6.8% hydroxypropyl) were kindly supplied by The Dow Chemical Company (Bomlitz, Germany). Sunflower oil was purchased from Deoleo S.A. (Córdoba, Spain).

2.1. Oleogel preparation

1)Emulsion template approach. The oleogel obtained by the emulsion template was prepared as previously described (Espert et al., 2020). Three emulsions with different oil content (18%, 33% and 47%

w/w), each with a cellulose concentration of 1.5% (w/w), were prepared. Briefly, the cellulose was added to the oil and dispersed via a Heidolph stirrer (RZR 1) (Heidolph Instruments, Germany) for 2 min at low speed (200 rpm). Then water at 10 °C was added and homogenized by a high-speed disperser (Ultraturrax T-18, IKA, Germany) for 1 min at 16500 rpm. After homogeneization, the color of the mixture turned into milky white, which means the emulsion was prepared successfully. The emulsion was collected and placed in an aluminum mold (245 × 140 mm) and heated into a forced-convection oven (Binder GmbH, Germany) at 60 °C for 48 h to remove moisture until the final humidity was below 0.5% (w/w). Finally, the dried samples with a final oil concentration of 92%, 96%, and 97% (w/w) were sheared with a high-speed dispersing machine (Moulinex, Groupe SEB, France) to form the oleogel.

2) Foam template approach. The method referred to by Oh and Lee (2018) with slight modifications was employed. 6 g cellulose was dissolved in 94 g hot water (85°C), and then 200 g cool water (below 10 °C) was added and the mixture was dispersed with a stirrer (RZR 1, Heidolph Instruments, Germany) at 400 rpm for 10 min. The resulting solution was homogenized using a high-speed disperser (Ultraturrax T-18, IKA, Germany) at 16500 rpm for 2 min, and finally, the sample was lyophilized using a laboratory freeze dryer (Lyobeta 6 PL, Telstar, Spain). The freeze-dried sample was minced with a grinding machine. Finally, the required oil to achieve 92%, 96%, and 97% oil concentration in the final oleogels was added slowly to the freeze-dried samples and stirred until a uniform oleogel was formed.

2.2. Visual appearance

Photos of the different oleogels were taken by a digital camera with a 1x objective to compare their appearance and morphological characteristics.

2.3. Microstructure

The microstructure of the samples with the highest oil concentration (96%) was studied by light microscopy (LM) using a Nikon Eclipse 80i light microscope (Nikon Co., Ltd., Tokyo, Japan) with a built-in camera (Exwave HAD, model No. DXC-190, Sony Electronics Inc., Park Ridge, New Jersey, USA. UU.). The samples were cut with a stainless-steel cutter to obtain thick sections that were placed on a glass slide for microstructure observation. The images were captured with x4 magnification and stored at 1,280 × 1,024 pixels using the microscope software (NIS-Elements M, Version 4.0, Nikon, Tokyo, Japan).

For the scanning electron microscopy (SEM), both the foam and the emulsions oleogels were gold coated using POLARON E6100 Equipment (10^{-4} bar, 20 mA, 80 s) and observed in a Jeol JSM 6300 Scanning Electron Microscope at 15 kV and a working distance of 15 mm with x50 magnification.

2.4. Determination of oil binding capacity

10 g oleogel was placed on a filter paper. The total mass of the sample and filter paper was recorded after 24 h. The oil-binding capacity (OBC) of oleogel after 24 h was calculated from the following formula:

$$OBC(\%) = 100\% - \frac{W_t - W_0}{F_{oleogel}}(\%)$$

Where W_t stands for the mass of the filter and sample after 24 h, W_0 stands for the initial weight of the filter, and $F_{oleogel}$ stands for the weight of oil in oleogel.

2.5. Rheological measurements

The rheological measurements of the oleogels were determined on a control stress rheometer model AR-G2 (TA Instruments, Montreal, QC, Canada) equipped with a 40 mm hatch parallel plate geometry and a Peltier temperature control system. Stress and frequency tests were carried out at 20 °C. Oscillatory stress sweeps from 0.1 to 1000 Pa were performed at a constant frequency of 1 Hz to determine the linear viscoelastic region. Frequency sweeps (from 0.1-100 Hz) and temperature sweeps (from 20-90 °C, 1 Hz) were conducted in the linear viscoelastic region. Rheological data were recorded with TRIOS Software (TA Instruments, Montreal, QC, Canada). Each assay was carried out twice.

2.6. Texture analysis

Texture analysis of oleogels was evaluated with a texture analyzer (TA. XT. Plus texture analyzer, Stable Micro Systems Ltd. Surrey, UK). Oleogel samples were placed into a 2*2*2 cm cube mold and a cylindrical probe with a diameter of 1 cm was selected to penetrate the sample 6 mm at a speed of 1 mm/s. Hardness was analyzed by Exponent software (version 6.1.4.0, Stable Micro Systems Ltd.) and calculated as the maximum force obtained at 6 mm penetration.

2.7. Statistical analysis

Each experiment was repeated three times, and all results were analyzed by One-way ANOVA in SPSS 8.5 (OriginLab Corporation, Northampton, MA, USA). Tukey test was used to determine the effect of the increase of temperature among values ($p<0.05$) and data were represented as mean ± deviation (SD).

3 Results and discussion

3.1 Appearance

Figure 1 shows the appearance of emulsion-based and foam-based oleogels obtained with the two types of cellulose and three different oil contents. The appearance of the emulsion-based oleogels was not very much influenced by the type of cellulose and the oil contents, all the oleogels appeared as white granular crystalline solids (Fig.1A, 1B). The A4M sample showed some adhesion of the oleogel particles at the higher oil concentration (Fig. 1B). In the foam-based oleogels differences were found depending on the oil concentration and type of cellulose. At 92% oil content (Fig. 1C, 1D) oleogels showed white aggregated clusters, and fragments of cellulose could still be observed on the surface after fragmentation, implying that these points are not fully saturated with oil. When the oil content increased to 96%, the A4M foam-based oleogels appeared as a yellowish semi-solid gel, while the surface of the F4M oleogel was smoother and more elastic and the oil was strongly absorbed in the gel network, reflecting a more suitable spatial conformation formed by the broken cellulose fragments after oil adsorption. At 97% of oil content, F4M oleogel showed obvious oil leakage (Fig.1D), indicating that the maximum oil adsorption capacity of F4M oleogel was about 95%, which was slightly weaker than that of the A4M sample.

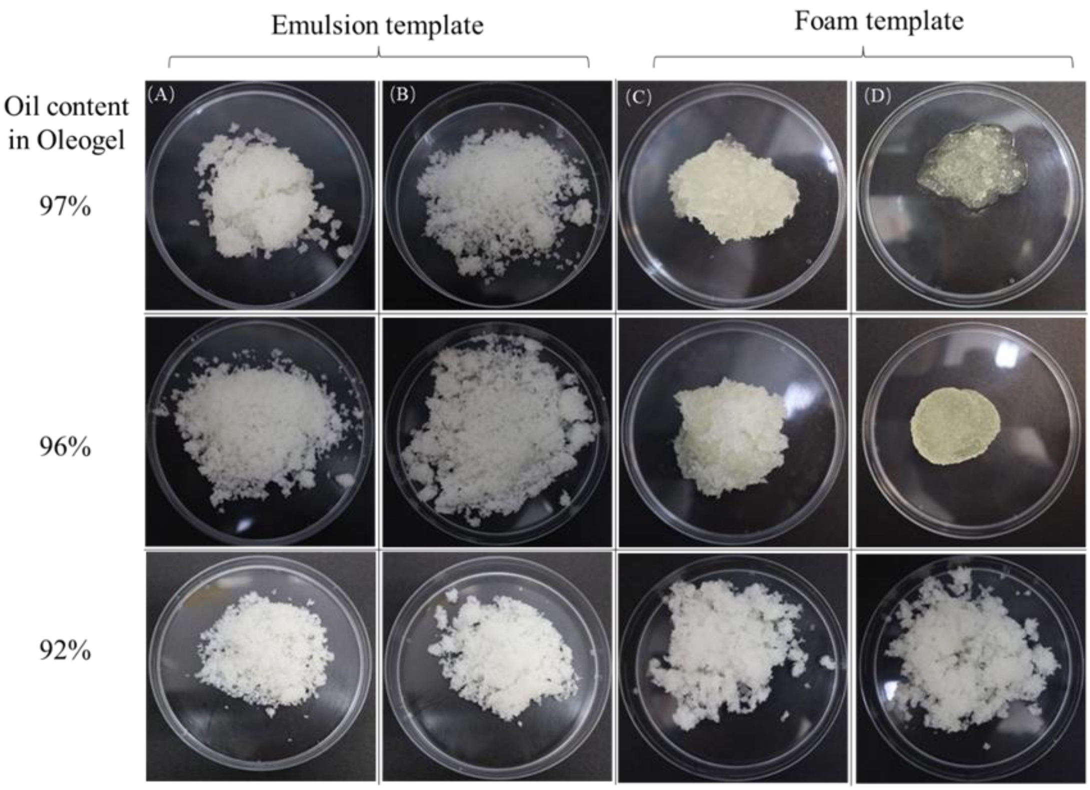

Figure 1. Appearance of cellulose-based oleogel obtained by the emulsion and foam template approaches. (A) A4M cellulose; (B) F4M cellulose; (C) A4M cellulose; (D) F4M cellulose.

3.2 Microstructure

A different microstructure was found among the A4M and F4M in the dry product obtained by the emulsion template and foam template approach with optical microscopy and SEM. In Fig. 2A, it can be seen that in the A4M dry product (with 96% oil content) droplets showed aggregation and an increase in droplet size (up to 50-200 µm in diameter), but exhibited relatively intact spherical droplet morphology and an un-flattened network spherical surface. In contrast, the structure of the F4M sample showed large-scale aggregation and flocculation (Fig. 2B) during the drying process, as well as the inability to observe a normal droplet structure. This may be related to F4M containing a considerable portion of the hydrophilic group itself, where the lipophilic segments of F4M chains were adsorbed on the surface of oil droplets during the formation of emulsions, while the hydrophilic segments stretched into the aqueous phase and formed trailing tails or loops, which makes the F4M emulsion droplet structure more vulnerable to losing stability in drying processes compared to the lipophilic A4M (Li, Al-Assaf, Fang, & Phillips, 2013; Wollenweber, Makievski, Miller, & Daniels, 2000). However, F4M with a rigid backbone structure was not easily bent and did not easily occupy enough interfacial area, resulting in only a few F4M chain segments being adsorbed on the surface of oil droplets (Meng, Qi, Guo, Wang, & Liu, 2018), so the emulsion droplet structure formed was easier to aggregation during the thermal drying process. Fig. 2C and 2D show the microstructure of the two cellulose dry foam samples, which are completely different from the emulsions, and a porous fibrous polymer network structure with inhomogeneity can be clearly observed in both samples. The difference is that the network structure of A4M is densified (Fig. 2C) and partially stacks are connected in a lamellar pattern, while the network structure of F4M foam is relatively sparse with larger pores and thicker mesh fibers.

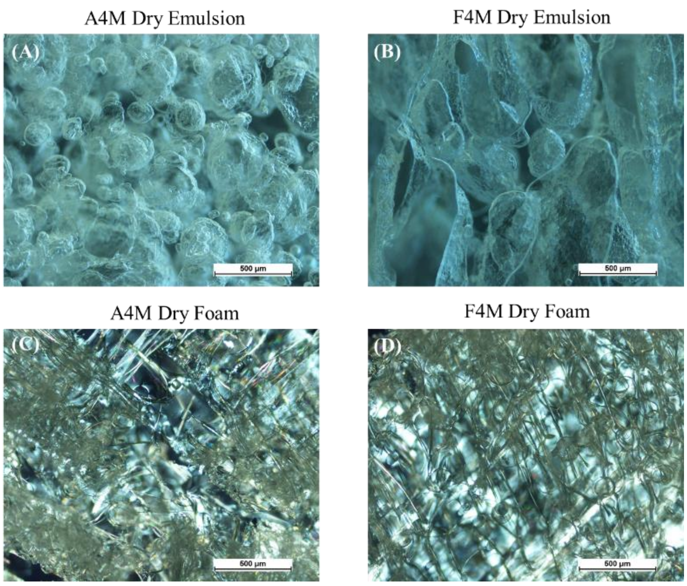

Figure 2. Light microscopy of the different cellulose-based dry products with 97% oil content.

SEM was employed to further analyze the effect of the preparation method and cellulose type on the microstructure of the oleogels. Fig. 3A showed the microstructure of the A4M dry product, with different-sized oil droplets distributed and captured in the polymer network. The irregular droplet structure was also observed for the F4M sample at high magnification (Fig. 3B), but some of the defined edge regions between the oil droplets were lost, indicating that coalescence occurred between the oil droplets during drying, suggesting that F4M is less resistant to thermal drying, causing a poorly homogeneous and unstructured oleogel (Bascuas, Hernando, Moraga, & Quiles, 2020a). The SEM of the two foam-based samples were completely different, A4M formed a complete paper-like fragment instead of a gridded structure containing porosity (Fig. 3C), in accordance with Patel, Schatteman, Lesaffer, & Dewettinck, (2013). They assumed that it was the emergence of Ostwald maturation and coalescence destabilization of A4M during the lyophilization process leading to inhomogeneous pore distribution and size and the formation of a needle-like structure. It is remarkable that the foam prepared with F4M with a porous sponge structure is clearly visible in each layer of the network structure and stacked into a three-dimensional structure with a relatively uniform size and distribution of pores (Fig. 3D). A similar structure was observed by Tanti, Barbut, & Marangoni (2016b) exploring the effect of different drying methods on HPMC and MC oleogels as stabilizers in peanut butter. During the preparation of the oleogels the dry foam was broken, but the network of small lamellar polymers remained and adsorbed liquid oils in a physical means thus forming a new gel network, meanwhile, the sophisticated three-dimensional structure provides a large surface area for the polymer/oil combination.

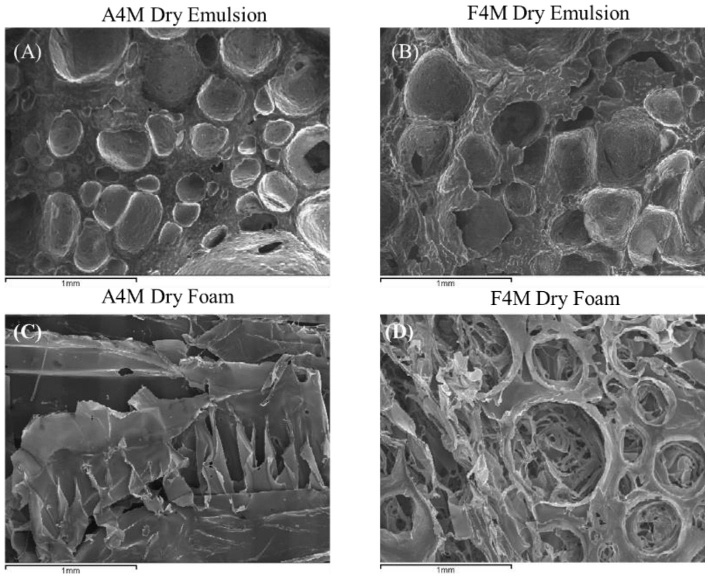

Figure 3. SEM images of the different cellulose-based samples.

3.3 Oil binding capacity

Oil binding capacity (OBC) reflects the ability of the oleogel to trap liquid oil, therefore is an essential parameter for assessing the physical stability of the oleogel network. Figure 4 shows the OBC of the foam template oleogels after 24 h. The increase in oil content was negatively correlated with OBC. The OBC of the A4M oleogels decreased from 99.9% to 91% when the oil content increased from 92% to 97%. In F4M oleogels the OBC decreased from 100% to 84%. The OBC results indicate that 92% oil content is the maximum oil percentage that can be retained in the foam oleogel structure. For higher oil concentrations (96% and 97%) the adsorption capacity of the foam oleogel is fulfilled and the excess oil is released. Thus, the maximum oil adsorption is reached at 92% oil. This phenomenon can also be observed in the appearance of the foam oleogels (Fig. 1) where a yellow color is observed at the higher oil concentrations (96% and 97%), while a white snowflake shape without the yellow color is observed at the optimum 92% oil concentration. Overall, the oil adsorption capacity of A4M foam-based oleogels is significantly higher than that of F4M, which indicates a more compact network structure in A4M oleogels with a stronger restraining force to prevent oil leakage in comparison to F4M. Jiang, Du, Li, Liu, and Meng (2021) suggested that the oil adsorption capacity of HPMC foam-based oleogels is mainly determined by the capillary forces that make up the functional network structure, and the correlation between capillary force strength and pore size clearly affects spontaneous absorption because the strength is inversely proportional to pore size (Mosquera, Rivas, Prieto, & Silva, 2000).

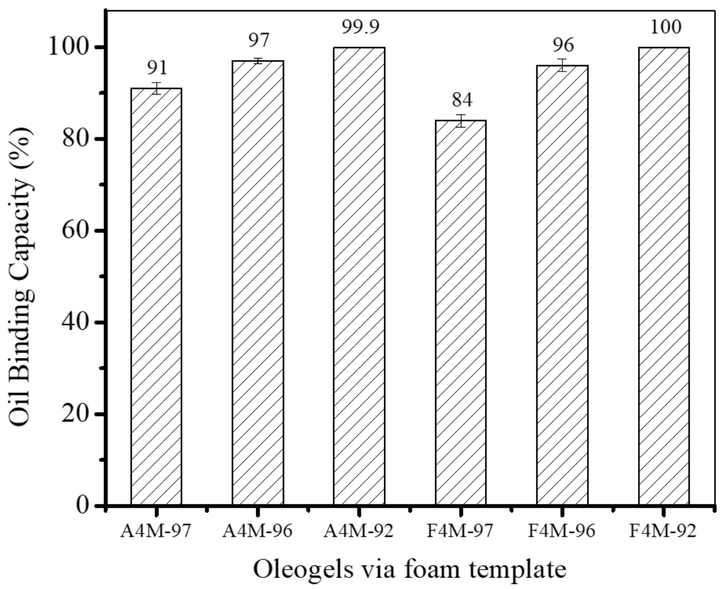

Figure 4. Effect of cellulose type and oil content in the oil binding capacity (OBC) of foam template oleogels; A4M and F4M refer to the type of cellulose, and numbers 92, 95 and 96 refer to oleogel oil concentration.

The OBC of all the emulsion template oleogels was 100% (data not shown in Figure 4). The differences in the OBC between emulsion and foam template methods are in agreement with their appearance in Figure 1. In the emulsion template oleogels a white powder is obtained at all oil concentrations, although for 92% the white color is more intense. Bascuas, Salvador, Hernando, & Quiles (2020b) obtained oil loss percentages of 10%

in emulsion template oleogels using hydroxypropyl methylcellulose (HPMC) and xanthan gum (XG) as structuring agents. The higher OBC of emulsion template oleogels of the present work can be related to the different methodologies employed to obtain the initial emulsion. Meng, Qi, Guo, Wang, & Liu (2018) employed different cellulose to prepare emulsion-based oleogels with oil loss even up to 19%.

3.4. Rheological measurement

3.4.1 Stress sweep

The stress sweeps corresponding to the different oleogels are shown in Figure 5. In all the oleogels, G' values were over 10 times higher than G'' values, indicating the predominant solid-liked behavior of the oleogels. The linear viscoelastic region (LVR) was negatively correlated with the oil content, which indicates that the structural resistance to the applied stress of the oleogels with 92.3% (w/w) oil content is higher than 95.6% and 96.9%, indicating a stabilized structure with higher resistance to the applied stress at the lowest oil content. Also, in all the oleogels G' and G'' values gradually decrease with the increase of oil concentration. The increased weakness of the oleogel structure with the increase in oil content might be associated with the decrease in the relative concentration of the cellulose ether, leading to a weaker network structure (Oh & Lee, 2018). F4M oleogel showed higher structural resistance in comparison to A4M, which could be explained due to the superior interfacial properties of HPMC (F4M oleogel) which will result in more homogenous droplets and a stronger gel network structure.

In comparison to the emulsion template oleogels, the LVR of the foam template oleogels was slightly greater indicating the highest strength of the foam-based oleogels. The lowest values of the viscoelastic functions and the lowest LVR were found in the A4M emulsion oleogel with the highest oil content (96%).

For oil concentrations lower than 96%, the difference in G' value between AFM and F4M samples was not significant. However, when the oil content increased to 96%, the G' value of A4M was much higher ($8x10^4$ Pa) than that of F4M ($5x10^4$ Pa), which is associated with a higher oil retention rate of A4M. The highest strength and oil binding capacity of the oleogels obtained with the A4M could be associated with its higher hydrophobic properties in comparison to F4M. This is attributed to the fact

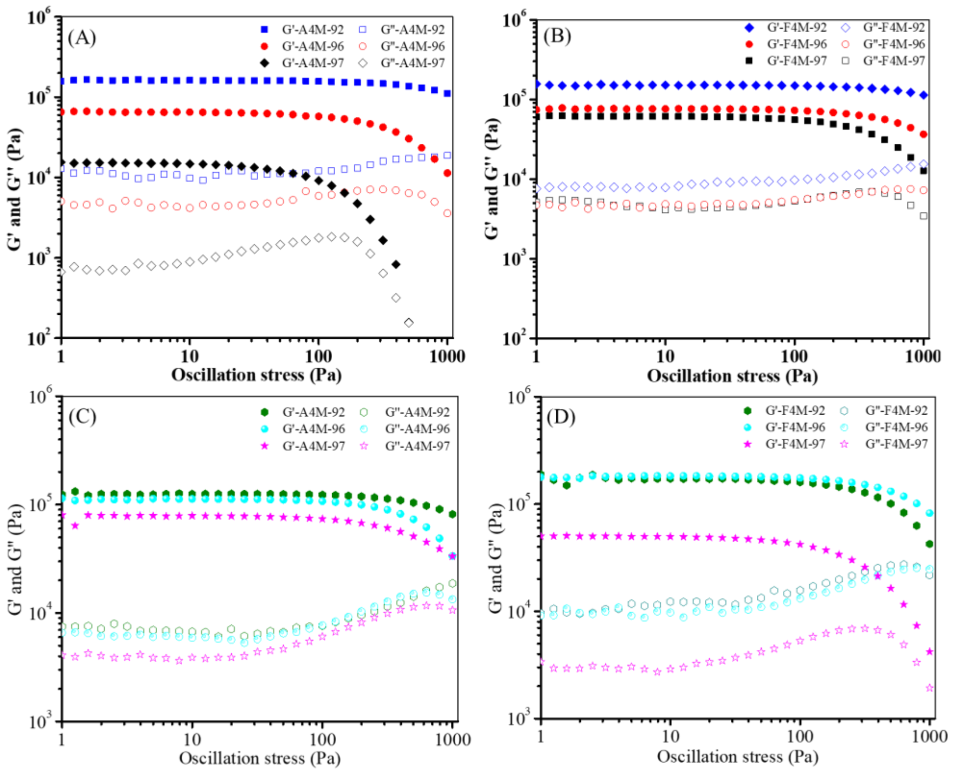

Figure 5. Effect of cellulose type and oil content in the stress sweeps. (A) and (B) are the emulsion template oleogels corresponding to A4M and F4M cellulose, respectively; (C) and (D) are the foam template oleogels corresponding to A4M and F4M cellulose oleogels, respectively.

that MC forms a separate polymer network after lyophilization treatment, which can be verified in Fig. 3. The polymer networks further formed the independent polymer flake networks after absorbing oils (Tanti, Barbut, & Marangoni, 2016b), resulting in a more complex three-dimensional network and having a higher gel stability than physically crushed emulsion-based oleogels. Surprisingly, the weakening effect produced by high oil content on gel strength was more noticeable in F4M foam-based oleogels, although at lower oil concentrations it showed high gel strength (Fig 5D). When the oil content increased to 97%, G' values of A4M foam-based oleogel were much higher than that of F4M, which is associated with its higher hydrophobic properties.

3.4.2 Frequency sweep

The frequency dependence of G' and G" of the different oleogels are shown in Figure 6. G' was higher than G" in all the frequency sweeps studied. The slope of the trend line of G' versus frequency was close to 0 in all the systems, indicating a low-frequency dependence associated with high gel strength. Similar results were obtained by Tanti, Barbut, & Marangoni (2016a) using hydroxypropyl methylcellulose and methylcellulose to prepare oleogels to replace shortening in sandwich cream via foam template method, where HPMC oleogels showed higher gel strength than MC oleogels. Similarly to the results found in the stress sweep tests, the overall gel strength of foam-based oleogels was generally higher than that of emulsion-based, especially at the highest oil concentration.

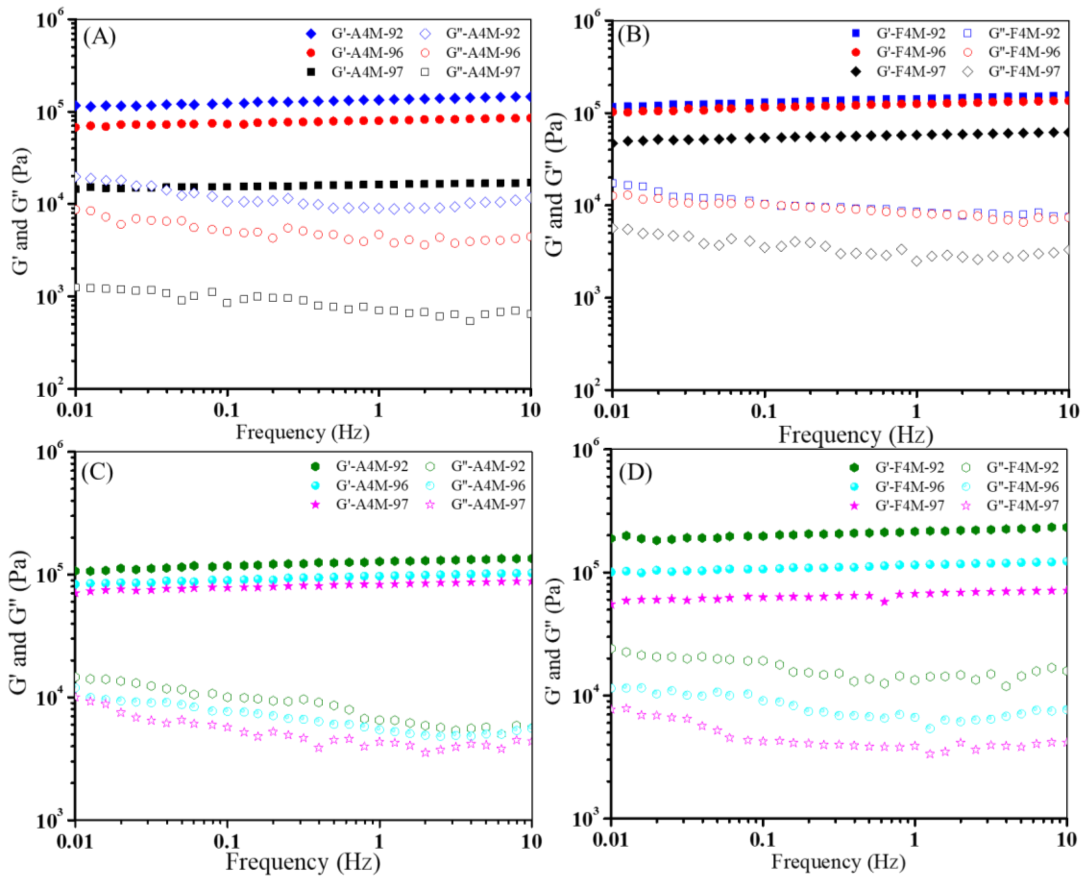

Figure 6. Effect of cellulose type and oil content in the frequency sweeps. (A) and (B) are emulsion template oleogels prepared with A4M and F4M cellulose; (C) and (D) are foam template oleogels prepared with A4M and F4M cellulose.

The dynamic moduli of all samples at 1 Hz were statistically compared (Table 1). In general foam-based oleogels showed significantly higher values of G' and G" than emulsion-template oleogels at the same oil content. Foam-template oleogels, F4M at 92% oil had the highest G' value (2.3×10^5 Pa). Increasing the oil content resulted in a significant decrease in both G' and G". This result is more noticeable in emulsion-based oleogels, especially in A4M with 97% oil. Tan δ informs about viscoelasticity which is related to the strength of the internal structure of the gel. The higher value of tan δ (closer to 1) indicated a weaker internal solution structure (Bascuas et al., 2021). All the oleogels showed tan δ values lower than 0.1, with no significant differences among them. These lower values of tan δ

Table 1. Viscoelastic rheological parameters (at 1 Hz) of the different oleogels.

Samples	Emulsion template approach						Foam template approach					
	A4M			F4M			A4M			F4M		
	92%	96%	97%	92%	96%	97%	92%	96%	97%	92%	96%	97%
G' (Pa)	123571 ± 11499^{b}	71891 ± 8782^{d}	14869 ± 1606^{f}	133794 ± 9081^{b}	124526 ± 691^{b}	59777 ± 1868^{e}	149882 ± 3246^{b}	112254 ± 14656^{c}	83165 ± 3453^{d}	230177± 16415^{a}	123572 ± 7428^{b}	73936 ± 6593^{d}
G''(Pa)	8133 ± 484^{b}	3576 ± 210^{e}	758 ± 60^{g}	8543 ± 458^{b}	7760 ± 38^{b}	3566 ± 102^{f}	8964 ± 192^{b}	5476 ± 414^{c}	4297 ± 42^{d}	11547 ± 517^{a}	5981 ± 106^{c}	3631 ± 181^{e}
Tan δ	0.07 ± 0.02^{a}	0.05 ± 0.01^{a}	0.05 ± 0.02^{a}	0.07 ± 0.03^{a}	0.06 ± 0.02^{a}	0.06 ± 0.02^{a}	0.06 ± 0.03^{a}	0.05 ± 0.03^{c}	0.05 ± 0.01^{a}	0.05± 0.03^{a}	0.05 ± 0.01^{a}	0.05± 0.03^{a}

a-g Means with the different letters for each raw indicate a significant difference between oleogels ($p < 0.05$).

indicate a great predominancy of the elastic properties versus the viscous properties reflecting the predominant solid-like structure of the oleogels.

3.4.3 Temperature sweep

The effect of the increase in temperature from 20 to 90 ºC on the oleogel viscoelastic properties was investigated to determine the temperature sensitivity of the oleogel structure (Figure 7). In the emulsion-based oleogels, values of G' and G" showed only a very slight decrease with the increase in temperature indicating high thermal stability. The foam template oleogels also showed very good thermal stability, although slightly lower than the emulsion template oleogels. In the foam template oleogels at a temperature higher than 50 ºC, the G' values showed a slight decrease, which was a result of the gel network structure melting and collapsing upon heating, leading to a decrease in gel strength.

The excellent thermal stability of cellulose oleogels prepared both by the emulsion and the foam template approaches is a positive advantage in terms of their future application as fat replacers in food applications. Previous studies in other oleogels types revealed a lack of thermal stability. For example, oleogels prepared using beeswax as a gelling agent showed significant gel structure damage (sharp decrease in G' value) at 50 °C, which was caused by the melting of the gelling agent crystals (Gómez-Estaca, et al). Also, oleogels prepared using ethylcellulose or waxes were thermally reversible (Gómez-Estaca et al., 2019; Rodríguez-Hernández, Pérez-Martínez, Gallegos-Infante, Toro-Vazquez, & Ornelas-Paz, 2021; Tavernier, Doan, Van der Meeren, Heyman, & Dewettinck, 2018). The thermal results obtained revealed that the cellulose ether oleogels obtained by both the foam and the emulsion template approaches would be a promising option when thermal stability is a requirement.

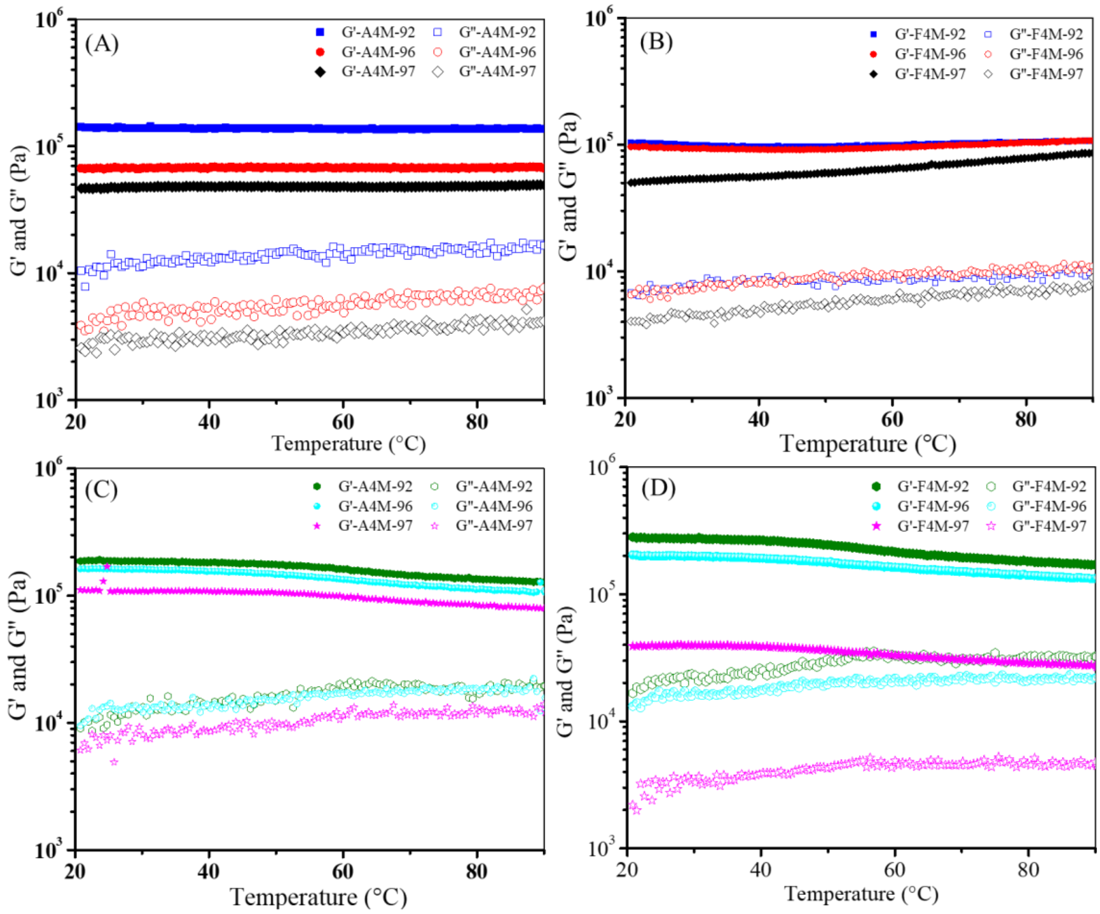

Figure 7. Effect of cellulose type and oil content in the temperature sweeps. (A) and (B) are the emulsion template oleogels corresponding to A4M and F4M cellulose, respectively; (C) and (D) are the foam template oleogels corresponding to A4M and F4M cellulose oleogels, respectively.

3.5. Texture measurement

The force/time curves during the penetration test of the different oleogels are shown in Figure 8. Penetration force curves showed an upward trend, indicating that the oleogel had a compact and stable structure. The maximum force value of the emulsion-based oleogels decreased significantly with increasing oil content (Table 2), which was due to the cellulose content of the emulsion being relatively reduced with the increase in the oil content, which weakened the gel network leading to a decrease in the hardness of the gel (lower values of maximum force). This is in agreement with the rheological results. Similarly, other authors also found a positive correlation between the oleogels elastic values and hardness (Li et al., 2021; Tanti, Barbut, & Marangoni, 2016a). The maximum force of F4M emulsion oleogels was higher than that of A4M for the same oil content, the reason being that the F4M showed a large aggregation of emulsion droplets into chunks and the formation of larger oil droplets in the dried oleogel (Fig. 2) and a stronger granularity of the gel fragments after shearing, resulting in a higher hardness.

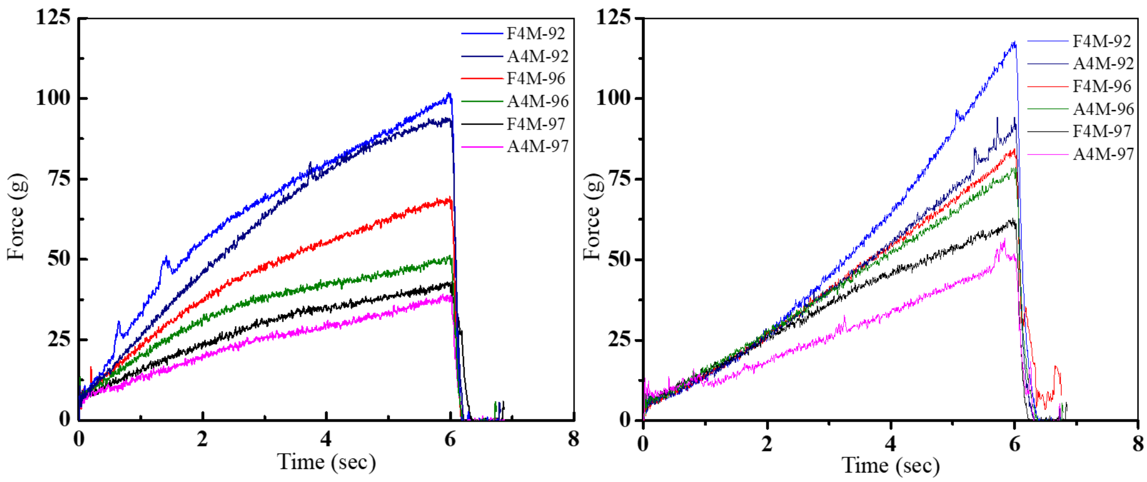

Figure 8. Penetration curves of emulsion template (A) and foam template (B) oleogels.

A similar phenomenon was also observed in the foam-based oleogels (Fig. 8B). Hardness of the foam-based oleogels was higher than that of the emulsion-based oleogel samples when compared at the same oil level (except for 92%). The reason for the pattern may be related to the formation mechanism of the oleogels. In foam-based oleogel a solid gel with good viscoelasticity (Fig. 2) formed by adsorbing liquid oils and fats through a three-dimensional cellulose network structure (A4M) or a cellulose stack structure (F4M) filled with pores, which has a strong resistance to deformation, while the emulsion-based oleogel shows a solid granular texture after shearing and a relatively loose structure in the unit volume, leading to a slight difference in hardness.

Table 2. The hardness of oleogels obtained by emulsion and foam template approaches.

Cellulose type	Oil content (%)	Max. Force (g)	
		Emulsion template	Foam template
F4M	92	101.90 ± 1.80^{B}	117.80 ± 2.07^{aA}
	96	69.57 ± 1.15^{cB}	84.46 ± 1.46^{cA}
	97	42.76 ± 0.94^{eB}	62.33 ± 1.22^{eA}
A4M	92	94.11 ± 1.43^{bA}	91.84 ± 1.19^{bA}
	96	51.34 ± 1.08^{dB}	78.43 ± 1.94^{dA}
	97	38.86 ± 1.26^{fB}	51.77 ± 1.04^{fA}

$^{a-f}$ Means with different letters for each column indicate significant differences between oleogels ($p < 0.05$).

$^{A-B}$ Means with different letters for each raw indicates significant differences between oleogels ($p < 0.05$).

4. Conclusion

The structure and physical properties of cellulose oleogels with different oil contents prepared by the emulsion template and the foam template approaches were evaluated. The oleogel obtaining method and oil content had more effect on the oleogel structure than the type of cellulose. The methodology to obtain the oleogels affected the structural properties of the final oleogels. The emulsion template oleogels were solid-like, non-fluid, and had 100% oil retention capacity. In contrast, the foam template oleogels were semi-solid, and their oil retention capacity decreased with increasing oil content. The gels prepared by both methods have excellent gel strength and low dependence on frequency and temperature. The variation of the methodology, oil content, and type of cellulose allows the obtention of oleogels with different properties and functions, so a wide range of semi-solid or solid-like fat products with a healthy lipid profile suitable for food applications could be obtained.

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Physicochemical stability of sunflower oil-based oleogels prepared by different indirect oleogelation approaches

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Abstract

To reduce the potential health hazards associated with conventional plasticized fats, researchers have been pursuing the development of healthy fats containing lower levels of saturated fatty acids and zero trans fats, with the expectation of improving the nutritional profile by replacing traditional solid fats while maintaining the texture and structure of the food. Oleogels, which are physically immobilized healthy liquid oils to provide a plastic fat-like property, have great potential for application in food formulations. In this study, sunflower oil oleogels by indirect method using Hydroxypropyl Methyl Cellulose (HPMC) were prepared to assess their feasibility as an alternative to traditional plastic fats by exploring the structural stability and oxidative stability of the fat with storage time. The results showed that the texture of the oleogels prepared by the emulsion template method became harder after four weeks, but their mixtures with shortening had textural properties similar to shortening, whereas the texture of the oleogels prepared by the foam template method as well as their mixtures with shortening were softer. The melting behavior of emulsion-based oleogels with shortening blends was not affected by time. Oxidative stability showed that both foam-based oleogels and emulsion-based oleogel shortening mixtures have excellent oxidative stability. The above results indicate the potential of oleogels as an alternative to conventional plasticized fats.

Keywords: Cellulose ether, oleogel, texture, oxidative stability.

1. Introduction

The development of plastic fats that can provide the consistency of conventional solid fats, such as *trans* fats or hydrogenated fats, but with a healthier lipid profile is of great interest to the food industry. One of the most recently explored alternatives is the structuring of liquid oils or oleogelification. Oleogels are defined as solid-like systems where a continuous liquid phase is entrapped or immobilized in a three-dimensional network supported by oleogelators. Reviews such as those published by Li et al. (2022) or Perța-Crișan et al. (2023) summarise the types of products reformulated with edible oleogels. Some of these food matrices include meat products, bakery, confectionery, spreads, and milk-based products. The goal for all of them was to improve texture, reduce saturated/trans fats, or even provide 'clean label' options.

Low molecular weight oil gelators (LMOG) such as waxes, fatty acids, or fatty alcohols, and high molecular weight oil gelators (HMOG) such as proteins and polysaccharides are the most common oleogelators used in the food industry (Hashemi et al., 2024). Depending on the type of oil used and the type of oleogelator, as well as the oleogelation mechanism, the oleogel will display a different technofunctionality (Li et al., 2022).

Although the simplest way to gel an oil would be direct gelation with LMOG (or ethylcellulose), this method has important limitations. It requires the use of high temperatures (above the melting point or glass transition point), leading to the deterioration of the oil (Davidovich-Pinhas, Barbut, & Marangoni, 2016; Gravelle, Barbut, & Marangoni, 2012). Also, gelators used are often not recognized as food grade and are not well perceived by consumers. For this reason, alternatives such as indirect methods are used for the preparation of oleogels (Tan et al., 2023).

The use of polysaccharides as structuring agents or stabilizers is well-established in the food industry due to their Generally Recognized As Safe (GRAS) status and consumer perception (Davidovich-Pinhas, 2019; Nishida, Uauy, Kumanyika, & Shetty, 2004). Since most food polymers are hydrophilic in nature, they are inefficient for structuring oils due to their limited dispersibility in oil and require additional procedures. Therefore, the formulation of polymer-based oleogels is achieved using indirect methods, such as foaming and emulsion approaches. Indirect template approaches are mainly categorized into two types, the emulsion-template (ET) approach and the foam-template (FT) approach. The former involves the formation of a water-in-oil (O/W) or water-in-oil (W/O) emulsion first via the gelator, and then the removal of the aqueous phase to form a stable oleogel (Espert, Salvador, & Sanz, 2020), while the latter utilizes a gelator to construct a stable bubble system, and then freeze-drying to remove the aqueous phase forming a foam structure, which ultimately adsorbs the liquid oil to form a porous oleogel (Wang et al., 2023).

In both cases, the oil droplets are tightly packed in the polymeric network. In these indirect methods, mostly cellulose derivatives have been used as a structural due to their oil gelation capability (Feichtinger & Scholten, 2020; Martins, Vicente, Cunha, & Cerqueira, 2018).

In addition to parameters such as the type and proportion of oleogelator and processing parameters, the properties and the proportion of the liquid oil have a significant effect on the behavior of oleogel (Huang, Guo, Gong, & Zhang, 2023; Li et al., 2022). The triacylglycerol (TAG) composition of oils is directly related to the final physical characteristics of oleogels (Martins et al., 2018; Mert & Demirkesen, 2016). One of the most commonly used is sunflower oil, due to its ease of production and its composition in monounsaturated and polyunsaturated fatty acids (MUFAs and PUFAs). While providing high levels of healthy unsaturated fatty acids, it also presents significant production and storage challenges, as polyunsaturated fatty acids are susceptible to oxidation, which can negatively affect the nutrition, flavor, and odor of the food product.

Hence, the present work aimed to study the effect of storage time and the obtaining method (FT approach and ET approach) on the structural and stability properties of oleogels formulated with high oleic sunflower oil and hydroxypropyl methylcellulose (HPMC) as an oleogelating agent, and consequently to explore the feasibility of mimicking the behavior of conventional fats by oleogels, especially in terms of texture and stability, to provide the appropriate structure.

2. Materials and methods

2.1. Ingredients

Emulsions and oleogels were prepared with hydroxypropyl methylcellulose (HPMC), water, and high oleic sunflower oil. HPMC ("Methocel K4M"; 4000 cP) was supplied by Dow Chemical Company (Midland, MI, Estados Unidos) and sunflower oil (Fontasol) (Sovena España S.A.U., Sevilla, España) was purchased from a local supermarket. Commercial shortening (SH) (Vandemoortele, Belgium) was used to make the oleogel/fat blends. All volatile standard compounds (2,3-Butanedione, Butanal, Acetic acid, Pentanal, Hexanal, Butanoic acid, Heptanal, 2-octenal, Nonanal, Decanal, Pentanoic acid, 2-Pentylfuran, Hexanoic acid) with > 97% purity were purchased from Sigma-Aldrich (Merck, Darmstadt, Germany).

2.2. Oleogels preparation

Emulsion template approach (ET)

An o/w emulsion composed of 47% oil, 51.5% water, and 1.5% HPMC was made. This emulsion was prepared by first dispersing the HPMC in oil using a stirrer (RZR 1, Heidolph Instruments, Germany) at 280 rpm for 5 min. Then water was gradually added at 10 °C to hydrate the cellulose effectively under continuous stirring. Finally, the mixture was emulsified with an Ultra-Turrax homogenizer (Model T-18, IKA, Germany) at 6500 rpm for 15 s and 17500 rpm for 60 s. The emulsion obtained was placed in aluminum trays and dehydrated at 60 °C (24-48h) with a forced convection oven (KB115 BINDER, Germany) obtaining a dry film of about 10 mm. The percentage of moisture (H) was determined using Equation 1, by weight difference between the emulsion (fresh sample) and the dry product obtained (dry sample).

$$H\ (\%) = \frac{((0.515 * fresh\ sample) - (fresh\ sample - dry\ sample)) * 100}{(0.515 * fresh\ sample)} \quad (1)$$

The dehydrated emulsion film was then minced using a manual mincer (Moulinex 123 AD560120, Paris, France) in 5 cycles of 3 s each. The obtained oleogel (ETOG) was deposited in molds and stored in a temperature-controlled room at 20 °C for 28 days.

Foam template approach (FT)

In this method, the hydration of cellulose was first carried out by preparing a solution of 1.5% cellulose ether and 98.5% water. For this, HPMC was dissolved in 1/3 of the total water at 80 °C. It was then hydrated with the rest of the water (at 1 °C) by stirring (RZR 1, Heidolph Instruments, Germany) at 1000 rpm for 5 min. Subsequently, it was frozen at -80 °C and freeze-dried (Lyobeta 6PL 2021, Telstar, Spain) for 24 h to form a solid sheet foam.

The foam obtained was then minced using a grinder (Moulinex A320R1, Paris, France) in 4 cycles (6 s each). The oil (97 %) was then added under constant stirring (RZR 1, Heidolph Instruments, Germany) at 280 rpm. The obtained oleogel (FTOG) was deposited in molds and stored in a temperature-controlled room at 20 °C for 28 days.

2.3. Oleogel-shortening blend preparation

Oleogel-shortening (OG-SH) blends were prepared in a 50/50 (w/w) ratio. For this purpose, shortening was first melted in a thermostatic bath (J.P. Selecta, S.A., Spain) at 80 °C. Then, it was allowed to cool to <40 °C and gradually added to each oleogel, stirring manually with a glass rod. The mixture obtained was deposited in small silicone molds and stored in a stability chamber (20 ℃) for 28 days.

2.4. Samples description

Five samples were developed: control (commercial shortening), oleogel obtained with the emulsions template approach (ETOG), oleogel obtained with the foam template approach (FTOG), emulsion template oleogel/shortening 50/50 blend (ETOG-SH) and foam template oleogel/shortening 50/50 blend (FTOG-SH).

2.5. Texture analysis

Texture analyses were performed with a TA-TX plus texturometer (Stable Micro Systems, Godalming, UK) equipped with Texture Exponent software (version 6.1.16.0; Stable Micro Systems, Godalming, UK. A 30 kg load cell was used and all measurements were carried out at 20ºC. A penetration test was performed using a cylindrical probe (P/10) which penetrated the sample up to a distance of 8 mm at 1 mm/s. Measurements were performed in triplicate on day 1 (T_0), day 7 (T_1), day 14 (T_2), day 21

(T_3) and day 28 (T_4). Force vs. time was plotted and the area under the curve (AUC) was calculated, as an indicator of the hardness of the oleogels and blends.

2.6. Thermal behaviour

Thermal behaviour was evaluated by Differential Scanning Calorimetry (DSC) using a Q2000 calorimeter (TA Instruments, USA). 10 mg of each sample were placed in hermetic DSC pans and an empty pan was used for reference. The heating rate was 5 °C/min, and the temperature ranged between 20 °C and 80 °C. Thermograms were analyzed using TA Universal Analysis software (TA instruments, USA). The maximum melting temperature (T_p), and the change in enthalpy associated with the melting process (ΔH_M) were calculated. Measurements were performed in triplicate on days 1 (T_0), 7 (T_1), 14 (T_2), 21 (T_3), and 28 (T_4).

2.7. Analysis of volatile compounds

The volatile compounds present in the headspace of oleogel samples were extracted using a solid-phase microextraction (SPME) device equipped with an 85 μm Carboxen/ Polydimethylsiloxane fiber (Supelco, Bellefonte, PA) installed in an automatic sampler (Gerstel MPS2 multipurpose sampler, Gerstel, Germany). The analysis of volatile compounds was achieved in gas chromatography (GC) (Agilent HP 7890 Series II, Hewlett-Packard, Palo Alto, CA) equipped with a mass selective detector (MS) (HP 5975C Hewlett-Packard, PA). Three grams of oleogel sample were weighed into 20 ml headspace vials (Gerstel, Germany) and analyzed according to the protocol described by Perea-Sanz, López-Díez, Belloch, and Flores (2020). The vial sample was equilibrated at 37 °C for 30 min and then, the SPME fiber was exposed to headspace for 60 min. Fiber with extracted volatile compounds was injected into the GC inlet maintained at 240 °C in splitless mode and compounds were separated on a DB-624 capillary column (30 m x 0.25 mm x 1.40 μm, Agilent Technologies, Santa Clara, CA, USA) and analyzed using the MS detector. The compounds eluted from GC using a temperature program have been made as indicated in Perea-Sanz, López-Díez, Belloch, and Flores (2020). Detection was done in scan mode and by electron impact at 70 eV, and data were acquired in the range of 29–400 amu. Identification of volatile compounds was performed by comparison of mass spectra from the library database (NIST'17) and calculation of linear retention indices (Van Den Dool & Kratz, 1963) using the series of n-alkanes C8-C22 (Aldrich, Merck, Germany). The oleogel samples were analyzed on day 1 (baseline), day 14 (week 2), and day 28 (week 4) and each oleogel sample was analyzed in triplicate. Quantification was performed in scan mode using either total ion area (TIC) on an arbitrary scale, and the data was expressed as a percent of the area (TIC) at which the compound was initially detected in the sample during the storage time.

2.8. Statistical analysis

One-factor analysis of variance (ANOVA) was performed to evaluate differences between samples (control, ETOG, ETOG-SH, FTOG, and FTOG-SH) initially and over time (T0, T1, T2, T3, and T4). Means were compared using Tukey's test with a significance of $P<0.05$. Statistical analysis was performed with statistical software (XLSTAT 2018, Addinsoft, Barcelona, Spain).

3. Results

3.1 Texture of oleogels and blends over time

The physical properties (e.g., hardness) of conventional solid fats are critical to the texture and mouthfeel of the final product. However, during storage, they may undergo crystal structure changes, oxidation, or hydrolysis reactions under the influence of the environment (Zhao, Wei, Xue, & Meng, 2023), leading to softening or brittleness due to changes in fatty acid composition or fat structure. Therefore, the periodical determination of solid fat penetration is not only instrumental in monitoring the physical state of the fat but also effective in predicting quality changes in storage, so as to establish a reasonable shelf-life for the product, in order to avoid excessive changes in fat hardness that may affect the usability or the consumer experience (Zetzl, Marangoni, & Barbut, 2012).

Figure 1 shows the penetration profiles of the oleogels and blends with respect to the conventional fat control. In the control sample (Fig. 1A), there is an increase in texture values with increasing storage time and the profile also showed a maximum peak in force followed by a decrease, reflecting an initial breakage of the structure. However, there is probably a first layer on the surface that has become hardened over time. Once it is overcome, there is no longer an increase in force with penetration. It can be seen in Table 1 that after four weeks its AUC increased significantly ($p<0.05$). This may be due to the recrystallization or migration of fats in the shortening, where the fat crystals may be rearranged into a more stable crystalline form, which leads to an increase in hardness. In contrast to shortening, oleogels showed force profiles characteristic of a compact but ductile gel structure. The force increased with the distance of penetration,

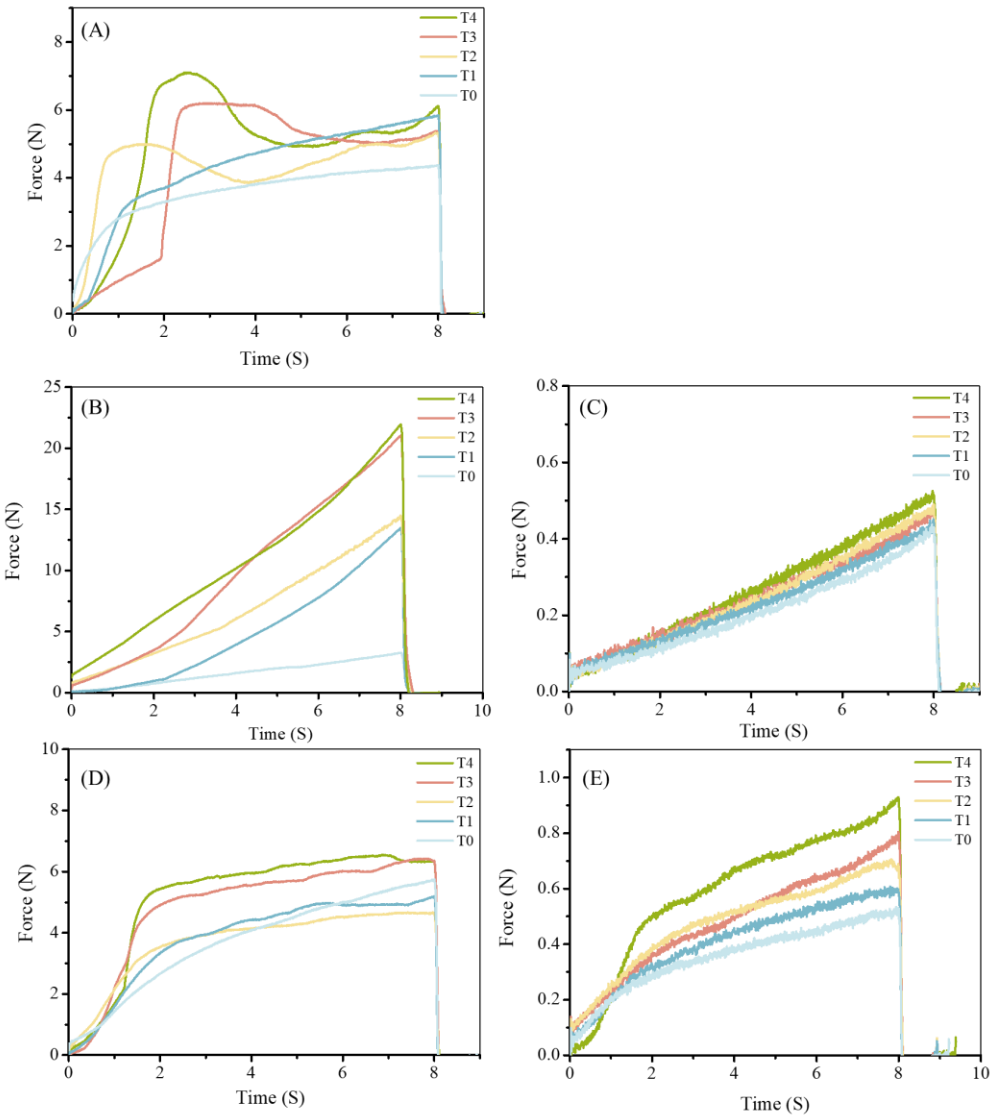

Figure 1. Penetration of different fats as a function of storage time. Control (A), ET (B), FT (C), ET O-S (B), FT O-S (C).

without any peak that could indicate structure breakage (Fig. 1B, C, D, E). The type of oleogel manufacturing process influenced the texture of the oleogel and oleogel-shortening blends. Systems obtained by the emulsion template approach (ET) showed higher AUC values ($p<0.05$) than those obtained by the foam template approach (FT) (Table 1). This difference is probably due to the functionality of the cellulose and the disposition of the oil in the network formed by the cellulose. In the case of ET samples, the initial emulsion already contains the oil emulsified by the cellulose, and is subsequently dehydrated and sheared, therefore, the cooperative effect of the phenomena of fat recrystallization and cross-linking of polysaccharide colloid network in the oleogel, could made the structure of the oleogel more compact and stable. However, in FT samples the oil is absorbed by the previously freeze-dried hydrated cellulose network but it is not retained as much as in the emulsion matrix, where it is retained from the beginning in the polysaccharide network, for that, the consistency of this foam is much lower than that of the dehydrated emulsion.

On the other hand, ET samples showed an increase in force values with storage time whereas the FT samples had been maintaining a tiny penetration and the AUC only showed a slight increase after four weeks, because the solid foam structure formed physically adsorbs the liquid oil through the porous foam structure, so the changes in the physical properties of the oils during the storage process (e.g. crystallization or migration of fats) have relatively minor effects on the hardness of the oleogel and showed very low penetration values (Li, Liu, & Lin, 2021; Shi et al., 2021).

Tabla 1. AUC values were obtained for the different oleogel formulations and mixtures at different storage times.

Samples	AUC (N s)				
	T_0	T_1	T_2	T_3	T_4
Control	30.30±3.10^{Ba}	34.93±2.63^{Aba}	35.21±1.13^{Abb}	38.64±4.85^{ABb}	39.61±4.56^{Ab}
ET OG	12.85±0.88^{Cb}	23.82±2.68^{Cb}	52.36±5.10^{Ba}	76.70±1.73^{Aa}	77.08±7.28^{Aa}
ETO-S	29.14±1.41^{Ba}	30.49±1.55^{Ba}	29.22±1.42^{Bb}	39.33±3.57^{Ab}	42.71±2.89^{Ab}
FT OG	1.63± 0.16^{Bc}	1.79± 0.04^{ABc}	1.86±0.20^{ABc}	1.75 ±0.25^{ABc}	2.17±0.13^{Ac}
FTO-S	2.85±0.14^{Cc}	3.27±0.12^{Cc}	4.15±0.29^{Bc}	4.11± 0.26^{Bc}	4.76±0.05^{Ac}

Average values (standard deviation) in the same row (A, B, C) or column (a, b, c) with different letters are significantly different ($p<0.05$). AUC: area under the curve.

After four weeks, the ETOG-SH sample was the most control-like system, with a significantly similar penetration profile and AUC values. However, systems obtained by the FT approach showed very low penetration values and even when conventional fat was incorporated into the FTOG-SH blend, the texture was not improved.

3.2 Thermal properties of blends

Figure 2 shows the melting profiles of the different OG-SH blends and shortening control stored at 20 ºC. The curves of 100% oleogel samples (ETOG, FTOG) are not shown. These samples, containing only liquid oil are crystal-free, i.e., no melting peaks were observed in the temperature range used. The thermograms of the initial (T0) and stored samples (T1, T2, T3, T4) showed a broad melting range with a main endothermic peak corresponding to the melting of solid fat crystals. Typically, a wide melting range is highly desirable in roll-in shortenings as it provides adequate functionality and good mouthfeel in the finished baked product (Macias-Rodriguez & Marangoni, 2016). Previous studies (Litwinenko, Rojas, Gerschenson, & Marangoni, 2002; Martini & Herrera, 2008) reported a similar melting profile in vegetable oil-based shortening. Both blends (ETOG-SH and FTOG-SH) showed shallower and wider endotherms. However, control endotherms were broad but sharper, with higher melting enthalpy (Table 2), indicating that more crystals were formed. This higher enthalpy was predictable, as the shortening has a higher content of more saturated fatty acids (NorAini et al., 1995). In previous research on oleogels, this peak was attributed to the melting of the monoglycerides employed in their preparation (Giacomozzi, Carrín, & Palla, 2021). Considering the composition of shortening used in oleogels, sunflower, soybean, and palm oil are present, as well as mono- and diglycerides of fatty acids as additives. This leads to a higher crystallized fat content with a higher enthalpy (Nilchian et al., 2020). Blend formulated with FT (FTOG-SH) presented the lowest enthalpy. As previously described (Martini & Herrera, 2008), lower enthalpy values suggest that crystallization is delayed or inhibited. Probably that explains the lower AUC of the FT blend found.

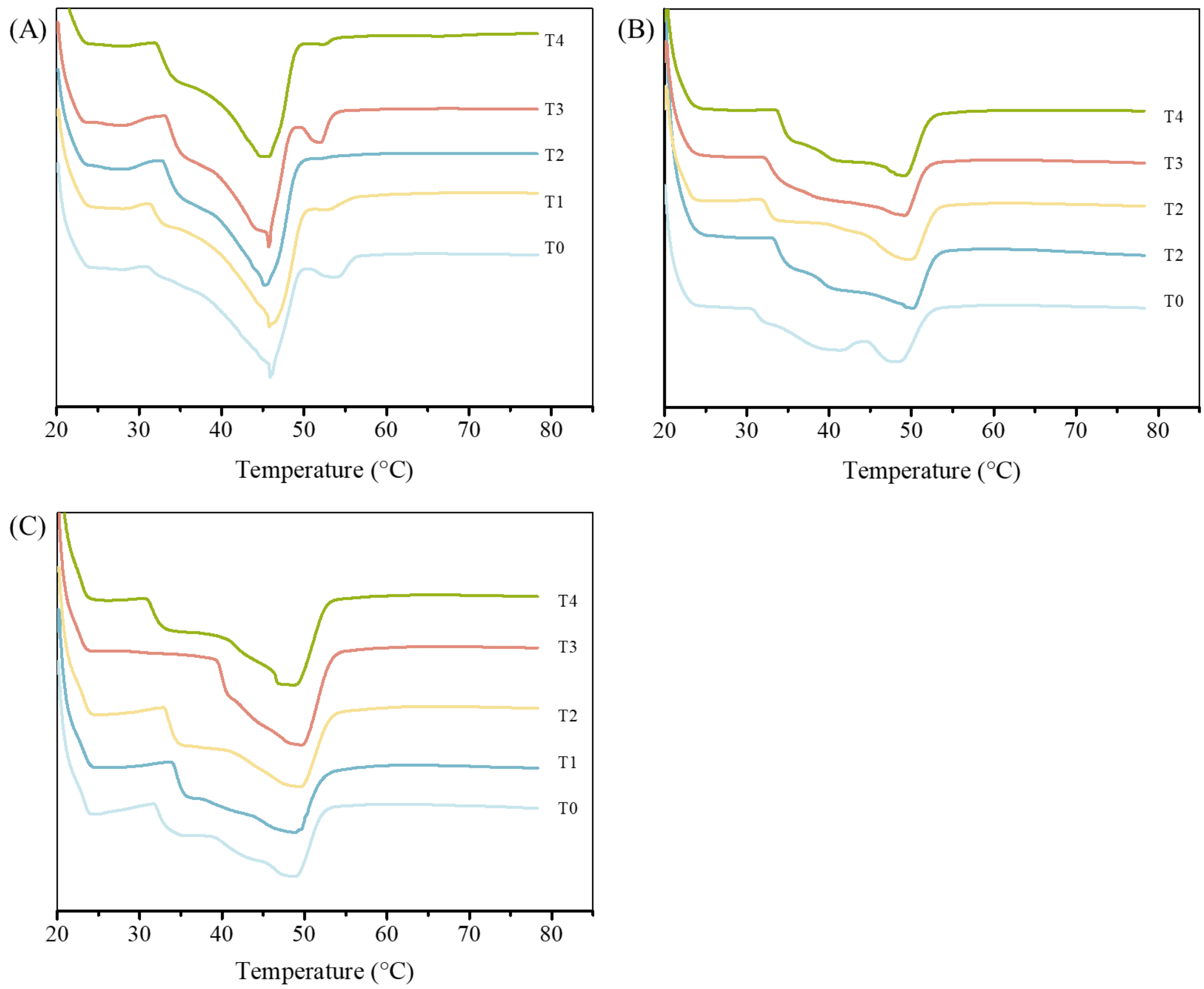

Figure 2. Melting profile of the different blends over time. Control (A), ETO-S (B), FTO-S (C).

The temperature of the major melting peak indicates where the major phase transformation of solid to liquid takes place (NorAini et al., 1995). In this case, there is an increase in the maximum temperature of the melting peak in the blends. Thus, the presence of oleogel affected the enthalpy and melting temperature of the fat in the blend matrix.

Regarding the effect of storage, no significant differences ($p>0.05$) were found in melting parameters between the different times (Table 2). There was only a slight increase in enthalpy in the control sample (shortening), although it was not considered significant. Temperatures for melting peaks had no significant differences. This fact suggested that, although there was a change in texture, there was no change in the amount of crystallized material during storage (Giacomozzi et al., 2021).

Table 2. Evolution in time of the enthalpy (ΔHm) and temperature (°C) of melting of mixtures.

	ΔH_m (J/g)			T_p (°C)		
	Control	ETO-S	FTO-S	Control	ETO-S	FTO-S
T_0	18.07±1.67^{Aa}	12.16±0.75^{ABa}	9.99±2.13^{Ba}	45.54±0.49^{Ba}	48.93±0.81^{Aa}	48.32±0.66^{ABa}
T_1	20.14±4.81^{Aa}	13.68±0.97^{Aa}	12.12±1.73^{Aa}	46.00±0.30^{Ba}	49.48±0.23^{Aa}	48.18±0.81^{Aa}
T_2	24.96±1.29^{Aa}	12.13±1.05^{Ba}	11.80±1.94^{Ba}	45.40±0.18^{Ba}	49.59±0.94^{Aa}	49.23±0.35^{Aa}
T_3	23.92±2.19^{Aa}	14.94±2.52^{ABa}	12.70±2.14^{Ba}	46.03±0.45^{Ba}	48.76±0.54^{Aa}	49.40±0.35^{Aa}
T_4	26.46±1.23^{Aa}	12.79±2.40^{Ba}	12.44±1.98^{Ba}	45.62±0.35^{Ba}	48.54±0.83^{Aa}	48.64±0.11^{Aa}

Average values (standard deviation) in the same row (A, b) or column (a, b) with different letters are significantly different ($p<0.05$).

3.3 Analysis of volatile compounds

The oxidation or degradation of fatty acids generates a large number of compounds, which can produce changes in the physicochemical and organoleptic properties of fat (Jeleń, Obuchowska, Zawirska-Wojtasiak, & Wasowicz, 2000). In particular, primary oxidation products such as hydroperoxides are formed first, and then these primary oxidation products are decomposed or react with each other and with other compounds to produce numerous secondary oxidation products such as aldehydes, ketones, alcohols, epoxides, polymers, and other compounds (Hwang, 2020). Although these secondary oxidation products are the compounds with the lowest concentrations, they are the most damaging, generating unpleasant aromas and flavours. One of the most commonly used methods to measure lipid oxidation is peroxides determination, but it has been found that it does not accurately display oxidative stability at all oxidation stages. Therefore, it is highly recommended to measure secondary oxidation products (Hwang, 2020). The oxidative stability of the sample during storage was investigated to evaluate the role of the oleogelator in the matrix. To identify differences in their release, the profile of volatile organic compounds was analyzed qualitatively by GC-MS. Thirteen compounds were identified during the storage. Table 3 showed the variation of the main volatile compounds found in the oleogel and blends stored at 20 ºC for 4 weeks.

The unsaturated aldehydes 2-heptanal, 2-octenal, and 2-decanal can be considered the main responsible for the sensory defect or rancidity, followed by saturated aldehydes such as pentanal, hexanal, heptanal, octenal, and nonanal (Kotsiou & Tasioula-Margari, 2015; Park, Bemer, & Maleky, 2018; Yi, Kim, Lee, & Lee, 2017) In addition, acetic, butanoic and hexanoic acids also contribute to the rancid flavor profile.

Some compounds were found in common in the different samples, such as butanal, pentanal, hexanal, butanoic acid, heptanal and nonanal. Previous studies have demonstrated the contribution of these compounds to sensory deterioration or oxidation of vegetable oils (Park et al., 2018; Petersen et al., 2012). One of the main degradation products of linoleic acid (the main polyunsaturated fatty acid in sunflower and soybean oil) is hexanal, which increased during storage (Snyder & Mounts, 1990). Furthermore, in the case of high oleic sunflower oil, there is a large amount of oleate; so, the nonanal formed from the decomposition of oleate hydroperoxides is higher in this type of oil (Snyder et al., 1990). Palm oil also presents a great amount of oleic acid. Therefore, both samples containing only oil (OG) and those containing shortening (with palm oil) (ETOG-SH and FTOG-SH blends) showed high nonanal values (Snyder & Mounts, 1990).

As can be seen in Table 3, volatile compounds characteristic of oxidation were observed in the control group (shortening) at the beginning, since commercial shortening contains small amounts of unsaturated fatty acids and moisture, which oxidize with air to produce volatile compounds. It should be noted that shortening was melted at about 60 °C to break the crystals and prepare both the control and the OG-SH blends for subsequent molding. This increase in temperature may have been the cause of the appearance of these oxidation compounds since the beginning. The content of the oxidized compounds varied with storage time, with significant increases in pentanal, hexanal, nonanal, and decanal after four weeks with respect to values obtained at the initial time. This indicates that a slight oxidation of the commercial fat occurred over time. Except for some variation in some volatile compounds, a high number of compounds can be observed over a longer storage time. For some compounds (2,3-butanedione, butanal, and acetic acid, which have a high volatility) a decrease from the initial time value can be observed. This is probably due to the aromas presented in the commercial fat used, which are lost when exposed to the environment. Specifically, 2, 3-butanedione was found in the samples containing shortening (control, ETOG-SH, and FTOG-SH). This compound is associated with a buttery odor (Rigler & Longo, 2010), and these flavourings can be lost when exposed to the environment, as observed in these samples (Table 3). The reduction of this compound was also observed in previous studies (Kallio, Leino, & Salorinne, 1989).

Comparing oleogels, results on volatile compounds indicate that FTOG had higher oxidative stability than ETOG. Solid oleogels may have great oxidative stability as compared to liquid oils presumably because of the smaller chances of collision between unsaturated fat molecules and oxygen molecules (Yi, Kim, Lee & Lee, 2017). The presence of the cellulose network in the oleogel would decrease the rate of secondary oxidation through a decrease in molecular mobility by acting as hurdles within oleogels.

Nonetheless, the ETOG was subjected to drying at 60°C for about 48 hours. This factor has probably been the trigger for the higher lipid degradation. On the contrary, the oleogels formulated by the foam template approach (FTOG), as were not subjected to high temperatures during their elaboration, presented a low abundance of oxidation volatile compounds.

These differences were more noticeable in pentanal, hexanal, heptanal, and 2-octenal. Pentanoic acid, hexanoic acid, and 2-pentylfuran, which were not found in FTOG, also appear in ETOG. Pentanoic acid and 2-pentylfuran are mainly formed from linoleic acid hydroperoxides (Holler et al., 2023) and hexanoic acid has been reported to be the result of a secondary decomposition of hexanal (Monroy Soto et al., 2019) and they were formed in the highest concentration in sunflower oil (Timm-Heinrich, Xu, Skall Nielsen, & Jacobsen, 2003). In contrast, FTOG formed by the adsorption of sunflower oil via the porous foam structure showed a significant decrease in oxidation compounds with storage time, except for an increase in the relative content of nonanal, which may be attributed to

Table 3. Relative content of volatile compounds in fat as a function of storage time.

Variation (%)	Control			ET OG			FT OG			ET OG-SH			FT OG-SH		
	T_0	T_2	T_4	T_0	T_2	T_4	T_0	T_2	T_4	T_0	T_2	T_4	T_0	T_2	T_4
2,3-Butanedione	100^{a}	94^{a}	48^{b}	100^{a}	220^{a}	145^{a}	100^{a}	13^{b}	9^{b}	100^{a}	35^{b}	14^{c}	100^{a}	106^{a}	43^{b}
Butanal	100^{a}	50^{a}	133^{a}	100^{a}	62^{b}	69^{b}	100^{a}	25^{b}	33^{b}	100^{a}	35^{b}	46^{b}	100^{a}	153^{a}	194^{a}
Acetic	100^{a}	138^{a}	132^{a}	100^{a}	19^{c}	49^{b}	-	-	-	100^{a}	70^{b}	69^{b}	100^{a}	27^{b}	20^{c}
Pentanal	100^{b}	151^{ab}	190^{a}	100^{c}	264^{b}	329^{a}	100^{a}	61^{b}	57^{b}	100^{a}	69^{b}	83^{ab}	100^{a}	200^{a}	152^{ab}
Hexanal	100^{b}	139^{b}	207^{a}	100^{c}	289^{b}	324^{a}	100^{a}	47^{b}	52^{b}	100^{a}	104^{a}	105^{a}	100^{a}	209^{a}	166^{a}
Butanoic	100^{b}	125^{a}	122^{ab}	100^{b}	119^{b}	268^{a}	100^{a}	125^{a}	113^{ab}	100^{a}	82^{ab}	80^{b}	100^{a}	103^{a}	80^{b}
Heptanal	100^{a}	94^{a}	90^{a}	100^{b}	245^{b}	432^{a}	100^{a}	25^{b}	31^{b}	100^{a}	106^{a}	92^{a}	100^{a}	86^{ab}	65^{b}
2-octenal	100^{a}	105^{a}	171^{a}	100^{b}	113^{b}	706^{a}	-	-	-	100^{a}	52^{b}	56^{b}	100^{a}	49^{a}	70^{a}
Nonanal	100^{c}	335^{b}	474^{a}	100^{b}	163^{b}	264^{a}	100^{c}	226^{b}	380^{a}	100^{b}	224^{b}	395^{a}	100^{c}	336^{b}	664^{a}
Decanal	100^{a}	218^{a}	278^{a}	-	-	273^{a}	-	-	-	100^{a}	297^{a}	404^{a}	100^{a}	81^{a}	68^{a}
Pentanoic	-	-	-	-	100^{b}	990^{a}	-	-	-	100^{a}	77^{b}	74^{b}	-	-	-
2-Pentylfuran	-	-	-	100^{b}	156^{b}	521^{a}	-	-	-	100^{a}	86^{a}	54^{a}	-	-	-
hexanoic acid	-	-	-	100^{b}	360^{b}	3894^{a}	-	-	-	100^{a}	58^{b}	65^{b}	-	-	-

Average values (standard deviation) in the same row (a, b, c) with different letters are significantly different ($p<0.05$).

the fact that the porous foam structure can inhibit fat oxidation to a certain extent. Blend of shortening with ETOG showed no increase in volatile compounds except for nonanal and decanal. Compounds associated with the oxidation of unsaturated fatty acids were also reduced compared to the ETOG. This may be due to the fact that the shortening fully mixed with the oil droplets of ETOG formed a new fat layer on the external layer of the emulsion droplets, which inhibited the oxidation of ETOG, especially the secondary decomposition of hexanoic acid. Although the degree of oxidation of FTOG was low, when it was mixed with shortening, the volatile compounds increased from the values at an initial time, especially hexanal, heptanal. In addition, the compounds associated with the oxidation of the unsaturated oil are reduced compared to oleogel alone. It is possible that the temperature at which OG-SH blending occurs affects the stability of the FTOG oil, which is less integrated into the cellulose network than in the case of ETOG.

4. Conclusions

This study evaluated the effect of storage time and oleogel processing method (*foam template* and *emulsion template*) on the structural properties and stability of HPMC-sunflower oil-based oleogels, and OG-SH blends. The texture of the oleogels was affected by time, as they became harder at the end of the storage time (four weeks). The FT method produced oleogels with a very smooth texture, even when mixed with the shortening to obtain FTOG-SH blend. On the contrary, the blend made with the oleogel obtained by the ET approach presented texture properties similar to shortening control. The melting behaviour of the OG-SH blends was not affected by time. Although FTOG had the minimum variation in term of oxidative volatile compounds during storage, the ETOG-SH mixture also exhibited the highest oxidative stability. Combining with other factors such as mechanical properties, it can be found that the mechanical properties, melting characteristics, and oxidative stability of ETOG-SH were comparable to those of the shortening control, and would offer great potential as a saturated fat substitute to improve the formulation of food products.

CRediT authorship contribution statement

Q. Wang: methodology, Investigation and Writing – original draft. M. Espert: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. T. Sanz: Supervision, Investigation, Funding acquisition. M. Flores: Methodology, Writing – review & editing, Supervision, Investigation. A. Salvador: Writing – review & editing, Supervision, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that there is no conflict of interest.

Data availability

The authors do not have permission to share data.

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Chapter 2

Oleogels application in cream cheese

Effect of cellulose ether emulsion and oleogel as healthy fat alternatives in cream cheese. Linear and nonlinear rheology, texture, and sensory properties

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Abstract

The suitability of oil-in-water (o/w) hydroxypropyl methylcellulose (HPMC)-based emulsions and oleogels to reduce total fat and saturated fat content in cream cheese was studied. The effect of HPMC emulsions and oleogels on the spreadability, viscoelasticity, and sensory acceptability of cream cheese was evaluated. Small-amplitude oscillatory shear (SAOS) and large-amplitude oscillatory shear (LAOS) tests were performed to investigate linear and nonlinear rheology. All cheeses showed a predominance of G' versus G'' with a light dependence of both moduli with frequency in the linear viscoelastic region (LVR). Fat replacement with emulsion or oleogel significantly reduces the values of G' and G'' at the LVR, yield point, and flow point, and increases spreadability. This effect was greatest for the oleogel substitution. However, the incorporation of emulsion or oleogel did not significantly affect tan δ, yield stress, yield strain, flow stress, and flow strain. The elastic and viscous evolution during the transition from SAOS to LAOS was similar in all cheeses, despite their differences in spreadability. At large deformation, all samples showed strain-stiffening and shear-thinning behavior. Similar sensory acceptability was found among the oleogel and emulsion cheeses and the control. The similar nonlinear rheological properties among cheeses do not explain the differences in spreadability properties but explain their similar sensory acceptability. Furthermore, the purchase intention for oleogel and emulsion cheeses increases when consumers receive information on the type and amount of fat.

Keywords: *Cream cheese, oleogel, emulsion, large-amplitude oscillatory shear (LAOS), sensory evaluation.*

1. Introduction

Cream cheese is a semi-soft dairy product with a wide diversity in flavor and form that varies with the ingredients of the formulations (Wendin, 2000). Fat is an essential ingredient that provides many textures, spreadability, and ease of being mixed with other constituents. However, excessive fat consumption, mainly saturated fat, and *trans* fatty acids can increase the risk of several chronic diseases such as obesity, cardiovascular disease, and cancer (Demirkesen & Mert, 2020; Espert, Hernández, Sanz, & Salvador, 2021). The growth of obesity has also increased consumer awareness to adopt healthier diet strategies, resulting in increased demand for low-fat foods (Espert, Salvador, & Sanz, 2020; Mert & Demirkesen, 2016). However, in cream cheese, fat reduction has been associated with textural and flavor changes that affect consumer's purchase intention (Ningtyas, Bhandari, Bansal, & Prakash., 2019). Ningtyas, Bhandari, Bansal, and Prakash. (2018) used β-glucan (BG) and phytosterols (PS) as fat substitutes, showing that BG increased the viscosity and hardness of reduced-fat cream cheese, whereas PS improved its spreadability. Zetzl, Marangoni & Barbut (2012) directly used liquid oils rich in unsaturated fatty acids to replace saturated fats, but the textural properties of the final product were not satisfactory. The structure of these fat replacers differed from that of traditional solid fats, decreasing the sensory properties of cheese (Ningtyas et al., 2019).

In previous studies, cellulose ether emulsions and sunflower oil-based oleogels have been used successfully to reduce total fat and saturated fat content in different foods (Espert et al., 2021). In comparison to butter: 55% saturated fat and 80% total fat, cellulose ether emulsions contain: 3.8% saturated fat and 47.5% total fat (sunflower oil) and oleogels contain: 96.7%

total fat and 7.8% saturated fat, so replacement one by one of butter by oleogels reduces saturated fat, and replacement of butter by emulsion reduces saturated fat and total fat.

Oleogelation represents a promising technique for structuring liquid oils into gels with a three-dimensional network (Patel et al., 2014), which possesses solid fat-like characteristics capable of replacing the traditional triacylglycerol crystalline fat network. Bemer et al. (2016) explored the possibilities of oleogels prepared with rice bran wax or ethylcellulose incorporated with vegetable oil to be used in cream cheese products. The total fat content of all oleogel cream cheeses was reduced by 25% compared to the control, indicating that vegetable-based oleogels can effectively improve the fatty acid composition of cream cheese products. In another study, Clifford Park (2018) used rice bran wax (RBW) and high-oleic soybean oil oleogels as fat substitutes in cream cheese, stating that thermal processing and storage had a minor effect on the degradation of rice bran wax oleogels, which could contribute to their potential application in dairy products.

The composition of cheese deeply affects its texture. Variations in the composition of fat content can alter the balance between fat, protein, carbohydrate, and water, inducing a perceptible textural change (Banks & Weimer, 2007) and affecting the rheology, spreadability, and organoleptic properties of cream cheese in different dimensions. Small-amplitude oscillation shear (SAOS) is conducted in the linear viscoelastic area to measure the mechanical properties of food products (Bayarri, Carbonell & Costell, 2012). Ningtyas, Bhandari, Bansalet & Prakash (2017) reported the impact of fat globules in the protein network on the texture and consumer acceptance of cream cheese. Cheese with different fat content had favorable viscoelasticity, non-Newtonian, and shear-thinning behaviors. However, the limitation of SAOS is that it cannot provide near-realistic information on viscoelasticity under large deformations related to food processing or oral processing once the amplitude exceeds the linear elastic region. Therefore, large-amplitude oscillation shear (LAOS) can fulfill these expectations and has become an ideal method to simulate food processing or variation of eating experience by controlling the amplitude and frequency to change the strength or timescale, so the type and intensity of physical movement in the sample is more realistic and closer to real conditions. Structural information provided by SAOS measurements are enlarged by LAOS. The nonlinear mechanical response of kashar cheese for different applications was explored at strain values ranging from 0.196% to 359% (Yildirim-Mavis et al., 2022). Zad Bagher Seighalani & Joyner (2019) compared the variability of different types of cheeses in terms of nonlinear viscoelastic parameters using Lissajous curves. Melito, Daubert & Foegeding (2013) determined the nonlinear viscoelastic properties of reduced-fat and low-fat Cheddar cheeses and investigated their correlation with rheological, sensory, and oral processing properties. Furthermore, the preparation of vegetable oil oleogels was successfully used to produce cream cheese with a high unsaturated fat content and a low saturated fat content using carnauba wax (K. Moon, 2021) and rice bran wax or ethylcellulose (Bemer et al., 2016). Anvari & Joyner (Melito) (2019) also found that low-fat cheeses prepared with emulsions showed greater nonlinearity with smaller critical stress and modulus values under LAOS. Comprehensive reports on the effects and correlations of fat substitution on texture, rheological properties, and sensory characteristics of low-fat cream cheese products have not been reported. Therefore, the purpose of this study was to verify for the first time the feasibility of HPMC emulsions and oleogels as a substitute for saturated fat in cream cheese formulations and to understand the relevance of SAOS and LAOS in the texture and sensory acceptability of cream cheese. The effects of these fat replacers in cream cheese were investigated using a combination of SAOS, LAOS, spreadability, and sensory evaluation, to better understand the relationship between the structure of cream cheese and the final quality.

2. Materials and methods

2.1 Materials

Hydroxypropyl methylcellulose (HPMC) (29% methoxyl, 6.8% hydroxypropyl) was supplied by The Dow Chemical Company (Bomlitz, Germany). High-oleic sunflower oil (Deoleo S.A., Córdoba, Spain), whole milk (Gaza, Zamora, Spain), vinegar (Sabater, Murcia, Spain), butter (Central Lechera Asturiana, Spain) (composition per 100 g: 82 g of fat included 55 g of saturated fat, 0.4 g of sugar, 0.6 g of protein, and 0.03 g of salt), and salt were purchased from a local supermarket.

2.2 Preparation of emulsion, oleogel and fat blends

HPMC emulsion and oleogel were prepared, as previously reported by Wang et al. (2023). In summary, 3 g of HPMC powder was dissolved in 103 g of sunflower oil, then 94 g of cold water (10 °C) was gently added to the oil phase while continuously stirring with a Heidolph stirrer (Heidolph Instruments GmbH & Co. KG) at 300 min^{-1} for 2 min. The viscous emulsion formed was subsequently homogenized using an Ultra-Turrax T18 homogenizer (IKA, Germany) at 16,500 rpm for 1 min. The above emulsion (1.5% HPMC, 47% oil content, 51.5% water content, w/w) was then placed in a 60 °C drying oven (Binder GmbH, Germany) for 48 h to achieve a moisture content lower than 0.5%. The solid obtained after crushing was oleogel (3% HPMC and 97% oil content, w/w). For the preparation of 50/50 emulsion and fat blends (EM-50%) or 50/50 oleogel fat blends (OL-50%), 10 g of butter was semi-melted in a water bath at 40 °C and mixed with 10 g of oleogel or 10 g of emulsion and stirred uniformly. Cream cheese prepared with 100% butter as a fat source was used as control, 100% emulsion and 100% oleogel-prepared cream cheese were labeled as EM-100% and OL-100%, respectively.

2.3 Cream cheese-making process

Five hundred grams of whole milk was stirred and heated at 90 °C for 10 min. 10 g of vinegar was then added to adjust the acidity of the milk to pH 5.0, and the mixture was filtered with gauze over 30 min. 120 g of the solids collected (curd) were placed in a food processor (Thermomix 31, Vorwrek, Wuppertal, Germany) and 15 g of fat (butter, oleogel, emulsion, or fat blend), and 0.5 g of salt were added. Last, all ingredients were mixed at a speed of 200 rpm for 1 min to obtain the cream cheese. All cream cheeses were stored at 4 °C prior to all tests.

2.4 Spreadability

A TA.XT. Plus texture analyzer (Stable Micro Systems Ltd. Surrey, UK) equipped with a 90° conical spread test probe (TA-425 TTC Spreadability RIG) was used for the experiments. Before measurement, the cream cheeses were filled bubble-free into the inner cavity of the cone sample holder and gently flattened with a spatula to avoid air incorporation. The sample temperature during the texture measurements was 10 °C. As during the holding process, the sample temperature increased to more than 10 °CC, the sample inside the holder was placed again in the refrigerator at 4 °C for approximately 10 minutes, as the necessary time to achieve a sample temperature of 10ºC. The test conditions were as follows, test speed: 1

mm/s, test distance: 22.5 mm, and trigger force: 1.0 g. Measurements were conducted by pressing the sample between the two cones with a male cone and returning to the initial position to obtain force versus time data to calculate the maximum force and area under the curve. The maximum force represented the firmness of the sample. The area under the curve (AUC) represented the ease of the shearing process referred to as spreadability.

2.5 Rheological measurements

All rheological tests on cream cheese samples were conducted on a controlled stress rheometer model AR-G2 (TA Instruments, Montreal, QC, Canada) equipped with a 40 mm rough parallel plate geometry and a Peltier temperature control system. All samples were measured at 10 °C, with a 1 mm gap setting and 5 min of equilibration before each test. Three measurements were made on each sample from different batches. Strain sweeps were performed at 1 Hz in a strain amplitude of 0.01 to 1000%, and Fourier transform rheology and orthogonal stress decomposition (Ewoldt, Hosoi, & McKinley, 2008) were used on the raw waveform data to evaluate linear and nonlinear responses to strain. Frequency sweeps inside the linear viscoelastic region (LVR) were performed from 10 to 0.01 Hz. The information on the yield point and flow point of all samples was recorded. γ_y, and σ_y were the values of the shear stress and strain at the linearity limit of the LVE region (yield point). γ_f, and σ_f were the values of the shear stress and strain at the crossover point (G'=G", flow point).

2.6 Sensory evaluation

Ninety students and fellows from the Institute of Agrochemistry and Food Technology (IATA-CSIC) were invited to evaluate the sensory characteristics of cream cheese. The sensory test was conducted in a standardized sensory evaluation room with 10 separate booths. Samples were prepared the day before and refrigerated at 4 °C. Five samples identified with a random computer-assigned code were tested. A nine-point hedonic scale from 1 (extremely disliked) to 9 (extremely liked) was used to measure the appearance, texture, taste, spreadability, and overall rating acceptability of the cream cheese, as well as the flavor of cream cheese coated with crackers. All participants will be required to read and sign the informed consent form prior to the start of the test. Before each test, participants were notified to take a 30-s interval and rinse their mouths before evaluating the next sample to minimize interference between samples.

A questionnaire with a 5-point scale was used to assess the intention to purchase cream cheese, with 0 indicating that it would not be purchased and 5 indicating it would definitely be purchased. First, participants were evaluated without being given information about the cream cheese recipe. Similarly, a 30s interval was required between each sample and mouth rinsing before the next sample could be evaluated. The second part of the test was carried out with the participants being informed about the cream cheese recipe information and the steps were the same as in the first part.

2.7 Data analysis

The rheological data were processed with TRIOS 5.4 software (TA Instruments, USA). The results were analyzed by one-way analysis of variance (ANOVA) using the XLSTAT software system (2019.2.2). Significant differences between means ($p \leqslant 0.05$) were analyzed with Tukey's test. Data were represented as mean ± deviation (SD). All tests were repeated at least three times to ensure the accuracy of the experimental data. Principal Component Analysis (PCA) was performed to correlate instrumental parameters and sensory attributes.

3. Results and discussion

3.1 Spreadability

Spreadability is a texture property required in cream cheese. It represents the ease of distributing the cheese in a layer over a surface. Spreadability is negatively correlated with firmness (maximum force) and with the area under the penetration curve. Higher values of firmness and area under the curve (AUC) indicate a lower spreadability. The firmness and AUC values of the different formulations studied are shown in Table 1. Cream cheese prepared with 50% emulsion or 50% oleogel did not significantly differ from the control. The lowest firmness and area were found with the complete replacement of butter by oleogel (OL-100%). The replacement of butter by the emulsion also significantly decreases the firmness and area values at 100% replacement compared to the control, although the effect was lower than for the oleogel. In OL-50% and EM-50%, only the AUC value corresponding to OL-50% was significantly lower than that of the control. Furthermore, the 100% emulsion cream cheese was not significantly different from the 50% oleogel cream cheese. The increase in cheese spreadability due to the total replacement of butter by the oleogel and the emulsion could be explained by a casein matrix-breaking effect, or as a reduction of the fat crystal in butter, which increased softness, as speculated by other authors. Bemer et al. (2016) reported that cheese made from oleogel using RBW or ethylcellulose had higher spreadability. The increased size of the fat globules would weaken the interaction between the proteins in the internal network, resulting in a softer texture of the cheese product (Noronha, O'Riordan & O'Sullivan, 2008). Anvari & Joyner (Melito) (2019) considered that emulsions with negative charges or neutralized interfaces inhibited the interaction between casein and oil phases during cheese making, reducing the strength of the casein network. Using hydrocolloids as fat substitutes in cheese decreases the density and continuity of the matrix. By binding to water molecules and forming colloidal lumps or networks throughout the protein matrix, the fat replacers based on hydrocolloids act as casein matrix-breakers (Everett & Auty, 2008). Joyner, Francis, Luzzi & Johnson (2018) suggested that flowable emulsions could weaken cheese structure as flocculated droplets generated more and larger voids in the microstructure of the cheese, which disrupted the continuity of the casein matrix, resulting in the internal microstructure of the cheese being more vulnerable to rupture, causing the cheese to become softer (Anvari & Joyner (Melito), 2019). However, other studies have found an improvement in the cheese firmness caused by some hydrocolloids (Hosseini-Parvar, Matia-Merino, & Golding, 2015). The increase in spreadability due to the total replacement of butter by the oleogel and the emulsion could also be explained due to the disruption of the underlying structure of the colloidal network constructed by shortening the crystalline particles (Patel, Nicholson & Marangoni, 2020), thus reducing the mechanical properties of cream cheese and making it softer. Spreadability was an essential factor to be considered in the improvement of cream cheese formulations because favorable spreadability not only benefited the production and processing of cream cheese, but also made the cream cheese smoother and easier to spread uniformly, which would enhance the texture and aesthetics of the food products, and thus increased the attractiveness of the cream cheese products to the consumers.

Table 1. Mean values of the spreadability test parameters of the different cream cheeses at 10 °C.

Samples	Firmness (N)	AUC (N s)
Control	86.27 ± 14.25^{A}	170.47 ± 29.40^{A}
OL-50%	77.99 ± 7.19^{AB}	135.29 ± 19.20^{B}
EM-50%	89.01 ± 5.79^{A}	151.45 ± 6.86^{AB}
OL-100%	54.37 ± 6.49^{C}	94.37 ± 7.67^{C}
EM-100%	65.26 ± 3.69^{B}	132.46 ± 10.40^{B}

* Control: cream cheese prepared with butter; OL-50%: cream cheese prepared with 50% oleogel and 50% butter; EM-50%: cream cheese prepared with 50% emulsion and 50% butter; OL-100%: cream cheese prepared with 100% oleogel; EM-100%: cream cheese prepared with 100% emulsion. Different letters in the same column represent significant differences according to the Turkey test ($p < 0.05$).

3.2 Amplitude sweeps of cream cheeses

To comprehensively analyze the effect of emulsion and oleogel on the viscoelastic properties of cream cheese, the variation of the storage modulus (G') and loss modulus (G") of the cheese during a strain amplitude sweep was studied (Figure 1). All cream cheese samples presented a predominance of G' versus G" in the LVR. In both oleogel and emulsion cheeses, a decrease in G' was observed with an increasing level of butter substitution. Like the spreadability parameters, at 100% butter substitution, both G' and G" of cream cheese prepared with oleogels were lower than those prepared with emulsions. Section 3.1 mentions that the breaking effect in the cheese protein matrix explains this, especially for the oleogel over the emulsion.

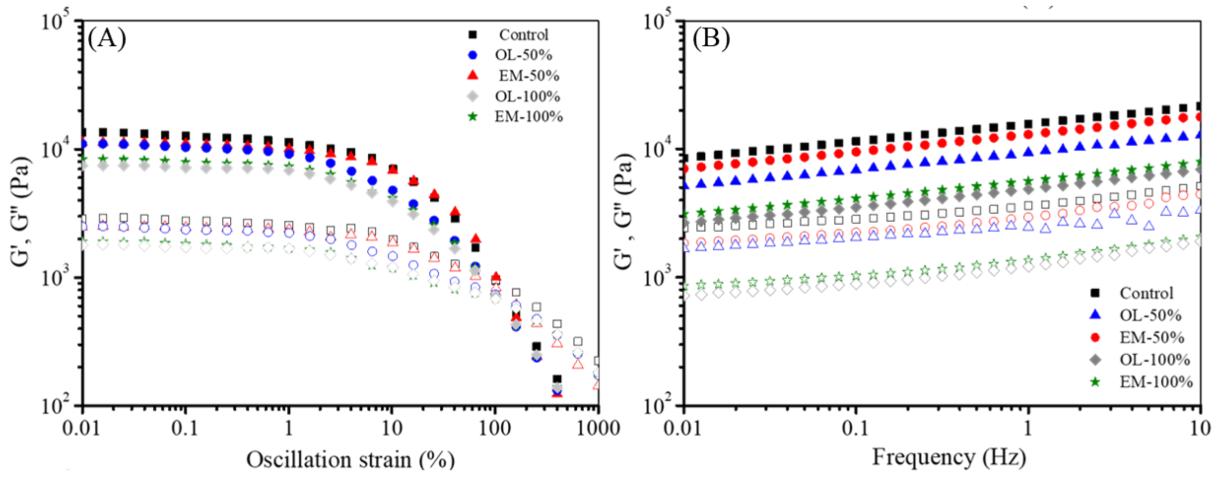

Figure 1. Strain sweep (A) and frequency sweep (B) of the different cheeses, ■ represents G', □ represents G".

To characterize the LVR, mean values of constant storage modulus (G'_0) and loss tangent (tan δ_0) corresponding to the plateau region were calculated (Table 2). The highest G'_0 values were found in the control cheese with no significant differences compared with 50% oleogel cheese. The increase in replacement from 50% to 100% significantly decreases G'_0 for both oleogel and emulsion, indicating a decrease in network rigidity compared to the control cheese. Values of tan δ_0 in the linear region were between 0.22-0.24, implying a solid-like behavior, with no significant differences among samples.

Above a critical strain value, both G' and G" decreased when strain amplitude increased, denoting the end of the LVR. To quantify the extension of the LVR, values of yield stress (σ_y) and corresponding strain (γ_y) were calculated (Table 2). The yield point was calculated considering a 5% deviation from the plateau (Mezger, 2020). These yield values determine the starting point for weakening of gel strength (Yousefi & Razavi, 2015). No significant differences in σ_y and γ_y were found among samples, indicating that all types of cheese require similar stress to reach the same strain value and that the extent of their linear behavior response is similar. Yield stress values between 30 and 40 Pa had to reach small strain values, from 0.3% to 0.5%.

At higher strain values, a crossover between G' and G" defined as the flow point, was observed. The values of the flow point, the corresponding strain (γ_f), and stress (σ_f) are also shown in Table 2. Like to G'_0, the values of the flow point (G' = G") decrease with increasing butter replacement, although no significant differences were found between the control and the sample with 50% oleogel. Furthermore, there was no significant difference between the three cream cheese groups prepared from 50%-emulsion as well as 100% emulsion and 100% oleogel, but the G' values were significantly lower than those of the control and 50% oleogel groups. No clear differences were found in γ_f and σ_f among cheeses, probably associated with the high coefficient of variation of these parameters, values of around 1000 Pa were required to reach a deformation of approximately 110%.

3.3 Frequency sweep of cream cheeses

The effect of frequency in the values of G' and G" in the linear region was shown in Figure B. For all formulations, the values of G' were always higher than G" along the complete frequency sweep studied with a light dependence of both G' and G" when frequency increased, revealing a cheese viscoelastic behavior typical of soft gels. Addition of oleogel and emulsion to replace butter in cream cheeses decreased G' and G" values, and the effect increased by increasing butter replacement. No changes in the ratio G"/ G' associated with butter replacement were observed (Table

2), where no significant differences of tan δ_0 calculated at 1 Hz were found between the control and the oleogel and emulsion cheeses.

3.4 LAOS rheology analysis of cream cheeses

In oscillatory strain sweep tests conducted over a wide deformation strain amplitude range (from 0.01 to 1000%), both the linear and nonlinear deformation regimes of all cheese are shown (Figure 1A). Due to the light frequency dependence of both G' and G" observed in the frequency sweep (Figure 1B), measurements were conducted only at a single frequency of 1 Hz.

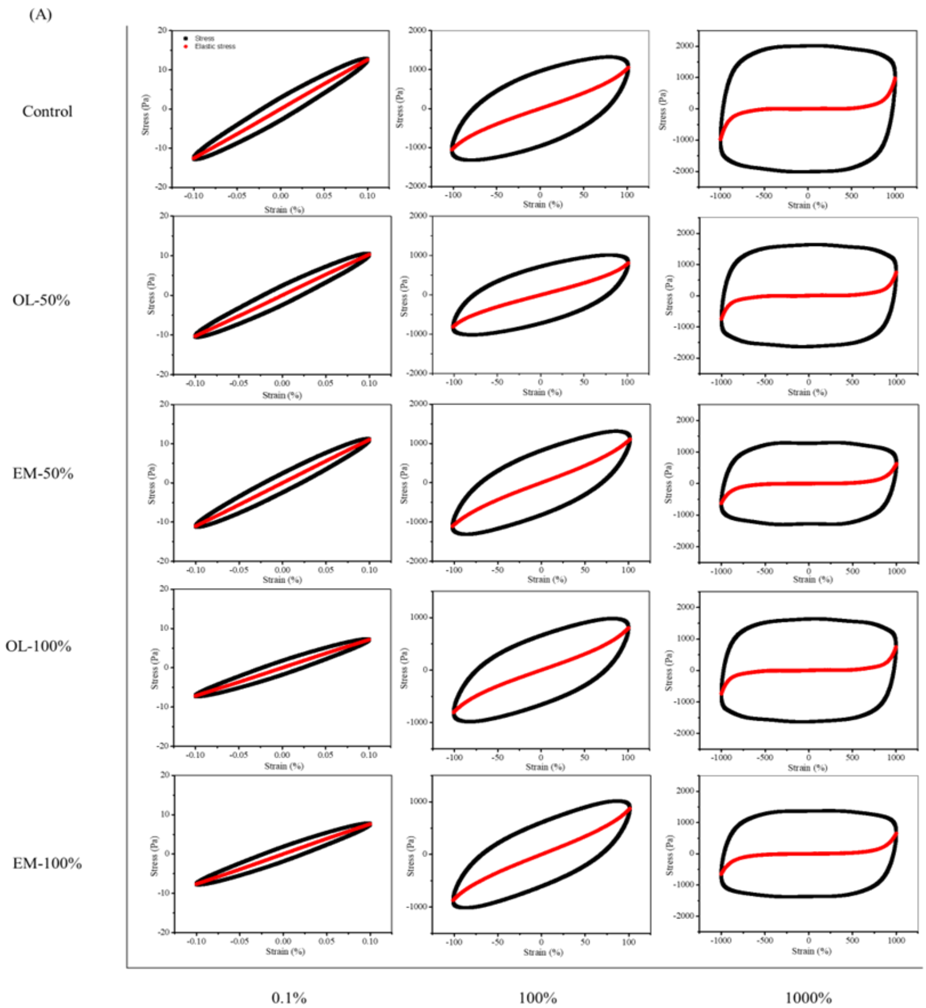

Figure 2A. Normalized elastic Lissajous–Bowditch (stress-strain) curves for cream cheeses for 0.1, 100, and 1000% strain amplitudes.

To further investigate the rheological behaviors of samples in the strain amplitude range from SAOS to LAOS, Lissajous–Bowditch plots (Joyner & Meldrum, 2016; Szopinski & Luinstra, 2016) were used to qualitatively analyze the elastic and viscous variation of samples over the strain interval, providing insight into the structural transformation of the material under large deformations and consequently anticipate the behaviors of the material during processing and application. Strain values of 0.1%, 100%, and 1000% were selected to investigate the transition from linear to nonlinear behavior of cream cheese. The total stress response as a function of strain (elastic Lissajous–Bowditch curves) and the total stress as a function of strain rate (viscous Lissajous–Bowditch curves) are shown in Figures 2A and 2B, respectively. These curves show separately the elastic and viscous stress contributions. The elastic Lissajous–Bowditch plots for all cream cheeses were elliptical at 0.1% strain, indicating an ideal viscoelastic behavior. The viscoelastic behavior of cream cheese shifted from the linear to the nonlinear region as the strain increased to 100% (near the intersection of G' and G"). The gradual enlargement of the ellipse area indicated an enhancement of nonlinear behavior for all samples resulting from the input of strain energy, leading to energy dissipation (Yazar et al., 2019). Finally, the elastic Lissajous–Bowditch plot of all cream cheeses varied from an ellipse to a sub-parallelogram as the strain rose to 1000%, which indicated an increase of viscous dissipation and a transfer from an elastic to a viscous predominant behavior (Fuongfuchat et al., 2012). Joyner & Meldrum (2016) believed that the nonlinearity increase observed at higher strains could be attributed to microstructural deformation, which resulted in permanent deformation and fluidity and exhibited a viscous dominant behavior in Lissajous.

Table 2. Mean values of parameters that characterize strain sweeps for the different cheeses studied. G0' and tan δ0 correspond to the storage modulus and loss angle for the plateau region in LVR and γy, γf, σy, σf correspond to the strains and stresses at the yield point and the flow point, respectively.

Sample	LVR-Yield point				Flow point		
	G'_0 (Pa)	tan δ_0	γ_y (%)	σ_y (Pa)	G' = G" (Pa)	γ_f (%)	σ_f (Pa)
Control	11760 ± 863^{A}	0.22 ± 0.01^{A}	0.31 ± 0.14^{A}	37.40 ± 8.42^{A}	805 ± 121^{A}	101 ± 6^{B}	1180 ± 119^{AB}
OL-50%	11039 ± 41^{A}	0.23 ± 0.00^{A}	0.37 ± 0.05^{A}	42.01 ± 5.53^{A}	869 ± 118^{A}	109 ± 8^{AB}	1357 ± 238^{A}
EM-50%	8401 ± 534^{B}	0.23 ± 0.00^{A}	0.44 ± 0.09^{A}	37.59 ± 7.38^{A}	604 ± 28^{B}	119 ± 8^{A}	1021 ± 34^{BC}
OL-100%	5771 ± 862^{D}	0.24 ± 0.00^{A}	0.49 ± 0.11^{A}	29.72 ± 10.25^{A}	587 ± 60^{B}	109 ± 2^{AB}	909 ± 103^{C}
EM-100%	7250 ± 310^{C}	0.23 ± 0.01^{A}	0.35 ± 0.10^{A}	28.93 ± 7.06^{A}	612 ± 43^{B}	116 ± 10^{AB}	1003 ± 61^{BC}

* Control: cream cheese prepared with butter; OL-50%: cream cheese prepared with 50% oleogel and 50% butter; EM-50%: cream cheese prepared with 50% emulsion and 50% butter; OL-100%: cream cheese prepared with 100% oleogel; EM-100%: cream cheese prepared with 100% emulsion. Different letters in the same column represent significant differences according to the Turkey test ($p < 0.05$).

The viscous Lissajous–Bowditch curve represents the stress as a function of the strain rate. The variation in the viscosity of cream cheese in the strain interval is shown in Figure 2B. All cream cheeses exhibited a deformed elliptical shape at low strain rates, as strain grew, the elliptical area gradually decreased and ultimately inclined to an S-shape, which indicated a nonlinear behavior of the sample with viscous shear thinning (Ewoldt et al., 2008; Q. Li et al., 2021; Szopinski & Luinstra, 2016). At the highest strains, the rheological behavior of cream cheese is more flow-oriented (Yazar et al., 2019).

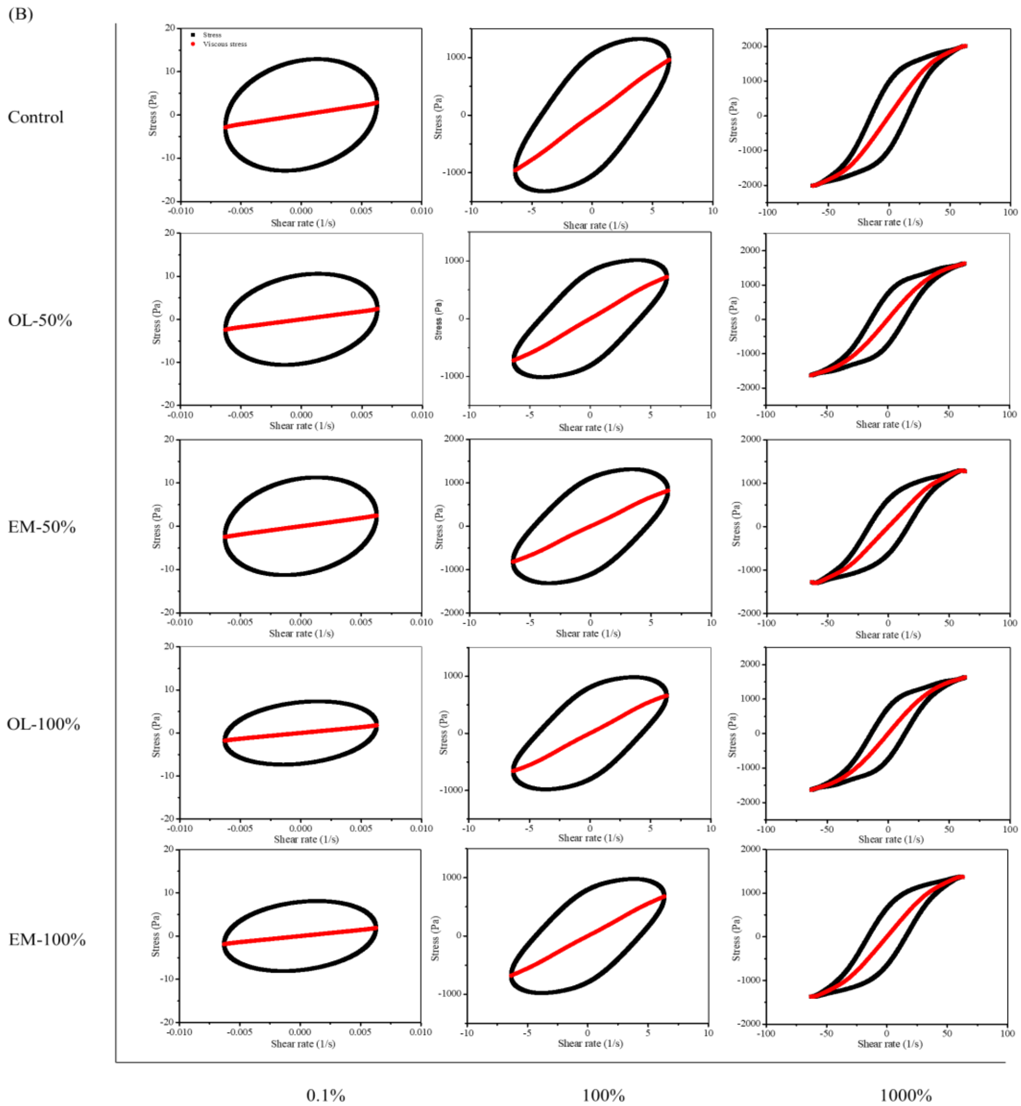

Figure 2B. Normalized viscous Lissajous–Bowditch (stress-strain rate) curves for cream cheeses for 0.1, 100, and 1000% strain amplitudes.

To evaluate the nonlinear behavior of samples over the entire strain range, Ewoldt, Winter, Maxey & McKinley (2010) defined the stress-stiffness ratio (S-value) and shear-thickening ratio (T-value). The S ratio corresponds to the relative differences in the minimum strain elastic modulus, G'_M, and the large strain elastic modulus, G'_L; and the T ratio corresponds to differences in the minimum strain rate viscosity, η'_M, and the large strain rate viscosity, η'_L (Ewoldt et al., 2008; Yazar et al., 2019).

$$S = \frac{G'_L - G'_M}{G'_L}$$

$$T = \frac{\eta'_L - \eta'_M}{\eta'_L}$$

$S > 0$ shows intracycle strain stiffening, which means the deformation rate decreases when increasing strain; $S < 0$ shows intracycle strain softening, i.e. deformation rate increases when increasing strain. In contrast, $T > 0$ represents intracycle shear thickening (increasing viscosity with increasing strain rate) and $T < 0$ corresponds to intracycle shear thinning (decreasing viscosity with increasing strain rate) (Duvarci, Yazar & Kokini, 2017).

As shown in Figure 3, the S values of all samples remained approximately 0 in the LVR (strain < 10%), and then the S values of all cream cheeses exhibited a strain-stiffening behavior as the strain increased. Similar results were shown by Precha-Atsawanan et al. (2018). In terms of T values, in all samples, a decrease is observed with increasing strain ($T < 0$), showing a remarkable shear-thinning behavior. The absolute value of T was always much lower than the value of S during the large deformation occurrence, indicating that the nonlinear behavior of cream cheese under large deformation was strain stiffening predominant.

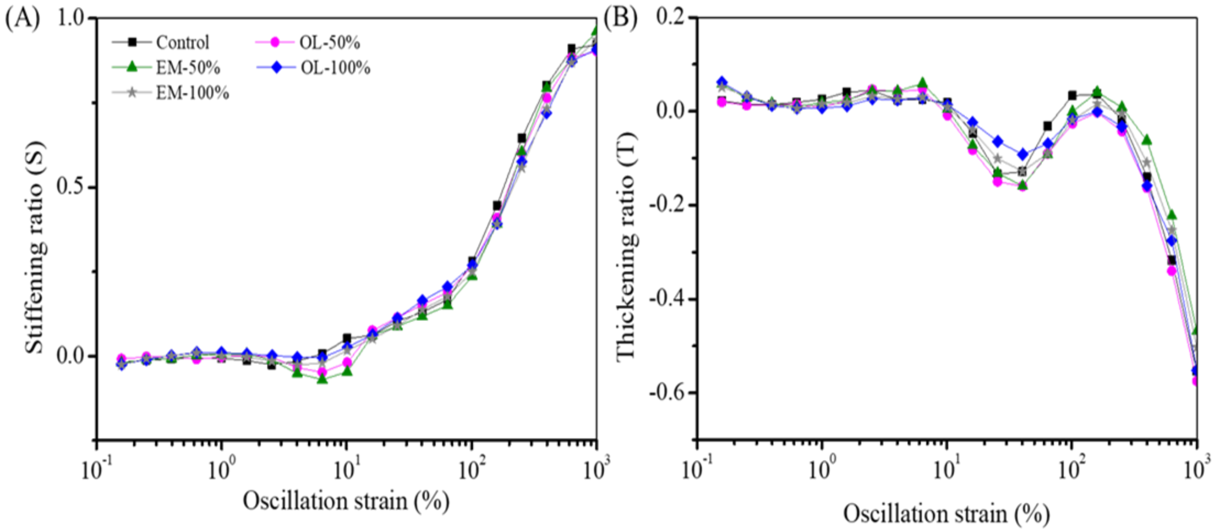

Figure 3. Variation of Stiffening ratio (plot A) and Thickening ratio (plot B) with strain of cream cheese prepared with the different fat sources.

3.5 Sensory evaluation

The mean values of the sensory acceptability scores for the appearance, texture, spreadability, and flavor of the cream cheese are shown in Table 3. No significant differences among the different types of cheese were found in appearance ($p > 0.05$). In terms of texture, the average score of the OL-100% group was significantly different from the average scores of the OL-50%, EM-50%, and EM-100% groups. Oleogel cream cheese (100%) showed the significantly lowest flavor acceptability, this may be due to the fact that the flavor of the oleogel itself had some effect on the cream cheese, but did not appear in the other samples. As for spreadability, all samples prepared with oleogel and emulsion exhibited significantly higher spreadability compared to the control group, which was consistent with the previous instrumental texture results. Regarding the flavour of the cream cheese with cracker spread and the overall score, it was shown that there was no significant unfavorable effect of emulsion or cream on the cream cheese, and even the flavor with cracker was significantly higher for the

Table 3. Sensory acceptability scores for the different cream cheeses.

Sample	Appearance	Texture	Flavor (Only cheese)	Spreadability (with cracker)	Flavor (with cracker)	Total score
Control	6.48 ± 1.49^{A}	6.16 ± 1.64^{AB}	6.46 ± 1.35^{AB}	6.28 ± 1.72^{C}	6.70 ± 1.29^{B}	6.50 ± 1.35^{BC}
OL-50%	6.80 ± 1.30^{A}	6.77 ± 1.42^{A}	6.79 ± 1.30^{AB}	7.65 ± 1.16^{AB}	7.26 ± 1.19^{A}	6.99 ± 1.24^{AB}
EM-50%	6.73 ± 1.50^{A}	6.53 ± 1.54^{A}	6.90 ± 1.23^{A}	7.37 ± 1.50^{B}	7.23 ± 1.23^{A}	7.15 ± 1.21^{A}
OL-100%	6.82 ± 1.34^{A}	5.73 ± 1.88^{B}	5.44 ± 1.66^{C}	7.32 ± 1.45^{B}	6.54 ± 1.46^{B}	6.04 ± 1.62^{C}
EM-100%	7.71 ± 1.35^{A}	6.46 ± 1.55^{A}	6.36 ± 1.51^{B}	7.10 ± 0.96^{B}	6.79 ± 1.23^{AB}	6.68 ± 1.45^{AB}

* Control: cream cheese prepared with butter; OL-50%: cream cheese prepared with 50% oleogel and 50% butter; EM-50%: cream cheese prepared with 50% emulsion and 50% butter; OL-100%: cream cheese prepared with 100% oleogel; EM-100%: cream cheese prepared with

50% oleogel and 50% emulsion cheeses compared to the control group. Moreover, cream cheeses produced with 100% emulsion or oleogel could completely replace the conventional fat in cream cheese as their flavor scores with cracker and total scores were not significantly different from the control group.

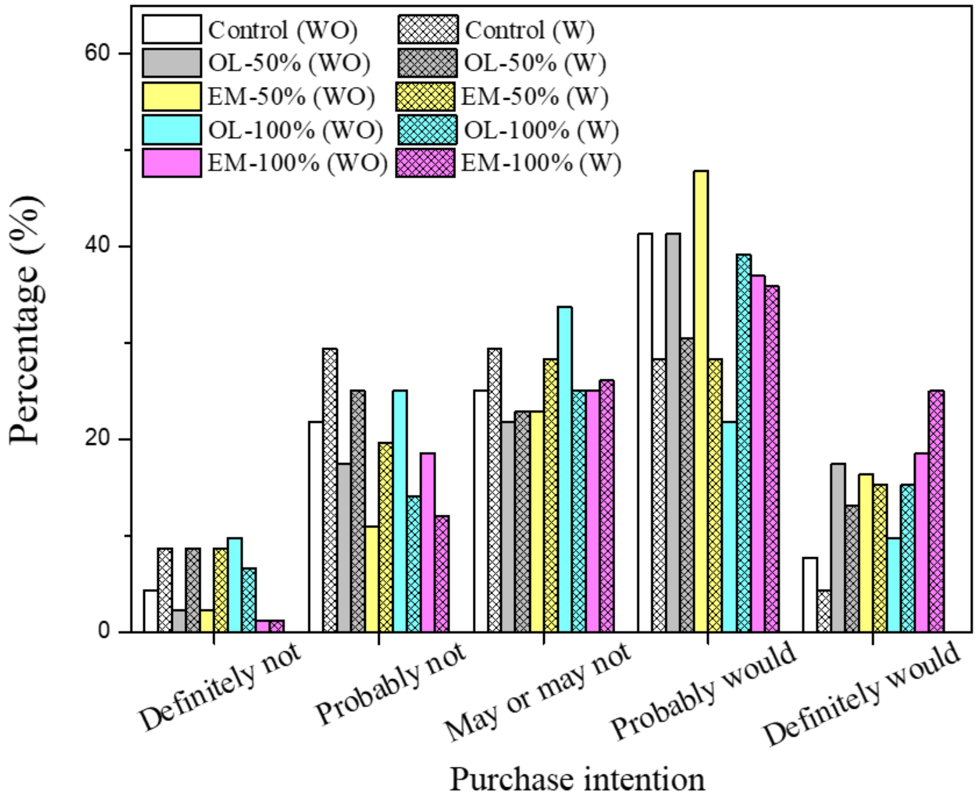

Figure 4. Intention to purchase the different cream cheeses. WO means that the test was carried out without information about the cream cheese recipe. W means that the test was conducted with the information about the cream cheese recipe.

Figure 4 shows the purchase intention of consumers before and after being informed of the cream cheese fat formulation. The percentage of unwillingness to buy control, 50% oleogel, and 50% emulsion cheese increased after consumers were informed about the type of fat, whereas the percentage of probably or definitely would purchase decreased. In contrast, the percentage of definitely would purchase 100% emulsion-prepared cream cheese increased from 18.5% to 25%, followed by cheese with 100% oleogel, which increased from 9.8% to 15.2%. This increase in purchase intention of the emulsion and oleogel cheeses indicates the importance given by consumers to the nutritional aspects, especially for a healthier fat profile with a reduction in the content of saturated fatty acids.

The correlation among instrumental texture parameters, rheological parameters inside and outside the linear viscoelastic region, and the consumers' acceptability were studied by PCA (Figure 5). The first two components explained 70.93% of the overall variability. The first dimension (F1) accounted for 46.39% of the variability and separated the samples according to their emulsion and oleogel content. The control and the samples with 50% replacement (EM-50% and OL-50%) are closely displayed on the right side of the plot and associated with the instrumental parameters: Firmness, AUC, Slaos, Tlaos, Ssaos, and Tmaos, and to the sensory parameters: global acceptability, texture acceptability, and flavor acceptability. The EM-100% appears separated in the positive part of the second component (24.54%) associated with spreadability, appearance acceptability, and Tsaos. Finally, sample OL-100% appeared separated in the negative part of F1 and not related to any of the instrumental and sensory parameters.

The results above demonstrated the feasibility of replacing fat with oleogels or emulsions in cream cheese manufacturing. The increase in the purchase intention after the nutritional information was given to the consumer supports the potential of oleogel and emulsion replacers as alternatives to conventional solid fat in dairy products.

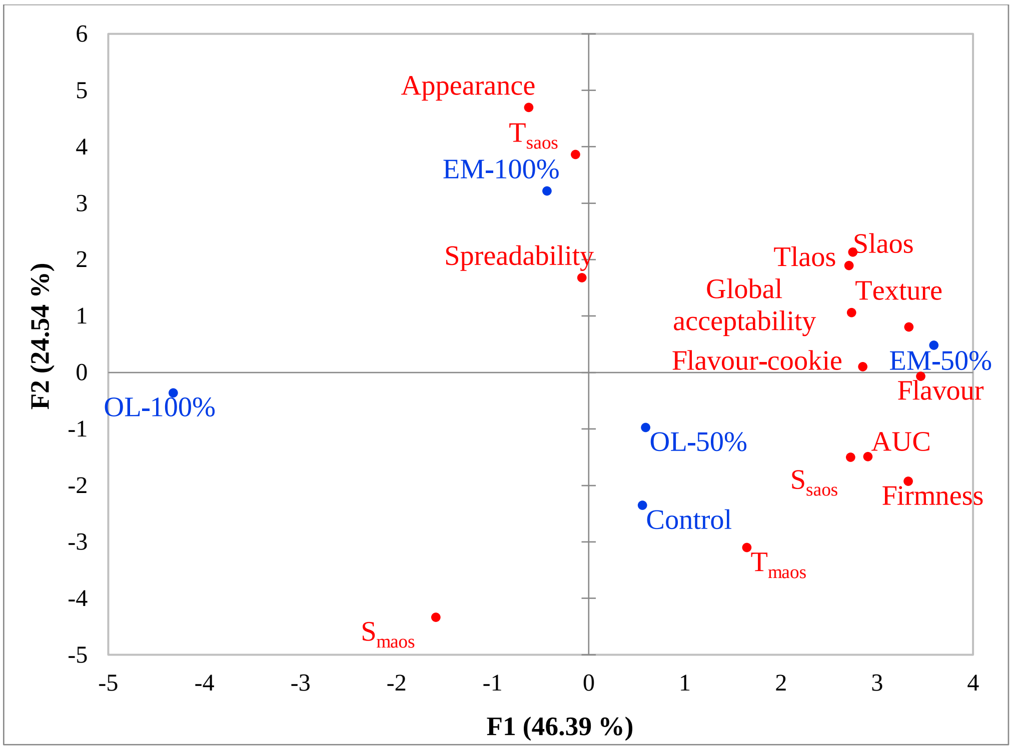

Figure 5. Principal Component Analysis (PCA) of samples, texture instrumental parameters, rheology parameters, and sensory acceptability.

4 Conclusions

This study validated the feasibility of employing HPMC oleogels and emulsions as substitutes for traditional fats in the production of cream cheese with reduced saturated fatty acids (oleogels and emulsions) and low-fat cream cheese (emulsions). The impact on spreadability, linear and nonlinear rheological behavior, and consumer acceptance of the products was assessed. The results indicated that oleogels and emulsions could enhance the spreadability of cream cheese, making it easier to spread. Rheological tests revealed that the mechanical strength of cream cheese decreased with an increasing proportion of oleogels and emulsions. Furthermore, under the same proportion, the storage modulus of oleogel cream cheese was smaller than that of emulsion cream cheese, suggesting a softer texture. Lissajous curves illustrated the transition from linear viscoelastic response to nonlinear response within the range of 0.1% to 1000%. All cream cheese samples exhibited nonlinear strain-stiffening and shear-thinning behavior, with no discernible differences between the different cheeses in the nonlinear region. Sensory evaluations showed that cream cheese prepared with oleogels and emulsions had minimal negative effects compared to the control group and even improved scores in spreadability, cream cheese flavor on biscuits, and overall assessment. Purchase intention assessments also indicated an increased willingness to buy cream cheese prepared with 100% emulsion and 100% oleogel after participants were informed about the type and amount of fat in the formulations. This study demonstrated the significant potential of replacing traditional fats with HPMC emulsions and oleogels in cream cheese formulations, providing insights into the development of healthier, low-saturated fatty acid or low-fat cream cheeses without compromising product quality.

Acknowledgments

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Chapter 3

Oleogel application in puff pastry

Sunflower oil-based oleogel as fat replacer in croissants: textural and sensory characterization

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Abstract

Croissants are made using solid fats that predominantly contains saturated fatty acids and *trans* fatty acids. In this study, an oleogel consisting sunflower oil structured with hydroxypropyl methylcellulose was used as a conventional fat replacer in puff pastry thus improving the nutritional profile. Oleogel (OG)-shortening (SH) blends were prepared as fat replacer for partial (50, 60, 70%) and full shortening (100%) substitution. Physical characterisation was conducted using texture profile analysis and penetration tests to evaluate the oleogel effect on a baked croissant matrix structure. Sensory analysis was also performed to evaluate the organoleptic properties of the croissant. Shortening replacement using oleogel results in croissants with lower saturated fat content, less bite firmness, and texture behavior like croissants using commercial shortening. The presence of oleogel of up to 100% did not contribute negatively to the firmness or springiness of the croissants, although they became chewier and more cohesive as the oleogel increased. In terms of sensory perception, the SH50:OG50 croissant sample was the most similar to the solid fat control. The use of sunflower oil-cellulose-based oleogel was suitable for the formulation of puff pastry products with a healthier fat profile while maintaining the physical and sensory characteristics such as conventional croissants.

Keywords: oleogel, shortening replacer, hydroxypropyl methylcellulose, croissant, texture

1. Introduction

Laminated dough products, such as croissants, have many plastic fats rich in saturated fatty acids. Their unique structure is composed of alternative thin fat and dough layers and provides a desirable light, delicate, and flaky texture when baked, highly appreciated by consumers (Simovic, Pajin, Seres, & Filipovic, 2009). Puff pastry fat must have certain specific structural characteristics, such as predetermined plasticity, firmness, and solid fat content profile (Simovic, Pajin, Seres, & Filipovic, 2009). Laminated dough products comprise many thin, alternating layers of fat and dough formed by repeated rolling and folding. Therefore, fats used in laminated dough production are often referred to as “roll-in fats”. Upon baking, the layering causes each individual dough layer to bake separately, creating the characteristic visual separation of the layers and the flaky texture (Mattice & Marangoni, 2017). Thus, fat plays a key role in puff pastry and cannot be replaced without adversely affecting aspects such as appearance, texture, structure and flavour of the reduced-fat puff pastry (Pimdit, Therdthai, & Jangchud, 2008).

Butter is the traditional fat used for puff pastry, but its high costs and difficult handling during industrial processing have led to the development of fat blends specifically manufactured for its replacement (Silow, Zannini, Axel, Belz, & Arendt, 2017). These fat blends are mainly derived from vegetable oils and fats and offer improved processability (fat plasticity). However, processes that confer these oils a solid texture, such as partial hydrogenation, generate a high proportion of *trans* fatty acids, which are associated with increased risks of several conditions, including coronary heart disease, cancer, diabetes, allergies, and poor foetal development (Simovic, Pajin, Seres, & Filipovic, 2009; Wickramarachchi, Sissons, &

Cauvain, 2015). Other alternatives like complete hydrogenation, transesterification, or using vegetable oils or fats do not contain *trans* fatty acids but are rich in saturated fatty acids. Therefore, there is a need in the food industry to develop environmentally friendly and cost-effective strategies to reduce or replace highly saturated fat.

There are several approaches to reducing the fat in pastry products, based on carbohydrate, protein, or fat mimetics. These attempts reported poor success when a single fat replacer was used to achieve all the functions of fat in puff pastry (Wickramarachchi, Sissons, & Cauvain, 2015). In particular, fat replacement in laminated pastries (such as croissants) has been a long-standing goal in industry.

In terms of nutrition and health, the ideal scenario would be to use liquid oil, rich in unsaturated fatty acids, to replace solid fat rich in saturated fatty acids. Nevertheless, it cannot generally be directly replaced with liquid oils without negatively impacting the physical and organoleptic properties of the end product (Wang, Gravelle, Blake, & Marangoni, 2016; Mert & Demirkesen, 2016). Using vegetable oil produces baked goods with greasier and less crispy characteristics and decreases the storage stability of the products, mainly due to oil oxidation (Jang et al., 2015). Furthermore, the mechanical behaviour of a fat substitute must be solid-like during initial deformation, followed by viscous liquid flow once the network deforms at the yield point—the melting temperature of the shortening substitute must be greater than the working temperature of the dough. Moreover, the consistency of the shortening material must be like the dough to obtain a flaky pastry (Blake and Marangoni, 2020). Gabriele et al. (2008) attempted to develop an emulsion formulated using olive oil, emulsifier, and hydrophilic thickener agents, but the large differences in rheological properties showed the need for further improvement of this replacer.

A way of using liquid oil to replace solid fat is to impart a solid consistency using an indirect oleogelification process using hydrocolloids. Recently, sunflower oil oleogels with cellulose ether, as the only structuring agent, have shown promising mechanical and oil retention properties (Espert, Salvador & Sanz, 2020). In this study, sunflower oil cellulose ether oleogels are used for the partial or total replacement of the solid fat used in the production of croissants. The textural and sensory properties of the reformulated croissants were compared with a commercial roll-in shortening based product to evaluate the effect of the oleogel in the final quality of croissants.

2. Materials and methods

2.1. Materials

The materials used for the production of the oleogel include sunflower oil (high oleic acid content) (Capicua, Compañía Oléicola, SAU, Sevilla, Spain), hydroxypropyl methylcellulose (HPMC) (Methocel® F4M Food Grade, 29 g/100 g methoxyl and 6.8 g/100 g hydroxypropyl (The Dow Chemical Co., Bomlitz, Germany)), and water. Laminating shortening (Hojaldambar® B90, Vandemoortele Ibérica S.A., Barcelona, Spain), pasteurised egg product (Derivados de Ovos, S.A., Pombal, Portugal), whole milk (Gaza, Zamora, Spain), fresh yeast (Lallemand, Madrid, Spain), wheat flour (Diexpa, Valencia, Spain), sugar (Disem, Valencia, Spain), and salt were used to prepare the croissants.

2.2. Preparation of the oleogel

Oleogels were prepared using the emulsion template approach with cellulose ether (HPMC) as the only structuring agent according to the methodology described in Espert, Salvador and Sanz, 2020). An emulsion of oil (47% w/w) in water (51.5% w/w) stabilised with hydroxypropyl methylcellulose (1.5% w/w) was prepared under specific conditions. First, cellulose ether was dispersed in the oil using a Heidolph stirrer (RZR 1) (Heidolph Instruments, Germany) at 280 rpm for 5 min. Water at 10 ºC was gradually added to hydrate the mixture under continuous stirring for 30 s. After, the mixture was homogenised using a high-energy dispersing unit (Ultraturrax T-18, IKA, Germany) at 6500 rpm for 15 s and at 17,500 rpm for 60 s. This emulsion was subjected to total evaporation of the aqueous phase in a forced convection oven at 60 ºC (Binder GmbH, Germany). Subsequently, the dried product was sheared using an A320R1 mincer (Moulinex, Groupe SEB, France), giving a final oil-concentrated oleogel (approx. 98%).

2.3. Preparation of the SH-OG blend

Different blends were prepared by partially (50, 60, and 70%) and totally (100%) replacing shortening (SH) with oleogel (OG) (SH50:OG50, SH40:OG60, SH30:OG70, and SH0:OG100). A shortening system without the addition of oleogel (SH100:OG0) was used as a control.

To prepare the SH:OG blends, the shortening was melted in a thermostatic water bath (JP Selecta S.A., Barcelona, Spain) at 45 °C. Then it was mixed with the oleogel under continuous stirring at the lowest speed (Heidolph RZR 1, Heidolph Instruments, Germany). The blend obtained was finally spread on an aluminium mould and stored at refrigeration temperature (4 °C). To obtain the control blend, the shortening was placed between two baking papers and spread out, forming a rectangle using a rolling pin, giving it the same shape as the mixtures. It was also stored at 4 °C.

2.4. Preparation of croissant dough

The proportions used for the preparation of the croissant dough were 250 g of wheat flour, 15 g of yeast, 35 g of sugar, 125 g of cold whole milk, 60 g of pasteurised eggs, 2 g of salt, and 125 g of fat (100%, 50%, 40, 30, and 0% for the blends SH100:OG0, SH50:OG50, SH40:OG60, SH30:OG70, or SH0:OG100, respectively).

To prepare the dough, part of the total fat (25g) (shortening or SH:OG blend), sugar, salt and pasteurised egg were mixed for 10 s at speed 6 using a food processor (Thermomix TM31, Vorwrek, Wuppertal, Germany). Subsequently, the yeast was diluted in cold milk and added with the flour to the previous mixture, mixing for 20 s at speed 6.

After obtaining the dough, it was kneaded by hand for 10–15 min to obtain a homogeneous dough, which was then wrapped in plastic film and kept in the refrigerator for 8 h. After the refrigeration time, the dough was extended using a rolling pin and then the rest of the fat (shortening or previously prepared SH-OG blend (2.3 section)) was incorporated into the centre of the extended dough for laminating (Figure 1). To start the lamination step, the dough was folded to retain the SH:OG blend inside. It was turned 90° horizontally and spread again with the rolling pin from the centre to the sides to spread the fat uniformly. The dough was then folded in three layers and allowed to rest in the refrigerator for 20 min. The rolling and folding steps were repeated three more times until four folds were complete. Then, the folded dough was extended into a rectangle (approximately 42 cm × 22 cm) and cut into 7 cm triangles. In each triangle, a 2 cm vertical cut was made in the middle of the base and rolled into the characteristic croissant shape. The raw croissants were placed in the refrigerator for 20 minutes. Finally, the croissant surface was brushed with pasteurised egg and was placed in a preheated oven and baked at 180 °C for approximately 20 min.

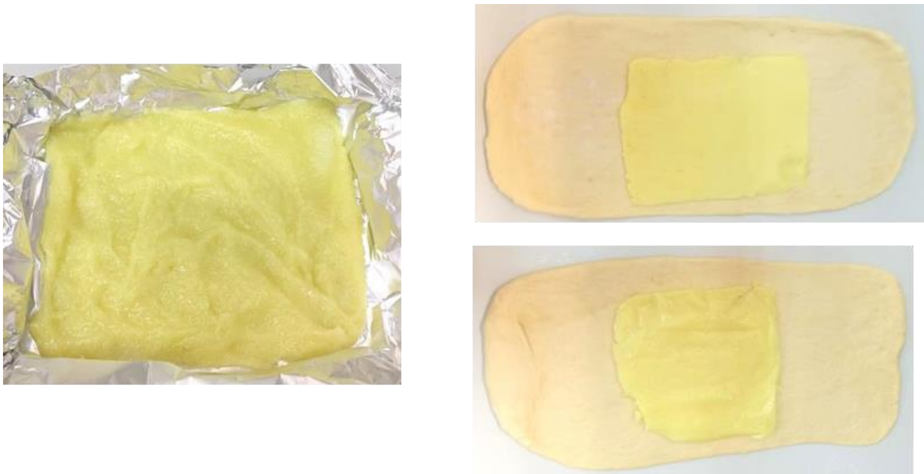


Figure 1. The visual appearance of the fat-oleogel blend (SH50:OG50) (a) and the doughs prepared for lamination with the control blend (SH100:OG0) (b) and with the fat-oleogel blend (SH50:OG50).

2.5. Texture characterisation of croissants

The texture of the baked croissants was determined using a TA-XT Plus texture analyser equipped with Texture Exponent software (Stable Microsystems, Godalming, UK).

Tests were conducted at room temperature (20 ± 1 ºC) 24 h after preparation. Ten croissants per formulation were used for measurement to ensure the reproducibility, and three repetitions of each sample were evaluated on different days.

To evaluate the firmness of the croissant, penetration tests were conducted using Volodkevich bite jaws (HDP/VB) to simulate the action of an incisor tooth biting through a croissant. A penetration distance of 30 mm was used at a speed of 1 mm s^{-1}. Hardness was calculated as the breaking force peak obtained (N).

A Texture Profile Analysis (TPA) test was also conducted to see how the samples behave when being chewed. Double compression tests were performed using a 75 mm diameter aluminium plate (P/75). The test speed was 1 mm s^{-1} with a strain of 50% of the original sample height and a 5 s interval between the two compression cycles. From the TPA curves, the three primary texture parameters were obtained: hardness (the peak force during the first compression cycle), springiness (the height that the food recovers during the time that elapses between the end of the first bite and the start of the second bite), and cohesiveness (the ratio of the positive force area during the second compression portion to the positive force area during the first compression), as well as chewiness (hardness × cohesiveness × springiness).

2.6. Sensory evaluation

The sensory analysis of the croissant samples was conducted using a Free Choice Profile (FCP) analysis. A total of 10 consumers were recruited from the "Instituto de Agroquímica y Tecnología de Alimentos" (IATA-CSIC). Consumers gave written informed consent before the start of the study.

The analysis was conducted in two sessions. The first session was conducted to generate the individual vocabulary of each consumer to indicate the descriptors that characterised each sample (Repertory Grid method) (Tarancón, Sanz, Salvador, &Tárrega, 2013). For this purpose, each consumer received two samples of croissants (SH100: OG0 and

SH0:OG100), and they were asked to describe differences and similarities in terms of appearance, texture, and taste. An individual list of attributes was obtained from each consumer, which was then used to evaluate each croissant sample in a second session. In this session, consumers were asked to rate their own list of attributes for each of the five croissant samples (SH100:OG0, SH50:OG50, SH40:OG60, SH30:OG70, and SH0:OG100) using a 10 cm unstructured line scale with the anchors ‘Not perceived’ and ‘Very intense’ for each attribute. In both sessions, samples were presented with random three-digit codes for each sample and served at room temperature. Mineral water was provided to clean the palate between samples.

2.7. Statistical data

The raw data obtained were statistically analysed using a one-way analysis of variance (ANOVA) to evaluate the effects of the different percentages of SH or OG on the mechanical properties of the croissants. To analyse the significant differences between the different samples, Tukey's test was applied (significance at $p < 0.05$). The results from the Free Choice Profile analysis were analysed using the Generalized Procrustes Analysis (GPA) technique. Statistical analyses were performed using XLSTAT software (2019.2.2, Addinsoft, Barcelona, Spain).

3. Results

3.1. Visual appearance

The croissants were cut transversely, and photos were taken to compare the internal and external structure. Figure 2 shows that there are no major differences in the lamination of the croissants baked with the different

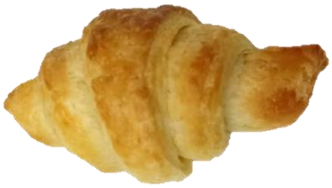
SH/OG	CRUST	CRUMB
100/0		
50/50		
40/60		
30/70		
0/100		

Figure 2. Visual appearance of the croissants obtained with different SH/OG ratio (SH: shortening; OG: oleogel).

SH:OG blends. However, the crumb differs between the control croissant (100% shortening) and the SH:OG blend croissants. This difference is probably due to the control dough having more air in its structure than the rest of the doughs, due to its higher solid fat content. Demirkesen & Mert (2020) stated that plasticity of shortening incorporates air bubbles during mixing, giving a smooth texture and a high volume in bakery products. The presence of oleogel (at all concentrations) reduces the aerated texture of the crumb and provides a more compact internal structure. There were no significant differences in the crust's appearance among the different oleogel substitution.

3.2. Texture analysis

3.2.1 Firmness determination

Firmness is a useful parameter to describe the texture and internal structure of puff pastry (Silow, Zannini, & Arendt, 2016). Peak firmness or maximum force peak for each croissant type is presented in Table 1. This peak firmness describes the force applied to completely bite through the sample. The penetration profile of each sample (Force versus time) is shown in Figure 3, which shows that all croissants break during the test, although the maximum peak force was not produced simultaneously. Samples with the highest fat content (SH100:OG0) provided the highest force values, indicative of the firmest texture. This could be due to the characteristic firmness of solid puff pastry fat at room temperature (20 ± 1 ºC). However, the lowest hardness values were observed in sample SH0:OG100 (Table 1), suggesting that oleogel in the croissants decreases the force required for penetration. This might be related to the absence of solid fat crystals in the fat blend, leading to a lower consistency in the croissant matrix, which translated in a softer croissant texture. As the concentration of oleogel increases, the hardness of the croissants decreases, although no significant differences were found in force values among the croissants formulated with SH-OG blends. Therefore, despite their more compact appearance, a reduction in croissant firmness is seen when oleogels are added to croissants. These results are not in line with previous studies on baked products. Jung et al. (2020) explained that the dense crumb structure of bread reformulated with oleogel would cause a significant increase in firmness. Although few studies focus on using oleogels as a fat substitute in puff pastry, Sim et al. (2021) recently found that ethyl cellulose oleogels (extensively characterised in recent years) failed to generate a puff pastry cake with a suitable texture. In baked products such as biscuits or cakes, the use of oleogels results in products with firmer texture (Kim et al., 2017; Mert & Demirkesen, 2016; Sim, Wong, & Henry, 2021).

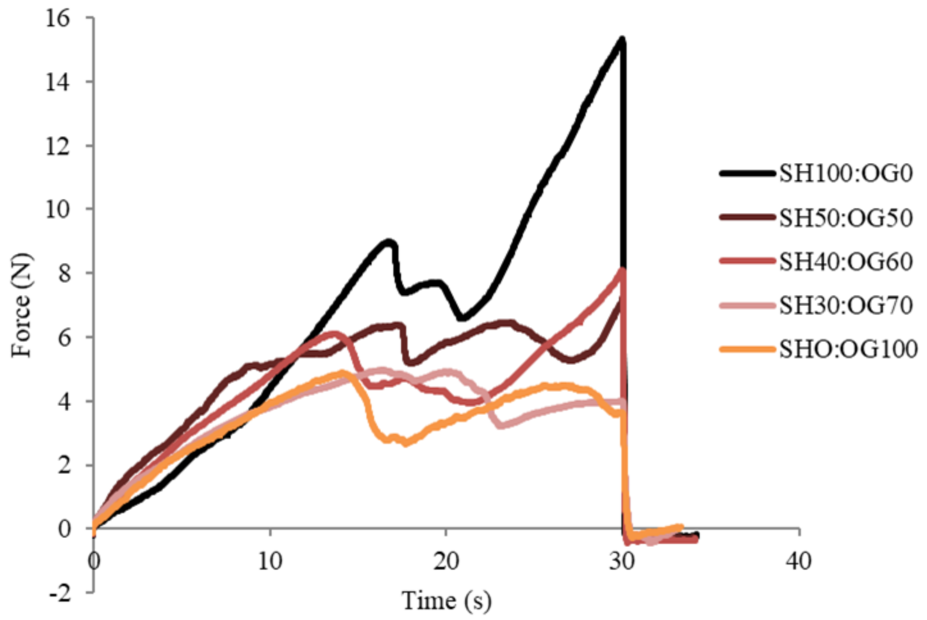


Figure 3. Penetration profile (force vs time) of the different croissants formulated (SH: shortening; OG: oleogel).

3.2.2 Texture profile analysis

Figure 4 and Table 1 show the TPA curves and parameter data for the tested croissants, respectively. No significant differences ($p < 0.05$) were found in the hardness and springiness of the croissants. Although some works show that the use of oleogels significantly affects the texture of the baked product, especially the firmness (Hwang, Singh, & Lee, 2016; Kim et al., 2017), the use of this oleogel did not show a change in the hardness and elasticity of the final product, even at a 100% replacement of traditional fat.

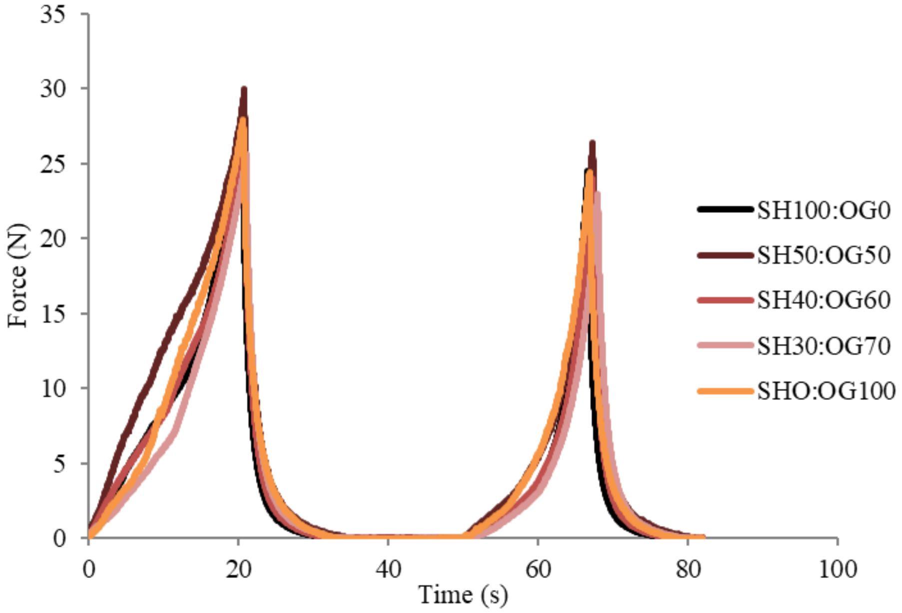


Figure 4. TPA curves for the different croissants formulated (SH: shortening; OG:oleogel).

However, an increase in oleogel proportions results in an increase in the cohesiveness, especially when compared to the control sample. Cohesiveness quantifies the internal strength of the food structure and provides information on the ability of a material to stick to itself (Lu, Lee, Mau, & Lin, 2010). Higher cohesiveness values in samples with more oleogel would indicate that more energy was required for the second compression. The higher cohesiveness of the oleogel croissant could be related to their more compact crumb structure. Compared to the control, the oleogel croissant's more compact network is more difficult to crumble. In contrast, the lower cohesiveness values in the control croissant could be explained by the presence of a crumb with weaker internal bonds that, once broken, cannot reform. Chewiness represents the amount of energy needed to disintegrate food to swallow. The TPA results also showed an increase in chewiness values with an increase in the proportion of oleogel, indicating that these samples offer greater resistance

Table 1. Texture values obtained from penetration and TPA measurements for the croissants formulated with different SH:OG ratios.

SH:OG ratio	**Penetration**	**TPA**			
	Max. peak firmness(N)	Hardness (N)	Springiness	Cohesiveness	Chewiness(N)
100:0	7.91^{A} (2.40)	27.68^{A}(2.67)	0.77^{A}(0.04)	0.43^{C}(0.02)	9.29^{B} (1.20)
50:50	6.32^{AB}(1.84)	27.13^{A}(3.24)	0.82^{A}(0.04)	0.47^{BC}(0.02)	10.53^{A} (1.80)
40:60	6.16^{AB}(1.92)	26.28^{A}(2.37)	0.78^{A}(0.02)	0.48^{B} (0.02)	9.89^{B} (1.41)
30:70	4.87^{B} (1.06)	25.87^{A}(3.91)	0.85^{A}(0.18)	0.50^{AB}(0.02)	11.73^{AB}(3.28)
0:100	4.79^{B} (1.31)	28.82^{A}(2.71)	0.84 (0.01)	0.53^{A} (0.04)	12.92^{A} (1.36)

Values in parentheses are standard deviations. ABC Values with the same letter in the same column indicate that there are no significant differences between samples ($p < 0.05$) according to Tukey's test. SH: shortening; OG: oleogel.

to chewing, as expected from the values of hardness, cohesiveness, and appearance of the croissant crumb. Patel et al. (2014) and Pehlivanoglu et al. (2018) also showed an increase in chewiness when using liquid oil structured by shellac or wax in baked cakes. Therefore, the oleogel in this study could replace shortening without significant changes in hardness and springiness, even at 100% replacement. However, it led to a slight increase in cohesiveness and chewiness. Some authors found no significant differences in cohesiveness when using different levels of fat substitution;

some others showed increasing elasticity values with higher fat substitutions, while others reported decreasing values or no differences when fat was substituted. These results indicate that texture parameters differ as a function of the fat substitute used (Belorio, Sahagún, & Gómez, 2019).

3.3.2 Sensory analysis

Free-choice profiling (FCP) is a sensory technique where each subject quantifies the perceived qualities of products using his or her own individual list of terms (Tarancón, Sanz, Salvador, & Tárrega, 2013). The consumers used a wide variety of terms to describe the differences (voluminous, uniform/regular, compact, brown color, laminated, glossy, brioche, crunchy, butter, croissant taste, and firm/hard). The two-dimensional Generalised Procrustes Analysis (GPA) plot obtained from the analysis of the consumer assessment of the different croissants is shown in Figure 5. The individual sensory attributes explained by each dimension and the number of times they were mentioned are listed next to each dimension.

Dimension 1 accounted for 51.33% of the total variance, indicating that most differences between croissants perceived were explained by this dimension and were mainly related to the descriptors of appearance, texture, and taste. In the positive part of this dimension, descriptors such as "laminated/airy appearance", "voluminous appearance", "crunchy texture", "buttery flavor", and "typical croissant flavor" appeared, which referred mainly to SH100:OG0 croissants, and to a lesser extent, to croissants with SH50:OG50. Whereas on the negative side of this axis, terms such as "uniform/regular appearance", "compact", "brown color", and "brioche flavor" appeared, which characterised the samples

SH40:OG60, SH30:OG70, and SH0:OG100. These results are related to the crumb appearance and TPA data which revealed that increasing oleogel concentration resulted in higher crumb compaction and thus increased cohesiveness and chewiness.

Dimension 2 accounted for 19.55% of the total variance. The positive part of this axis was mainly related to appearance, highlighting the descriptor "bulky", which was described in croissants SH50:OG50 and SH0:OG100, whereas in the negative part, descriptors from all the categories studied (appearance, texture, and flavour) appeared, highlighting "typical croissant flavor", which surprisingly was named in all the study samples, except in sample SH0:OG100.

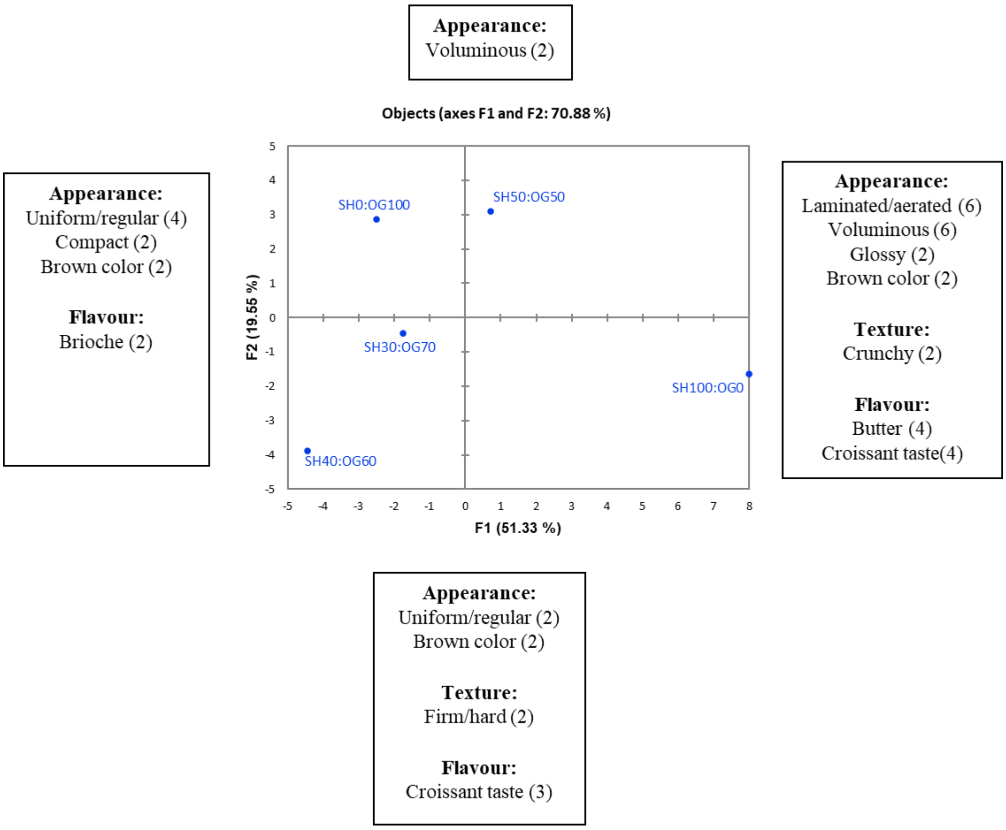


Figure 5. Two-dimensional GPA plot of the differences between croissants perceived by consumers. Descriptors correlated (R>0.6) with the two dimensions of the average space are listed on the boxes and the number of times that the descriptor was mentioned, if more than once (SH:shortening; OG:oleogel).

Therefore, it can be concluded that the samples prepared with the different percentages of oleogel presented similar descriptors to the control, although they were much more compact, with the sample prepared with SH50:OG50 being the most similar to the control. These results may be in agreement with those obtained by Simovic, Pajin, Seres, & Filipovic (2009), who concluded that the addition of a minimum amount of margarine (55%) in the formulation of laminated doughs can lead to excellent results in terms of acceptability. Likewise, no negative descriptors were found for the samples, except for the mention of the term firm/hard in the samples with the highest percentage of oleogel, although it only had a frequency of mention of two.

Conclusions

The partial and complete substitution of conventional shortening with a sunflower oil-cellulose-based oleogel in croissants was investigated. Four blends composed of commercial shortening (SH) and oleogel (OG) in different ratios (SH100:OG0, SH50:OG50, SH40:OG60, or SH30:OG70, and SH100:OG0) were evaluated.

The addition of this shortening replacement results in croissants with lower saturated fatty acids, lower firmness to bite, and a texture behaviour similar to that of the selected commercial shortening. Oleogel incorporation of up to 100% did not contribute negatively to the firmness or springiness texture of the croissants. However, as the level of fat replacement by oleogel increased, the croissants became chewier and more cohesive. Regarding sensory perception, croissants made with the SH:OG blend presented similar descriptors to the control, although they were considered more compact. The SH50:OG50 croissant sample was the most similar to the solid fat control.

These results demonstrated sunflower oil-cellulose-based oleogels could be effective in replacing shortening at up to 100% without significant deterioration in the quality properties of croissants. Therefore, the substitution of solid conventional fat by structured vegetable oil can be a promising strategy to reduce consumption of saturated and *trans* fats in puff pastry bakery products, while maintaining the functional and sensory properties provided by hard stock lipids.

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Author Contribution

M. Espert: Conceptualization, Methodology, Formal analysis, Writing – original draft, preparation, Writing – review & editing. Q. Wang: Conceptualization, Methodology, Formal analysis, Writing – original draft. T. Sanz: Conceptualization, Methodology, Investigation, and, Funding acquisition. A. Salvador: Conceptualization, Methodology, Investigation, Funding acquisition, Supervision, Writing – review & editing.

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Data Availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on request.

Conflict of interest

The authors declare no competing interests.

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Shortening replacement by emulsion and foam template hydroxypropyl methylcellulose (HPMC)-based oleogels in puff pastry dough. Rheological and texture properties

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Abstract

Shortening plays an essential function in the formulation of sweet laminated bakery products but has a potential health risk due to their high percentage of saturated fatty acids. In this paper, the feasibility of hydroxypropyl methylcellulose (HPMC) oleogels prepared with the emulsion template (ET) and the foam template (FT) approaches as fat sources in a puff pastry dough was investigated. Spreadability and thermal properties of control shortening, 100% ET and FT oleogels, and shortening/oleogel (50/50) blends were measured. The different systems were applied as the fat source in a puff pastry dough, and their effect on rheological and texture properties was investigated. Results showed that partial replacement of shortening with oleogels could significantly decrease the firmness values (from 115 to 26 N) ($P<0.05$) and increase the spreadability of shortening. The methodology to prepare the oleogel (FT or ET) also significantly affected the texture parameters, FT blends had the highest spreadability with significantly lower firmness values and area under the curve. Thermal values showed that both oleogels could slightly increase the melting point of shortening from 47 to 50 °C. The replacement of shortening with oleogel decreases the viscoelasticity of puff pastry dough and increases its thermal stability but does not significantly change dough viscoelasticity in the shortening/oleogel mixture. These results indicated that both oleogels have promising potential to replace shortening in puff pastry dough formulations, but the ET oleogel showed a more similar behavior to the control shortening than the FT oleogel.

Keywords: fat replacer, oleogelation, physical properties, cellulose, laminated dough

1. Introduction

Laminated bakery products are highly appreciated worldwide for their characteristic light and flaky texture (Selaković et al., 2021) and have become an indispensable segment of Western food culture. Fat (shortening, margarine, butter) is wrapped around the basic dough (flour, salt, water) and then repeatedly rolled and folded to form a laminated dough comprised of alternating layers of dough and thin layers of fat. The fat is also called rolling fat because of its unique folding and rolling method of production, which requires excellent softness and plasticity to enable layering without breaking the dough layers, but not being too soft to leak out under pressure (Mattice & Marangoni, 2017). The layered structure enables each individual dough layer to be baked separately, and the water turns into steam during baking, causing the expansion of the dough layers to create visual layering and flaky texture characteristics (Ana E. de la Horra, 2015; Gabriele et al., 2008; Šoronja-Simović et al., 2017). In the absence of shortening, the gluten and starch granules will stick together and make the dough stiff and low-volume (Lim et al., 2017). In contrast, shortening envelops the gluten particles, which causes a discontinuity in the protein and starch structure and lubricates the gluten particles, forming a small, soft, inflated product. Butter is commonly considered a favorable rolling fat, but the high cost and restricted plasticity range limit its large-scale production in laminated doughs (Mattice & Marangoni, 2017), so shortening is becoming the priority for preparing industrial laminated dough products. It provides not only functionality but also texture and lubrication. However, the problem currently confronted is the high amount of saturated fatty acids present in rolling fats (Lai & Lin, 2007; Silow et al., 2017). It is well-recognized that the excessive intake of saturated fatty acids can be harmful to health, increasing the risk of cardiovascular disease and leading to obesity and diabetes (DiNicolantonio et al., 2016; Hamley, 2017). Hence, there has been a tremendous effort in the search for alternative fat sources with healthy fat profiles without altering the typical food quality properties. Vegetable oils liquid at room temperature because of their low saturated fatty acid content, cannot be employed in the preparation of laminated doughs where high plasticity fats are required. Also, due to the high unsaturation, liquid vegetable oils are prone to oxidation, and their storage stability is significantly reduced.

Oleogels are an alternative to conventional solid fat. Oleogels are generated by wrapping liquid oil in a three-dimensional gel network using gelators and could have rheological, viscoelastic characteristics similar to those of solid fats. Typical food gelators include waxes, fatty acids, proteins, or polysaccharides, as well as their complexes. The differences in gelling agent properties lead to various oleogel preparation methodologies. Hydrophobic gelators like waxes and fatty acids are mostly added directly to the oil phase, whereas hydrophilic gelators like polysaccharides need indirect methodologies, as they are not able to interact directly with the oil. The most common indirect methodologies for obtaining oleogels with hydrophilic polysaccharides are the emulsion-template and foam template approaches.

The application of oleogel as fat source in baked food is limited to specific foods, such as cookies (Li et al., 2021; Mert & Demirkesen, 2016b; Zhao et al., 2020), cakes (Aliasl Khiabani et al., 2020; Ashok R. Patel, 2014; Oh et al., 2017), and muffins (Lim et al., 2017; Oh & Lee, 2018). Most of the attention was focused on the oleogels and the final product's sensory properties. However, there are no studies about the effect of oleogels on the dough's physical properties before baking, which is highly correlated with the quality of the final product (Mironeasa & Mironeasa, 2019; Zhang et al., 2022). Knowledge about the structural effects induced by oleogel and by shortening/oleogel blends incorporated in the dough will be of great importance for the further development of oleogels in bakery product applications.

Cellulose was recognized as a promising natural polysaccharide oleogelator with healthy food properties (Elleuch et al., 2011; Yang Jiang, 2018). Ethylcellulose can be directly soluble in the oil phase to form oleogels but requires a high temperature above 140°C (glass transition temperature). Moreover, its oleogel plasticity and oil adsorption ability are relatively weaker compared to conventional shortening. The cellulose ethers hydroxypropyl methylcellulose (HPMC) and methylcellulose (MC) have attracted enormous interest for their excellent surface activity and foaming structure that can effectively prepare stabilized oleogels with high oil retention capacity (Bascuas, Hernando, et al., 2020; Bascuas, Salvador, et al., 2020; Meng et al., 2018). Its amphiphilic properties come from the partial substitution of the hydroxyl group by hydroxypropyl and methoxyl groups. In puff pastry, Blake & Marangoni (2015) found that the consistency of the shortening must be like the dough to obtain a flaky pastry. HPMC emulsion template oleogels were successfully used as shortening replacer in a croissant formula; the croissant became chewier and more cohesive as the oleogel increased. A replacement level of 50% provided the most similar sensory perception (Espert et al., 2023).

The methodology to obtain MC and HPMC oleogels affected their physicochemical properties. The emulsion template oleogels showed lower values of the viscoelastic moduli and higher oil retention capacity than the foam template oleogels, although no significant differences were found in viscoelasticity (G''/G'), in both oleogels, a predominancy of the elastic versus the viscous component was found. The obtaining method and the initial oil content had more effect on the oleogel structure than the type of cellulose (Wang et al., 2023).

This paper focuses on the comparison of HPMC oleogel obtaining methodology (emulsion and foam template approaches) in their application as shortening replacers in a puff pastry dough formula. Oleogels and oleogel/shortening (50/50) blends were characterized and applied as fat sources to prepare a puff pastry dough. The texture and rheological properties of the different doughs were compared. The different fat sources' physical properties were related to the corresponding doughs' physical properties. Results will provide useful information for further development and application of oleogels as total or partial shortening replacers in cereal-baked food formulations.

2 Methods and materials

2.1 Materials

Hydroxypropyl methylcellulose (29% methoxyl, 6.8% hydroxypropyl) was supplied by The Dow Chemical Company (Bomlitz, Germany). Sunflower oil (oleic acid over 70%) was purchased from Deoleo S.A. (Córdoba, Spain). Shortening Hojaldambar (palm, sunflower, and soy oil with variable proportions; emulsifier (E471), flavorings, and coloring (carotenes)) was obtained from Vandemoortele Europe NV (Gent, Belgium). Flour, sugar, milk, liquid egg, and salt were bought from a local Carrefour supermarket (Valencia, Spain).

2.2 Preparation of oleogels

1)Emulsion-template approach (ET). The preparation method of ET oleogels with 96% (w/w) oil content was carried out as previously described by (Espert et al., 2020; Wang et al., 2023). In brief, 3g HPMC powder was dissolved in 94g sunflower oil, then 103g drinking water at 10 °C was added to the oil, and the mixture was stirred at 200 rpm for 2 min using a Heidolph stirrer (RZR 1, Heidolph Instruments, Germany) to obtain an initial emulsion. The initial emulsion was further homogenized by a high-speed disperser (Ultraturrax T-18, IKA, Germany) at 16500 rpm for 1 min and the resultant milky white emulsion was dried in a 60°C forced-air convection oven (Binder GmbH, Germany) for 24-48 h to reach a moisture content of less than 0.5% (w/w). Finally, the dried sample was crushed with a high-speed disperser (Moulinex, Groupe SEB (France)) to obtain the oleogel.

2) Foam-template approach (FT). The FT oleogels were prepared according to the method of Oh & Lee (2018) with slight modifications. 4.5 g of HPMC powder was dissolved in 95.5 g of hot water (>85°C), and subsequently 200 g of cool water (<10°C) was slowly added. The entire dissolution process was carried out with a mixer (RZR 1, Heidolph Instruments, Germany) at 400 rpm for 10 min. The solution was homogenized at 16500 rpm for 2 min using a high-speed disperser (Ultraturrax T-18, IKA, Germany) and was lyophilized to remove water with a freeze-dryer (Lyobeta 6 PL, Telstar, Spain). The resulting foam was then minced with a kitchen grinder (Moulinex, Groupe SEB, France). Subsequently, 96 g sunflower oil was mixed thoroughly with 4 g of the chopped foam sample until a uniform oleogel was formed.

2.3. Preparation of oleogel/shortening blends

The shortening (62.5g) was gently softened by heating in a 40 °C water bath for 10 minutes to form a semi-solid, and then an equivalent amount of oleogel was added and mixed thoroughly to form a 50/50 shortening/oleogel blend. Finally, the blend was placed in a square mold 15 cm x 10 cm before it solidified and stored in the fridge for subsequent testing and dough preparation. The same protocol was also applied to control shortening. 100% oleogel samples were directly placed into the mold.

2.4 Spreadability measurements

The spreadability of the oleogel and shortening/oleogel blends was determined by a texture analyzer TA. XT plus (Stable Micro Systems Ltd. Surrey, UK) equipped with a TTC Spreadability Rig. The test was performed in compression mode with a penetration depth of 25 mm, a test speed of 1 mm/s, and a post-test speed of 10.0 mm/s. Prior to measurement, the sample was placed into the inner cavity, gently flattened with a spatula to avoid air incorporation, and then stored at 4 °C for 24 h. Measurements were carried out by pressing the sample with a conical probe and returning it to the initial position. Force versus distance data was recorded, and then the maximum force, the area under the curve (AUC), and stickiness were calculated.

2.4 Thermal properties

Thermal analysis was carried out with a Q2000 Differential Scanning Calorimeter (DSC) (TA Instruments, New Castle, USA) according to a previous methodology (Espert et al., 2021) with slight modifications. 11-15 mg of the sample was weighed into an aluminum pan and then sealed with a press. An empty pan was used as the control. Samples (10-15 mg) were hermetically sealed in an aluminum pan and heated from 20 to 130 °C at the rate of 5 °C/min under a nitrogen atmosphere. All results were recorded and analyzed by the Universal Analysis 2000 software (TA Instruments, New Castle, DE).

2.5 Dough-making procedure

The dough formula was composed of 250 g flour, 35 g sugar, 1 g salt, 15 g yeast, 60 g egg, 125 g milk, and 125 g fat. Fats employed were: shortening (control), a blend made with shortening and oleogel (50/50), and 100% oleogel. Both ET and FT oleogels were tested. Sugar, salt, eggs, and 25 g of the corresponding fat were added to a food processor (Kenwood titanium major kitchen machine, KM020, UK) for mixing 10 s at speed 6 (Kenwood titanium major kitchen machine, KM020, UK). Then, the flour and the yeast previously diluted with the milk were added and mixed at speed 6 for 20 s. The dough was then kneaded by hand for 10-15 min until a homogeneous texture was obtained. The dough was covered with plastic film and placed in the refrigerator at 4 ºC to ferment for 8 h. Subsequently, the dough was rolled into a 40 cm × 15 cm flat rectangle. A square of fat/blends (100 g) was placed in the center of the dough square and the sides of the dough were folded towards the middle of the fat square so as to envelop it into one entity completely. After that, the dough with the fat was rolled into a rectangle, folded into three layers, and placed in the refrigerator for 20 minutes. This final step was repeated three times to obtain the final dough.

2.6 Dough rheological properties

The rheological properties of the dough were measured by an AR-G2 rheometer (TA Instruments, Montreal, QC, Canada) equipped with a 40 mm diameter hatch parallel plate geometry and a Peltier temperature control system. All tests were performed at 20°C except for the temperature sweep. The oscillatory stress sweep range was set from 0.1 to 1000 Pa at 1 Hz and the frequency sweep range was set from 10 to 0.01 Hz at stress inside the linear viscoelastic region. Temperature sweeps from 20-90°C at a heating speed of 5 ºC at 1 Hz was carried. The auto-strain option of the rheometer was selected for the temperature sweep to better control the linear viscoelastic response along the entire temperature sweep. Storage (G') and loss modulus (G'') data were recorded by TRIOS software (TA Instruments, Montreal, QC, Canada).

2.7 Dough texture analysis

Texture analysis of the dough was evaluated using a texture analyzer TA. XT plus (Stable Micro Systems Ltd. Surrey, UK), with slight modifications of the method of Sudha et al. (2007). A dough with a diameter of 4 cm and a thickness of 0.6 cm was scooped using a circular mold and placed on the platform, and a cylindrical probe with a diameter of 75 mm (P/75) was used to perform a TPA test. The sample was compressed twice at a rate of 1 mm/s for 5 seconds and the textural parameters (hardness, springiness, cohesiveness, and resilience) were analyzed by Exponent software (version 6.1.4.0, Stable Micro Systems Ltd.).

2.8 Statistics Analysis

Each test was performed three times on batches prepared on different days. All results were analyzed by One-way ANOVA in SPSS 8.5. $P<0.05$ represented a significant difference, and data were represented as mean ± deviation (SD).

3 Results and discussion

3.1 Spreadability analysis of blends

Spreadability profiles and values of firmness, stickiness, and area under the force-time curve were shown in Figure 1 and Table 1. Data of emulsion template oleogels (100% ET oleogels) were not shown as they could not be accurately measured due to their inability to evacuate air during measurement. Pure shortening showed the highest firmness and AUC significantly. Both 100% foam template oleogel (FT oleogel) and shortening/oleogel blends showed significantly lower values of firmness and AUC than the control shortening. The firmness values of the shortening/ET oleogel blend were approximately half those of pure shortening, indicating a higher spreadability. Furthermore, the significantly lower firmness and AUC values of the shortening/FT blends compared to the shortening/ET blends indicated that the approach of oleogel preparation significantly affected the blends' texture. Lower firmness values and work of shear indicated more spreadable fat, suggesting that partial (50%) substitution of shortening with oleogel could effectively improve the spreadability. 100% FT oleogels had the highest stickiness, followed by shortening/FT oleogel blend and control shortening. Shortening/ ET oleogel blend showed the lowest stickiness.

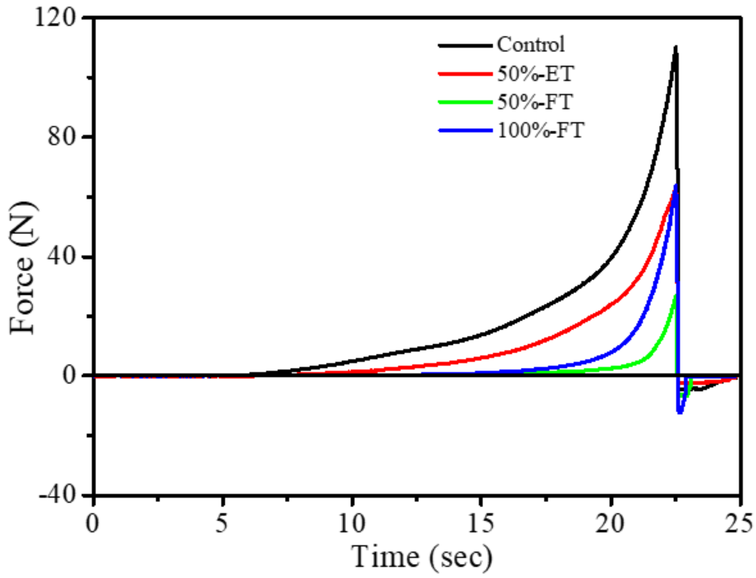

Figure 1. Spredeability profile of shortening, shortening/oleogel (50/50) blends and 100% oleogel. (Control: shortening; 50%-ET: blend 50% shortening-50% ET oleogel; 50%-FT: blend 50% shortening-50% FT oleogel; 100%-FT: FT oleogel).

Table 1. Values of firmness, AUC, and stickiness were obtained from the spreadability test for control shortening, shortening/oleogel blends, and 100% oleogels. ET: emulsion template; FT: foam template.

Sample	Firmness (N)	Area under the curve (N/s)	Stickiness (N)
Control shortening	115.02±0.15[a]	339.92±0.56[a]	5.02±1.38[c]
Shortening / ET oleogel blend	63.85±3.64[b]	122.72±6.64[b]	2.35±0.18[d]
Shortening/ FT oleogel blend	26.46±8.69[c]	27.92±2.32[d]	7.84±1.03[b]
100% ET oleogel	-	-	-
100% FT oleogel	65.92±10.86[b]	97.20±16.54[c]	12.57±1.83[a]

[abcd] For each column, values with different letters are significantly different ($p < 0.05$).

3.2 Thermal analysis of blends

To further investigate the properties of the oleogel/shortening blends, differential scanning calorimetry was employed to analyze the melting behavior of the different systems. Thermal profile of all samples is shown in Figure 2. The shortening control sample showed two endothermic peaks, which appeared at approximately 17 °C and 47 °C, respectively. Mattice & Marangoni (2017) described a similar profile when exploring the behavior of different fat sources, where the endothermic peaks of hydrogenated shortening were around 18 °C and 50 °C. Contrary to shortening, in both FT and ET oleogels no thermal transitions were observed in the studied

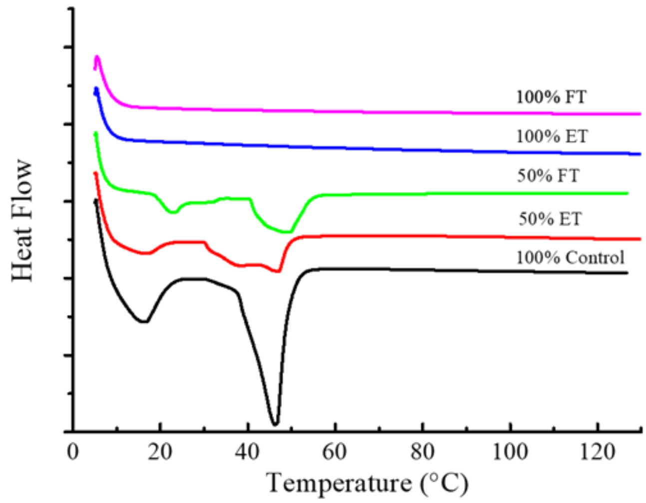

Figure 2. Thermal profile of control shortening, shortening/oleogel (50/50) blends, and 100% oleogel.

temperature range. In shortening/oleogel blends, a significant change in the shortening calorimetric profile was observed. The second peak becomes smaller and broader in both shortening/oleogel blends (Figure 2). A significant decrease in enthalpy (from 31 to 13 J/g in 100% ET oleogel and to 11 J/g in 100% FT oleogel) was observed. Also, an increase in melting temperature, with a maximum temperature of the peak from 47 to 48 ºC

(ET oleogel) and to 50 ºC (FT oleogel) (Table 2). The effect of oleogel on the shortening melting temperature and the shape of the melting curve indicated an interaction between the two available matrices of shortening and oleogel, probably due to an alteration of fatty acid composition or in the crystallization behavior of the shortening (Mert & Demirkesen, 2016b), which influenced the thermal profile.

Table 2. Thermal parameters of control shortening and shortening/oleogel (50/50) blends.

Sample	Peak temperature (°C)	Enthalpy (J/g)
Control shortening	47.0 ± 0.8^{b}	31.1 ± 5.1^{a}
Shortening / ET oleogel blend	48.0 ± 1.0^{b}	13.1 ± 0.2^{b}
Shortening / FT oleogel blend	50.0 ± 0.3^{a}	11.3 ± 0.8^{c}

^{abc} For each column, values with different letters are significantly different ($p < 0.05$).

3.2 Rheology analysis of the dough

The effect of total (100% oleogel) and partial (50/50 shortening/oleogel blends) shortening replacement by both FT and ET oleogels in the rheological properties of a puff pastry dough was studied. The effect of stress amplitude, frequency, and temperature in the viscoelastic functions G' and G" were shown in Figure 3A. All doughs exhibited solid-like properties with values of storage modulus G' greater than loss modulus G" over the entire frequency sweep studied. The extension of the dough's linear viscoelastic region (LVR) became progressively narrower as the shortening level was reduced (higher oleogel content). The shortening sample showed the highest extension of the LVR, followed by the shortening/oleogel blends, being the FT oleogel the one with the lowest resistance to the applied stress. The ET oleogel dough showed a wider LVR than the FT oleogel dough, indicating that the ET oleogel had greater resistance to the applied deformation. The highest spreadability found in the oleogel/shortening blends agrees with the lowest dough resistance to the applied stress.

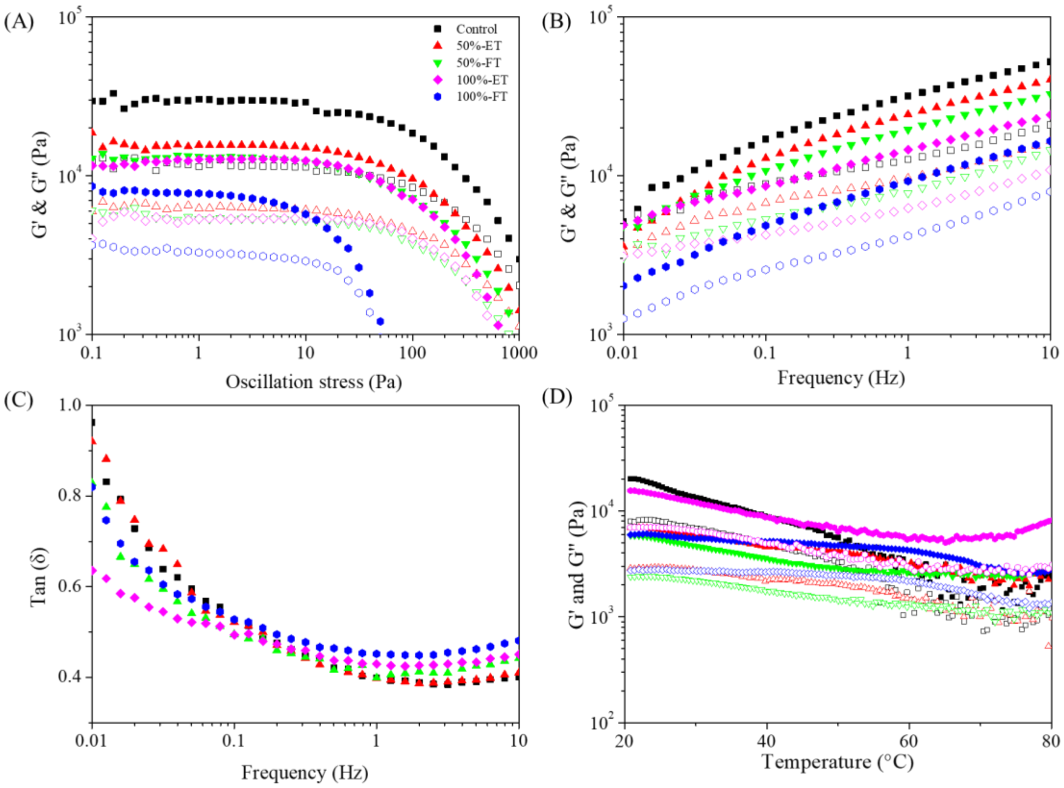

Figure 3. Rheological properties of dough prepared with shortening, shortening/oleogel (50/50) blends and 100% oleogel as fat sources (■ represents G', □ represents G''). (A) stress sweep, (B) frequency sweep, (C) loss tangent and (D) temperature sweep. Control: dough with shortening; 50%-ET: dough with 50% ET oleogel and 50% shortening; 50%-FT: dough with 50% FT oleogel and 50% shortening; 100%-ET: dough with ET oleogel, 100%-FT: dough with 100% FT oleogel.

Figure 3B showed that both dynamic viscoelastic parameters (G' and G") of all doughs increased linearly with increasing frequency, indicating a typical viscoelasticity behavior of soft gels. The viscoelasticity and gel strength of the control shortening dough were the highest among all doughs, which might be due to the existence of solid fat crystals and higher aeration (Mert et al., 2016b). The highest viscoelasticity of the control shortening dough was in line with the highest hardness and lowest spreadability shown in the texture measurement of control shortening. The replacement of shortening with both oleogels decreased the viscoelastic parameters of doughs, being the G' of doughs prepared with 50% ET oleogels significantly higher than that of 50% FT oleogel doughs (Table 3). The FT oleogel was formed by adsorbing liquid oil through a porous sponge-like cellulose network structure (Jiang et al., 2021; Wang et al., 2023). FT oleogel showed lower oil retention capacity than ET oleogel (Wang et al., 2023). This lower oil retention capacity of the FT oleogel would be related to a higher oil release during the dough rolling, which could coat the flour to form a fatty film, blocking the interaction between gluten proteins and the hydration between proteins and water molecules, thereby inhibiting the formation of gluten and making the dough softer (Ghotra et al., 2002; Mert & Demirkesen, 2016b). Figure 3C showed the evolution of tan δ with frequency, which informs about the viscoelasticity, the ratio between viscous and elastic moduli (G"/G'). Values of tan δ were lower than 1 in all the samples, indicating a predominance of the elastic moduli. At 1 Hz, tan δ values of all doughs prepared with oleogel were higher (closer to 1) than those prepared with shortening, indicating that shortening induced a higher increase in dough elasticity than both types of oleogel. However, no significant differences in tan δ were found between the control shortening dough and shortening/oleogel dough, which indicated that although the incorporation of oleogel decreases the values of G', no effect in the dough viscoelasticity was found in blends. In the case of 100% oleogel, differences in tan δ were significant but small (tan δ was 0.39 for control shortening dough, 0.44 for 100% ET oleogel dough, and 0.45 for 100% FT oleogel dough), implying that control shortening dough had a higher predominance of elastic behavior. In practice, appropriate dough formation could be carried out with all the fat sources (control shortening, 100% oleogel, and 50% shortening/oleogel blends). Therefore, the existing differences in the viscoelastic properties of the dough allow for proper handling, although easier handling was observed in blends in comparison to the 100% oleogel dough. Pehlivanoglu et al. (2018) found similar conclusions when exploring different oleogels as shortening replacers in cakes; oleogels prepared with rice bran and candle wax made the cake batter more appropriate in terms of viscosity.

Table 3. Viscoelastic parameters (at 1 Hz) of control shortening dough, oleogel doughs (100%ET or 100%FT), and shortening/oleogel (50/50) blend doughs.

Sample doughs	G' (Pa)	G'' (Pa)	Tan δ
Control shortening	29161 ± 2398[a]	11533 ± 1063[a]	0.395 ± 0.004[b]
Shortening/ET oleogel blend	24312 ± 412[b]	9771 ± 241[b]	0.398 ± 0.005[b]
Shortening/FT oleogel blend	19177 ± 194[c]	8024 ± 297[c]	0.419± 0.02[b]
100%-ET	12805 ± 1149[d]	5663 ± 562[d]	0.444±0.015[a]
100%-FT	10021± 105[e]	5157 ± 238[e]	0.451±0.008[a]

[a-e] For each column, means values with different letters indicate a significant difference ($p < 0.05$).

The effect of oleogel incorporation on the viscoelastic behavior of the dough during heating was shown in Figure 3D. When the dough was heated, a clearly different behavior was observed between shortening and oleogel doughs. G' decreased with increasing temperature in all the doughs. However, in shortening dough an increase in the slope of the decay of G' was found around 45 ºC, revealing the effect of shortening melting. This decrease in G' at 45 ºC was accompanied by an increase in G'', indicating the reduction in the shortening dough viscoelastic properties upon heating.

In 50% and 100% oleogel doughs, the initial soft decrease of G' and G'' before 45 ºC was observed, but upon this temperature, no further decrease was observed, and the viscoelastic functions remained stable. As a consequence of the reduction in the viscoelastic properties of the shortening dough with temperature, at higher temperatures (around 60 ºC) the oleogel doughs showed higher viscoelasticity than the control shortening dough. Therefore, shortening replacement by oleogel in dough could improve its thermal stability.

3.3 Texture of the dough

The effect of control shortening, 100% oleogels, and 50/50 shortening/oleogel blends on the puff pastry dough texture properties was shown in Table 4. As well as rheological results, the control shortening dough showed the highest hardness (10.60 ± 1.40 N). It is well known that shortening forms a barrier around gluten proteins that prevent extensive cross-linking of the gluten (Mert & Demirkesen, 2016a). The lowest viscoelasticity and the lowest dough hardness in the presence of oleogels, indicated that the oil present in the oleogel avoids the development of the gluten network, even to a greater extent than shortening, creating a softer dough structure than the one created by shortening. Hardness of the dough prepared from the different shortening/oleogel blends decreased to about 6 N. Significant differences were found among the two types of 100% oleogel doughs, being the lowest hardness found in the FT oleogel, which could be explained due to the lowest oil retention capacity of the FT oleogel, as previously described (Wang, et al., 2023). Lowest oil retention capacity means higher oil loss during rolling dough forming. The released oil could not only inhibit the development of gluten protein but also affect the fluidity and ductility of the dough (Mert & Demirkesen, 2016a), resulting in a loose and soft dough. Accordingly, the dough prepared from 100% FT oleogels had the lowest hardness (4.41 ± 0.27 N), which is also consistent with the results of rheological tests on the dough.

Table 4. Texture parameters of control shortening dough, shortening/oleogel (50/50) blend doughs and oleogel doughs (100% ET or 100% FT).

Sample dough	Hardness (N)	Springiness	Cohesiveness	Resilience
Control shortening	10.60±1.40^{c}	0.53±0.05^{a}	0.51±0.03^{a}	0.123±0.007^{d}
Shortening /ET oleogel blend	6.66±1.00^{b}	0.74±0.16^{b}	0.56±0.07^{a}	0.118±0.024^{b}
Shortening / FT oleogel blend	5.93±0.36^{b}	0.93±0.03^{c}	0.81±0.04^{b}	0.121±0.004^{c}
100%-ET	8.43±0.62^{c}	0.93±0.09^{cd}	0.82±0.02^{b}	0.091±0.003^{a}
100%-FT	4.41±0.27^{a}	0.98±0.01^{d}	0.87±0.05^{b}	0.118±0.009^{b}

The structural system to fix the oil is different in both types of oleogels. In the foam-based oleogel a cellulose porous structure was first formed and the oil was trapped in a second step, whereas in the ET oleogel the oil is initially entrapped in an o/w emulsion, and the water evaporated in a second step. In the case of MC and HPMC oleogels the oil retention capacity was initially higher in the ET than in the FT, which will also explain an easier oil release during the FT dough lamination process. Hardness of the dough prepared by the ET oleogel was 8.43 ± 0.62 N, which was not significantly different compared to shortening ($P>0.05$). The cohesiveness and springiness of the dough increased significantly with a higher degree of oleogel substitution, for both types of oleogels. As for the effect of oleogel on the dough resilience no effect was found.

4 Conclusion

This paper investigated the suitability of HPMC oleogels prepared by the emulsion and the foam template approaches to partial or total replace shortening in a puff pastry dough formulation. Mixing oleogel with shortening increases spreadability, reduces hardness and increases the melting point compared to control shortening. In puff pastry dough, a decrease in viscoelastic parameters and hardness was observed with the incorporation of oleogel, denoting that similarly to the effect of shortening, the oil present in the oleogel interacts with gluten avoiding the development of a strong gluten network. No significant differences were found in viscoelasticity (tan δ) among the shortening dough and oleogel/shortening doughs. Dough thermal stability was increased in the presence of oleogel, as no fat melting occurs in the absence of shortening. A relationship among the spreadability properties of the shortening, ET oleogel, and shortening/oleogels blends with puff pastry dough texture and rheological properties was found. The most similar behavior to the shortening dough in terms of texture and rheological behaviour was found for the shortening/ET oleogel blend. The difference among the behavior of the FT and the ET doughs was associated to the lowest oil retention capacity of the FT oleogel structure, which will favor oil release during the rolling process necessary to obtain puff pastry doughs.

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Shortening replacement by emulsion and foam template hydroxypropyl methylcellulose (HPMC)-based oleogels in puff pastry. Texture and sensory properties

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Abstract

Shortening in puff pastry products contains high levels of saturated and even *trans*-fatty acids that may be hazardous to human health. One efficient way to reduce such unhealthy fat in food is to employ gelators to structure liquid oils for the production of oleogels, thereby replacing shortening. In this paper, two types of HPMC (Hydroxypropyl Methyl Cellulose) oleogels (*emulsion template* and *foam template*) were used to replace shortening in puff pastry. Full-HD images, TPA (Texture Profile Analysis) and penetration tests, as well as TDS (Time-Dominant Sensation) sensory analysis, were used to assess the products' cross-sectional morphology, texture, and sensory attributes. The appearance of baked pastry made with 50/50 (shortening/oleogel) was similar to the control (100% shortening). In contrast, the crumb texture of baked pastry prepared with 100% oleogel was more compact and less airy than control. All samples showed similar firmness. TPA test showed that puff pastry made with 100% foam-based oleogel did not substantially differ to the control group, while samples prepared with emulsion-based oleogels were significantly harder and chewier than the control. Regarding sensory analysis, all puff pastries were mainly perceived as "crunchy" during chewing. The increase in oleogel content resulted in denser pastry, but the 50/50 foam template samples were "easier to chew". Attribute "compact" also became one of the main perceptions when the oleogel content increased to 100%, which would be related to the dense structure observed in the crumb morphology. This study confirms the feasibility of HPMC oleogels as healthy fat source in puff pastry.

Keywords: Oleogel; HPMC; puff pastry; texture profile analysis**;** temporal dominance sensations.

1. Introduction

Puff pastry products have gained great popularity among consumers mainly due to their light and flaky layered structure (Selaković et al., 2021; Silow et al., 2016; Simovic et al., 2009) resulting from the specific recipe and process of making puff pastry. Examples of puff pastry are croissants and Danish pastry (Grujić et al., 2008; Sanz et al., 2015). Puff pastry consists of two parts: the dough and the fat, the former is made of flour, milk, sugar, yeast, and a limited amount of fat (10% in flour mass basis). The molded rolled fat (40-50% in flour mass basis) is then topped with the dough and repeatedly folded, rolled out, and chilled to produce an overlapping structure of dough and fat layers (Bousquieres et al., 2014; Silow et al., 2017; Simovic et al., 2009). Typical pastry fats include butter and shortenings. However, it is known that butter and shortening contain high levels of saturated fatty acids, which may have adverse health effects such as obesity, cancer, hyperlipidemia, and coronary heart disease when consumed over a long period of time (Mozaffarian & Clarke, 2009; Siri-Tarino et al., 2015). Hence, numerous manufacturers and researchers have devoted significant efforts to finding feasible ways to decrease saturated and trans fats on pastry foods.

It is definitely a great challenge to find fat substitutes that satisfy the requirement of reducing harmful fats while maintaining a comparable taste and texture to conventional puff pastry products. Traditional puff pastry fat is crucial to the quality of the product, the fat in dough can fix the structure of the dough, while the rolled-in fat can separate the dough layers, preventing coagulation by repeated folding and inhibiting water's evaporation to ensure the final product's expansion in volume (Lefébure et al., 2013; Šoronja-Simović et al., 2017). Consequently, the alteration of fat may lead to changes in the structure, color, mouthfeel and even texture of the product, affecting its organoleptic properties (Mamat & Hill, 2014). Consumers' purchase of food products is based on their subjective perception and physical properties. Besides, the textural perception of baked goods is closely associated with the food formulation ingredients, hence the substitution of shortening with other fats enriched with high unsaturated fatty acids would lead to sensory changes in the product during oral processing (Yılmaz & Öğütcü, 2015a). Dynamic texture analysis methods, specifically temporal dominance of sensation (TDS) analysis, have proven to be an effective technique for describing the emergence, dominance, and change over time of different sensations during oral processing of food (Gao et al., 2017; Gao et al., 2018). During the sensory evaluation, participants are requested to collect and record the perceived dominant attributes from a predetermined list of various attributes using the corresponding sensory software while tasting the samples. The results are presented as curves of dominance versus time and compared to chance levels (theoretical proportions of a randomly selected attribute) and significance levels (minimum proportions significantly greater than chance levels) to evaluate the significance of the dominant attribute. Numerous reports have been published utilizing TDS for sensory evaluation, such as cream cheese (Ningtyas et al., 2019), biscuits (Bénédicte Le Calvé, 2019), cookies (Li et al., 2021), bread (Puerta et al., 2021; Rind & Miano, 2018), etc. TDS studies regarding bread were about the effects of flour, salt, and shortening on bread's sensory, rheological, and textural properties (Panouille et al., 2014). However, as far as we know, there are no studies investigating the dynamic texture of puff pastry during oral processing. It is expected that texture-related attributes are the ones that may be most affected with chewing time when replacing saturated fat with oleogels. In fact, a croissant is expected to be chewy and crunchy without being hard and the addition of oleogel could result in a more compact and denser crumb. Therefore, it is considered interesting to evaluate the dominant temporal sensations during chewing of croissant samples made with the developed oleogels compared to a control.

Many reports have shown that oleogels have a promising potential to replace butter or shortening. Oleogelation is a technology to structure liquid oils into thermally reversible three-dimensional network structured solid-like fats with viscoelastic properties by gelators, which could fulfill the demand for plasticity and spreadability of solid fats in various food applications (Sylwia Onacik-Gur, 2020; Yılmaz & Öğütcü, 2015b; Zetzl et al., 2012). Hydroxypropyl Methyl Cellulose (HPMC) has been proven to be an effective emulsifier and thickening agent, its amphiphilic structure enables to build a bridge between the water and oil phases, with the hydrophilic groups interacting with water molecules and the hydrophobic groups interacting with the oil phase to form stable emulsion. Bascuas et al. (2021) reported that oleogels formulated with HPMC and xanthan gum as a substitute for coconut oil did not damage the texture and flavor of chocolate cream. In another study, oleogels prepared from HPM and Methyl Cellulose (MC) effectively prolonged the shelf life of peanut butter (Tanti et al., 2016). In a muffin formulation, hydroxypropyl methylcellulose oleogels improved the aeration of the product and there was no adverse effect of oleogels on the softness and chewiness of the muffins at substitution percentages below 50% (Oh & Lee, 2018).

The physical properties of HPMC oleogels depend on their obtention methodology. Differences were found in the oil retention, texture and rheological properties among emulsion template and foam template oleogels. In a previous study, the effect of HPMC oleogel obtention methodology (foam template or emulsion approaches) on physical properties was compared (Wang et al., 2023). Thermal properties and spreadability of oleogel-shortening blends, and their influence on the rheological properties of fresh puff pastry dough were investigated. The objective of the present article is to evaluate the effect of the emulsion template and foam template oleogels on the texture and sensory properties of baked croissant (as model of puff pastry).

2. Materials and Methods

2.1 Materials

Hydroxypropyl methylcellulose (29% methoxyl, 6.8% hydroxypropyl) were purchased by The Dow Chemical Company (Bomlitz, Germany). Sunflower oil with high levels of oleic acid (over 70% w/w) was purchased from Deoleo S.A. (Córdoba, Spain). Shortening (vegetable oils (palm; sunflower; soybean), mono- and diglycerides of fatty acids, flavorings and coloring (carotenes)) was obtained from Vandemoortele Europe NV (Gent, Belgium). Flour, sugar, milk, liquid egg and salt were purchased from local Carrefour supermarket (Valencia, Spain).

2.2 Oleogel preparation

Foam template approach. Foam-template (FT) oleogels were prepared as previously reported (Wang et al., 2023). 3g HPMC powder was weighed accurately and dissolved in 197g water (HPMC content is 1.5% w/w). A Heidolph stirrer (RZR 1, Heidolph Instruments, Germany) at 200 rpm was used to stir the solution for 10 minutes to make it fully hydrated. Then the solution was homogenized under a high-speed homogenizer (Ultraturrax T-18, IKA, Germany) at 16500 rpm for 2 min to form foam samples, and the collected samples were lyophilized using a lyophilizer (Tesltar, Lyobeta 6 PL), for 72 h to obtain dry foam samples. The dry foam samples were crushed in a pulverizer and mixed with sunflower oil. 8 g of dry foam were added to 192 g of sunflower oil with high levels of oleic acid and mixed thoroughly to obtain a foam-based oleogel sample with 96% (w/w) oil content.

Emulsion template approach. Emulsion-template (ET) oleogels were prepared as previously reported (Wang et al., 2023). The HPMC with a mass fraction of 1.5% was dispersed entirely in 47% sunflower oil, and 51.5% water was added and stirred into an initial milky emulsion by using a Heidolph stirrer (RZR 1, Heidolph Instruments, Germany) at 200 rpm. The final emulsion sample was homogenized via a high-speed homogenizer (Ultraturrax T-18, IKA, Germany) at 16500 rpm for 1 min, and the resulting emulsion was dried in a force-air convection oven ((Binder, Alemania) at 60 °C for 48 h to remove water. Finally, the dry emulsion was ground by a grinder to obtain an emulsion-based oleogel with 96% (w/w) oil content.

2.3 Puff pastry making

The formulation of puff pastry was as follows: 250 g flour, 35 g sugar, 1 g salt, 15 g yeast, 60 g liquid eggs, 125 g milk, and 125 g fat (100% shortening (control), a mixture of 50% shortening and 50% oleogel, or 100% oleogel). Briefly, the sugar, salt, eggs, and 25 g of the corresponding fat were mixed in a food processor (Thermomix TM31, Vorwrek, Wuppertal, Germany) at speed 6 for 10 seconds. Then, the flour and the milk with the yeast dissolved were added and mixed on speed 6 for 20 seconds. Then took out the dough and kneaded it for 10-15 minutes. After kneading, cover the dough with plastic film and ferment it in the refrigerator at 4 °C for 8 hours. Then, the dough was rolled into a rectangle with a rolling pin, and 100 g of fat cubes were added, ensuring that the fat was completely enveloped in the dough. The dough was then rolled into a rectangle, folded into three layers, then placed in the refrigerator for 20 minutes at 4°C, and the procedure was repeated three times. The dough was rolled out to a rectangular shape of 50x24cm (L*W) and cut into triangles of 8x24cm (L*W) with a 2cm deep slit in the middle of the bottom to enable the croissants to be shaped. Before baking, they were brushed with beaten egg to give them a more pleasant color and baked at 180°C for 18 minutes. In order to easily differentiate the samples, abbreviations of fat composition were used to name the samples. Control: pastry made with shortening; ET-50%: pastry made with 50% ET oleogel and 50% shortening; FT-50%: pastry made with 50% FT oleogel and 50% shortening; ET-100%: pastry made with 100% ET oleogel; FT-100%: pastry made with 100% FT oleogel.

2.4 Visual appearance of the inner puff pastry structure

The inner structure of the pastries was explored by an EVO Cam II macroscope (Vision Engineering, Woking, UK) equipped with a 2-megapixels digital colour camera. A slice of each croissant sample was illuminated episcodically with an integrated LED-ring by visible light. The lens used was 0,45 X Objective lens (2190560). Images were acquired with ViPlus software v1.00.82 (2018, Vision Engineering) and processed by the Nis Elements BR 3.2 software (Nikon corporation, Japan) to substitute the background to pure black. Main image properties were: RGB 32 bits, a frame size of 1920*1080 pixels. The image dimensions of field of view were 8.2*4.6 cm and the x-y spatial resolution value was 43.19 microns/pixel. Calibration bar is 1 cm lenght.

2.5 Texture of puff pastry

Texture analysis of the pastries was conducted by a texture analyzer TA. XT. Plus (Stable Micro Systems Ltd. Surrey, UK) equipped with Texture Exponent software (version 6.1.4.0, Stable Micro Systems Ltd.). Tests were conducted at room temperature (20 ± 1 °C) 24 h after preparation. To ensure the accuracy of the experimental data, the assays were carried out on three different days with three repetitions of each formulation. Whole croissant samples, including crust and crump were used.

Penetration test

The penetration test was performed with the specific Volodkevich Bite Jaws (HDP/VB) probe (Stable Micro Systems, Godalming, UK) to evaluate the firmness/hardness of the pastry crust. This probe simulates the action of the incisors in biting down the food. The penetration distance of the test was 30 mm, the test speed was 1 mm/s and the speed back was 10 mm/s. Hardness was calculated as the maximum penetration force obtained (N).

Texture profile analysis

A texture profile analysis (TPA) (Stable Micro Systems, Godalming, UK) test was also conducted to evaluate how the samples behave when being chewed. Double compression tests were performed using a 75-mm diameter aluminium plate (P/75). The test speed was 1 $mm \cdot s^{-1}$ with a strain of 50% of the original sample height and a 5 s interval between the two compression cycles. Retraction speed was 10 $mm \cdot s^{-1}$ before and after the test. From the TPA curves, the three primary texture parameters: hardness (the peak force during the first compression cycle), springiness (the height that the food recovers during the time that elapses between the end of the first bite and the start of the second bite) and cohesiveness (the ratio of the positive force area during the second compression portion to the positive force area during the first compression), and the secondary texture parameter, chewiness (hardness × cohesiveness × springiness) were obtained.

2.6 Sensory analysis

Temporal Dominance of Sensations

Sensory analysis of the different puff pastries was carried out using the Temporal Sensory Dominance (TDS) method, which identified the dynamic sensations that were considered dominant during product consumption through a list of attributes. The dominant attribute was the one attracting attention at a specific time.

The assay was performed in a fully computerized tasting room equipped with individual booths within "Instituto de Agroquímica y Tecnología de Alimentos" (IATA-CSIC). Ten trained participants were recruited from the staff of the Institute, and the whole assay was replicated three times on different days with the Compusense 20 software (Compusense Inc., Guelph, ON, Canada). For selection of terms and panel instruction and training, four preliminary sessions were conducted in order to explain the TDS technique and the notion of temporality of sensations and give the assessors the chance to test the data collection software and familiarize themselves with it. In the first session the panelists were introduced to the notion of the temporality of sensations and to the TDS technique and had to describe all the in-mouth sensations they felt while tasting the most different samples (control, FT 100% and ET 100%). In the second session, the most frequently cited attributes were selected (spongy, sweet, fatty, soft, crunchy, compact/dense, dry, easy to chew, and sticky) and their definitions were developed (Table 1). During the third and fourth sessions the panelists were

Table 1. List of attributes and their definitions used in TDS test.

Attributor	Definitions
Spongy	The product is easy to compress; products feel full of air
Sticky	Adhere to the palate and the teeth during chewing
Dry	The sensation of dryness due to lack of saliva; absence of water
Crunchy	Low pitch sound produced on crust fracture during mastication
Soft	It presents no resistance under the teeth/requires a weak force to be chewed.
Compact/Dense	Describe a solid containing little cells filled with gas; high density
Easy to chew	Property of a food bolus that easy to chew
Sweet	Basic taste of sugar
Greasy	The taste of cooked vegetable oil

able to understand the dominance and sequence concepts and participated in a simulated TDS session with several samples of croissants in order to solve questions and get used to the computer program and methodology. For formal assessment, TDS evaluation took place in sessions held on two different days in order to conduct two replications. During the formal assessment, a list of the nine sensory attributes presented to the panelist was displayed on the computer. Then, the panelists were given five sample halves placed on a dish (control, FT 50% and 100%, ET 50% and 100%), labeled with a randomly generated three-digit code. The panelists placed the sample into the mouth and simultaneously pressed the "Start" button to start the timer. They were asked to choose the most dominant sensation from the list of attributes for each moment while tasting the croissant. Panelists could choose each attribute based on its sensation, choosing the same attribute for the same sample or not choosing any attribute as dominant until they finished any mouthfeel.

At that time, they would press the stop button, ending the evaluation. Participants had one-minute intervals to rinse the mouth before evaluating the following sample, and the order of attributes for each participant was variable to avoid bias in the list order.

2.7 Statistical analysis

Each experiment was repeated three times, and One-way ANOVA analyzed all results in SPSS 8.5. All data were shown as mean ± deviation (SD), and $P<0.05$ indicated a significant difference.

3. Results and discussion

3.1 Visual appearance of the baked puff pastry

The appearance of a product often determines the consumer's purchase intention. A subtle and attractive appearance not only can attract attention and arouses interest in purchasing, but also stimulate the appetite, thereby increasing anticipation and appreciation of the product. Figure 1 showed the appearance and cross-section images of croissants made from shortening (Control), two types of 50% shortening/oleogel blends (ET-50% and FT-50%), and two types of oleogel (ET-100% and FT- 100%), respectively. From the appearance of crust, the croissants had a classic croissant shape and coloring, and there was minimal visual variation among the five croissants made with different fats, which indicates that it was feasible to use emulsion-based or foam-based oleogel to partially or completely replace the shortening in pastry products. Cross-sectional images showed that the color of the crumb was somewhat related to the shortening, with the control crumb having a light-yellow color. As the shortening content decreased (50%), the product becomes paler in color the closer it is to the crust. The crumb color of the croissants prepared from 100% ET oleogel was almost beige, and unexpectedly the product prepared from 100% FT oleogel had a distinctly light-yellow color. The difference in crumb color might be related to the differences in the initial color of the fat, shortening would brighten the product due to its own certain natural yellow pigment content. As its content decreased (50% oleogel/shortening) the color became lighter. When shortening was completely replaced in the formulation, the light-yellow color of the product prepared from the white 100% ET oleogel was the weakest, and the crumb of product made with 100% FT oleogel still displayed a color slightly less than the control because of its inherent yellowish coloration with vegetable oils (Wang et al., 2023).

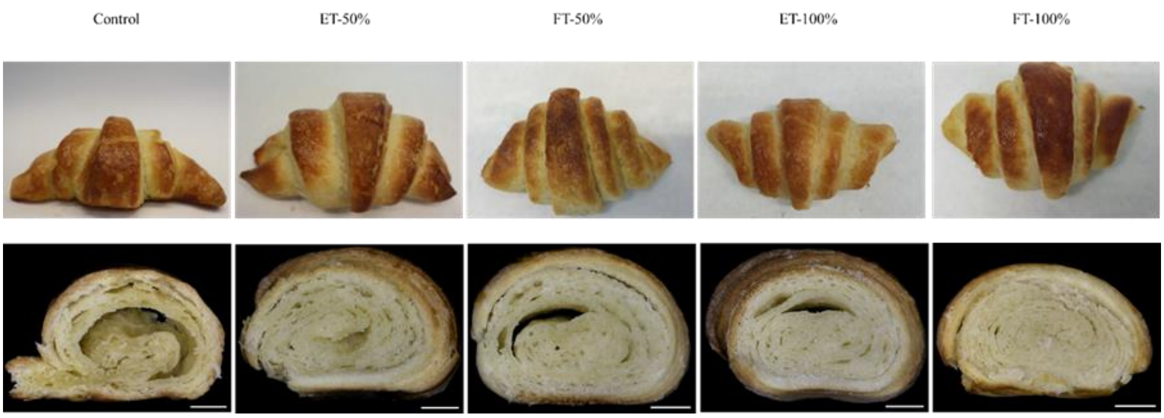


Figure 1. Appearance and cross-sectional images of pastries prepared with shortening and oleogels.

As for aeration, the pore structure decreased as the shortening content decreased. This was due to the fact that shortening was evenly distributed in the dough to form a multi-layered structure through the process of folding and flattening several times in puff pastry preparation. These multiple layers allowed more expansion for gases in the puff pastry, which in turn created more air cells (Ghotra et al., 2002b; Larsson, 1980; Mert & Demirkesen, 2016a). However, emulsion-based oleogels and foam-based oleogels have neither such superior plasticity as shortening, so as the shortening content was reduced, or even completely replaced by 100% oleogel, the interior of the product became progressively denser, with fewer air pockets, resulting in a more compact structure.

3.2 Penetration test

Table 2. Firmness of pastries prepared with shortening and HPMC oleogels.

Samples*	Max. Force (N)
Control	4.24±0.40[a]
ET-50%	4.15±0.29[a]
ET-100%	4.77±0.56[a]
FT-50%	3.82±0.71[a]
FT-100%	4.65±0.86[a]

* Control: croissant prepared with 100 % shortening as fat source; ET-50%: croissant prepared with 50% emulsion template oleogel and 50% shortening; ET-100%: croissant prepared with 100% emulsion template oleogel; FT-50%: croissant prepared with 50% foam template oleogel and 50% shortening; FT-100%: croissant prepared with 100% foam template oleogel.

[a] Means values with different letters indicate significant differences between samples ($p < 0.05$) according to Tukey’s test.

The maximum peak force is related to firmness or hardness, indicating the force required to penetrate and break the structure of the pastry, which is related to the force used by the incisors in biting; the highest its value, the hardest the croissant is. Significance analysis of the maximum peak was performed by multiple tests (Table 2). The mean maximum force values of all samples were not significantly different from those of the control group, indicating that the method of oleogel preparation and the substitution ratio in the formulation had no significant effect on puff pastry firmness.

3.3 Texture profile analysis

TPA test was used to compare the texture parameters of puff pastry prepared from shortening and oleogel, such as firmness, springiness, cohesiveness and chewiness. Figure 2 showed that the hardness of pastry made with 50% ET oleogel was higher than the other samples. The specific parameters of firmness, springiness, cohesiveness and chewiness obtained after TPA analysis are shown in Table 3. There was no significant difference in all textural parameters between the 50/50 shortening/oleogel and the control samples, indicating that the reduction of 50% shortening does not significantly affect the pastries texture. The hardness, cohesiveness, and chewiness of samples prepared with 100% ET oleogels were significantly higher than the other groups of samples ($P<0.05$). Surprisingly, there was no significant difference ($P>0.05$) in the hardness and springiness of the puff pastry made with 100% FT oleogel compared to the control group, whereas cohesiveness and chewiness were significantly higher than the control group ($P<0.05$), and did not differ significantly from the samples prepared with 100% ET oleogel ($P>0.05$).

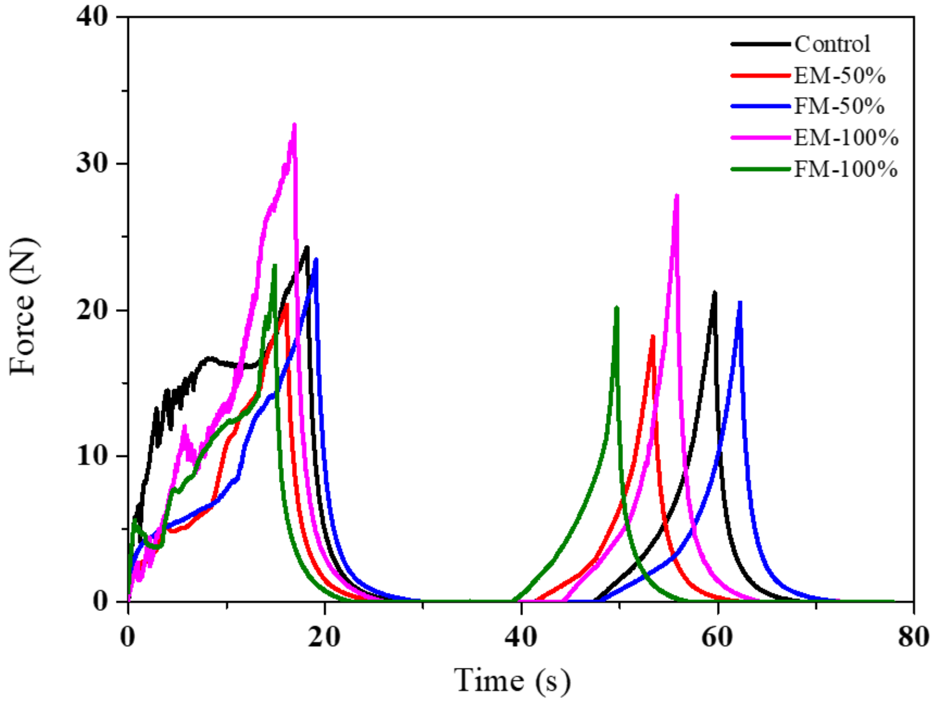


Figure 2. Textural profile analysis curves of pastries prepared with shortening and oleogels.

The possibility causing the raised cohesiveness and chewiness of pastry products prepared from the two 100% oleogels was that the structure of the oleogel might have interacted with the protein network, affecting the structure of the dough, which structural change might impact on the chewiness, making the bread chewier and more cohesive. Also, shortening is helpful in forming a crunchy pastry due to the fact that it can be evenly distributed in the dough as a solid or semi-solid fat at room temperature, thus providing the product with a unique multi-layered crunchy texture and mouthfeel. When shortening is completely replaced by oleogel, the structure of the pastry may change and lose some of its crunchy character, which may also result in a higher chewiness and cohesiveness of the product. Shortening with a high content of fat crystals provides lubrication in the dough, which would inhibit the cross-linking of the gluten protein network, making it easier to process and roll out (Ghotra et al., 2002b; Lim et al., 2017). The substitution of shortening with oleogel could serve a comparable function to a certain extent. However, granular emulsion-based oleogels may form a granular distribution of fat in the pastry, resulting in

Table 3. TPA parameters of pastries prepared with shortening and HPMC oleogels.

Samples*	Hardness (N)	Springiness	Cohesiveness	Chewiness (N)
Control	22.07±2.83[a]	0.70±0.07[a]	0.38±0.03[a]	5.10±0.61[a]
ET-50%	22.22±3.62[a]	0.74±0.04[a]	0.39±0.04[a]	4.41±0.52[a]
FT-50%	24.65±1.56[a]	0.74±0.05[a]	0.40±0.05[ab]	4.64±0.70[a]
ET-100%	29.08±2.27[b]	0.76±0.05[a]	0.46±0.02[b]	6.57±0.48[b]
FT-100%	20.01±1.41[a]	0.72±0.01[a]	0.47±0.03[b]	6.64±0.90[b]

* Control: croissant prepared with 100 % shortening as fat source; ET-50%: croissant prepared with 50% emulsion template oleogel and 50% shortening; ET-100%: croissant prepared with 100% emulsion template oleogel; FT-50%: croissant prepared with 50% foam template oleogel and 50% shortening; FT-100%: croissant prepared with 100% foam template oleogel.

[a-b] Means with different letters for each column indicate significant differences between samples ($p < 0.05$) according to Tukey's test.

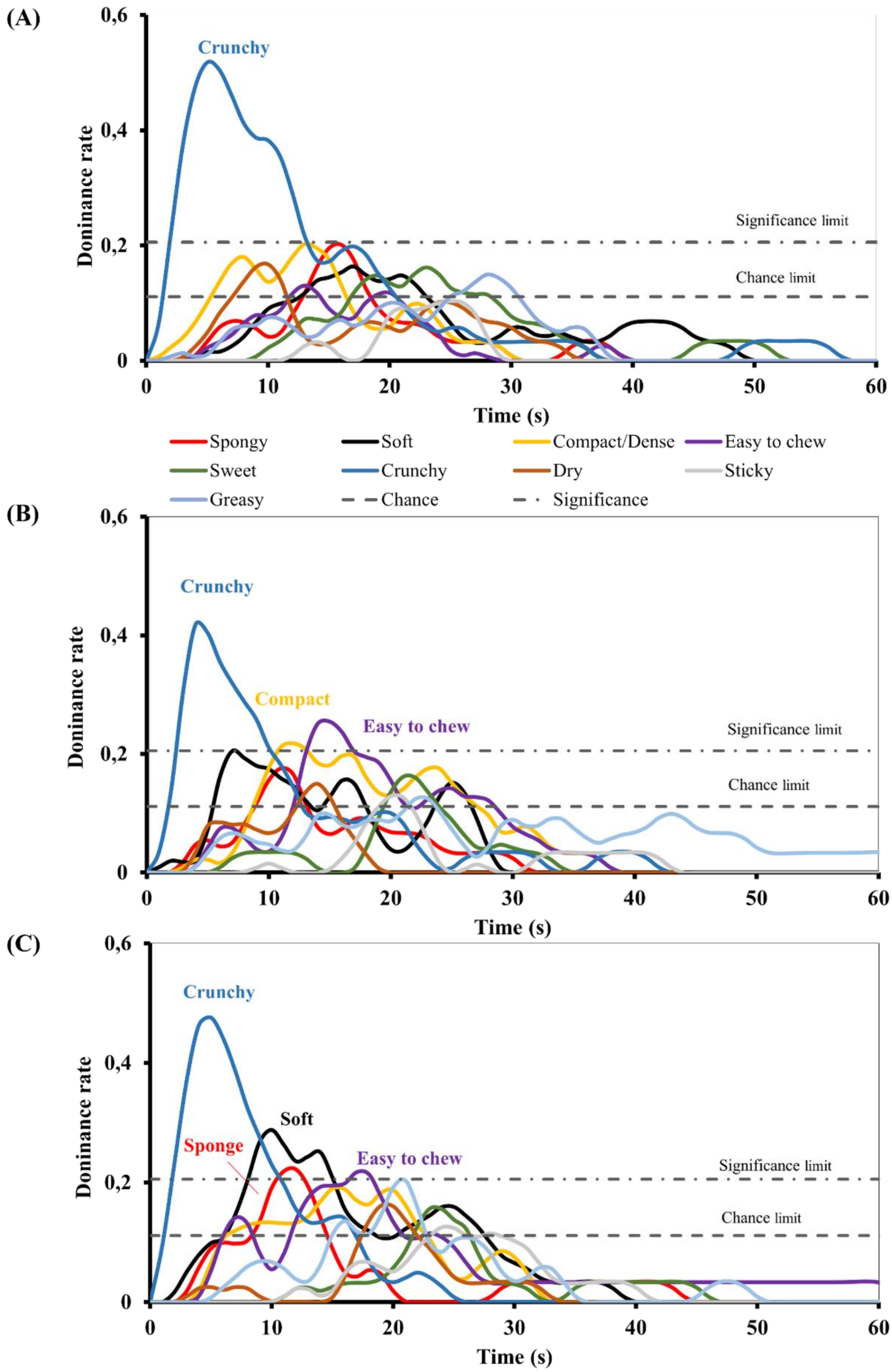
an increase in the hardness of the pastry. In contrast, foam-based oleogels produced by adsorbing liquid oil through a porous foam structure are inherently soft and easier to distribute in a uniform pattern in the pastry, which provides lubrication and reduces the formation of partial hardness. The springiness of pastry products is mainly determined by the composition of the dough and the conditions during processing, including factors such as flour, moisture content, fat content, fermentation process, processing method, and baking conditions, one possible explanation for the non-significant change in the springiness of the two 100% oleogel-prepared pastries is that the effect of the oleogel on the above-mentioned variables was not substantial enough to influence the springiness (Ashok R. Patel, 2014; Oh et al., 2017; Renzyaeva, 2013).

3.4 Temporal domination of sensory

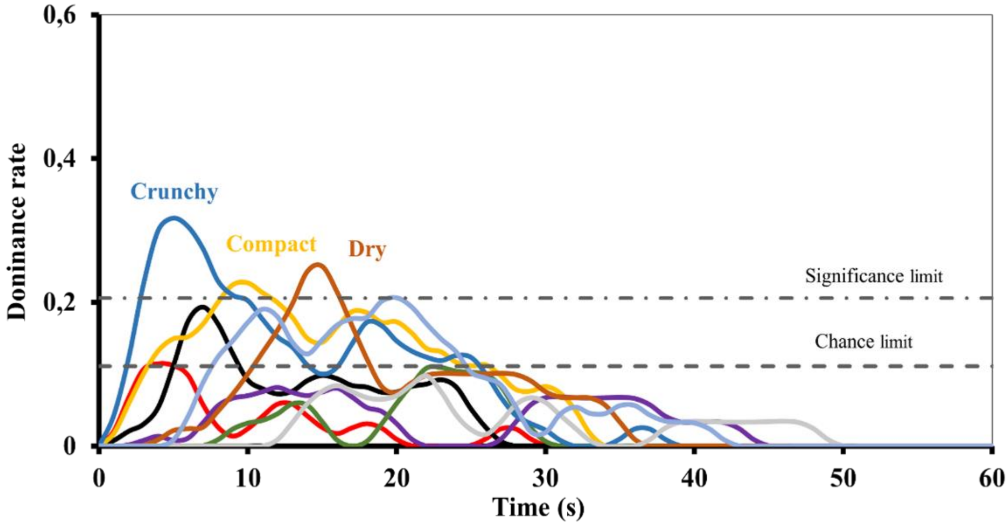
The dynamic variation of the dominant sensation of puff pastry made from different ratios of shortening and oleogel was shown in Figure 3. To ease the interpretation of the TDS curves, two lines of "chance level" and "significant level" are added to the figure. The former corresponds to the rate of dominance accessible by chance for an attribute, while the TDS curve for an attribute exceeding the "significance level indicated that the attribute was considered significantly dominant. In all samples tested, samples prepared with shortening (Fig. 3A) were the least complex product, with crunchy being considered the only attribute significantly dominant throughout the perception.

With the partial replacement of the oleogels (50/50 shortening/oleogel), crunchy and easy to chew became the dominant perception of the samples (Fig. 3B). Shortening deficiency might promote the adhesion between starch and protein granules (Mohanan et al., 2020) resulting in a less crumbly croissant in favor of a softer and firmer texture, which made the pastry less prone to crumbling when chewed. The superiority of the foam-based oleogels versus the emulsion-based oleogels was attributed to the soft and spongy attributes (Fig. 3C), which may be relevant to the highly porous structure of the foam-based gels themselves (Wang et al., 2023). Foam-based oleogels contain air bubbles in their structure, and these bubbles are uniformly distributed in the samples, which means that foam-based oleogels can provide good dispersion of air bubbles in baked products, offering a better softness.

Besides, puff pastry prepared with 100% ET oleogels had significant dry attribute besides compact (Fig. 3D), which was due to the fact that shortening was uniformly distributed in the dough through repeated folding and rolling, assisting in the formation of air cells and a fluffy structure in the puff pastry, as well as contributing to the expansion of the puff pastry. Also, the moisture in the shortening might have some lubricating effect on the formation of the dough, which could hydrate with the starch in the flour to form a colloid that would be helpful in moisturizing the proteins (Larsson, 1980; Mert & Demirkesen, 2016a). These moisture molecules can be more evenly distributed in the dough in the presence of shortening, further reducing the viscosity of the dough. Therefore, when 100% oleogel was used to completely replace shortening, it not only resulted in a compact internal structure of the puff pastry, but also could lead to a reduction in moisture as well as uneven distribution, resulting in a dry texture. In contrast, the porous structure of the foam-based oleogel could trap moisture and effectively minimize the loss of moisture from the dough, enabling the pastry made from 100% foam-based oleogel to keep moist during baking and exhibit the subjective attributes of soft and sticky (Fig. 3E). The above results demonstrated the feasibility of structured sunflower oil to replace solid fats in baking recipes with a substitution of up to 100%. The puff pastry prepared with 50% FT oleogel were similar to the control that had the optimum mouthfeel, which maintained the excellent crunchiness of samples, and also improved the softness, aeration and chewiness of the product.


(A)
Crunchy
Significance limit
Chance limit
Doninance rate
Time (s)
Spongy
Soft
Compact/Dense
Easy to chew
Sweet
Crunchy
Dry
Sticky
Greasy
Chance
Significance
(B)
Crunchy
Compact
Easy to chew
Significance limit
Chance limit
Doninance rate
Time (s)
(C)
Crunchy
Soft
Sponge
Easy to chew
Significance limit
Chance limit
Doninance rate
Time (s)

(D)



(E)

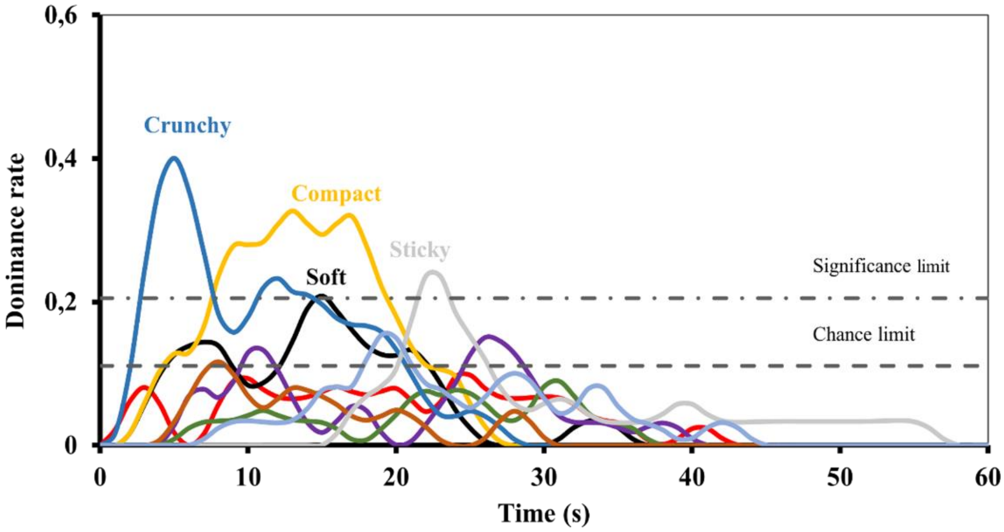


Figure 3. The temporal dominance of sensations curves of pastries prepared with shortening (A), 50% shortening/ET oleogel (B), 50% shortening/FT oleogel (C), 100% ET oleogel (D) and 100% FT oleogel (E), respectively.

These results are based on the fact that shortening has the effect of trapping air to improve the aeration and crunchiness of the baked product, and the absence of shortening inevitably leads to a lower crunchiness and higher compactness (Panouille et al., 2014). Therefore, crunchy and compact became the most dominant attributes of pastries after the introduction of the oleogel. These results agree with the visual appearance of baked pastry and texture results.

4 Conclusion

In this work, vegetable oil-cellulose oleogels obtained by both emulsion template and foam template were used as shortening substitutes in puff pastry to evaluate their effect on physical and sensory properties of final product. The increase of HPMC oleogel substitution, leads to a denser and less aerated internal puff pastry structure. The puff pastry prepared from foam-template oleogels exhibited superior textural properties compared to the emulsion-template oleogels. TDS showed that 100% oleogels resulted in crunchy and compact being the main perceived attribute of puff pastry, but 50/50 shortening-oleogels made them more chewable. At the same time, foam template oleogels also contributed to softer being the main perceived attribute compared to emulsion-based oleogels. Hence, HPMC oleogels show the potential to replace shortening in puff pastry processing, especially foam-based oleogels, in terms of texture as well as sensory and other technical aspects.

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034449Reversible thermal behaviour of vegetable oil cellulose ether emulsions as fat replacers

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4. SUMMARY AND DISCUSSION Of RESULTS

4. Summary of results and general discussion

The present thesis aims to investigate the feasibility of cellulose ethers, hydroxypropylmethylcellulose (HPMC), and methylcellulose (MC), to act as oleogelators in sunflower oil oleogels to formulate conventional fat replacers that have better lipid profile. The effects of the oleogel obtention methodology, type of cellulose ether, and initial oil content, in the texture, rheological, microstructure, oil retention properties, and stability were studied. Subsequently, the oleogels developed were applied in two different foods: cream cheese, a spreadable and creamy semisolid food, and croissant, a puff pastry food.

The results of the thesis are structured around three main sections: 1) the structure, properties, and oxidative stability of cellulose ether oleogels, 2) their application in cream cheese, and 3) their application in croissants.

4.1 Structure, properties, and oxidative stability of cellulose ether oleogels

In this section, the effect of obtention methodology, type of cellulose ether, initial oil concentration, and oxidative stability are studied. These contents have been included in the following two scientific articles:

- Paper 1: Wang, Q. Espert, M., Larrea, V., Quiles, A., Salvador, A., Sanz, T. Comparison of different indirect approaches to design edible oleogels based on cellulose ethers. Food Hydrocolloids 134, 108007 (2023).

-Paper 2: Wang, Q., M. Espert, M., Flores, M., Sanz, T., Salvador, A. Physicochemical stability of sunflower oil-based oleogels prepared by

different indirect oleogelation approaches. Food Hydrocolloids (2024) (send to publication).

MC and HPMC are hydrocolloids, so they have an affinity for water and their thickening and gelling abilities will not be developed in an oil medium. To obtain oleogels with hydrocolloids as oleogelling agents, indirect methods are required. Two indirect methodologies were evaluated: the emulsion template approach (ET) and the foam template approach (FT). In the ET, the hydrocolloid structure is developed in an emulsion system, and the oleogel is obtained after water removal and final mixing. In the FT, the hydrocolloid is first developed in a water phase, secondly, water is eliminated and third the oil phase is mixed with the dehydrated hydrocolloid structure. Another factor that may affect the oleogel structure and properties is the amount of oil initially present in the emulsion (ET) or the amount of oil initially mixed with the dehydrated hydrocolloid structure (FT). The effect of the type of cellulose, MC, or HPMC was also investigated.

There were clear visual differences in the appearance of the ET and FT oleogels. The FT oleogels appearance was affected by the oil concentration and the type of cellulose, At the lowest oil concentration (92%) FT oleogels showed white aggregated clusters, at 96% oil the MC FT oleogel formed a yellowish semi-solid gel, while HPMC oleogel was smoother and more elastic with the oil strongly absorbed in the gel network. Finally, at 97% oil content the FT oleogels showed obvious oil leakage.

Evaluation of the microstructure of the oleogel facilitates an in-depth study of its formation, gelation mechanism, and properties, as well as an understanding of the interaction mechanism of the different components at the molecular level to form a stable three-dimensional network structure.

A different microstructure was found among the MC and HPMC in the dry product obtained by the ET and FT approaches with optical microscopy and SEM. The FT dry powder showed a porous fibrous polymer network in both MC and HPMC. In the ET dry product, the microstructure showed aggregation of oil droplets, which was higher in HPMC and lower in MC, where oil droplets remained spherical.

SEM images of dry FT MC showed a lamellar structure, in contrast with the porous foam structure of HPMC, which was attributed to the fact that the molecular structure of HPMC contained both methoxyl and hydroxypropyl substituents and that the hydrophilic-hydrophobic equilibrium enabled the formation of stable foams, thus promoting a more homogeneous oleogel structure. The molecular chain of MC, on the other hand, has a relatively rigid structure due to only methoxyl substituents. The lower molecular flexibility may lead to a looser network structure formed during gelation, this foam structure may be easily disrupted during lyophilization, resulting in the formation of flaky structures.

The oil-binding capacity of oleogels was influenced by several factors. The first was the preparation technique, where the three-dimensional network structure of the oleogel played a major role in determining its capacity to retain fat. The ET can form a spatial interfacial layer at the oil-water interface through the gelling agent, which can effectively inhibit the aggregation and flocculation of droplets, thus forming homogeneous and stable oil droplets, achieving an oleogel with high mechanical strength and strong oil binding ability to minimize losses after dehydration. HPMC and MC oleogels prepared by the ET approach contained almost 100% lipid retention capacity. However, in the FT, a porous, sponge network structure with the ability to absorb liquid oil should be formed. The size and distribution of pores in the network affect the oil-binding ability. Smaller and more uniform pores help to fix the oil and reduce leakage. The SEM images revealed some differences in the spatial structure of the dry foams formed by MC and HPMC. The MC formed a denser porous structure with higher oil retention ability than the HPMC. Oil content did not exhibit any effect on the oil holding capacity of the ET oleogels, whereas it significantly affected the FT oleogels. Initial oil content of 96% (w/w) seemed to be the critical oil content for HPMC and MC dry foams, which an oil retention capacity of 96% (HPMC) and 97% (MC). If the initial oil content increased to 97%, a significant decrease in the oil retention capacity appeared, with 91% oil retention in the MC oleogel, and 84% in the HPMC oleogel.

The rheological properties of the oleogel have a significant impact on the stability of the product, and favorable rheological properties allow it to be stored without phase separation, sedimentation, or other undesirable changes, thus maintaining its physical stability and consistency. G' values of all oleogels were significantly higher than the G'' values, which indicated that the predominant behavior of the oleogels was solid-like. For ET oleogels, the linear viscoelastic region (LVR) was negatively correlated with the initial oil content. The G' and G'' values of all the oleogels decreased gradually with increasing oil concentration. HPMC oleogels showed higher structural resistance compared to MC (92% and 96% oil content, w/w), and a relatively stronger gel network structure. For both cellulose oleogels, the slope of the trend line of G' with respect to frequency was close to 0, suggesting a low-frequency dependence associated with high gel strength. The G' and G'' values of FT oleogels were significantly higher than those of ET oleogels at the same oil content. The highest G' value was found for the FT HPMC oleogel with 92% oil content.

Increasing the oil content leads to a significant decrease in G' and G". The results of the temperature sweeps showed only a very slight decrease in the values of G' and G" with increasing temperature, indicating that the oleogels are highly thermally stable. The FT oleogel also showed very favorable thermal stability, but somewhat lower than the ET oleogel.

The penetration profile of the oleogel linearly increased with time, indicating that the oleogels had a compact and stable structure. The maximum force value of the ET oleogel decreased significantly with increasing oil content, which was attributed to the relative decrease in cellulose content in the emulsion with increasing oil content, resulting in the weakening of the gel network, leading to a decrease in the hardness of the gel (decrease in the maximum force value). The higher maximum force value of the HPMC oleogel than for MC oleogels at the same oil content was associated with a larger number of aggregated clusters in HPMC emulsion droplets, which formed larger oil droplets in the dry oleogel. Also, the gel fragments were more granular after shear and thus stiffer. A similar phenomenon was observed in the FT oleogel. On the other hand, for the same oil content (92% excluded), the FT oleogels were harder than the ET oleogels.

Spreadability properties were measured in a conventional shortening, in FT oleogels, and in 50/50 ET and FT oleogel/shortening blends. Pure ET oleogels could not be accurately measured. Spreadability is one of the required characteristics of conventional plasticized fat. It is related to the uniform distribution of the fat and determines the degree of crispness and layering of products like pastries, cookies, and pastries. High spreadability can allow the fat to be evenly distributed in the dough, avoiding the problem of uneven texture and improving the overall product texture. At the same time, it also makes the food products expand better during baking, forming a desirable appearance and internal structure. Consequently, spreadability is an important evaluation parameter in the application of oleogel as a fat substitute.

Pure shortening showed the highest firmness and a significant AUC. 100% FT oleogel and shortening/oleogel blends had significantly lower firmness and AUC values than pure shortening. The firmness values of the shortening/ET oleogel blends were approximately half that of the pure shortening, indicating higher spreadability. In addition, the firmness values and AUC values of the shortening/FT oleogel mixtures were significantly lower compared to the shortening/ ET oleogel mixtures, suggesting that the method of preparation of the oleogel has a significant impact on the texture of the mixtures. The texture and stability of food products depend heavily on the fat melting and crystallization properties.

The thermal properties of shortening, 100% HPMC FT and ET oleogel, and a composite fat made up of shortening and the above-mentioned two types of oleogels (50/50, w/w) were compared. Shortening showed two endothermic peaks at 17 °C and 47 °C, respectively, while no thermal transition was found in any of the 100% HPMC oleogels in the studied temperature range. In shortening/oleogel blends, the second peak becomes smaller and broader with a significant decrease in enthalpy. Furthermore, the melting temperature rose, resulting in a maximum peak temperature increase from 47 ºC to 48 ºC for the fat composed of ET oleogel and shortening and 50 ºC for that made of FT oleogel and shortening. The effect of the oleogel on the melting temperature and the shape of the melting curve of shortening suggests that there was an interaction between the shortening and the oleogel matrices, which affected the crystallization behavior of the shortening.

Finally, oleogel oxidation stability was studied. The oxidation or degradation of fatty acids generates a large number of compounds, which can produce changes in the physicochemical and organoleptic properties of fat. To identify differences in their release, the profile of volatile organic compounds was analyzed qualitatively by GC-MS. Thirteen compounds were identified during the storage. Comparing oleogels results on volatile compounds indicated that FT oleogel had higher oxidative stability than ET oleogel. The presence of the cellulose network in the oleogel would decrease the rate of secondary oxidation through a decrease in molecular mobility by acting as hurdles within oleogels. Nonetheless, the ET oleogel was subjected to drying at 60°C for about 48 hours. This factor has probably been the trigger for the higher lipid degradation. On the contrary, the oleogels formulated by the FT approach, as were not subjected to high temperatures during their elaboration, presented a lower oxidation. These differences were more noticeable in pentanal, hexanal, heptanal, and 2-octenal. Pentanoic acid, hexanoic acid, and 2-pentylfuran, which were not found in FT oleogel, also appear in ET oleogel.

4.2 Oleogels application in cream cheese

HPMC emulsions and oleogels were investigated as substitutes for butter in cream cheese formulations. Rheology, texture, and sensory acceptability of cream cheese were evaluated. These results have been included in the third research paper of the thesis:

*-Paper 3: Q. Wang, M. Espert, M.J. Hernández, A. Salvador & T. Sanz***.** *Effect of cellulose ether emulsion and oleogel as healthy fat alternatives in cream cheese. Linear and nonlinear rheology, texture, and sensory properties. Food Hydrocolloids, 150, 109740 (2024).*

The rheological properties of all cream cheese samples presented a predominance of G' versus G" in the LVR. In both oleogel and emulsion cheeses, a decrease in G' was observed with an increasing level of butter substitution. At 100% butter substitution, both G' and G" of cream cheese prepared with oleogels were lower than those prepared with emulsions. Above a critical strain value, both G' and G" decreased when strain amplitude increased, denoting the end of the LVR. No significant differences in yield stress (σ_y) and the corresponding strain (γ_y) were found among samples, indicating that all types of cheese require similar stress to reach the same strain value and that the extent of their linear behavior response is similar. Yield stress values between 30 and 40 Pa had to reach small strain values, from 0.3% to 0.5%. At higher strain values, a crossover between G' and G" defined as the flow point, was observed. The values of the flow point (G' = G") decrease with increasing butter replacement, although no significant differences were found between the control and the sample with 50% oleogel. Furthermore, there was no significant difference between the three cream cheese groups prepared from 50%-emulsion as well as 100% emulsion and 100% oleogel, but the G' values were significantly lower than those of the control and 50% oleogel groups.

In the frequency sweeps, the values of G' were always higher than G" along the complete frequency sweep studied with a light dependence of both G' and G" when frequency increased, revealing a cheese viscoelastic behavior typical of soft gels. Addition of oleogel and emulsion to replace butter in cream cheeses decreased G' and G" values, and the effect increased by increasing butter replacement.

The LAOS results showed that the elastic Lissajous–Bowditch plots for all cream cheeses were elliptical at 0.1% strain, indicating an ideal viscoelastic behavior. The viscoelastic behavior of cream cheese shifted from the linear to the nonlinear region as the strain increased to 100% (near the intersection of G' and G"). Finally, the elastic Lissajous–Bowditch plot of all cream cheeses varied from an ellipse to a sub-parallelogram as the strain rose to 1000%, which indicated an increase of viscous dissipation and a transfer from an elastic to a viscous predominant behavior.

The stress-stiffness ratio (S-Value) of all samples remained approximately 0 in the LVR (strain < 10%), and then the S values of all cream cheeses exhibited a strain-stiffening behavior as the strain increased. In terms of T values, in all samples, a decrease is observed with increasing strain (T < 0), showing a remarkable shear-thinning behavior. The absolute value of T was always much lower than the value of S during the large deformation occurrence, indicating that the nonlinear behavior of cream cheese under large deformation was strain stiffening predominant.

Spreadability is negatively correlated with firmness (maximum force) and area under the penetration curve. Higher values of firmness and AUC indicate lower spreadability. When butter was totally substituted with either an oleogel or an emulsion, the hardness and AUC of the products were reduced in comparison to butter, which served as the control. Cream cheeses produced with oleogel or emulsion in partial replacement of butter (50% degree of replacement, w/w) did not differ much from the control. The ductility and hardness of cream cheeses made with 100% emulsion exhibited no significant differences when compared to those prepared with 50% oleogel. This was attributed to the increased spreadability of the cream cheese after the substitution of butter for oleogel and emulsion, which could be caused by the disruptive effect of the casein matrix or by the reduction of fat crystals in the butter, thereby increasing the softness as speculated by other reports. Lastly, sensory evaluation of cream cheese was investigated. Sensory appearance, texture, spreadability, flavor, and acceptability scores of the oil cheeses were studied by consumers in a hedonic test. In terms of appearance, no significant differences were found among all cream cheeses. In terms of, the mean scores of the product's texture in the 100% oleogel group were significantly different from the mean scores of the products prepared in the oleogel/butter (50/50, w/w), emulsion/butter (50/50, w/w) and 100% emulsion. Cream cheese made with 100% oleogel showed the significantly lowest flavor acceptability, this may be due to the fact that the flavor of the oleogel itself had some effect on the cream cheese, but did not appear in the other samples. As for spreadability, all samples prepared with oleogel and emulsion exhibited significantly higher spreadability compared to the control group, which was consistent with the previous instrumental texture results. Regarding the flavor of the cream cheese with cracker spread and the overall score, it was shown that there was no significant unfavorable effect of emulsion or cream on the cream cheese, and even the flavor with cracker was significantly higher for the 50% oleogel and 50% emulsion cheeses compared to the control group. Moreover, cream cheeses produced with 100% emulsion or oleogel could completely replace the conventional fat in cream cheese as their flavor scores with crackers and total scores were not significantly different from the control group. As for purchase intention, after consumers were informed of the type of fat, the percentage of unwillingness to purchase cheese in the control, oleogel/butter (50/50, w/w), and emulsion/butter (50/50, w/w) groups increased significantly, while the percentage of likely or sure purchases decreased. In contrast, the percentage that would definitely purchase 100% emulsion made cream cheese increased from 18.5% to 25%, followed by 100% oleogel made cheese from 9.8% to 15.2%. This increase in purchase intention of the emulsion and oleogel cheeses indicates the importance given by consumers to the nutritional aspects, especially for a healthier fat profile with a reduction in the content of saturated fatty acids.

Therefore, oleogels and emulsions might potentially replace butter in a cream cheese formulation.

4.3 Oleogel application in puff pastry

One of the food applications were a spreadable, plastic, solid fat is specially required is puff pastry. Puff pastry structure is composed of alternative thin fat and dough layers, which are the responsible of the desirable light, delicate, and flaky texture when baked. Laminated dough products comprise many thin, alternating layers of fat and dough formed by repeated rolling and folding. Upon baking, the layering causes each individual dough layer to bake separately, creating the characteristic visual separation of the layers and the flaky texture. Puff pastry could be considered the most challenging food in terms of saturated fat reduction.

Research into the application of hydroxypropyl methyl cellulose (HPMC) ether oleogels as a spreadable, plastic, solid fat in croissant is included in the three last papers of the thesis:

-Paper 4: M. Espert, Qi Wang, T. Sanz, and A. Salvador. Sunflower oil-based oleogel as fat replacer in croissants: textural and sensory characterization. Food and Bioprocess Technology 16(14), 1943-1952 (2023).

*-Paper 5**:** Q. Wang, M. Espert· A. Salvador and T. Sanz. Shortening replacement by emulsion and foam template hydroxypropyl methylcellulose (HPMC)-based oleogels in puff pastry dough. Rheological and texture properties. Current research in Food Science 7, 100558 (2023).*

-Paper 6: Q. Wang, S. Bobadilla, M. Espert, T. Sanz and A. Salvador. Shortening replacement by hydroxypropyl methylcellulose-based oleogels obtained by different indirect approaches. Texture and sensory properties of baked puff pastry. Food hydrocolloids 153, 109936 (2024).

In the first two articles of this section (papers 4 and 5), the oleogel obtention methodology and level of shortening replacement on dough rheological properties were studied. HMPC FT and ET oleogels were used to prepare pastry doughs with total and partial (50/50 shortening/oleogel mixtures) replacement of shortening. The rheological results show that all doughs exhibit solid-like properties, with values of the elastic modulus, G', greater than the viscous modulus, G'', in the entire frequency range studied. The extension of the dough's LVR became progressively narrower as the shortening level was reduced (higher oleogel content). The shortening sample showed the highest extension of the LVR, followed by the shortening/oleogel blends, being the FT oleogel the one with the lowest resistance to the applied stress. The ET oleogel dough showed a wider LVR than the FT oleogel dough, indicating that the ET oleogel had greater resistance to the applied deformation. The highest spreadability found in the oleogel/shortening blends agrees with the lowest dough resistance to the applied stress/strain. The G' of dough prepared with 50% ET oleogel was significantly higher than that of 50% FT oleogel dough. The lower viscoelasticity in the presence of oleogels allows for proper handling, although easier handling was observed in the blends in comparison to the 100% oleogel dough. Research about the texture and sensory analysis of the baked croissants prepared with oleogels was included in the last two papers (5 and 6). Fats play a vital role in puff pastry products, which not only allow puff pastry to expand and form a unique multilayered structure during baking but also provide a crispy texture and enriched flavour.

Moreover, the melting point, uniformity of distribution, and operational characteristics of fats determine the workability of the dough and the final baking quality. Modification of the type or proportion of fat significantly affects the layer separation, crispness, and flavor of the puff pastry, and could cause the texture to become softer, coarse, or undefined layers. Hence, it is essential to explore the textural properties of croissants prepared with oleogel. The textural parameters such as hardness, cohesiveness, adhesiveness, and chewiness were compared between the different croissant formulations. The oleogel prepared with the ET was first selected to substitute shortening in the croissant formulation, with the percentage of shortening substitution ranging from 50%, 60%, 70%, and 100% in descending order. No significant difference ($p < 0.05$) was found between the oleogels in terms of hardness and springiness. However, as the level of fat replacement by oleogel increased, the croissants became chewier and more cohesive. Cohesiveness quantifies the internal strength of the food structure and provides information on the ability of a material to stick to itself. The higher cohesiveness of the oleogel croissant could be related to its more compact crumb structure. Compared to the control, the oleogel croissant's more compact network is more difficult to crumble. In contrast, the lower cohesiveness values in the control croissant could be explained by the presence of a crumb with weaker internal bonds that, once broken, cannot reform. Chewiness represents the amount of energy needed to disintegrate food to swallow. An increase in chewiness values with an increase in the proportion of oleogel was found, indicating that these samples offer greater resistance to chewing, as expected from the values of hardness, cohesiveness, and appearance of the croissant crumb. In summary, the oleogel could replace shortening without significant changes in hardness and springiness, even at 100% replacement, however, the increase in oleogel concentration led to a slight increase in cohesiveness and chewiness.

In the last paper, the FT oleogel was further used to replace shortening and compared with the ET oleogel to explore the effect of different types of oleogel on the texture of the puff pastry product. The results showed that there was no significant difference in all textural parameters between the 50/50 shortening/oleogel and the control samples, indicating that the reduction of 50% shortening does not significantly affect the pastry texture. The hardness, cohesiveness, and chewiness of samples prepared with 100% ET oleogels were significantly higher than the other groups of samples ($P<0.05$). Surprisingly, there was no significant difference ($P>0.05$) in the hardness and springiness of the puff pastry made with 100% FT oleogel compared to the control group, whereas cohesiveness and chewiness were significantly higher than the control group ($P<0.05$), and did not differ significantly from the samples prepared with 100% ET oleogel ($P>0.05$).

The possibility causing the raised cohesiveness and chewiness of pastry products prepared from the two 100% oleogels was that the structure of the oleogel might have interacted with the protein network, affecting the structure of the dough, which structural change might impact the chewiness. Also, shortening is helpful in forming a crunchy pastry due to the fact that it can be evenly distributed in the dough as a solid or semi-solid fat at room temperature, thus providing the product with a unique multi-layered crunchy texture and mouthfeel. When shortening is completely replaced by oleogel, the structure of the pastry may change and lose some of its crunchy character, which may also result in a higher chewiness and cohesiveness of the product. However, ET oleogels may form a granular distribution of fat in the pastry, resulting in an increase in the hardness of the pastry. In contrast, FT oleogels produced by adsorbing liquid oil through a porous foam structure are inherently soft and easier to distribute in a uniform pattern in the pastry. The springiness of pastry products is mainly determined by the composition of the dough and the conditions during processing, including factors such as flour, moisture content, fat content, fermentation process, processing method. No significant change in the springiness of the two 100% oleogel croissants was observed, however, the ET croissant were significantly harder and chewier than the FT oleogel croissant.

Finally, two different sensory evaluation methods, namely Free Choice Profile (FCP) and Temporal Dominance of Sensations (TDS), were used to evaluate croissant products prepared using ET oleogel and FT oleogel as shortening substitutes, respectively.

FCP is a sensory technique where each subject quantifies the perceived qualities of products using his or her own individual list of terms. The consumers used a wide variety of terms to describe the differences: voluminous, uniform/regular, compact, brown color, laminated, glossy, brioche, crunchy, butter, croissant taste, and firm/hard. The two-dimensional Generalised Procrustes Analysis (GPA) plot was obtained from the analysis of the consumer assessment of the different croissants explained 77.88% of the variance. In the formulation of croissants prepared using ET oleogels with various degrees of shortening substitution (50%, 60%, 70%, 100%), it was found that dimension 1 accounted for 51.33% of the total variance, indicating that most differences between croissants perceived were explained by this dimension and were mainly related to the descriptors of appearance, texture, and taste. In the positive part of this dimension, descriptors such as "laminated/airy appearance", "voluminous appearance", "crunchy texture", "buttery flavor", and "typical croissant flavor" appeared, which referred mainly to shortening croissants (control), and to a lesser extent, to croissants with 50/50 (shortening/oleogel). Whereas on the negative side of this axis, terms such as "uniform/regular appearance", "compact", "brown color", and "brioche flavor" appeared, which characterized the samples 40/60 (shortening/oleogel), 30/70 (shortening/oleogel), and 100% oleogel. Dimension 2 accounted for 19.55% of the total variance. The positive part of this axis was mainly related to appearance, highlighting the descriptor "bulky", which was described in croissants 50/50 (shortening/oleogel), and 100% oleogel, whereas in the negative part, descriptors from all the categories studied (appearance, texture, and flavor) appeared, highlighting "typical croissant flavor", which surprisingly was named in all the study samples, except in sample 100% oleogel.

Therefore, it can be concluded that the samples prepared with the different percentages of ET oleogel presented similar descriptors to the control, although they were much more compact, with the sample prepared with 50/50 (shortening/oleogel) being the most similar to the control.

After exploring the effect of ET oleogel replacing shortening on the sensory properties of croissant products using FCP and obtaining the result that 50% degree of substitution gave the optimum product in terms of palatability, in another work, the difference in the organoleptic properties of the croissant products from the substitution of shortening by ET oleogel and FT oleogel using TDS was made. TDS analysis was used in this paper to analyze the dynamics of the main sensory attributes of puff pastry products prepared with oleogel using the two indirect methods to substitute shortening, with the degree of substitution considered only at 50% and 100%. It could be found that with the partial replacement of the oleogels (50/50 shortening/oleogel), crunchy and easy to chew became the dominant perception of the samples. The superiority of the foam-based oleogels versus the ET oleogels was attributed to the soft and spongy attributes, which may be relevant to the highly porous structure of the FT oleogels themselves. FT oleogels contain air bubbles in their structure, and these bubbles are uniformly distributed in the samples, which means that FT oleogels can provide good dispersion of oil in baked products, offering better softness. Besides, puff pastry prepared with 100% ET oleogels had significant dry attributes besides compact, which was due to the fact that moisture molecules can be more evenly distributed in the dough in the presence of shortening. Therefore, when 100% ET oleogel was used to completely replace shortening, it not only resulted in a compact internal structure of the puff pastry but also could lead to a reduction in moisture as well as uneven distribution, resulting in a dry texture. In contrast, the porous structure of the FT oleogel could trap moisture and effectively minimize the loss of moisture from the dough, enabling the pastry made from 100% FT oleogel to keep moist during baking and exhibit the subjective attributes of soft and sticky. The above results demonstrated the feasibility of structured sunflower oil to replace solid fats in baking recipes with a substitution of up to 100%. The puff pastry prepared with 50% FT oleogel was similar to the control, with optimum mouthfeel, crunchiness, softness, aeration, and chewiness.

4.4 Prospects

The results of this thesis demonstrate that oleogels are a feasible alternative to reduce the saturated fatty acid content in both cheese and croissants, being a healthier alternative to conventional fats. However, there are many interesting topics in this area which remain to be solved. First of all, the stability of oleogel in storage and usage is still a technological difficulty. Drying techniques, necessary to remove the water from the oleogel structure are also a technological difficulty, which may have an effect on energy costs and the stability of certain types of oils. Secondly, a multitude of factors affect the structure and characteristics of the oleogels themselves; thus, additional optimization is required to guarantee uniformity in quality during commercial production and to prevent variations in texture and functional attributes.

In terms of their food applications, more research is required for oleogels to be fully comparable to shortening in the manufacturing of dough pastry food. For 50% replacement of conventional fat, cellulose ether oleogels allow the obtention of suitable dough rheological properties as well as texture and sensory properties of the croissants; however, 100% replacement has limitations in terms of both manufacturing and final sensory properties. In addition, there is still a long way to go for further development and optimization of oleogelators, for example, research on new alternative sources completely free of additives and more contribution to a sustainable manufacturing process.

5. CONCLUSIONS

The main conclusions of this thesis are:

OLEOGELS PROPERTIES

- The methodology to obtain cellulose ether oleogels affected the final oleogel rheology, texture, microstructure, and oil retention capacity. The emulsion template oleogels were solid-like, non-fluid, and had 100% oil retention capacity. The foam template oleogels were semi-solid, and their oil retention capacity decreased with increasing oil content. The emulsion template oleogel microstructure exhibited spherical oil droplet morphology, for methylcellulose, and irregular for hydroxypropylmethylcellulose, while in the foam template powders, a porous fibrous polymer network is observed.

- Initial oil content had an important effect on the rheological properties of the oleogels. At the lowest oil content, a more stabilized oleogel structure with higher resistance to the applied stress was found. G’ and G’’ gradually decreased with the increase in oil concentration.

- The hydroxypropylmethylcellulose and methylcellulose oleogels prepared by emulsion template and foam template approaches showed high gel strength and low dependence on frequency and temperature. The type of cellulose did not have a significant effect on the oleogel properties.

- Hydroxypropylmethylcellulose oleogel/shortening blend obtained with an emulsion template approach presented similar mechanical properties, melting characteristics, and oxidative stability to shortening control samples after a storage of four weeks at 20ºC.

CREAM CREESE APPLICATION

- Hydroxypropylmethylcellulose oleogels and emulsions were validated as replacers of traditional fat, for example, butter, in the production of cream cheese. Oleogels reduced saturated fatty acids and emulsions reduced saturated fatty acids and total fat content.
- Oleogels and emulsions decreased cheese cream mechanical strength and enhanced spreadability properties in comparison to the control, being the effect more noticeable for oleogels, which showed the lowest elastic modulus.
- Lissajous curves illustrated the transition from linear viscoelastic response to nonlinear response within the range of 0.1% to 1000%. All cream cheese samples exhibited nonlinear strain-stiffening and shear-thinning behavior, with no discernible differences between the different cheeses in the nonlinear region.
- Sensory evaluations showed that cream cheese prepared with oleogels and emulsions had minimal negative effects compared to the control cream cheese and even improved scores in spreadability, cream cheese flavor on biscuits, and overall assessment. Purchase intention indicated an increased willingness to buy cream cheese prepared with 100% emulsion and 100% oleogel after participants were informed about the type and amount of fat in the formulations.

CROISSANT APPLICATION

- Replacement of shortening by both emulsion template and foam template hydroxypropylmethylcellulose oleogels reduced the dough's viscoelastic properties, showing the foam template oleogel dough the lowest resistance to the applied deformation. The easier handling was found in the 50% blend of shortening and oleogel for both oleogel types.

- The level of replacement of shortening by hydroxypropylmethylcellulose oleogel had no effect on the external appearance of the bakery products, but it did have an effect on the aeration and compactness of the products, with complete replacement of shortening by the oleogel resulting in a firmer product with less aeration.

- No significant differences were found in croissant hardness and springiness between the control croissant and the 100% emulsion template oleogel. However, as the level of fat replacement by oleogel increased (50, 60, 70, and 100%) the croissant became chewier and more cohesive, which was associated with their more compact structure.

- The texture of croissants made with either foam template hydroxypropylmethylcellulose oleogel or emulsion template hydroxypropylmethylcellulose oleogel at 50% level of shortening replacement was not significantly different from the control croissant.

- The Temporal Dominance Sensation sensory analysis showed that oleogel at 50% level of replacement was optimal with the best overall mouthfeel found in the 50% foam template oleogel. Replacement of 100% resulted in compact being the main perceived attribute.

6. ANNEXES

Publications

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Comparison of different indirect approaches to design edible oleogels based on cellulose ethers

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ABSTRACT

Growing public concern about the adverse health effects of overconsumption of saturated fat has contributed to the rising research interest in the field of using healthy oils to construct edible structured oils (oloegels) as fat-based alternatives. In this study two indirect methodologies (the emulsion template approach and the foam template approach) were investigated to prepare oleogels with hydroxypropyl methylcellulose and methylcellulose as gelling agent at three different oil concentrations. Microstructure, texture, rheology, and oil retention capacity were measured to evaluate the structural and physicochemical properties of oleogels. Results showed that the emulsion-based oleogel effectively inhibited the aggregation of droplets. The dry emulsion showed independent droplets and an oil retention capacity of 100%. In foam-type oleogels the oil retention rate was negatively correlated with the oil content. The oleogels prepared by both methods have excellent mechanical properties and gel strength, with a predominance of the elastic versus the viscous behavior. Hydroxypropyl methylcellulose and methylcellulose had different degrees of influence on the structure and mechanical properties of the two oleogels. The results of this paper provide guidance for the development and application of cellulose-based oleogels as healthy alternatives to saturated fat.

1. Introduction

Solid fat such as shortenings, butter, palm fat, cocoa butter etc., are widely used in bakery products, chocolate, spread sauces, quick-frozen food, snacks, and other industrial foods due to their ability to endow technological and organoleptic properties (flavor, taste, texture, etc.) (Feichtinger & Scholten, 2020; Gómez-Estaca et al., 2019; Naeli, Milani, Farmani, & Zargaraan, 2022). Solid fat functional properties depend to a large extent on the crystal network structure of the high melting point components in the fat used. Without saturated fatty acid (SFA), these fats would not be able to provide the required structure and texture. However, excessive intake of saturated fat has potential risks for cardiovascular disease (Adili, Roufegarinejad, Tabibiazar, Hamishehkar, & Alizadeh, 2020), diabetes (Oh, Lee, Lee, & Lee, 2019), or metabolic syndrome (Bascuas et al., 2021), which seriously endangers human health.

An alternative to conventional solid fat is oleogelation. Oleogelation confers solid properties to a liquid oil and requires the use of gelators or structurants to form a three-dimensional network polymeric structure to trap the liquid oil (Davidovich-Pinhas, Barbut, & Marangoni, 2015; Li et al., 2021). In recent year, the development of edible oleogels based on polymers has been flourishing. Initially, researchers focused on small fat-soluble molecules e.g., waxes (Yılmaz & Öğütcü, 2015), mono-glycerides, diglycerides, long-chain fatty acids (Martins, Vicente, Cunha, & Cerqueira, 2018) or long-chain fatty alcohols (Lupi et al., 2013). Later, the interests gradually shifted from small polymers to edible natural polymers being developed due to their more plentiful and economical availability (Matalanis & McClements, 2013), such as proteins (de Vries, Gomez, van der Linden, & Scholten, 2017; de Vries, Jansen, van der Linden, & Scholten, 2018; Mohanan, Tang, Nickerson, & Ghosh, 2020), polysaccharides (Patel et al., 2014), hydroxypropyl methylcellulose (HPMC), and methylcellulose (MC) (Patel & Dewettinck, 2015; Zetzl et al., 2014).

The methodologies to prepared oleogels with polysaccharides as structure agents required indirect approaches, as the oil cannot directly interact with the polysaccharide. In the direct methods, the gelling agent is directly mix with oil to form a gel at the appropriate temperature (Shi et al., 2021). The emulsion template approach and the foam template approach are two of the indirect methodologies available. The emulsion template approach involves forming an emulsion and, subsequently

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Effect of cellulose ether emulsion and oleogel as healthy fat alternatives in cream cheese. Linear and nonlinear rheology, texture and sensory properties

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A R T I C L E I N F O

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Sensory evaluation

A B S T R A C T

The suitability of oil-in-water (o/w) hydroxypropyl methylcellulose (HPMC)-based emulsions and oleogels to reduce total fat and saturated fat content in cream cheese was studied. The effect of HPMC emulsions and oleogels on spreadability, viscoelasticity, and sensory acceptability of cream cheese was evaluated. Small-amplitude oscillatory shear (SAOS) and large-amplitude oscillatory shear (LAOS) tests were performed to investigate linear and nonlinear rheology. All cheeses showed a predominance of G' versus G" with a light dependence of both moduli with frequency in the linear viscoelastic region (LVR). Fat replacement with emulsion or oleogel significantly reduces the values of G' and G" at the LVR, yield point, and flow point, and increases spreadability. This effect was greatest for the oleogel substitution. However, incorporation of emulsion or oleogel did not significantly affect tan δ, yield stress, yield strain, flow stress, and flow strain. The elastic and viscous evolution during the transition from SAOS to LAOS was similar in all cheeses, despite their differences in spreadability. At large deformation, all samples showed strain-stiffening and shear-thinning behavior. Similar sensory acceptability was found among the oleogel and emulsion cheeses and the control. The similar nonlinear rheological properties among cheeses do not explain the differences in spreadability properties, but explain their similar sensory acceptability. Furthermore, the purchase intention for oleogel and emulsion cheeses increases when consumers receive information on the type and amount of fat.

1. Introduction

Cream cheese is a semi-soft dairy product with a wide diversity in flavor and form that varies with the ingredients of the formulations (Wendin, 2000). Fat is an essential ingredient that provides many textures, spreadability, and with ease of being mixed with other constituents. However, excessive fat consumption, mainly saturated fat and *trans* fatty acids, can increase the risk of several chronic diseases such as obesity, cardiovascular disease, and cancer (Demirkesen & Mert, 2020; Espert, Hernández, Sanz, & Salvador, 2021). The growth of obesity has also increased consumer awareness to adopt healthier diet strategies, resulting in increased demand for low-fat foods (Espert, Salvador, & Sanz, 2020; Mert & Demirkesen, 2016). However, in cream cheese, fat reduction has been associated with textural and flavor changes that affect consumer's purchase intention (Ningtyas, Bhandari, Bansal, & Prakash., 2019). Ningtyas, Bhandari, Bansal, and Prakash. (2018) used β-glucan (BG) and phytosterols (PS) as fat substitutes, showing that BG increased the viscosity and hardness of reduced-fat cream cheese, whereas PS improved its spreadability. Zetzl, Marangoni, and Barbut (2012) directly used liquid oils rich in unsaturated fatty acids to replace saturated fats, but the textural properties of the final product were not satisfactory. The structure of these fat replacers differed from that of traditional solid fats, decreasing the sensory properties of cheese (Ningtyas, Bhandari, Bansal, & Prakash, 2019).

In previous studies, cellulose ether emulsions and sunflower oil-based oleogels have been used successfully to reduce total fat and saturated fat content in different foods (Espert et al., 2021). In comparison to butter: 55% saturated fat and 80% total fat, cellulose ether emulsions contains: 3.8% saturated fat and 47.5% total fat (sunflower oil) and oleogels contains: 96.7% total fat and 7.8% saturated fat, so replacement one by one of butter by oleogels reduces saturated fat, and replacement of butter by emulsion reduces saturated fat and total fat.

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RESEARCH

Sunflower Oil-based Oleogel as Fat Replacer in Croissants: Textural and Sensory Characterisation

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Abstract

Croissants are made using solid fats that predominantly contain saturated fatty acids and *trans* fatty acids. In this study, an oleogel consisting of sunflower oil structured with hydroxypropyl methylcellulose was used as a conventional fat replacer in puff pastry thus improving its nutritional profile. Oleogel (OG)-shortening (SH) blends were prepared as a fat replacer for partial (50, 60, 70%) and full shortening (100%) substitution. These replacements implied a reduction of up to 45% of saturated fat and an increase of up to 47% of unsaturated fat, especially monounsaturated fatty acids. Physical characterisation was conducted using texture profile analysis and penetration tests to evaluate the oleogel effect on a baked croissant matrix structure. Sensory analysis was also performed to evaluate the organoleptic properties of the croissant. Shortening replacement using oleogel resulted in croissants with lower saturated fat content, lower bite firmness, and a texture profile similar to croissants made with commercial shortening. The presence of oleogel up to 100% did not contribute negatively to the firmness or springiness of the croissants, although they became chewier and more cohesive as the oleogel increased. In terms of sensory perception, the SH50:OG50 croissant sample was the most similar to the solid fat control. The use of sunflower oil-cellulose-based oleogel was suitable for the formulation of puff pastry products with a healthier fat profile while maintaining the physical and sensory characteristics of conventional croissants.

Keywords Oleogel · Shortening replacer · Hydroxypropyl methylcellulose · Croissant · Texture

Introduction

Laminated dough products, such as croissants, have many plastic fats rich in saturated fatty acids. Their unique structure is composed of alternative thin fat and dough layers and provides a desirable light, delicate, and flaky texture when baked, highly appreciated by consumers (Simovic et al., 2009). Puff pastry fat must have certain specific structural characteristics, such as predetermined plasticity, firmness, and solid fat content profile (Simovic et al., 2009). Laminated dough products comprise many thin, alternating layers of fat and dough formed by repeated rolling and folding. Therefore, fats used in laminated dough production are often referred to as "roll-in fats". Upon baking, the layering causes each individual dough layer to bake separately, creating the characteristic visual separation of the layers and the flaky texture (Mattice & Marangoni, 2017). Thus, fat plays a key role in puff pastry and cannot be replaced without adversely affecting aspects such as appearance, texture, structure, and flavour of the reduced-fat puff pastry (Pimdit et al., 2008).

Butter is the traditional fat used for puff pastry, but its high costs and difficult handling during industrial processing have led to the development of fat blends specifically manufactured for its replacement (Silow et al., 2016). These fat blends are mainly derived from vegetable oils and fats and offer improved processability (fat plasticity). However, processes that confer these oils a solid texture, such as partial hydrogenation, generate a high proportion of *trans* fatty acids, which are associated with increased risks of several conditions, including coronary heart disease, cancer, diabetes, allergies, and poor foetal development (Simovic et al., 2009; Wickramarachchi et al., 2015). Other alternatives like complete hydrogenation, transesterification, or using vegetable oils or fats do not contain *trans* fatty acids but are

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Shortening replacement by emulsion and foam template hydroxypropyl methylcellulose (HPMC)-based oleogels in puff pastry dough. Rheological and texture properties

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ABSTRACT

Shortening plays an essential function in the formulation of sweet laminated bakery products, but has a potential health risk due to their high percentage of saturated fatty acids. In this paper, the feasibility of hydroxypropyl methylcellulose (HPMC) oleogels prepared with emulsion template (ET) and foam template (FT) approaches as fat sources in a puff pastry dough was investigated. Spreadability and thermal properties of control shortening, 100% ET and FT oleogels and shortening/oleogel (50/50) blends were measured. The different systems were applied as the fat source in a puff pastry dough, and their effect on rheological and texture properties was investigated. Results showed that partial replacement of shortening with oleogels could significantly decrease the firmness values (from 115 to 26 N) ($P < 0.05$) and increased the spreadability of shortening. The methodology to prepare the oleogel (FT or ET) also significantly affected the texture parameters. FT blends had the highest spreadability with significantly lower firmness values and area under the curve. Thermal values showed that both oleogels could slightly increase the melting point of shortening from 47 to 50 °C. The replacement of shortening with oleogel decreases the viscoelasticity of puff pastry dough and increases its thermal stability but does not significantly change dough viscoelasticity in the shortening/oleogel mixture. These results indicated that both oleogels have promising potential to replace shortening in puff pastry dough formulations, but the ET oleogel showed a more similar behavior to the control shortening than the FT oleogel.

1. Introduction

Laminated bakery products are highly appreciated worldwide for their characteristic light and flaky texture (Selaković et al., 2021). Fat (shortening, margarine, butter) is wrapped around the basic dough (flour, salt, water) and then repeatedly rolled and folded to form a laminated dough comprised of alternating layers of dough and thin layers of fat. The fat is also called rolling fat because of its unique folding and rolling method of production, which requires excellent softness and plasticity to enable layering without breaking the dough layers, but not being too soft to leak out under pressure (Mattice and Marangoni, 2017). The layered structure enables each individual dough layer to be baked separately, and the water turns into steam during baking, causing the expansion of the dough layers to create visual layering and flaky texture characteristics (de la Horra et al., 2015; Gabriele et al., 2008; Šoronja-Simović et al., 2017). In the absence of shortening, the gluten and starch granules will stick together and make the dough stiff and low-volume (Lim et al., 2017). In contrast, shortening envelops the gluten particles, which causes a discontinuity in the protein and starch structure and lubricates the gluten particles, forming a small and soft inflated product. Butter is commonly considered a favorable rolling fat, but the high cost and restricted plasticity range limit its large-scale production in laminated doughs (Mattice and Marangoni, 2017), so shortening is becoming the priority for preparing industrial laminated dough products. It provides not only functionality but also texture and lubrication. However, the problem currently confronted is the high amount of saturated fatty acids present in rolling fats (Lai and Lin, 2007; Silow et al., 2017). It is well-recognized that the excessive intake of saturated fatty acids can be harmful to health, increasing the risk of cardiovascular disease and leading to obesity and diabetes (DiNicolantonio et al., 2016; Hamley, 2017). Hence, there has been a tremendous effort in the search for alternative fat sources with healthy fat profiles without altering the typical food quality properties. Vegetable oils liquid at room temperature because of their low saturated fatty acid

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Shortening replacement by hydroxypropyl methylcellulose-based oleogels obtained by different indirect approaches. Texture and sensory properties of baked puff pastry

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Temporal dominance sensations

ABSTRACT

Shortening in puff pastry products contains high levels of saturated and even *trans*-fatty acids that may be hazardous to human health. One efficient way to reduce such unhealthy fat in food is to employ gelators to structure liquid oils for the production of oleogels, thereby replacing shortening. In this paper, two types of HPMC (Hydroxypropyl Methyl Cellulose) oleogels (*emulsion template* and *foam template*) were used to replace shortening in puff pastry. Full-HD images, TPA (Texture Profile Analysis) and penetration tests, as well as TDS (Time-Dominant Sensation) sensory analysis, were used to assess the products' cross-sectional morphology, texture, and sensory attributes. The appearance of baked pastry made with 50/50 (shortening/oleogel) was similar to the control (100% shortening). In contrast, the crumb texture of baked pastry prepared with 100% oleogel was more compact and less airy than control. All samples showed similar firmness. TPA test showed that puff pastry made with 100% foam-based oleogel did not substantially differ to the control group, while samples prepared with emulsion-based oleogels were significantly harder and chewier than the control. Regarding sensory analysis, all puff pastries were mainly perceived as "crunchy" during chewing. The increase in oleogel content resulted in denser pastry, but the 50/50 foam template samples were "easier to chew". Attribute "compact" also became one of the main perceptions when the oleogel content increased to 100%, which would be related to the dense structure observed in the crumb morphology. This study confirms the feasibility of HPMC oleogels as healthy fat source in puff pastry.

1. Introduction

Puff pastry products have gained great popularity among consumers mainly due to their light and flaky layered structure (Selaković et al., 2021; Silow et al., 2016; Simovic et al., 2009) resulting from the specific recipe and process of making puff pastry. Examples of puff pastry are croissants and Danish pastry (Grujić et al., 2008; Sanz et al., 2015). Puff pastry consists of two parts: the dough and the fat, the former is made of flour, milk, sugar, yeast, and a limited amount of fat (10% in flour mass basis). The molded rolled fat (40–50% in flour mass basis) is then topped with the dough and repeatedly folded, rolled out, and chilled to produce an overlapping structure of dough and fat layers (Bousquieres et al., 2014; Silow et al., 2017; Simovic et al., 2009). Typical pastry fats include butter and shortenings. However, it is known that butter and shortening contain high levels of saturated fatty acids, which may have adverse health effects such as obesity, cancer, hyperlipidemia, and coronary heart disease when consumed over a long period of time (Mozaffarian & Clarke, 2009; Siri-Tarino et al., 2015). Hence, numerous manufacturers and researchers have devoted significant efforts to finding feasible ways to decrease saturated and trans fats on pastry foods.

It is definitely a great challenge to find fat substitutes that satisfy the requirement of reducing harmful fats while maintaining a comparable taste and texture to conventional puff pastry products. Traditional puff pastry fat is crucial to the quality of the product, the fat in dough can fix the structure of the dough, while the rolled-in fat can separate the dough layers, preventing coagulation by repeated folding and inhibiting water's evaporation to ensure the final product's expansion in volume (Lefébure et al., 2013; Šoronja-Simović et al., 2017). Consequently, the alteration of fat may lead to changes in the structure, color, mouthfeel and even texture of the product, affecting its organoleptic properties (Mamat & Hill, 2014). Consumers' purchase of food products is based on

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