UNIVERSIDADE ESTADUAL DE CAMPINAS

FACULDADE DE ENGENHARIA DE ALIMENTOS

JULIO CESAR BARBOSA ROCHA

OBTENTION AND CHARACTERIZATION OF ORGANOGELS OF SOYBEAN OIL STRUCTURED USING VEGETABLE WAXES AND INTERESTERIFIED FAT UNDER CONTROLLED CRYSTALLIZATION CONDITIONS

OBTENÇÃO E CARACTERIZAÇÃO DE ORGANOGÉIS DE OLEO DE SOJA ESTRUTURADOS UTILIZANDO CERAS VEGETAIS E GORDURA INTERESTERIFICADA SOB CONDIÇÕES CONTROLADAS DE CRISTALIZAÇÃO

Campinas

2017

JULIO CESAR BARBOSA ROCHA

OBTENTION AND CHARACTERIZATION OF ORGANOGELS OF SOYBEAN OIL STRUCTURED USING VEGETABLE WAXES AND INTERESTERIFIED FAT UNDER CONTROLLED CRYSTALLIZATION CONDITIONS

OBTENÇÃO E CARACTERIZAÇÃO DE ORGANOGÉIS DE OLEO DE SOJA ESTRUTURADOS UTILIZANDO CERAS VEGETAIS E GORDURA INTERESTERIFICADA SOB CONDIÇÕES CONTROLADAS DE CRISTALIZAÇÃO

Thesis presented to the Faculty of Food Engineering of the University of Campinas in partial fulfillment of the requirements for the degree of Doctor in Food Technology.

Tese apresentada à Faculdade de Engenharia de Alimentos da Universidade Estadual de Campinas como parte dos requisitos exigidos para a obtenção do título de Doutor em Tecnologia de Alimentos.

Orientador: Prof. Dr. DANIEL BARRERA-ARELLANO

ESTE EXEMPLAR CORRESPONDE À VERSÃO FINAL DA TESE DEFENDIDA PELO ALUNO JULIO CESAR BARBOSA ROCHA E ORIENTADA PELO PROF. DR. DANIEL BARRERA-ARELLANO

CAMPINAS

2017

Agência(s) de fomento e nº(s) de processo(s): CNPq, 140517/2012-0

Ficha catalográfica
Universidade Estadual de Campinas
Biblioteca da Faculdade de Engenharia de Alimentos
Márcia Regina Garbelini Sevillano - CRB 8/3647

R582o
Rocha, Julio Cesar Barbosa, 1982-
Obtention and characterization of organogels of soybean oil structured using vegetable waxes and interesterified fat under controlled crystallization conditions / Julio Cesar Barbosa Rocha. – Campinas, SP : [s.n.], 2017.

Orientador: Daniel Barrera-Arellano.
Tese (doutorado) – Universidade Estadual de Campinas, Faculdade de Engenharia de Alimentos.

1. Organogel. 2. Cristalização. 3. Reologia. 4. Ceras. 5. Gordura. I. Barrera-Arellano, Daniel,1953-. II. Universidade Estadual de Campinas. Faculdade de Engenharia de Alimentos. III. Título.

Informações para Biblioteca Digital

Título em outro idioma: Otenção e caracterização de organogéis de óleo de soja estruturado com ceras vegetais e gordura interesterificada obtidos sob condições controladas de cristalização
Palavras-chave em inglês:
Organogel
Crystallization
Rheology
Waxes
Fat
Área de concentração: Tecnologia de Alimentos
Titulação: Doutor em Tecnologia de Alimentos
Banca examinadora:
Daniel Barrera-Arellano [Orientador]
Ana Paula Badan Ribeiro
Rosiane Lopes da Cunha
Marisa Aparecida Bismara Regitano d' Arce
Rita de Kássia de Almeida Garcia
Data de defesa: 24-02-2017
Programa de Pós-Graduação: Tecnologia de Alimentos

____

Prof. Dr. Daniel Barrera-Arellano (Orientador)
Faculdade de Engenharia de Alimentos –UNICAMP

____

Profa. Dra. Marisa Aparecida Bismara Regitano d’Arce (Membro titular)
Escola Superior de Agricultura Luiz de Queiroz – ESALQ/USP

____

Profa. Dra. Rita de Kassia Almeida Garcia (Membro titular)
Faculdade de Tecnologia de Capão Bonito – FATEC

____

Profa. Dra. Ana Paula Badan Ribeiro (Membro titular)
Faculdade de Engenharia de Alimentos –UNICAMP

____

Profa. Dra. Rosiane Lopes da Cunha (Membro titular)
Faculdade de Engenharia de Alimentos –UNICAMP

____

Profa. Dra. Ana Carla Kawazoe Sato (Membro suplente)
Faculdade de Engenharia de Alimentos –UNICAMP

____

Profa. Dra. Kelly Moreira Bezerra Gandra (Membro suplente)
Universidade Federal de Ouro Preto – UFOP

____

Dra. Carla Léa de Camargo Vianna Cruz (Membro suplente)
Instituto de tecnologia de Alimentos - ITAL

A Ata de defesa com as respectivas assinaturas dos membros encontra-se no processo de vida acadêmica do aluno.

Dedico esse trabalho à minha família pela paciência e apoio em todos esses anos.

Agradecimentos

Agradeço em especial à minha esposa Fernanda Oliveira pela paciência e apoio. Ao meu orientador Prof. Daniel Barrera-Arellano pela oportunidade de desenvolver esse trabalho e pela compreensão em todos os momentos difíceis.

Agradeço também ao pessoal do Laboratório de Óleos e Gorduras (DTA-FEA Unicamp)[1], Profa. Lireny Aparecida Guaraldo Gonçalves, Profa. Ana Paula Badan Ribeiro, Dr. Renato Grimaldi e Rosana Nogueira. A Kamila Ferreira Chaves por todo o apoio e ajuda. Ao Chiu Chi Ming, Glazielli Marangoni, Gabriel Deschamps Fernandes, Valter Stroppa pela amizade e apoio nos momentos difíceis.

---

[1] `https://www.fea.unicamp.br/laboleos/index.php`

Resumo

Organogéis são misturas que apresentam características de gel, compostas por agentes estruturantes e uma fase imobilizada, formando uma rede termorreversível autosustentada, onde esta fase imobilizada é um composto orgânico, o que o difere de outros géis formados basicamente por compostos hidrossolúveis. Os principais agentes estruturantes já estudados para formação de organogéis são os diacilgliceróis, monoacilgliceróis, álcoois e ácidos graxos e suas misturas, ceras e ésteres de cera, fitosteróis e orizanol, lecitina e triestearato de sorbitana, entre outros. O objetivo desta pesquisa foi desenvolver e caracterizar organogéis elaborados a partir de óleo de soja, gordura vegetal e ceras vegetais (cera de cana-de-açúcar, cera de carnaúba e cera de candelila), e a partir dos resultados obtidos gerar uma base de conhecimento para estudos posteriores sobre aplicação destes organogéis em produtos alimentícios. Organogéis estruturados com até 4% de cera vegetal (candelila, carnaúba e cana-de-açúcar) e adição de gordura vegetal nos teores de 5, 15 e 25%, os organogéis foram feitos utilizando condições controladas de cristalização (taxa de resfriamento e cisalhamento), as amostras foram analisadas quanto à estabilidade, propriedades reológicas, comportamento térmico, conteúdo de gordura sólida, dureza e morfologia. Os organogéis desenvolvidos somente com óleo de soja foram desenvolvidos para as ceras de cana-de-açúcar e candelila usando apenas cristalização estática. As análises térmicas mostraram uma temperatura de cristalização para os organogéis variando entre 43,7 e 44,57°C para a cera de cana-de-açúcar, 42,95 e 42,92°C para cera de candelila e 56,23°C para a cera de carnaúba, todas em 4% (m/m). As análises reológicas com cristalização estática mostraram que os materiais apresentaram um comportamento típico de gel com início da mudança de comportamento reológico em condições de temperatura similares às observadas na análise térmica com valores de 43,1 e 42,1°C para os géis de cana-de-açúcar e candelila respectivamente, a mesma análise para o organogel de cera de carnaúba mostrou a mudança de comportamento reológio em temperatura de aproximadamente 61°C, todos os organogéis apresentaram o comporamento esperado na varredura de frequências com os valores de G’ maiores que G". As mesmas medidas feitas usando cristalização com cisalhamento em 300s$^{-1”}$ até a temperatura de formação de gel seguido de cristalização estática. As amostras apresentaram comportamento similar à da cristalização estática, a inclusão de gordura interesterificada por sua vez aumentou os valores de G’ para as amostras, porém na análise de varredura de frequência foi observado uma maior sensibilidade à variações de frequência. A dureza foi maior para os géis de candelila, seguido dos géis de cana-de-açúcar e por últimos os de carnaúba. Os tamanhos de cristais observados na microscopia foram maiores para os organogéis de carnaúba e para os géis de cera de cana-de-açúcar quando comparados com os da cera de candelila. A formação de organogéis permitiu um aumento na estabilidade oxidativa da fase lipídica contínua. De maneira geral os organogéis apresentaram baixa resistência mecânica que foi melhorada pela inclusão da gordura vegetal, permitindo que a modificação da fase contínua amplia as possibilidades de aplicação para organogéis em produtos alimentícios.

Palavras-chaves: organogéis, cera de cana-de-açúcar, cera de candelilla, cera de carnaúba, estruturação de gorduras.

Abstract

Organogels are mixtures that present gel like characteristics, composed of a structuring agent and an immobilized phase, forming a self-sustained thermoreversible network, where this immobilized phase is an organic compound, which differs them from other gels basically formed by water-soluble compounds. The main structurant agents already studied for the formation of organogels are diacylglycerols, monoacylglycerols, alcohols, fatty acids and their mixtures, waxes and esters of wax, phytosterols and oryzanol, lecithin and sorbitan tristearate, among others. The objective of this research was to develop and characterize organogels made from soybean oil, vegetable fat and vegetable waxes (sugarcane wax, carnauba wax and candelilla wax), and from the obtained results generate a base of knowledge for further studies on the application of these organogels in food products. Organogels structured with up to 4% of vegetable wax (candelilla, carnauba and sugar cane) and addition of vegetable fat at levels of 5, 15 and 25%, the organogels were made using controlled conditions of crystallization (cooling rate And shear), the samples were analyzed for stability, rheological properties, thermal behavior, solid fat content, hardness and morphology. The organogels developed only with soybean oil were developed for sugar cane and candelilla wax using only static crystallization. Thermal analyzes showed a crystallization temperature for the organogels ranging from 43.7 to 44.57°C for sugar cane wax, 42.95 and 42.92°C for Candelilla wax and 56.23°C for carnauba wax, all at 4% (w/w). The rheological analyzes with static crystallization showed that the materials presented a typical behavior of gel with beginning of the change of rheological behavior in conditions of temperature similar to those observed in the thermal analysis with values of 43.1 and 42.1°C to The sugarcane and candelilla gels respectively, the same analysis for the carnauba wax organogel showed the change in rheological behavior at a temperature of approximately 61°C, all the organogels presented the expected behavior at the frequency sweep with values of G' greater than G". The same measurements were taken using shear crystallization in 300s^{-}1 to the gel-forming temperature followed by static crystallization.The samples exhibited behavior similar to that of static crystallization, tha inclusion os interesterified fat increased the G' and the frequency sweep showed that it made the material more frequency sensible. The hardness was higher for the candelilla gels, followed by the sugarcane gels and the latter for the carnauba gels, the inclusion of interesterified fats increased mechanical resistance. The crystal sizes observed in the microscopy were higher for the carnauba organogens and for the sugarcane wax gels, Of sugarcane when compared to candelilla wax. The formation of organogels allowed an increase in the oxidative stability of the continuous lipid phase. All organogels presented low mechanical resistance that was improved by the inclusion of vegetable fat, allowing the modification of the continuous phase, increasing the possibilities of application for organogels in food products.

Key-words: organogels, sugarcane wax, candelilla wax, carnauba wax, lipid structuring.

Lista de ilustrações

Lista de tabelas

Lista de abreviaturas e siglas

TAG	Triacilgliceróis
CLW	Cera de candelila
CRW	Cera de carnauba
SCW	Cera de cana-de-açúcar
HSA	Ácido Hidroxiesteárico

Sumário

Introdução

A vida moderna trouxe inúmeras comodidades, em especial a industrialização dos alimentos, que tornou mais baratos e acessíveis produtos que anteriormente eram apenas consumidos por uma minoria. Hoje é possível conseguir praticamente qualquer produto em um supermercado com extrema facilidade e isto tem levado a indústria a procurar matérias-primas com custo reduzido que gerem produtos de alta qualidade e nutricionalmente adequados.

Na busca por produtos de alta qualidade e aceitação pelo consumidor surgiu a tecnologia aplicada aos alimentos e logo novos ingredientes e processos foram criados em substituição aos antigos que eram apenas adaptações de processos artesanais. Uma das grandes evoluções na tecnologia de alimentos foi a modificação de produtos lipídicos em especial a hidrogenação, pois permitiu usar produtos de origem vegetal para obter produtos substitutos para as gorduras animais, que apresentam custos elevados, baixa disponibilidade e altos teores de ácidos graxos saturados e colesterol conhecidos como prejudiciais à saúde.

Posteriormente descobriu-se que os processos de hidrogenação formavam compostos até então pouco estudados; os ácidos graxos *trans* , que também se mostraram potencialmente prejudiciais à saúde em especial, por aumentarem o risco de doenças cardiovasculares, assim como as gorduras saturadas e o colesterol (CHRISTOPHE, 2005).

Com a descoberta do efeito deletério dos ácidos graxos *trans* formados na hidrogenação parcial, foram utilizados novos processos tecnológicos para a produção de gorduras vegetais com aplicação industrial, buscando-se manter um custo competitivo. As principais tecnologias utilizadas para essa finalidade são: fracionamento; a separação de diferentes componentes de uma gorduras usando a cristalização controlada dos TAGs presentes na gordura e separação por filtração de frações com menor ponto de fusão (oleína) e maior ponto de fusão (estearina) (SENANAYAKE; SHAHIDI, 2005b) e interesterificação; que consiste no rearranjo da distribuição dos ácidos graxos nos triacilgliceróis (TAGs), sem alterações no perfil de ácidos graxos.

A interesterificação ocorre por via química ou enzimática, na via química, os catalisadores mais utilizados para a reação são ligas de sódio ou potásio ou alcoolato de sódio. A troca pode ocorrer entre dois ou mais TAGs e também ésteres metílicos ou etílicos (POKORNÝ; SCHMIDT, 2011), a migração dos ácidos graxos durante a reação é aleatória levando à formação de produtos não específicos (YANG; FRUEKILDE; XU, 2005). Para a interesterificação, as fontes normalmente usadas de ácidos graxos saturados são os óleos vegetais totalmente hidrogenados ou as estearinas obtidas por processos de fracionamento.

O processo de interesterificação enzimática, por sua vez, utiliza lipases microbianas como catalisadores da reação. O processo permite uma redução no consumo de energia pelas condições de processo mais amenas e produção contínua pelo uso de enzimas imobilizadas. Existe também a possibilidade de utilizar lipases específicas sn-1,3 modificando o perfil aleatório da distribuição dos ácidos graxos nos TAGs formados após a reação, esse processo mantém os ácidos graxos da posição central do glicerol (sn-2) inalterados, de modo geral os processos de interesterificação catalisados por lipases são aplicados para produtos de elevado valor agregado como, por exemplo, substitutos e equivalentes de manteiga de cacau (SENANAYAKE; SHAHIDI, 2005a).

Apesar do aspecto positivo da redução dos ácidos graxos *trans* obtidos através do uso de processos de interesterificação, a formação de TAGs com ácidos graxos saturados na posição sn-2 do glicerol tem sido questionado, esse posicionamento (não usual nos TAGs de fontes naturais naturais) possuem um efeito nutricional negativo, estudos observaram que o aumento da quantidade de ácido palmítico na posição central da molécula do TAG (sn-2) permitiu uma maior absorção desses lipídios pelo organismo, levando a um aumento do potencial aterogênico em animais de laboratório (CHRISTOPHE, 2005; SUNDRAM; KARUPAIAH; HAYES, 2007; HUNTER, 2001), além disso a redução dos ácidos graxos *trans*, trouxe como consequência um aumento na presença de ácidos graxos saturados nos produtos lipídicos que independente do posicionamento no glicerol são reconhecidamente prejudiciais à saúde. Além disso com o uso de fontes lipídicas com quantidades maiores de ácidos graxos saturados ocorreu um aumento progressivo na ingestão desses, apesar da importância na redução do consumo de ácidos graxos *trans*, reconhecidamente capazes de aumentar os riscos de enfermidades cardíacas (FLICKINGER; HUTH, 2004), os ácidos graxos saturados também o são, mesmo que apresentando um risco menor que os ácidos graxos *trans* (STENDER; DYERBERG, 2004).

Em conjunto com a ampliação dos conhecimentos sobre os malefícios dos ácidos graxos saturados e *trans*, as indústrias de alimentos sofrem pressão de consumidores mais informados e dos órgãos reguladores. No ano de 2012 a agência nacional de vigilância sanitária no Brasil (ANVISA) definiu os novos parâmetros de rotulagem, exigindo a descrição do conteúdo de gordura *trans* (ANVISA, 2012), forçando os fabricantes a modificar as suas matérias-primas com o objetivo de manterem uma "rotulagem limpa", nos Estados Unidos a agência reguladora *Food and Drug Administration* (FDA), foi além e estabeleceu diretrizes para proibir a presença de ácidos graxos *trans* em alimentos (FDA, 2015).

Uma das alternativas que surgiram para eliminar a presença dos ácidos graxos *trans* sem aumentar o uso de ácidos graxos saturados foi a utilização de organogéis, que são materiais que possuem características de gel, porém a fase contínua imobilizada é um composto orgânico o que o difere de outros géis (hidrogéis), formados basicamente por compostos hidrossolúveis (ROGERS et al., 2007).

Os organogéis apresentam como vantagem a manutenção das características nutricionais do óleo inalteradas, em especial a manutenção dos ácidos graxos insaturados e das suas posições no glicerol o que os torna potencialmente mais adequados nutricionalmente que as opções usadas atualmente (SUNDRAM; KARUPAIAH; HAYES, 2007).

Os materiais lipídicos apresentam propriedades reológicas distintas, comportando-se como fluidos e como sólidos, o que os torna especiamente complicados para serem substituidos em produtos alimentícios isso devido à presença de redes cristalinas microscópicas que permitem que um material se mantenha rígido, mas ao mesmo tempo seja capaz de escoar sob um esforço mecânico (CHRYSAN, 2005).

Como parte da avaliação da viabilidade industrial da aplicação dos organogéis em produtos lipídicos, é de extrema importância compreender o seu comportamento físico e químico, uma vez que as gorduras utilizadas atualmente apresentam características bastante conhecidas e possíveis de serem previstas em especial, perfil de cristalização e comportamento térmico, permitindo inclusive a modelagem computacional do comportamento esperado (GARCIA, 2010).

Para avaliar este comportamento físico-químico é necessário o uso de metodologias analíticas específicas. De modo geral são utilizadas análises de DSC para análise de comportamento térmico, texturômetro, reômetro rotacional e viscosímetro para análise de comportamento reológico, microscopia óptica com luz polarizada para avaliação da estrutura microscópica, essas análises tem como objetivo observar a microestrutura formada pelos agentes estruturantes junto com a fase contínua lipídica e suas comparações com as gorduras comerciais.

Revisão Bibliográfica

Óleos e Gorduras Vegetais

Óleo de Soja

Com uma produção estimada para o ano de 2017 em 8 milhões de toneladas (ABIOVE, 2016), o óleo de soja é o produto lipídico mais importante economicamente no Brasil. Além disso, a soja com uma safra de 94,7 milhões de toneladas em 2016 e com um aumento de produção esperado de 9,6% para 2017, é o segundo maior volume de produção agrícola do país (IBGE, 2017) e o primeiro produto do país em volume de exportações sendo também o segundo maior exportador global do produto representando 40% de toda soja exportada no mundo de acordo com o Observatório Internacional de Complexidade Econômica (OEC, 2014). Com base nesses dados, podemos afirmar que o complexo soja é extremamente importante para a economia local e global.

O óleo de soja é composto majoritariamente por ácidos graxos insaturados com teores variando entre 79 e 88,4%, como mostrado na Tabela 1. Essa composição aliada ao grande volume de produção o torna especialmente interessante para ser utilizado como gordura industrial.

Tabela 1: Composição em ácidos graxos de óleo do soja (ANVISA, 2006).

Ácidos Graxos	Quantidade (%)
C12:0	0,1
C14:0	0,2
C16:0	8 - 13,5
C16:1	0,2
C18:0	2 - 5,4
C18:1	17 – 30
C18:2	48 – 59
C18:3	8,0
C20:0	0,1 - 0,6
C20:1	0,5
C22:0	0,7
C22:1	0,3
C24:0	0,5
Insaturados	79,0 – 88,4
Saturados	11,6 – 21,0

Óleos líquidos, como o de soja, possuem limitações de aplicação, ficando restrito basicamente à processos de fritura e algumas aplicações específicas, isso porque boa parte das aplicações industriais dependem da presença de estrutura no lipídio sendo necessário o uso de processos de modificação visando ampliar o leque de aplicações industriais como será discutido adiante.

Gorduras Vegetais Industriais

Os óleos e gorduras são alimentos essenciais na dieta, além de serem a principal fonte energética do organismo, aportam elementos indispensáveis, como vitaminas e esteróides precursores de hormônios, contribuindo também para a palatabilidade e aroma dos alimentos (GURR; HARWOOD, 1996). Além disso óleos e gorduras conferem consistência, características de fusão, atuam como meio de transferência de calor durante o processo de fritura, podendo afetar a estrutura, vida de prateleira e características sensoriais dos alimentos (YOUNG, 1985).

Gorduras industriais são, por sua vez, produtos obtidos à partir de modificações físicas ou químicas de matrizes lipídicas que resultam em materiais com características importantes para aplicações específicas, como por exemplo em margarinas ou recheios de biscoito, as caracteríticas que tornam as gorduras industriais importantes são em especial a consistência (dureza) e a plasticidade (espalhabilidade), sendo este comportamento fruto de uma complexa rede cristalina, que os ácidos graxos e TAGs saturados ou *trans* produzem quando em temperaturas abaixo do seu ponto de fusão (RYE; LITWINENKO; MARANGONI, 2005)

A estrutura cristalina da rede permite diferentes configurações que modificam tanto o comportamento reológico quanto térmico do material (NARINE; MARANGONI, 2002). Às diferentes formas de cristalização observadas em gorduras denomina-se polimorfismo, conforme mostrado na Figura 1, sendo que três formas cristalinas são comumente observadas para gorduras, chamadas de α, β' e β, cujas diferenças residem nas modificação da conformação dos cristais e organização das monocamadas (SATO; UENO, 2005). Como consequência, gorduras obtidas em diferentes hábitos polimórficos apresentam características distintas, uma vez que estrutura das gorduras está intimamente ligada ao comportamento térmico e mecânico, que por sua vez, são indicativos para aplicações industriais (SENANAYAKE; SHAHIDI, 2005a).

Análises de Gorduras Industriais

A determinação do comportamento das gorduras é de fato extremamente relevante para a adequada aplicação desses produtos, e de modo geral, as análises para gorduras industriais visam compreender melhor o comportamento físico e químico do material.

Dentre as determinações de comportamento físico, o conteúdo de gordura sólida é uma das análises mais utilizadas e consiste em avaliar a porção de uma determinada matriz lipídica que se encontra na forma de sólido cristalino, sendo que a relação entre

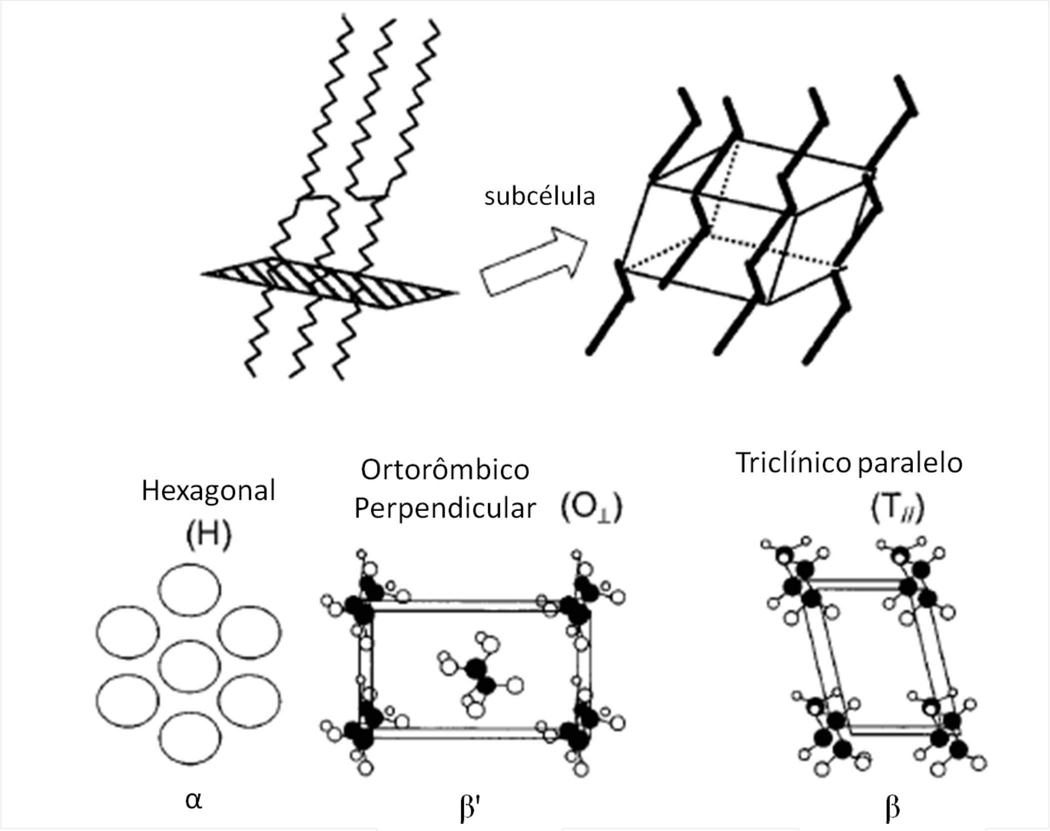

Figura 1: Organização dos hábitos polimórficos para gorduras (SATO; UENO, 2005).

a quantidade de gordura sólida e a textura de um material é direta, com o aumento do teor de sólidos, a força medida como textura do material será aumentada. No entanto, a textura também depende da força da rede formada pelos cristais (MATUSZEK, 2003). O teor de sólidos mensurado é uma fração do material que se encontra cristalizado, a análise é feita sob uma condição de temperatura controlada e os dados são utilizados para a construção de uma curva que é chamada de perfil de sólidos. A análise do perfil de sólidos em função da temperatura permite a determinação do uso de uma gordura industrial para aplicações específicas, por exemplo o perfil de uma manteiga de cacau será distinto de uma gordura para biscoito (CHRYSAN, 2005).

A determinação do teor de sólidos é usualmente realizada utilizando espectroscopia de ressonância magnética nuclear de baixa frequência (RMN), sendo metodologia oficial (AOCS, 2004). A determinação é feita em condições controladas de cristalização uma vez que as gorduras apresentam memória de cristalização e deseja-se garantir uma adequada comparação entre os materiais (DEMAN; DEMAN, 2002).

O conhecimento das propriedades térmicas do material é muito importante e usando a calorimetria diferencial de varredura (DSC), é possível mensurar a energia térmica (calor) necessária para modificar o estado físico de uma amostra, obtendo seu termograma, que consiste em um representação gráfico dos eventos térmicos, o gráfico apresenta "picos” de intensidade variável (CAMPOS, 2005). A análise dos termogramas, permite avaliar o perfil de fusão e cristalização de materiais lipídicos, além disso é possível observar fenômenos de transição polimórfica e mudanças de estado (HIMAWAN; STAROV; STAPLEY, 2006).

A rede cristalina formada pelas gorduras (como citado anteriormente) permite que tais materiais tenham um comportamento viscoelástico; se comportanto como sólidos ou líquidos dependendo das condições de cisalhamento e temperatura. O comportamento das gorduras define características de produtos com elevados teores de lipídios tais como margarinas, chocolates e *spreads*. A capacidade de fornecer a textura desejada para os produtos alimentícios é de modo geral mensurada pelo comportamento reológico do material, em especial a análise de textura. A compreensão dos indicadores reológicos para processamento, composição e estrutura é de extrema importância para a indústria, para que os processos possam ser aprimorados e a qualidade dos produtos melhorada (NARINE; MARANGONI, 1999).

A análise de textura avalia a resistência mecânica de um material à uma força normal, uma vez que estes materiais possuem comportamento tanto de sólidos (resistência mecânica) quando de fluidos (escoamento), desse modo é possível mensurar a força necessária para que um material possa escoar (STEFFE, 1996). Baseando-se nessas análises podemos intuir sobre as propriedades macroscópicas, em especial de dureza e espalhabilidade de um produto, por exemplo, de uma margarina que seja formulada à partir de uma determinada gordura (CHRYSAN, 2005).

Além das análises térmicas e reológicas a análise da microestrutura de óleos e gorduras é muito utilizada, pois a compreensão da rede formada pelos cristais e intuir sobre o comportamento macroscópico dos lipídios. A técnica explora o alto contraste entre o material sólido que refrata a luz e a fase líquida que não a refrata, por isso permite a observação de materiais cristalinos estruturados mesmo em baixas concentrações (CAMPOS, 2005).

A percepção sensorial de textura de um alimento está intimamente relacionada com o comportamento reológico intrumental da gordura, esse comportamento por sua vez, está relacionado com a presença de uma estrutura cristalina que se forma com a presença de ácidos graxos saturados ou *trans* que são reconhecidamente prejudiciais à saúde (SHI; LIANG; HARTEL, 2005).

Aspectos Nutricionais das Gorduras

A formação de uma rede cristalina é o que torna as gorduras sólidas ou semi-sólidas, porém esta rede apenas será desenvolvida devido à presença de ácidos graxos saturados ou *trans* na molécula do TAG, que são capazes de formar redes devido à sua conformação espacial diferenciada e alto ponto de fusão (RYE; LITWINENKO; MARANGONI, 2005).

A demanda pela redução do uso de ácidos graxos *trans*, em impulsionada em parte por ações de agências reguladoras como o FDA que visa a eliminação desses ácidos graxos nos produtos alimentícios (FDA, 2015) e no Brasil (ANVISA, 2012), causou um incremento no uso de fontes de ácidos graxos saturados misturados com óleos líquidos ou como matérias-primas para interesterificação para a manutenção das propriedades físicas de produtos de base gordurosa.

Os processos de interesterificação consistem no rearranjo da distribuição dos ácidos graxos no TAG, no processo, que ocorre sem incremento nos teores de ácidos graxos saturados, fazendo apenas a redistribuição dos ácidos graxos nas moléculas de glicerol (SREENIVASAN, 1978). Existem basicamente duas maneiras de realizar tal processo, a via química utilizando catalisadores e a via enzimática com o uso de enzimas específicas ou randômicas. No processo por via química, os catalisadores mais utilizados são ligas de sódio ou potásio ou alcoolato de sódio. A troca pode ocorrer entre dois ou mais TAGs e também ésteres metílicos ou etílicos (POKORNÝ; SCHMIDT, 2011). A migração randômica de ácidos graxos durante a reação leva à formação de produtos não específicos (YANG; FRUEKILDE; XU, 2005).

Por sua vez, o processo de interesterificação enzimática utiliza lipases microbianas como catalisadores da reação, permitindo uma redução no consumo de energia pelas condições de processo mais amenas e produção contínua pelo uso de enzimas imobilizadas. Existe também a possibilidade de utilizar lipases específicas sn-1,3, modificando o processo de obtenção randômico dos TAGs formados após a reação, mantendo os ácidos graxos da posição central sn-2 inalterados. De modo geral são usadas lipases específicas para produtos de alto valor agregado como, por exemplo, substitutos e equivalentes de manteiga de cacau (SENANAYAKE; SHAHIDI, 2005b).

O processamento de gorduras por processos não específicos de interesterificação tanto químico quanto enzimático, têm como principal questionamento a formação de isômeros com ácidos graxos saturados na posição sn-2 do glicerol, um resultado normal do processo randômico, porém esses isômetos têm sido objeto de diversos estudos sobre o possível efeito nutricional dos ácidos graxos saturados na posição central (CHRISTOPHE, 2005; KARUPAIAH; SUNDRAM, 2007). O aumento da quantidade de ácido palmítico (C16:0) na posição central da molécula do TAG (sn-2) permite uma maior absorção desses lipídios pelo organismo, levando a um aumento do potencial aterogênico em animais de laboratório (HUNTER, 2001).

Organogéis

Os organogéis são materiais viscoelásticos compostos por estruturantes e uma fase líquida apolar. São sistemas semi-sólidos, onde uma fase oleosa é imobilizada por uma rede tridimensional auto-sustentada do agente estruturante (DASSANAYAKE et al., 2009).

Os organogéis possuem diferentes estruturas formadas pelos mais diversos compostos orgânicos, sendo duas mais importantes: 1) dispersão de sólidos em uma fase líquida (pequenas partículas inertes, sólidos cristalizados, gotículas) ou 2) mecanismos específicos (comumente observado nos agentes estruturantes de baixo peso molecular). Ambos formam redes tridimensionais que são capazes de imobilizar a fase líquida. O tamanho e forma dessa estrutura estão diretamente relacionados com as características físicas do organogel obtido. A Figura 2 apresenta mecanismos observados para outros materiais que podem dar suporte à estruturação de organogéis (PERNETTI et al., 2007).

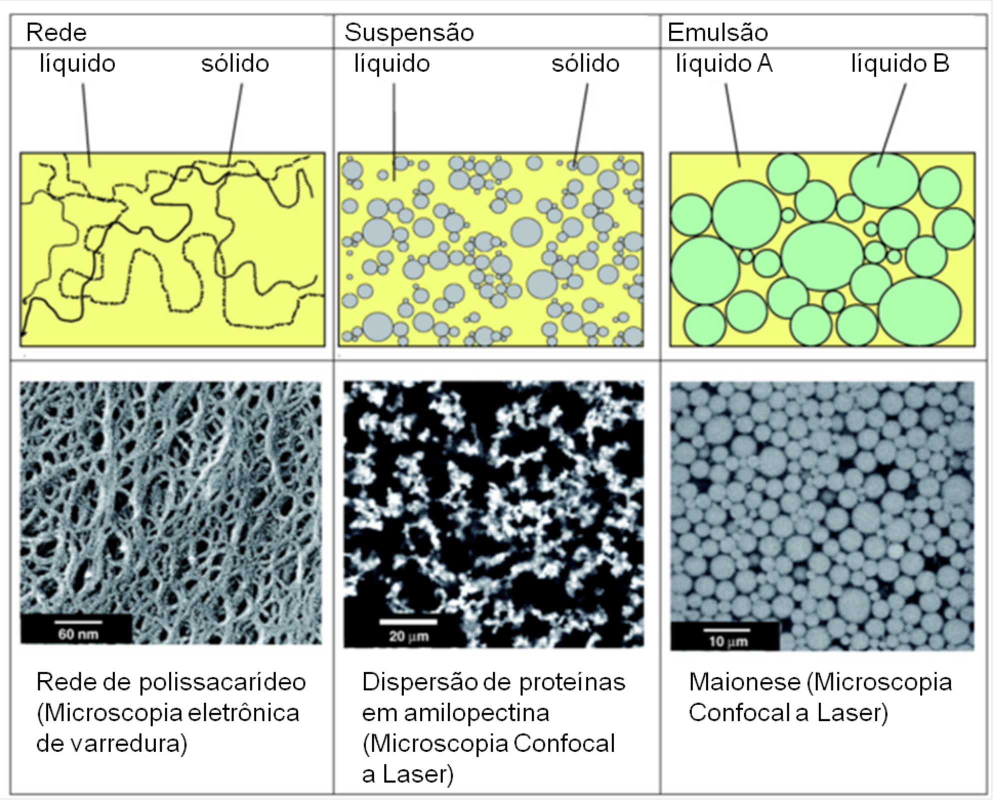

Figura 2: Mecanismos possíveis para a estruturação de óleos líquidos (PERNETTI et al., 2007).

Uma das principais características que tornam os organogéis interessantes é o seu potencial para melhorar as características físicas de um produto para uso industrial, sem incrementar seu teor de ácidos graxos saturados ou ácidos graxos *trans*, tornando possível desenvolver produtos com teores mais baixos de ácidos graxos saturados, mantendo suas características reológicas (ROGERS; WRIGHT; MARANGONI, 2009c).

Os organogéis podem ser formados por diversos tipos de agentes estruturantes e incluem, ácidos graxos hidroxilados, ácidos graxos, alcoóis graxos, misturas de ácidos e alcoóis graxos, misturas de fitoesteróis-orizanóis, monostearato de sorbitana, ceras e misturas de lecitina e triestearato de sorbitana (ROGERS, 2009). Via de regra, os principais compostos capazes de formar organogéis, possuem cadeias carbônicas bastante longas, como os ácidos graxos de cadeia longa, alcoóis graxos, ésteres de cera e alcanos (DANIEL; RAJASEKHARAN, 2003), considerados de baixo peso molecular menor do que 3000Da (ABDALLAH; WEISS, 2000).

Na Figura 3, temos diversos agentes estruturantes. Os ácidos graxos hidroxilados, ácidos graxos, alcoóis graxos, misturas de ácidos e alcoóis graxos, misturas de fitoesteróis-orizanóis, monostearato de sorbitana, ceras e misturas de lecitina e triestearato de sorbitana apresentam grande potencial para uso alimentício (HUGHES et al., 2009).

A produção de de organogéis, apesar de bastante simples, exige alguns cuidados, sendo necessário apenas a adição dos componentes do sistema (solvente e estruturante) em estado líquido, seguido de cristalização, Patel e Dewettinck (2016), revisaram diversos artigos com o mesmo procedimento para produção com diversos estruturantes. A questão é que apesar da aparente simplicidade as condições de produção, em especial a velocidade de cristalização e a presença ou não de cisalhamento podem causar muita variação nos organogéis obtidos.

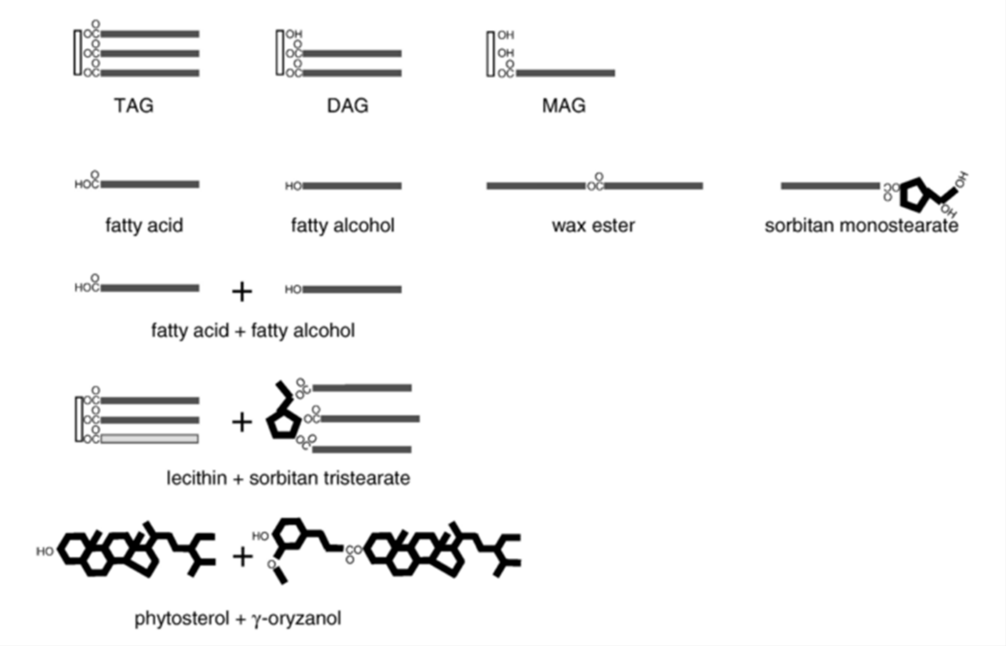

Figura 3: Materiais com capacidade para atuar como estruturantes (PERNETTI et al., 2007).

A seleção de um agente estruturante para desenvolvimento de produtos alimentícios deve ser criteriosa e levar em consideração as possíveis aplicações para esse material estruturado, além da inocuidade do estruturante e a sua eficácia em baixas concentrações. Na literatura é possível encontrar organogéis estruturados com ácido 12-hidroxiesterárico

(ROGERS, 2009), esteróis vegetais (BOT; AGTEROF, 2006), lecitinas (SCARTAZZINI; LUISI, 1988), mono e diacilgliceróis, misturas de lecitina com ésteres de sorbitana (MURDAN; GREGORIADIS; FLORENCE, 1999), ácidos e alcoóis graxos (SCHAINK et al., 2007) e ceras e ésteres de cera (DASSANAYAKE et al., 2009; ROCHA et al., 2013; TORO-VAZQUEZ et al., 2007; YıLMAZ; ÖğÜTCÜ, 2014b; HWANG et al., 2011). O uso de ceras para produzir organogéis também já se mostrou viável tecnicamente. Existem vários estudos avaliando a estabilidade e condições ideais para a formação desses sistemas. As ceras mais comumente utilizadas para esse fim são as de candelila (TORO-VAZQUEZ et al., 2007), cera de farelo de arroz e cera de carnaúba (DASSANAYAKE et al., 2009), cera de girassol (HWANG et al., 2011) e cera de cana-de-açúcar (ROCHA et al., 2013). Existem também trabalhos utilizando combinações de agentes estruturantes, como cera de candelila adicionada de tripalmitina (TORO-VAZQUEZ et al., 2009) e também componentes menos usuais como, por exemplo, o colesterol (PERNETTI et al., 2007).

Considerando o uso dos organogéis para fins alimentícios, o uso de ingredientes previamente aprovados pelas agências reguladoras e que apresentem capacidade como estruturante, é o caminho mais fácil. O uso de ceras vegetais como agentes estruturantes, por exemplo, traz o benefício de tais produtos já serem aprovados pelo FDA (2015) por exemplo, além de possuírem características tecnológicas favoráveis e por serem produtos de fácil obtenção e baixo custo quando comparados com outros agentes estruturantes.

Estruturação de organogéis

A estrutura formada por organogéis tem sido alvo de estudos nos últimos anos, onde a utilização da microscopia óptica de luz polarizada permite a observação de cristais do tipo agulha para a maioria dos estruturante estudados (PIEVE et al., 2010; ROCHA et al., 2013; BLAKE; CO; MARANGONI, 2014), tal estrutura é compatível com a formação de uma rede tridimensional (ZHANG; WEISS, 2015).

A observação das micrografias com mais detalhamento deixa claro esse perfil. A Figura 4 mostra uma micrografia usando luz parcialmente polarizada onde é possível observar como o estruturante modifica o tamanho dos cristais e a sua organização, porém a estrutura se mantem de alguma forma bastante similar com a presença dos cristais na forma de agulha e organizados como uma rede (BLAKE; CO; MARANGONI, 2014).

As mesmas estruturas foram observadas usando microscopia de luz polarizada, apresentado na Figura 5 que revela a presença da rede e com o contraste do campo escuro, observa-se também a presença de material não cristalizado da fase contínua líquida em preto (CAMPOS, 2005).

A formação das redes autossustentadas; *Self Assembled Fibrilar Networks* ou SAFiNs pela sua sigla em inglês foi estudada e modelada por Mallia e Weiss (2015), de

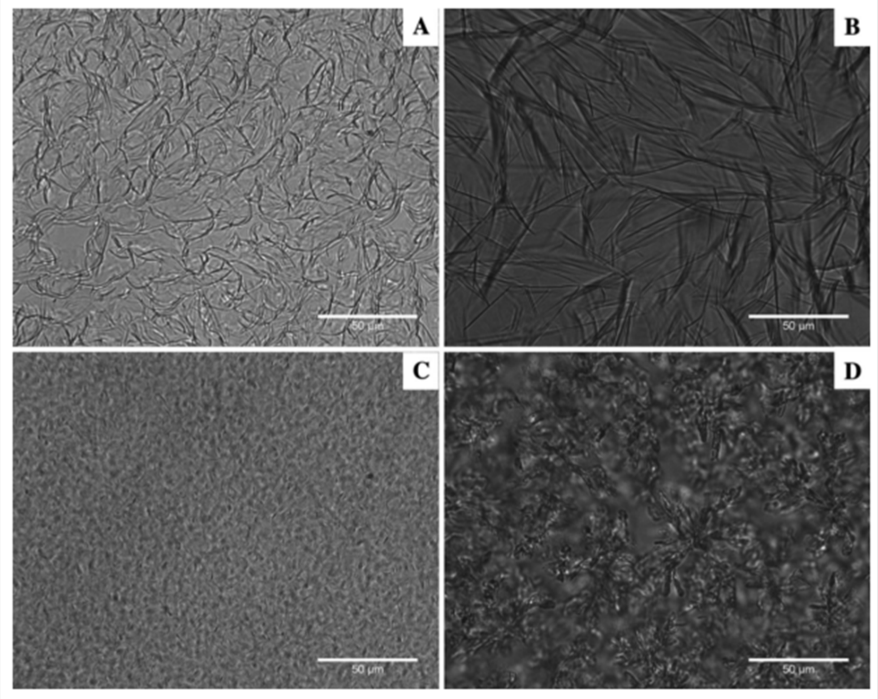

Figura 4: Micrografias de campo brilhante para organogéis de óleo de canola com ceras de farelo de arroz (a), girassol (b), candelila (c) e carnauba (d) a 10% m/m (BLAKE; CO; MARANGONI, 2014).

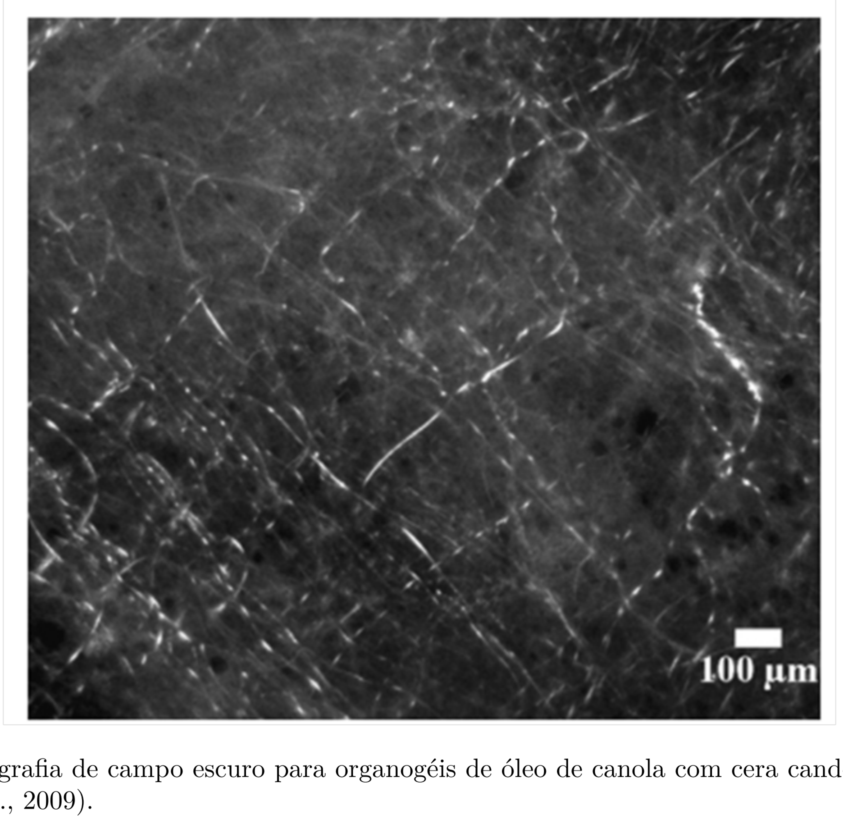

Figura 5: Micrografia de campo escuro para organogéis de óleo de canola com cera candelila a 2% m/m (HUGHES et al., 2009).

acordo com o modelo descrito e apresentado na Figura 6, existe a necessidade de aproximação entre os componentes que devido à presença de carga se juntam formando a rede, o mecanismo pode ser usado para explicar a ruptura da estrutura, levando-se em consideração que ela pode ocorrer tanto pela ação de trabalho mecânico, quanto por aumento da energia térmica no sistema.

O mecanismo de redes autossustentadas é atualmente a estrutura de organização de organogéis mais aceita, apesar de existirem outros modelos sugeridos como a formação de fibras pela presença de nanotubos (BOT et al., 2009). O modelo de formação de estrutura usando nanotubos sugere que a estrutura dos estruturantes é alinhada pelas caudas polares sofrendo uma modificação espacial formando uma fita que por sua vez dá origem à nanotubos por espiralamento, essas fitas espiraladas por suas vez formam as estruturas denominadas de *SAFiNs* (MALLIA; WEISS, 2015).

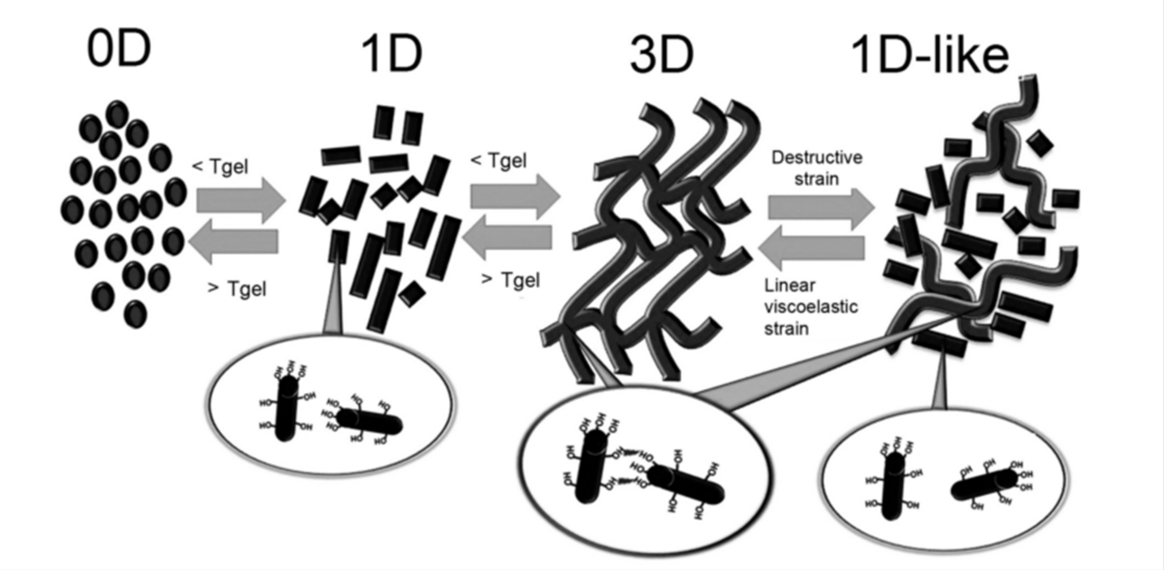

Figura 6: Mecanismo proposto para a formação de redes autossustentadas (MALLIA; WEISS, 2015).

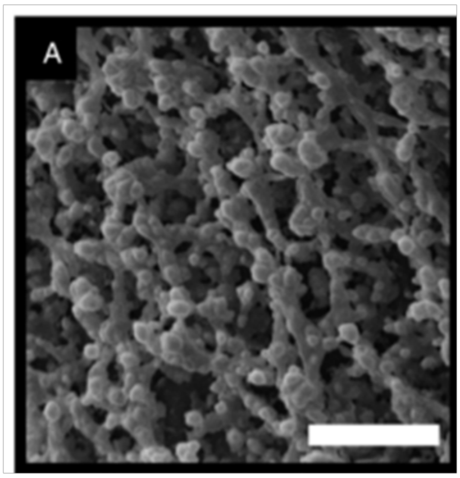

Figura 7: Estrutura observada para organogéis de ácido 12-hidroxiesteárico desengordurados (ROGERS; WRIGHT; MARANGONI, 2009b).

Rogers, Wright e Marangoni (2009a) sugerem uma abordagem mais tradicional com o alinhamento e crescimento do cristais em uma única dimensão, similar ao modelo sugerido para cristalização dos TAG e ácidos graxos (SATO; UENO, 2005) porém com diferentes tamanhos de monocamadas devido aos diferentes comprimentos de cadeias de cada molécula. Apesar das diferenças conceituais, ambos os modelos coincidem na formação de uma rede tridimensional. A presença de cristais no organogel de ácido 12-hidroxiesteárico (ROGERS; WRIGHT; MARANGONI, 2009b), onde observam-se as estruturas fibrilares é visualizada na Figura 7.

A formação de cristais do tipo agulha foi discutida por Blake e Marangoni (2015a), onde os autores obtiveram imagens da rede cristalina usando microscopia eletrônica de varredura (Cryo-SEM), como apresentada na Figura 8. O processo permitiu observar que os cristais da rede tridimensional são na verdade lamelas, que por sua vez quando observadas em duas dimensões pela microscopia óptica são observados como agulhas.

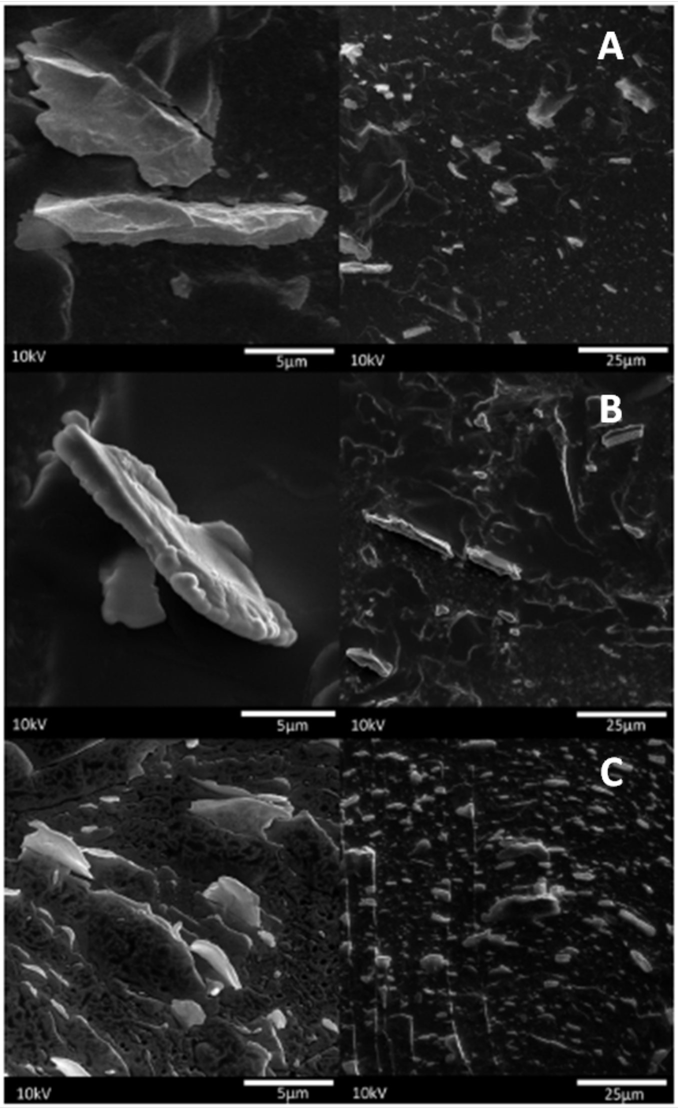

Figura 8: Micrografias (Cryo-SEM) de organogéis óleo de amendoim estruturado com ceras de farelo de arroz (A), girassol (B) e candelila (C) a 2% m/m (BLAKE; MARANGONI, 2015a).

Apesar do conhecimento existente sobre estruturação de organogéis existe ainda um campo para ser explorado, em especial se considerarmos as interações de agentes estruturantes e o efeito da composição da fase imobilizada.

Propriedades Reológicas

A dureza mensurada instrumentalmente tem relação direta com a textura avaliada pela percepção sensorial de um produto alimentício (ROUSSEAU; MARANGONI, 1999). Dessa forma a compreensão do comportamento reológico é fundamental para identificar possíveis aplicações para produtos alimentícios.

A determinação do comportamento reológico consiste em uma série de análises que podem ser feitas de diferentes maneiras, sendo as principais: a análise rotacional utilizando um sistema de cone e placas ou placas paralelas e ensaios com força normal do tipo compressão. As análises rotacionais permitem o controle adequado das taxas de cisalhamento e determinação da força de resistência à deformação considerando o torque mensurado pelo equipamento (STEFFE, 1996), essas análises também permitem mensurar a viscosidade do fluido ou seu comportamento durante o escoamento, que é de fundamental importância para determinar o comportamento do material durante as etapas de processamento industrial.

O comportamento de fluidos sob condições de trabalho mecânico são relevantes. A esse respeito, os fluidos podem ser dividos entre newtonianos e não-newtonianos. Fluidos newtonianos são materias que se comportam puramente como fluidos, tendo a sua viscosidade dependente apenas da temperatura, uma análise do comportamento permite observar uma relação linear entre a tensão de cisalhamento (σ) e a taxa de cisalhamento (γ) que passa pela origem. Fluidos não-newtonianos, por sua vez, são todos os outros que não se comportam dessa maneira, eles sofrem modificação do comportamento de escoamento com a modificação da taxa de cisalhamento, alguns materiais apresentam um aumento da viscosidade com o aumento da taxa de cisalhamento (são chamados de dilatantes) e outros apresentam uma redução, sendo identificados como pseudopláticos, o comportamento reológico permite observar quando os materiais se comportam como sólido ou líquido, ou seja o quando escoam ou resistem ao escoamento (STEFFE, 1996).

Entre os materiais pseudoplásticos, um grupo especial são os fluidos tixotrópicos, materiais que apresentam redução de viscosidade com o aumento da taxa de cisalhamento, que não é recuperada imediatamente, sendo por isso importante observar, além do comportamento sob cisalhamento o comportamento ao longo do tempo. Os organogéis especificamente, são materiais tixotrópicos, conforme observado na literatura (TORO-VAZQUEZ et al., 2007; ROCHA et al., 2013; PATEL et al., 2015; MALLIA; WEISS, 2015). Ainda no caso dos organogéis a presença de uma resistência inicial ao escoamento denominada *stress overshoot*, foi mensurada por Rocha et al. (2013) para organogéis de cera de candelila e de cana-de-açúcar.

Além do escoamento o comportamento dos organogéis ao longo do tempo usando varredura de frequências é relevante, uma vez que são tixotrópicos, e mostra que o material se comporta como esperado para um gel, justificando assim o seu nome, com valores de G' maiores que os do G", porém sem variação ao longo do tempo, ou seja com a manutenção dos valores para o angulo de fase (δ) praticamente constantes, conforme mostrado na Figura 9 (STEFFE, 1996).

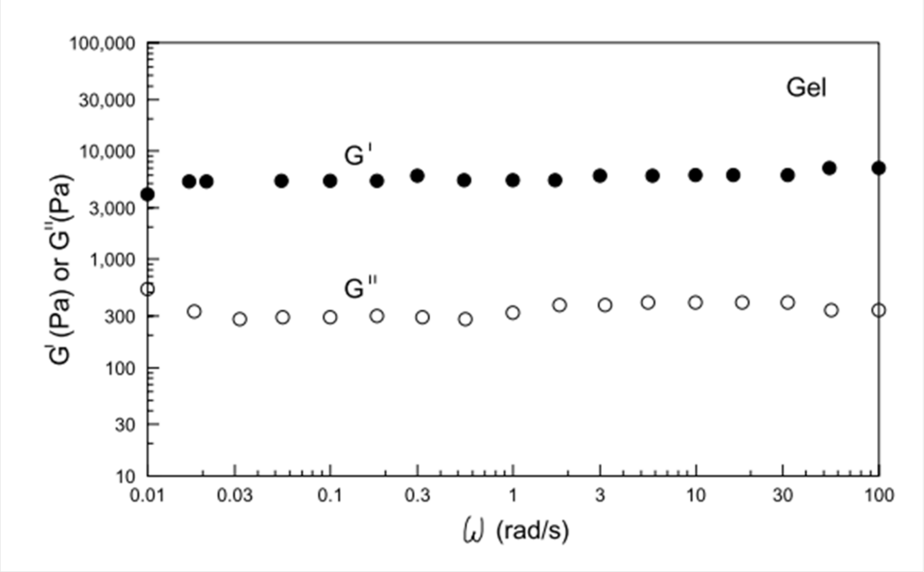

Figura 9: Varredura de frequências para um gel de ágar 1% (STEFFE, 1996).

O comportamento dos orgagéis na varredura de frequência com o comportamento típico de gel, foi observado com o uso de deformação constante para diferentes estruturantes, tais como ácido 12-hidroxiesteárico (MALLIA; BLAIR; WEISS, 2016), Rocha et al. (2013) verificaram o perfil para cera de cana-de-açúcar e para candelilla; Patel et al. (2015) avaliaram o comportamento para diversas ceras como girassol, carnauba, candelila, abelha e ceras de frutas e Doan et al. (2015) avaliaram o mesmo perfil para organogéis de cera de farelo de arroz. Esse comportamento de gel é algo esperado para o material, sendo portanto parte do comportamento desejado e uma maneira de determinar se o material é de fato um organogel ou apenas uma mistura estabilizada.

A relação entre a microestrutura e as propriedades macroscópicas dos materiais foram estudadas por Narine e Marangoni (2002), porém a relação entre as propriedades reológicas não foi totalmente relacionada com respeito a composição do lipídio que forma a rede, no caso dos autores as observações foram feitas para TAG. Para poder compreender completamente o fenômeno e prever as propriedades desses materiais plásticos é necessário que se caracterize e defina diferentes níveis da estrutura presentes no material e sua relação com as propriedades macroscópicas (NARINE; MARANGONI, 1999).

Assim como para gorduras estruturadas com TAGs, as condições de cristalização, tais como super resfriamento, taxa de cisalhamento e super saturação, causam modificações na estrutura cristalina e por sua vez nas propriedades macroscópicas do material obtido, em especial dureza e espalhabilidade (WRIGHT et al., 2001).

Análise de Organogéis

A avaliação de amostras organogéis, assim como outros materiais cristalizados, necessita que os materiais sejam processados consistentemente da mesma maneira, por exemplo, para observar as concentrações mínimas para a formação de organogéis, as condições de cristalização são essenciai, além da estabilidade por períodos mais longos, o que permite, por exemplo, descartar amostras e materiais que não formar organogéis estáveis sob determinadas condições (WRIGHT; MARANGONI, 2006).

A determinação do comportamento térmico é crucial para a compreensão de como materiais termorreversíveis se comportam, tais como os organogéis, nesse caso utiliza-se calorimetria diferencial de varredura (DSC), onde os eventos térmicos podem ser mensurados como picos com a determinação das temperaturas de transição e as energias necessárias (CAMPOS, 2005). Essa é uma das principais avaliações utilizadas para para óleos e gorduras, sendo por isso bastante aplicável em organogéis.

A existência de termorreversibilidade é uma das características dos organogéis (WRIGHT; MARANGONI, 2006), assim como em gorduras, logo essa propriedade é muito desejada para o uso de um material como eventual substituto de gorduras (SENANAYAKE; SHAHIDI, 2005b). A propriedade de termorreversibilidade é inerente ao processo de obtenção de organogéis, onde temos uma mistura de dois compostos no estado líquido, então espera-se que uma vez que o material retorne ao seu estado líquido, o comportamento de formação de gel se mantenha, essa propriedade foi mensurada para organogéis de cera de candelilla, arroz e carnaúba por Dassanayake et al. (2009), assim como para organogéis de ácido 12-hidroxiesteárico (ROGERS; WRIGHT; MARANGONI, 2009b).

Conforme citado no tópico Propriedades Reológicas, os organogéis possuem comportamento viscoelástico, assim como gorduras plásticas; ou seja são materiais que apresentam resistência, mas espalham quando sob ação de trabalho mecânico, uma característica típica de materiais semi-sólidos (SHAHIDI, 2009).

A espalhabilidade de materiais gordurosos é mensurada com base no *yield value* que pode ser considerado um parâmetro reológico de força limite para escoamento do material, usualmente determinado para margarinas e *spreads*, o parâmetro serve como referência para avaliar se um material é mais ou menos espalhável e consiste determinar a força máxima necessária para que um material comece a escoar (WRIGHT et al., 2001).

A capacidade de um determinado agente estruturante formar um organogel e o comportamento reológico e térmico resultante, vai levar em consideração o comportamento térmico do estruturante, da fase imobilizada e as interações física e química entre as duas fases (ABDALLAH; LU; WEISS, 1999).

A existência de uma estrutura microcristalina na formação dos organogéis pode ser constatada utilizando-se microscopia óptica de luz polarizada (DASSANAYAKE et al., 2009; ABDALLAH; SIRCHIO; WEISS, 2000), mas outras técnicas podem ser utilizadas, como por exemplo, a microscopia eletrônica de varredura (MIYAZAKI; YOSHIDA; MARANGONI, 2011; ROGERS et al., 2007; ROCHA, 2012).

A observação da microestrutura com uso de técnicas alternativas permite uma maior compreensão da existência da estrutura de plaquetas verificada por Blake e Marangoni (2015a) ou a presença de células vazias nos organogéis como observado por Rocha (2012) para organogéis de óleo de soja e cera de cana-de-açúcar a 4% (m/m) e apresentado na Figura 10. Como inconveniente das técnicas alternativas à luz polarizada tem-se a necessidade de trabalhar com organogéis devidamente cristalizados e que precisam ser "desengordurados", ou seja a fase contínua precisa ser retirada do material (ROGERS et al., 2007), de modo a permitir a adequada vizualização da microestrutura. Tal procedimento nem sempre é simples e pode ocasionar modificações na estrutura observada e eventualmente fenômenos de fusão e recristalização. É interessante notar que as estruturas observadas por Rogers, Wright e Marangoni (2009b) e Rocha (2012), apresentadas nas Figuras 7 e 10, respectivamente, são semelhantes apesar da diferença de estruturante utilizados.

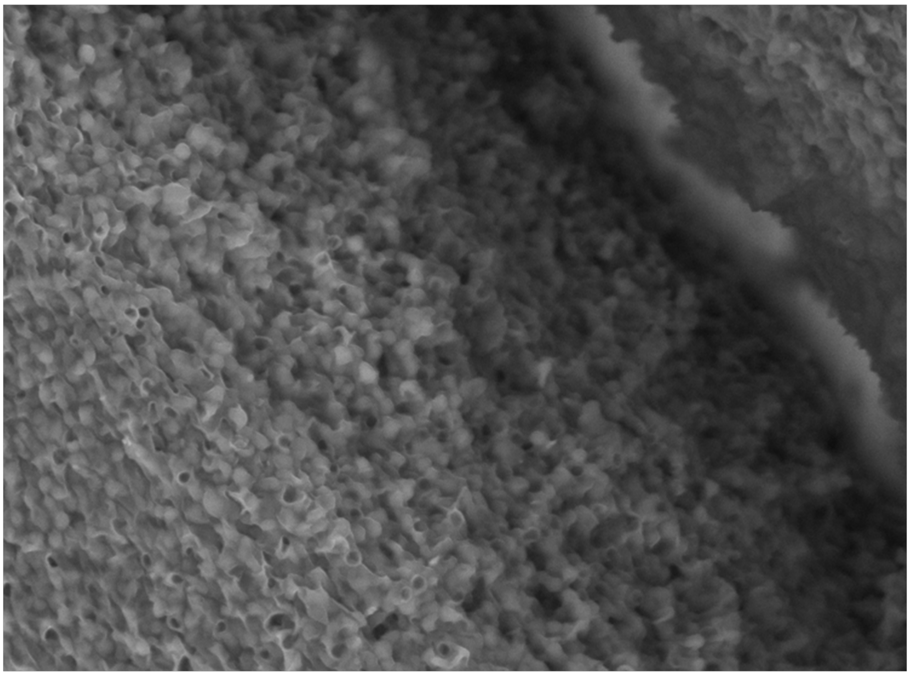

Figura 10: Organogel de óleo de soja estruturado com cera de cana-de-açúcar a 4% (m/m) (ROCHA, 2012)

.

Apesar de muito usual para gorduras vegetais de uso industrial, a análise do perfil de sólidos não é tão comum para organogéis, porém essa análise pode trazer informações relevantes, em especial se considerarmos a presença de teores de sólidos que podem ser percebidos sensorialmente. Conforme Guinard e Mazzucchelli (1996), a relação entre a presença de sólidos e percepção sensorial de textura deve ser considerada, em especial quando temos um produto semi-sólido.

As determinações de perfil de sólidos para organogéis são, de modo geral, apenas uma verificação. Quando avalia-se os valores mensurados por Mert e Demirkesen (2016), é possível observar que o método praticamente mede os valores adicionados do estruturante na faixa de temperatura estudada. A questão é que com o aumento dos teores de ácidos graxos saturados, existe a possibilidade de interação, esse efeito foi observado por Toro-Vazquez et al. (2009) onde a adição de um TAG totalmente saturado (tripalmitina), modificou o perfil de sólidos, com incremento dos valores 50% superior à quantidade adicionada de estruturante à -5°C, até o presente momento não há dados sobre redução do teor de sólidos com uso de diferentes estruturantes. Alterações desse tipo não foram observadas quando não há a adição de TAGs saturados.

Estruturantes para Organogéis

Os estruturantes ou organogelantes podem ser de diversas origens, os principais, como citado anteriormente, são compostos orgânicos de cadeia longa. Considerando-se apenas os materiais com potencial para aplicação em alimentos, têm-se alguns especialmente interessantes.

O uso de monoacilgliceróis (MAGs) para a produção de organogéis vem sendo estudada há algum tempo, os primeiros estudos feitos por Ojijo et al. (2004) se iniciaram com a busca de um substituto para gordura de margarinas com uso de cisalhamento. Os autores observaram que com o uso de um MAG com uma composição de 46% ácido palmítico e 53% ácido esteárico foi possível formar um organogel em azeite de oliva com o uso de cisalhamento até a faixa de 300s^{-1}, no estudo o cisalhamento foi utilizado apenas em temperaturas acima da temperatura de formação de gel, ou seja com o material ainda no estado líquido.

Pieve et al. (2010), utilizaram MAG composto de 60% ácido palmítico e 40% ácido esteárico para obtenção de organogéis, a fase contínua foi óleo de fígado de bacalhau. Os autores observaram a formação de um gel com características mecânicas relevantes, porém quando cisalhado a 20°C, o material perdeu estrutura; observou-se também que a formação do organogel melhorou a estabilidade oxidativa do óleo (Da Pieve et al., 2011).

A estabilidade oxidativa de óleo de peixe também foi estudada por Öğütcü, Arifoğlu e Yılmaz (2015), onde o óleo foi imobilizado usando MAG e cera de girassol, as concentrações dos estruturantes utilizadas foram relativamente altas 3, 7 e 10%. Os autores observaram que a cera produziu organogéis com maior dureza, além disso foi observado que os organogéis apresentaram comportamento reológico como o de cristais do tipo β', quanto à estabilidade oxidativa, os organogéis de cera de girassol foram melhores que os de MAG, porém os autores não apresentaram os dados do óleo puro.

Os MAGs também foram usados para obter produtos do tipo *spreads* e comparados com géis obtidos com cera de abelha nas concentrações de 3, 7 e 10%, usando como fase contínua óleo de avelãs (YıLMAZ; ÖğÜTCÜ, 2014b), com boa estabilidade durante um período de 90 dias, apesar da elevada quantidade dos estruturantes necessária para se obter os organogéis.

O efeito da formação de organogéis na migração de óleo em bombons recheados foi estudada por Si et al. (2016), onde a monoestearina foi utilizada em conjunto com um sistema triestearato de sorbitana:lecitina e óleo de soja como fase contínua. No estudo, o organogel conseguiu reduzir a migração de óleo para a camada externa no bombom de maneira significativa, um efeito esperado da imobilização da fase líquida.

É importante notar que apesar a estruturação formada pelo uso de MAGs em sistemas com água com a formação de emulsões do tipo *Pickering* como as estudadas por Batte et al. (2007) serem capazes de dar estrutura à fases lipídicas, estas não são consideradas organogéis, apesar de apresentarem bons resultados para estruturação com uso de 40% de água e 4% de monoestearina.

Outro estruturante que teve seu estudo iniciado nos anos 1990 é a lecitina, em especial para uso como veículo para transporte de princípios ativos de medicamentos transdérmicos (WILLIMANN et al., 1992), logo a abordagem não é nova, apesar de seu uso para alimentos ser bastante restrito ainda.

Lecitinas foram usadas junto com triestearato de sorbitana (STS) para desenvolver organogéis por Pernetti et al. (2007) nas concentrações de 6, 8 e 12% do total de estruturante, com as proporções de 100:0, 70:30, 60:40, 50:50, 40:60, 30:70 e 0:100 (m:m) considerando Lecitina:STS, com efeitos sinergísticos observados pelo aumento na textura, na faixa de 60:40 a 40:60 com o total de estruturante em 8% (m:m).

Outros materiais foram utilizados como por exemplo monoestearato de sorbitana (SMS) a 19% em óleo de amêndoas e também colesterol a 3,5% em parafina líquida (ALMEIDA; BAHIA, 2006). No estudo o óleo estruturado com SMS se manteve estável por 3 meses a 20°C, porém o mesmo material armazenado a 40°C apresentou separação de fases e escurecimento após 30 dias, enquanto a parafina líquida não exibiu modificações durante o período estudado pelos autores nas duas condições de temperatura. Apesar da menor estabilidade, os organogéis de SMS foram mais duros, mas não devemos desconsiderar a quantidade muito elevada de um estruturante, que possui limitações na quantidade permitida para aplicações alimentícias (FAO, 2000).

O uso de materiais combinados como estruturantes também tem sido estudado. A combinação de γ-orizanol com β-sitosterol nas concentrações de 6 a 8% foi estudada por Bot e Agterof (2006). Os autores usaram esses materiais para produzir organogéis, porém estes materiais estruturaram somente após um período de agitação, diferente do observado para outros estruturantes, o comportamento também foi diferente quanto as parâmetros G' e G", que foram menores do que os observados para organogéis obtidos apenas por resfriamento. Os organogéis obtidos mostraram-se translúcidos o que pode ser desejável para algumas aplicações.

Misturas de sitosterol com lecitina também foram utilizadas para a formação de géis por Han et al. (2013). A concentração utilizada no estudo, de 16% não é baixa, porém os autores conseguiram organogéis de boa estabilidade e com valores interessantes de G' e G". Também foi observado o comportamento de gel com a não variação dos valores de G' e G"com a variação da frequência.

Um material que tem recebido uma grande atenção é o ácido 12-hidroxiesteárico (HSA), apesar de o material ser aprovado apenas para uso como lubrificante na indústria de alimentos com migração eventual limitada em 5mg/kg de alimento (FDA, 2016; EFSA, 2010). Este material começou a ser estudado por Terech et al. (2000), porém os solventes utilizados para o estudo eram solventes orgânicos (tolueno, dodecano, nitrobenzeno e hexafluorobenzeno), deixando claro o objetivo da aplicação não alimentícia. O comportamento reológico dos géis observado pelos autores, permitiu definir que o material comporta-se como gel e que é capaz de atuar como estruturante, mesmo em baixas concentrações.

Os primeiros estudos com uso do HSA em óleos vegetais foram iniciados por Rogers, Wright e Marangoni (2008), onde o HSA foi utilizado para imobilizar óleo de canola. O HSA foi capaz de formar géis a partir de 0,5% (m:m) nos quais a estabilidade térmica e G' aumentaram com o aumento da concentração do estruturante, chegando ao máximo de 5%. Os autores observaram que o material se manteve estável por um período de 1 mês sem alterações significativas, em especial de exsudação de óleo. No ano seguinte mais informações sobre a microestrutura do material foram publicadas (ROGERS; WRIGHT; MARANGONI, 2009b) incluindo-se a observação das microestruturas fibrilares conforme apresentadas na Figura 7.

Buscando estruturantes adequados para uso alimentício, Toro-Vazquez et al. (2007), iniciaram estudos utilizando cera de candelila em óleo de cártamo. Esta cera é composta de uma mistura de alcanos, ácidos graxos, álcoóis graxos e ésteres e apresentou um elevado potencial para a produção de organogéis, atuando em baixas concentrações a partir de 1%. Os organogéis obtidos com esta cera apresentaram termoreversibilidade e a modificação do comportmento reológico mensurado como dureza. Devido aos bons resultados obtidos com a cera a investigação do papel do hentriacontano (C31) que é o alcano presente em maior quantidade na cera de candelila, foi estudado. Morales-Rueda et al. (2009), usaram o dotriacontano (C32) como padrão para comparação com os organogéis obtidos com a cera de candelila. Foram determinados os parâmetros reológicos, porém na análise de G' pelo tempo a cera de candelila se mostrou mais resistente além disso a cera também apresentou uma rede mais organizada, com cristais menores e mais interação, quando comparado com o alcano puro, o que está relacionado com comportamento reológico de sólido (NARINE; MARANGONI, 2002).

Além da candelila, outras ceras foram avaliadas, como a cera de farelo arroz e carnauba (DASSANAYAKE et al., 2009), cera de girassol e abelha (DOAN et al., 2015) a cera de cana-de-açúcar foi avaliada por Rocha et al. (2013). Os autores citados observaram que as ceras formaram organogéis que apresentaram as características observadas para os organogéis de cera de candelila, tais como a termoreversibilidade, a formação em concentrações variando entre 1 e 8%, além do comportamento independente do tempo observado pela determinação reológica de varredura de frequência. Nesses casos foi observado também que dependendo do estruturante, os valores mensurados em especial de força máxima e os módulos (G' e G"), foram bastante modificados, apesar da manutenção de perfis semelhantes, as microestruturas também foram similares, porém com cristais de tamanhos distintos, sendo que a candelila apresentou cristais menores, maior organização e valores mais altos de G' e força máxima.

A interação entre o estruturante e a fase contínua foi estudada também por Toro-Vazquez et al. (2009), que desenvolveram organogéis de cera de candelila com adição de um TAG saturado (tripalmitina), de modo a modificar a fração triacilglicerólica no organogel. Com o aumento dos teores de ácidos graxos saturados houve melhora significativa na resistência mecânica do material, assim como aumento na organização da estrutura cristalina deixando evidente que a composição em TAG da fase contínua deve ser levada em consideração ao planejar o uso de organogéis como fontes alternativas para gorduras.

Ainda pensando na possibilidade de uso de organogéis em processos industriais a compreensão do comportamento sob condições de cisalhamento precisou ser aprofundada. Pieve et al. (2010) desenvolveram organogéis com MAG sob cisalhamento, porém observaram que sob cisalhamento constante e intenso o material perdeu estrutura, de maneira semelhante Alvarez-Mitre et al. (2012) avaliaram organogéis de cera de candelila sob condições de cisalhamento e concluiram que o cisalhamento não deve ser efetuado durante todo o processo de formação do organogel. Os autores observaram que caso o cisalhamento seja efetuado no resfriamento, mas em temperatura superior à formação de gel (mensurada como transição térmica em DSC), os géis apresentaram maior dureza e organização estrutural. Do mesmo modo Blake e Marangoni (2015b), desenvolveram organogéis de ceras de farelo de arroz, girassol e candelila utilizando cisalhamento, observaram que o cisalhamento aplicado sob resfriamento lento e em condições moderadas ($50s^-1$) melhorou a qualidade dos organogéis estudados.

Aplicações de Organogéis em Alimentos

O potencial para aplicação de organogéis em alimentos já foi provado, porém até o presente momento apenas aplicações em pequena escala foram feitas para produtos alimentícios.

O desenvolvimento de sorvete usando organogel como substituto de gordura de leite estudado por ZULIM BOTEGA et al. (2013), para o produto estudado foi utilizado um organogel composto de 90% óleo de girassol alto oleico e 10% (m:m) de cera de farelo de arroz. As características do sorvete, tais como textura e resistência ao derretimento dependem em grande parte da presença de gordura sólida. O produto foi comparado com um produto comercial padrão usando gordura de leite e com um modelo usando apenas óleo de girassol alto oléico. Determinações utilizando microscopia eletrônica de varredura criscópica (Cryo-SEM), DSC e microscopia eletrônica de transmissão (TEM) foram realizadas. Considerando as caracteríticas tecnológicas, o produto obtido com o organogel apresentou um *overrun* mais alto quando comparado com o sorvete de óleo puro tornando-o visualmente mais agradável. De modo geral, nas condições estudadas o organogel foi capaz de induzir a formação de uma rede de glóbulos de gordura, o que é desejado para um sorvete, apesar de não apresentar resultados satisfatórios para todos os parâmetros esperados para um sorvete, em especial o derretimento que foi muito mais rápido quando comparado com o sorvete padrão.

Hwang et al. (2013) desenvolveram uma margarina usando óleo de soja e ceras de candelila, girassol e farelo de arroz como agentes estruturantes, levando ao desenvolvimento de um produto com potencial para aplicação como gordura base para margarinas. Nas condições do estudo, os autores observaram separação de fases para o produto obtido com cera de candelila. O organogel de cera de farelo de arroz, que apresentava boas caracteríticas como gel, não mostrou a consistência esperada para margarina, apesar de não ocorrer separação de fases, enquanto o organogel com a cera de girassol apresentou os melhores parâmetros para consistência e estabilidade. A consistência das margarinas com teores de 2-6% de cera de girassol foi similar a de uma margarina com 18-30% de gordura hidrogenada, onde os valores mínimos para um produto comercial do tipo *spread* foram obtidos com cerca de 2% de cera de girassol. Apesar do sucesso parcial no desenvolvimento da margarina, deve-se considerar que o processo utiliza de um cisalhamento muito intenso, sendo por isso necessário, algumas adequações ao processo produtivo com o objetivo de reduzir a ação do cisalhamento sobre o organogel, vale lembrar que o cisalhamento intenso em condições de temperatura inferiores à de formação de organogel, podem levar à ruptura da estrutura fibrilar (ALVAREZ-MITRE et al., 2012).

Chaves (2013) utilizou um planejamento experimental para desenvolver uma margarina usando organogéis de cera de candelila com óleo de soja e óleo de girassol alto oleico. Um total de 11 formulações foram feitas utilizando um processo modificado com menor cisalhamento durante a etapa de cristalização para evitar a perda de estabilidade, relatada em literatura, para margarinas usando processos tradicionais por Hwang et al. (2013) e para organogéis puros (ALVAREZ-MITRE et al., 2012). Diferentes concentrações de gordura vegetal, monoacilglicerol como emulsificante e cera de candelila, foram utilizadas. A fase oleosa foi mantida com 80% em massa para todas as formulações. As 11 amostras foram comparadas com três amostras comerciais, a estabilidade da emulsão, assim como os parâmetros reológicos de dureza e espalhabilidade foram comparadas e um modelo matemático para cada um dos parâmetros foi desenvolvido, além do cálculo da redução dos teores de ácidos graxos saturados. O planejamento experimental permitiu encontrar as condições para desenvolver um produto com as características reológicas semelhantes à dos produtos comerciais, essa formulação foi testada para validação do modelo matemático utilizando óleo de soja e óleo de girassol alto oleico com resultados dentro do esperado e com uma redução de ácidos graxos saturados de 30%.

Patel et al. (2014) demonstraram o potencial de aplicação para produtos alimentícios de organogéis obtidos à partir de óleo de girassol e goma-laca (0 - 6% m:m). Os autores prepararam uma base gordurosa para produtos emulsionados do tipo *spread*, como substituto de gordura para pasta de chocolate e como gordura alternativa para bolos. Emulsões com até 60% de água foram preparadas sem a necessidade de uso de emulsificante, onde a estabilização ocorreu devido à inclusão de gotículas de água na interface da goma-laca cristalizada. A pasta de chocolate foi preparada fazendo a substituição total do agente estabilizante de gordura e parcial do óleo de palma (27%) pelo organogel, o produto e apresentou boas características, em sem migração e separação de óleo, quando armazenada por 4 semanas a 30°C. O uso de uma emulsão (20%) para produzir bolos se mostrou equivalente, tanto nos parâmetros sensoriais, quanto de textura quando comparadas com o bolo padrão feito com margarina.

Yılmaz e Öğütcü (2014a) desenvolveram um produto do tipo *spread* usando óleo de avelãs estruturado com cera de abelhas e MAG nas concentrações de 3, 7 e 10%. Os dois materiais apresentaram elevada capacidade para formar organogéis estáveis e sem exsudação de óleo. Comparando o material obtido com organogel com uma margarina comercial foi observado que o pico da fusão mensurado como 41,86°C, variou entre 45.22 a 50.77°C para o organogel de cera de abelha e entre 37.32 e 52.68°C para o material estruturado com MAG; os valores aumentaram com o aumento da concentração dos estruturantes. Os valores observados para a variação de entalpia (ΔH) de fusão foram inferiores para os organogéis, quando comparados com um produto comercial, o que é uma evidência de menor resistência térmica desses produtos. Não foram observadas diferenças entre o ΔH de fusão e cristalização. A consistência não mostrou mudanças para o produto estruturado com cera de abelha durante o período de 90 dias. Os produtos obtidos com organogéis de MAG mostraram-se mais macios dos que os elaborados com a gordura comercial. A estrutura observada usando luz polarizada para os organogéis de cera de abelha foi similar à observada para organogéis de outras ceras, com a presença de cristais do tipo agulha. Os organogéis de MAG apresentaram cristais do tipo esferulito. Análises de difração de raio-x mostraram que os organogéis de cera de abelha se comportaram de modo similar ao esperado para organogéis de ceras com cristais distâncias similares à β'. A análise sensorial (aceitação do produto) indicou uma intenção de compra superior a 50% (YıLMAZ; ÖğÜTCÜ; YÜCEER, 2015). De modo semelhante azeite de oliva foi estruturado com cera de carnauba ou MAG (ÖUTCU; YıLMAZ, 2014) e como observado para o óleo de avelãs, o produto teve boa aceitação e estabilidade, porém as concentrações dos estruturantes utilizadas foram iguais a 3 e 7% (m/m).

Organogéis de cera de candelila com óleo de canola nas concentrações de 3 e 6% foram avaliados por Mert e Demirkesen (2016) como alternativa para gordura de biscoitos. Os biscoitos foram formulados usando óleo puro, organogel puro e mistura de gordura com organogéis nas razões de 30:70 e 40:60 (m:m). Os biscoitos produzidos com a substituição total com organogéis foram mais próximos em textura aos obtidos com a gordura comercial, quando comparados com os de óleo puro, ainda assim os biscoitos feitos com os organogéis não foram equivalentes aos obtidos com gordura comercial. Foi observado também que a adição de gorduras tornou os materiais mais sensíveis ao cisalhamento. De maneira simelhante Jang et al. (2015) desenvolveram biscoitos usando organogéis de óleo de canola com cera de candelila nas concentrações de 3 e 6%. Os autores observaram uma menor resistência térmica e as características reológicas da massa de biscoito mostraram redução nos parâmetros de G' e G". Como esperado os teores de ácidos graxos saturados foram bastante modificados, reduzido de 52,8% para 8% quando usado o organogel. Apesar dos biscoitos produzidos com organogel serem mais macios, eles foram bem aceitos pelos consumidores.

Yılmaz, Öğütcü e Yüceer (2015) também produziram biscoitos usando organogéis de óleo de avelã estruturado com ceras de girassol ou cera de abelhas com concentração de 5%, sendo a gordura padrão um substituto de manteiga de cacau (CBS). A análise sensorial mostrou que os consumidores preferiram o produto obtido com organogéis. A comparação das propriedades de textura instrumental e pela escala hedônica sensorial, mostraram produtos com características similares às do biscoito obtido com CBS, porém a massa foi mais macia para os biscoitos obtidos com os dois organogéis. Os biscoitos foram armazenados por 30 dias e analizados novamente com modificações mínimas nas suas características.

Um produto cárneo (similar a um patê) foi produzido por Lupi et al. (2014) usando organogéis. Óleo vegetal (oliva e girassol) foi estruturado com uma mistura de MAG com policosanois (uma mistura de alcoóis graxos de cadeia longa), nas concentrações de 0,1 a 0,5% (m/m) no produto final (0,5 e 2,5% da fase oleosa). A formulação foi comparada com um produto comercial e usou como base um material identificado como *"spicy spreadable sausage"*. Tecnicamente a formulação consiste em uma suspensão de gordura e carne em óleo líquido e o objetivo principal dos autores foi estabilizar esse produto usando uma fase líquida imobilizada. A avaliação reológica dos produtos mostrou que o policosanol foi mais efetivo para estabilizar o sistema mesmo na concentração mais baixa, fornecendo um produto com características similares às do produto comercial, mesmo sendo processado com cisalhamento. Apesar da maior eficiência na estabilização observada para o policosanol, o MAG também foi capaz de estabilizar o produto, o que deixa claro que os dois estruturantes possuem alto potencial e a escolha deva ser feita de acordo com as características desejáveis para o produto final.

Um produto do tipo *cream cheese* foi produzido por Bemer et al. (2016), para tal processo foram utilizadas organogéis de etilcelulose e de cera de farelo de arroz na concentração de 10% (m/m) e óleo de soja comum e alto oleico como a fase contínua. O produto foi feito usando os componentes dos organogéis e não um organogel já cristalizado. Ao todo foram produzidas 4 amostras, duas com cera de farelo de arroz e duas com etilcelulose que foram comparadas com amostras comerciais de *cream cheese* do tipo com gordura e sem gordura. Os produtos obtidos com organgéis tiveram uma redução de 25% no teor de gordura quando comparado com o produto comercial. A dureza e espalhabilidade dos produtos obtidos com os organogéis foram equivalentes ao produto comercial, a adesividade foi equivalente à do produto comercial para o *cream cheese* obtido com organogel cera de farelo de arroz, mas foi reduzida para o produto feito com organogel de etilcelulose. A verificação da incorporação do organogel na estrutura do *cream cheese* foi feita usando microscopia e os autores observaram similaridades à estrutura do produto comercial, mostrando que os organogéis são uma alternativa viável para a substituição de gordura em produtos do tipo *cream cheese*.

Um glacê e uma pasta americana foram produzidos por Melo, Chaves e Barrera-Arellano (2013), utilizando a tecnologia de organogéis. Uma mistura de óleo de soja (90%) e gordura interesterificada (10%) foi estruturada com cera de candelila na concentração de 4% (m/m), MAG (4%) e lecitina (0,5%). A fase lipídica foi fundida e posteriormente cristalizada para obter um organogel. A pasta americana e o glacê foram elaborados adicionando, açúcar (77,8 e 72,27%), amido (3,82 e 3,55%) e água (5,10 e 11,84%), respectivamente, ao organogel. Os produtos obtidos, quando comparados com produtos comerciais, apresentaram menores teores de gordura de 21,9 para 12,2% para a pasta americana e de 19,2 para 11,8% para o glacê; menores teores de ácidos graxos saturados 6,6 e 3,3% e de 8,5 para 3,0% para a pasta americana e o glacê respectivamente. Os produtos tiverem quantidades de ácidos graxos *trans* baixas o suficiente para serem considerados *zero trans*, enquanto as amostras comerciais apresentaram valores de 7,9% para a pasta americana e 4,1% para o glacê. Os valores para dureza e espalhabilidade na pasta americana formulada foram maiores aumentando de 21,2 para 34,3 kg para a dureza e 30,4 para 39,7 kg.s para a espalhabilidade, os mesmos parâmetros foram reduzidos no glacê de 2,3 para 0,72 kg para dureza e 1,6 para 0,6 kg.s para a espalhabilidade. Os autores observaram que foi possível produzir as duas coberturas usando organogéis mantendo características interessantes para aplicação.

Referências

ABDALLAH, D. J.; LU, L.; WEISS, R. G. Thermoreversible Organogels from Alkane Gelators with One Heteroatom. *Chemistry of Materials*, v. 11, n. 10, p. 2907–2911, 1999. ISSN 08974756. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/cm9902826>.

ABDALLAH, D. J.; SIRCHIO, S. a.; WEISS, R. G. Hexatriacontane Organogels. The First Determination of the Conformation and Molecular Packing of a Low-Molecular-Mass Organogelator in Its Gelled State. *Langmuir*, v. 16, n. 20, p. 7558–7561, oct 2000. ISSN 0743-7463. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/la000730k>.

ABDALLAH, D. J.; WEISS, R. G. n -Alkanes Gel n -Alkanes (and Many Other Organic Liquids). *Langmuir*, v. 16, n. 2, p. 352–355, jan 2000. ISSN 0743-7463. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/la990795r>.

ABIOVE. *Complexo Soja - Estatística Mensal Ano Safra 2010/11*. 2016. Disponível em: <http://www.abiove.org.br/site/index.php?page=estatisticaarea=NC0yLTE=>.

ALMEIDA, I. F.; BAHIA, M. F. Evaluation of the physical stability of two oleogels. *International journal of pharmaceutics*, v. 327, n. 1-2, p. 73–7, dec 2006. ISSN 0378-5173. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/16996708>.

ALVAREZ-MITRE, F. et al. Shearing as a variable to engineer the rheology of candelilla wax organogels. *Food Research International*, Elsevier Ltd, v. 49, n. 1, p. 580–587, nov 2012. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii-/S0963996912003341>.

ANVISA. *INSTRUÇÃO NORMATIVA Nº 49, DE 22 DE DEZEMBRO DE 2006*. 2006.

ANVISA. *Resolução RDC 54, DE 12 DE NOVEMBRO DE 2012*. 2012. 5 p.

AOCS. *Official methods and recommended practices of the American Oil Chemists Society*. 5. ed. Champaign, IL: AOCS Press, 2004.

BATTE, H. et al. Effect of processing conditions on the structure of monostearin–oil–water gels. *Food Research International*, v. 40, n. 8, p. 982–988, oct 2007. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996907000804>.

BEMER, H. L. et al. Vegetable organogels incorporation in cream cheese products. *Food Research International*, Elsevier B.V., v. 85, p. 67–75, 2016. ISSN 09639969. Disponível em: <http://dx.doi.org/10.1016/j.foodres.2016.04.016>.

BLAKE, A. I.; CO, E. D.; MARANGONI, A. G. Structure and Physical Properties of Plant Wax Crystal Networks and Their Relationship to Oil Binding Capacity. *Journal of the American Oil Chemists' Society*, v. 91, n. 6, p. 885–903, feb 2014. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007/s11746-014-2435-0>.

BLAKE, A. I.; MARANGONI, A. G. Plant wax crystals display platelet-like morphology. *Food Structure*, Elsevier Ltd., v. 3, p. 30–34, 2015. ISSN 22133291. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S2213329115000027>.

BLAKE, A. I.; MARANGONI, A. G. The Effect of Shear on the Microstructure and Oil Binding Capacity of Wax Crystal Networks. *Food Biophysics*, 2015. ISSN 1557-1858. Disponível em: <http://link.springer.com/10.1007/s11483-015-9398-z>.

BOT, A.; AGTEROF, W. G. M. Structuring of Edible Oils by Mixtures of γ -Oryzanol with β -Sitosterol or Related Phytosterols. *Journal of the American Oil Chemists' Society*, v. 83, n. 6, p. 513–521, 2006.

BOT, A. et al. Non-TAG structuring of edible oils and emulsions. *Food Hydrocolloids*, Elsevier Ltd, v. 23, n. 4, p. 1184–1189, 2009. ISSN 0268005X. Disponível em: <http://dx.doi.org/10.1016/j.foodhyd.2008.06.009>.

CAMPOS, R. Experimental Methodology. In: *Fat Crystal Networks*. Marcel Dekker, 2005. v. 41, n. 3, cap. 9, p. 267–348. Disponível em: <http://www.scielo.br/scielo-.php?script=sci_arttext\pid=S1516-93322005000300015\lng=pt\nrm>.

CHAVES, K. F. *PROCESSO SIMPLIFICADO DE FABRICAÇÃO DE MARGARINAS COM REDUZIDOS TEORES DE ÁCIDOS GRAXOS SATURADOS UTILIZANDO A TECNOLOGIA DE ESTRUTURAÇÃO DE ÓLEOS*. 75 p. Tese (Doutorado) — Universidade Estadual de Campinas, 2013.

CHRISTOPHE, A. B. Structural Effects on Absorption, Metabolism and Health Effects of Lipids. In: SHAHIDI, F. (Ed.). *Bailey's Industrial Oil and Fat Products*. 6th. ed. [S.l.]: John Wiley & Sons Inc., 2005. cap. 16, p. 535–553.

CHRYSAN, M. M. Margarines and Spreads. In: SHAHIDI, F. (Ed.). *Bailey's Industrial Oil and Fat Products*. 6th. ed. [S.l.]: John Wiley & Sons Inc., 2005. cap. 2, p. 33–82.

Da Pieve, S. et al. Effect of monoglyceride organogel structure on cod liver oil stability. *Food Research International*, Elsevier Ltd, v. 44, n. 9, p. 2978–2983, nov 2011. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii-/S0963996911004510>.

DANIEL, J.; RAJASEKHARAN, R. Organogelation of plant oils and hydrocarbons by long-chain saturated FA, fatty alcohols, wax esters, and dicarboxylic acids. *Journal of the American Oil Chemists' Society*, v. 80, n. 5, p. 417–421, may 2003. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10.1007/s11746-003-0714-0>.

DASSANAYAKE, L. S. K.; KODALI, D. R.; UENO, S. Formation of oleogels based on edible lipid materials. *Current Opinion in Colloid & Interface Science*, Elsevier Ltd, v. 16, n. 5, p. 432–439, oct 2011. ISSN 13590294. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S1359029411000756>.

DASSANAYAKE, L. S. K. et al. Physical Properties of Rice Bran Wax in Bulk and Organogels. *Journal of the American Oil Chemists' Society*, v. 86, n. 12, p. 1163–1173, sep 2009. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10-.1007/s11746-009-1464-6>.

DEMAN, J.; DEMAN, L. Texture of fats. In: A.G.MARANGONI; S.S.NARINE (Ed.). *Physical Properties of Lipids*. New York: Marcel Dekker, 2002. cap. 7, p. 191–215. Disponível em: <http://scholar.google.com-/scholar?hl=en\btnG=Search\q=intitle:Texture+of+Fats\1 http://scholar.google-.com/scholar?hl=en\btnG=Search\q=intitle:Te>.

DOAN, C. D. et al. Evaluating the Oil-Gelling Properties of Natural Waxes in Rice Bran Oil: Rheological, Thermal, and Microstructural Study. *Journal of the American Oil Chemists' Society*, Springer Berlin Heidelberg, v. 92, n. 6, p. 801–811, 2015. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007/s11746-015-2645-0>.

EFSA. Scientific Opinion on the safety evaluation of the substance poly (12-hydroxystearic acid) stearate , CAS No . 58128-22-6 for use in food contact materials 1. *EFSA Journal*, v. 8, n. 58128, p. 1–12, 2010.

FAO. *SORBITAN MONOSTEARATE.* 2000. 2 p. Disponível em: <http://www.fao.org-/ag/agn/jecfa-additives/specs/Monograph1/Additive-434.pdf>.

FDA. *FDA Cuts Trans Fat in Processed Foods.* 2015. 1–2 p. Disponível em: <http://www.fda.gov/ForConsumers/ConsumerUpdates/ucm372915.htm>.

FDA. *FOOD FOR HUMAN CONSUMPTION (CONTINUED).* 2016. Disponível em: <http://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=178-.3570>.

FLICKINGER, B.; HUTH, P. Dietary fats and oils: technologies for improving cardiovascular health. *Current atherosclerosis reports*, Springer, v. 6, n. 6, p. 468–476, 2004. Disponível em: <http://www.springerlink.com/index/G122Q7X878346708.pdf>.

GARCIA, R. d. K. d. A. Formulação de gorduras para aplicação em margarinas zero trans com redes neurais a partir de gorduras interesterificadas. p. 118, 2010.

GUINARD, J.-x.; MAZZUCCHELLI, R. The sensory perception of texture and mouthfeel. *Trends in Food Science & Technology*, v. 7, n. July, p. 213–219, 1996.

GURR, M.; HARWOOD, J. *Lipid Biochemistry: An Introduction.* 4th. ed. [S.l.]: Chapman & Hall, 1996. 162–243 p.

HAN, L.-J. et al. Rheological Properties of Organogels Developed by Sitosterol and Lecithin. *Food Research International*, Elsevier B.V., apr 2013. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996913002147>.

HIMAWAN, C.; STAROV, V. M.; STAPLEY, a. G. F. Thermodynamic and kinetic aspects of fat crystallization. *Advances in colloid and interface science*, v. 122, n. 1-3, p. 3–33, sep 2006. ISSN 0001-8686. Disponível em: <http://www.ncbi.nlm.nih.gov-/pubmed/16904622>.

HUGHES, N. E. et al. Potential food applications of edible oil organogels. *Trends in Food Science & Technology*, Elsevier Ltd, v. 20, n. 10, p. 470–480, oct 2009. ISSN 09242244. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0924224409002040>.

HUNTER, J. E. Studies on effects of dietary fatty acids as related to their position on triglycerides. *Lipids*, v. 36, n. 7, p. 655–68, jul 2001. ISSN 0024-4201. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/11521963>.

HWANG, H.-S. et al. Organogel Formation of Soybean Oil with Waxes. *Journal of the American Oil Chemists' Society*, v. 89, n. 4, p. 639–647, oct 2011. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007/s11746-011-1953-2>.

HWANG, H.-S. et al. Margarine from Organogels of Plant Wax and Soybean Oil. *Journal of the American Oil Chemists' Society*, v. 90, n. 11, p. 1705–1712, aug 2013. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007/s11746-013-2315-z>.

HWANG, H. S. et al. Preparation of margarines from organogels of sunflower wax and vegetable oils. *Journal of Food Science*, v. 79, n. 10, p. C1926–C1932, 2014. ISSN 17503841.

IBGE. *Prognóstico da Produção Agrícola Nacional, dos principais produtos, para safra 2017*. 2017. Disponível em: <http://www.ibge.gov.br/home/estatistica/indicadores-/agropecuaria/lspa/lspa_201612_1>.

JANG, A. et al. Evaluation of canola oil oleogels with candelilla wax as an alternative to shortening in baked goods. *Food Chemistry*, Elsevier Ltd, v. 187, n. 4, p. 525–529, nov 2015. ISSN 03088146. Disponível em: <http://www.scopus.com/inward/record-.url?eid=2-s2.0-84929206822\partnerID=40\md5=66b50062fe5bdd3516776fb9005fbfed https://www.jstage.jst.go.jp/article/jos/64/7/64_ess15053/_article http://xlink.rsc-.org/?DOI=C5FO01006C http://dx.doi.org/10.1016/>.

KARUPAIAH, T.; SUNDRAM, K. Effects of stereospecific positioning of fatty acids in triacylglycerol structures in native and randomized fats: a review of their nutritional implications. *Nutrition & metabolism*, v. 4, p. 16, jan 2007. ISSN 1743-7075. Disponível em: <http://www.pubmedcentral.nih.gov/articlerender-.fcgi?artid=1947992\tool=pmcentrez\rendertype=ab>.

KODALI, D. R. *Stabilization of Long Chain Polyunsaturated Oils*. 2010. 7 p.

LUPI, F. R. et al. Rheological design of stabilized meat sauces for industrial uses. *European Journal of Lipid Science and Technology*, v. 116, n. 12, p. 1734–1744, 2014. ISSN 14389312.

MALLIA, V. A.; BLAIR, D. L.; WEISS, R. G. Oscillatory Rheology and Surface Water Wave Effects on Crude Oil and Corn Oil Gels with (<i>R</i>)-12-Hydroxystearic Acid as Gelator. *Industrial & Engineering Chemistry Research*, v. 55, n. 4, p. 954–960, 2016. ISSN 0888-5885. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/acs.iecr-.5b04267>.

MALLIA, V. A.; WEISS, R. G. Structural bases for mechano-responsive properties in molecular gels of (R)-12-hydroxy-N-(ω-hydroxyalkyl)octadecanamides. Rates of formation and responses to destructive strain. *Soft Matter*, Royal Society of Chemistry, in press, p. 5010–5022, 2015. ISSN 1744-683X. Disponível em: <http://xlink.rsc.org-/?DOI=C5SM00353A>.

MATUSZEK, T. Rheological Properties of Lipids. In: *Chemical and Functional Properties of Food Lipids*. CRC, 2003. ISBN 978-1-4200-3199-7. Disponível em: <http://dx.doi.org/10.1201/9781420031997>.

MELO, C. A.; CHAVES, K. F.; BARRERA-ARELLANO, D. FORMULAÇÃO DE PASTA AMERICANA E GLACÊ COM BAIXO TEOR DE ÁCIDOS GRAXOS SATURADOS A PARTIR DA TECNOLOGIA DE ORGANOGÉIS. In: *SBOG 20 ANOS: NOVOS HORIZONTES PARA CIÊNCIA E TECNOLOGIA DE ÓLEOS E GORDURAS*. Florianópolis: [s.n.], 2013.

MERT, B.; DEMIRKESEN, I. Evaluation of highly unsaturated oleogels as shortening replacer in a short dough product. *LWT - Food Science and Technology*, Elsevier Ltd, v. 68, p. 477–484, 2016. ISSN 00236438. Disponível em: <http://linkinghub.elsevier.com-/retrieve/pii/S0023643815304205>.

MIYAZAKI, Y.; YOSHIDA, K.; MARANGONI, A. G. Online Only Supplement - Lecture Abstracts of the 9th Euro Fed Lipid Congress, Rotterdam 18-21 September 2011. *European Journal of Lipid Science and Technology*, v. 113, n. S1, p. 1–46, nov 2011. ISSN 14387697. Disponível em: <http://doi.wiley.com/10.1002/ejlt.201100363>.

MORALES-RUEDA, J. a. et al. Rheological Properties of Candelilla Wax and Dotriacontane Organogels Measured with a True-Gap System. *Journal of the American Oil Chemists' Society*, v. 86, n. 8, p. 765–772, jun 2009. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10.1007/s11746-009-1414-3>.

MURDAN, S.; GREGORIADIS, G.; FLORENCE, A. T. Novel sorbitan monostearate organogels. *Journal of Pharmaceutical Sciences*, v. 88, n. 6, p. 608–614, jun 1999. ISSN 00223549. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/10350496>.

NARINE, S. S.; MARANGONI, A. G. Relating structure of fat crystal networks to mechanical properties : a review. *Food Research International*, v. 32, 1999.

NARINE, S. S.; MARANGONI, A. G. Structure and mechanical properties of fat crystal networks. *Advances in food and nutrition research*, Elsevier, v. 44, p. 33–145, 2002. Disponível em: <http://www.sciencedirect.com/science/article/pii-/S104345260244003X>.

OEC. *OEC - Soybeans.* 2014. Disponível em: <http://atlas.media.mit.edu/en/profile-/hs92/1201/>.

OJIJO, N. K. O. et al. Effects of monoglyceride content, cooling rate and shear on the rheological properties of olive oil/monoglyceride gel networks. *Journal of the Science of Food and Agriculture*, v. 84, n. 12, p. 1585–1593, 2004. ISSN 00225142.

ÖğÜTCÜ, M.; ARIFOğLU, N.; YıLMAZ, E. Preparation and Characterization of Virgin Olive Oil-Beeswax Oleogel Emulsion Products. *Journal of the American Oil Chemists' Society*, v. 92, n. 4, p. 459–471, apr 2015. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007/s11746-015-2615-6>.

ÖUTCU, M.; YıLMAZ, E. Oleogels of virgin olive oil with carnauba wax and monoglyceride as spreadable products. *Grasas y Aceites*, v. 65, n. 3, p. 1–11, 2014. ISSN 19884214. Disponível em: <http://grasasyaceites.revistas.csic.es/index.php-/grasasyaceites/article/viewArticle/1505>.

PATEL, A. R. et al. Rheological Profiling of Organogels Prepared at Critical Gelling Concentrations of Natural Waxes in a Triacylglycerol Solvent. *Journal of Agricultural and Food Chemistry*, v. 63, n. 19, p. 4862–4869, 2015. ISSN 0021-8561. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/acs.jafc.5b01548>.

PATEL, A. R. et al. Polysaccharide-based oleogels prepared with an emulsion-templated approach. *ChemPhysChem*, v. 15, n. 16, p. 3435–3439, 2014. ISSN 14397641.

PATEL, A. R.; DEWETTINCK, K. Edible oil structuring: an overview and recent updates. *Food Funct.*, Royal Society of Chemistry, v. 7, n. 1, p. 20–29, 2016. ISSN 2042-6496. Disponível em: <http://xlink.rsc.org/?DOI=C5FO01006C>.

PERNETTI, M. et al. Structuring edible oil with lecithin and sorbitan tri-stearate. *Food Hydrocolloids*, v. 21, n. 5-6, p. 855–861, jul 2007. ISSN 0268005X. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0268005X06002499>.

PIEVE, S. da et al. Shear Nanostructuring of monoglyceride organogels. *Food Biophysics*, v. 5, n. 3, p. 211–217, 2010. ISSN 15571858.

POKORNÝ, J.; SCHMIDT, S. Plant Lipids and Oils. In: KOLAKOWSKA, A. (Ed.). *Chemical, Biological, and Functional Aspects of Food Lipids*. 2nd. ed. Boca Raton, Florida: Taylor and Francis, LLC, 2011. cap. 14, p. 249 – 269. ISBN 978-1-4398-0238-0. Disponível em: <http://www.crcnetbase.com/isbn/9781439802380>.

ROCHA, J. C. B. *Obtenção e caracterização de organogéis de óleo de soja preparados com cera de cana-de-açúcar e suas frações*. 109 p. — Universidade Estadual de Campinas, 2012.

ROCHA, J. C. B. et al. Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil. *Food Research International*, Elsevier Ltd, v. 50, n. 1, p. 318–323, jan 2013. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996912004541>.

ROGERS, M. A. Novel structuring strategies for unsaturated fats – Meeting the zero-trans, zero-saturated fat challenge: A review. *Food Research International*, Elsevier Ltd, v. 42, n. 7, p. 747–753, aug 2009. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996909000623>.

ROGERS, M. A. et al. A Novel Cryo-SEM Technique for Imaging Vegetable Oil Based Organogels. *Journal of the American Oil Chemists' Society*, v. 84, n. 10, p. 899–906, sep 2007. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10.1007/s11746-007-1122-9>.

ROGERS, M. A.; WRIGHT, A.; MARANGONI, A. G. Crystalline stability of self-assembled fibrillar networks of 12-hydroxystearic acid in edible oils. *Food Research International*, Elsevier Ltd, v. 41, n. 10, p. 1026–1034, dec 2008. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996908001427>.

ROGERS, M. A.; WRIGHT, A. J.; MARANGONI, A. G. Corrigendum to "Nanostructuring fiber morphology and solvent inclusions in 12-hydroxystearic acid/canola oil organogels" [Current Opinion in Colloid & Interface Science 14(1) (2009) 33–42]. *Current Opinion in Colloid & Interface Science*, Elsevier Ltd, v. 14, n. 3, p. 223, jun 2009. ISSN 13590294. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S1359029409000132>.

ROGERS, M. A.; WRIGHT, A. J.; MARANGONI, A. G. Nanostructuring fiber morphology and solvent inclusions in 12-hydroxystearic acid / canola oil organogels. *Current Opinion in Colloid & Interface Science*, Elsevier Ltd, v. 14, n. 1, p. 33–42, feb 2009. ISSN 13590294. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S1359029408000149>.

ROGERS, M. A.; WRIGHT, A. J.; MARANGONI, A. G. Oil organogels: the fat of the future? *Soft Matter*, v. 5, n. 8, p. 1594, 2009. ISSN 1744-683X. Disponível em: <http://xlink.rsc.org/?DOI=b822008p>.

ROUSSEAU, D.; MARANGONI, A. G. The effects of interesterification on physical and sensory attributes of butterfat and butterfat-canola oil spreads. *Science And Technology*, v. 31, n. 5, 1999.

RYE, G. G.; LITWINENKO, J. W.; MARANGONI, A. G. Fat Crystal Networks. In: SHAHIDI, F. (Ed.). *Bailey's Industrial Oil and Fat Products*. [S.l.]: John Wiley & Sons Inc., 2005.

SATO, K.; UENO, S. Polymorphism in Fats and Oils. In: SHAHIDI, F. (Ed.). *Bailey's Industrial Oil and Fat Products*. 6th. ed. [S.l.]: John Wiley & Sons Inc., 2005. cap. 3, p. 77–120.

SCARTAZZINI, R.; LUISI, P. L. Organogels from lecithins. *The Journal of Physical Chemistry*, v. 92, n. 3, p. 829–833, feb 1988. ISSN 0022-3654. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/j100314a047>.

SCHAINK, H. et al. Crystal network for edible oil organogels: Possibilities and limitations of the fatty acid and fatty alcohol systems. *Food Research International*, v. 40, n. 9, p. 1185–1193, nov 2007. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996907001202>.

SENANAYAKE, S.; SHAHIDI, F. Modification of fats and oils via chemical and enzymatic methods. In: Fereidoon Shahidi (Ed.). *Bailey's Industrial Oil and Fat Products*. 6th. ed. Wiley Online Library, 2005. cap. 17, p. 555–584. Disponível em: <http://onlinelibrary.wiley.com/doi/10.1002/047167849X.bio062/full>.

SENANAYAKE, S. N.; SHAHIDI, F. Dietary fat substitutes. In: SHAHIDI, F. (Ed.). *Bailey's Industrial Oil and Fat Products*. 6th. ed. John Wiley & Sons Inc., 2005. v. 14, n. 10, cap. 15, p. 503–533. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0271531705802398>.

SHAHIDI, F. *Bailey ' S Industrial Oil and Fat*. Hoboken, NJ: [s.n.], 2009. 2005–2006 p. ISBN 9786468600.

SHI, Y.; LIANG, B.; HARTEL, R. W. Crystal Morphology, Microstructure and Textural Properties of Model Lipid Systems. *J Am Chem. Soc.*, v. 82, n. 6, p. 399–408, 2005. Disponível em: <http://link.springer.com.proxy.lib.ohio-state.edu/article/10.1007/s11746-005-1084-3>.

SI, H. et al. Physical Properties of Soybean Oleogels and Oil Migration Evaluation in Model Praline System. *JAOCS, Journal of the American Oil Chemists' Society*, Springer Berlin Heidelberg, v. 93, n. 8, p. 1075–1084, 2016. ISSN 0003021X. Disponível em: <"http://dx.doi.org/10.1007/s11746-016-2846-1>.

SREENIVASAN, B. Interesterification of fats in margarine: effect on blood lipids, blood enzymes, and hemostasis parameters. *Journal of the American Oil Chemists' Society*, v. 55, n. 11, p. 796–805, aug 1978. ISSN 0954-3007. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/19442321>.

STEFFE, J. F. *Rheological methods in food process engineering.* 2nd. ed. Freeman Press, 1996. 418 p. ISSN 02608774. ISBN 0-9632036-1-4. Disponível em: <http://linkinghub-.elsevier.com/retrieve/pii/0260877494900906>.

STENDER, S.; DYERBERG, J. Influence of trans fatty acids on health. *Annals of nutrition & metabolism*, v. 48, n. 2, p. 61–6, jan 2004. ISSN 0250-6807. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/14679314>.

SUNDRAM, K.; KARUPAIAH, T.; HAYES, K. C. Stearic acid-rich interesterified fat and trans-rich fat raise the LDL/HDL ratio and plasma glucose relative to palm olein in humans. *Nutrition & metabolism*, v. 4, p. 3, jan 2007. ISSN 1743-7075. Disponível em: <http://www.pubmedcentral.nih.gov/articlerender-.fcgi?artid=1783656\tool=pmcentrez\rendertype=ab>.

TERECH, P. et al. Rheological Properties and Structural Correlations in Molecular Organogels. *Langmuir*, v. 16, n. 10, p. 4485–4494, may 2000. ISSN 0743-7463. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/la991545d>.

TORO-VAZQUEZ, J. F. et al. The Effect of Tripalmitin Crystallization on the Thermomechanical Properties of Candelilla Wax Organogels. *Food Biophysics*, v. 4, n. 3, p. 199–212, jun 2009. ISSN 1557-1858. Disponível em: <http://www.springerlink.com-/index/10.1007/s11483-009-9118-7>.

TORO-VAZQUEZ, J. F. et al. Thermal and Textural Properties of Organogels Developed by Candelilla Wax in Safflower Oil. *Journal of the American Oil Chemists' Society*, v. 84, n. 11, p. 989–1000, oct 2007. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10.1007/s11746-007-1139-0>.

WILLIMANN, H. et al. Lecithin organogel as matrix for transdermal transport of drugs. *Journal of Pharmaceutical Sciences*, v. 81, n. 9, p. 871–874, 1992. ISSN 00223549.

WRIGHT, A. J.; MARANGONI, A. G. Time, Temperature, and Concentration Dependence of Ricinelaidic Acid–Canola Oil Organogelation. *Journal of the American Oil Chemists' Society*, v. 84, n. 1, p. 3–9, dec 2006. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10.1007/s11746-006-1012-6>.

WRIGHT, A. J. et al. Rheological Properties of Milkfat and Butter Concise Reviews in Food Science. *Journal of Food Science*, v. 66, n. 8, 2001.

YANG, T.; FRUEKILDE, M.-B.; XU, X. Suppression of acyl migration in enzymatic production of structured lipids through temperature programming. *Food Chemistry*, v. 92, n. 1, p. 101–107, 2005.

YOUNG, F. Interchangeability of fats and oils. In: *Journal of the American Oil Chemists' Society.* Springer, 1985. v. 62, n. 2, p. 372–376. Disponível em: <http://www.springerlink.com/index/U62310V588484P20.pdf>.

YıLMAZ, E.; ÖğÜTCÜ, M. Comparative Analysis of Olive Oil Organogels Containing Beeswax and Sunflower Wax with Breakfast Margarine. *Journal of Food Science*, v. 79, n. 9, p. E1732–E1738, 2014. ISSN 00221147. Disponível em: <http://doi.wiley.com/10-.1111/1750-3841.12561>.

YıLMAZ, E.; ÖğÜTCÜ, M. Properties and Stability of Hazelnut Oil Organogels with Beeswax and Monoglyceride. *Journal of the American Oil Chemists' Society*, v. 91, n. 6, p. 1007–1017, 2014. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007-/s11746-014-2434-1>.

YıLMAZ, E.; ÖğÜTCÜ, M.; YÜCEER, Y. K. Physical Properties, Volatiles Compositions and Sensory Descriptions of the Aromatized Hazelnut Oil-Wax Organogels. *Journal of Food Science*, v. 80, n. 9, p. S2035–S2044, sep 2015. ISSN 00221147. Disponível em: <http://doi.wiley.com/10.1111/1750-3841.12992>.

ZHANG, M.; WEISS, R. G. Self-Assembled Networks and Molecular Gels Derived from Long-Chain, NaturallyOccurring Fatty Acids. *Journal of the Brazilian Chemical Society*, v. 00, n. 00, p. 1–17, 2015.

ZULIM BOTEGA, D. C. et al. The potential application of rice bran wax oleogel to replace solid fat and enhance unsaturated fat content in ice cream. *Journal of food science*, v. 78, n. 9, p. C1334–9, sep 2013. ISSN 1750-3841. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/24024686>.

Objetivos

Objetivos Gerais

O objetivo do trabalho foi obter e caracterizar organogéis produzidos utilizando ceras de cana-de-açúcar, carnaúba e candelila como estruturantes usando como fase contínua óleo de soja ou óleo de soja com gordura vegetal interesterificada, sob condições de cristalização estática ou com cisalhamento.

Objetivos Específicos

- Avaliar a estabilidade dos organogéis em condições diferentes de armazenamento;
- Determinar como a estruturação afeta a estabilidade oxidativa da fase contínua;
- Determinar o comportamento térmico dos organogéis;
- Determinar o comportamento reológico dos organogéi;
- Determinar o perfil de sólidos dos organogéis com adição de gordura vegetal interesterificada;
- Determinar o efeito da inclusão de gordura vegetal interesterificada na fase contínua do organogel na modificação das características mecânicas, além da estabilidade ao armazenamento e perfil de sólidos;
- Determinar a microestrutura dos organogéis.

Documentos Publicados ou a Publicar

Vegetable waxes organogels: A review

Julio Cesar Barbosa Rocha, Daniel Barrera-Arellano.

Revisão bibliográfica a ser submetida para o periódico Journal of Food Science and Technology

Vegetable waxes organogels: A review

Julio Cesar Barbosa Rocha[a], Daniel Barrera-Arellano[a]

[a]*Faculty of Food Engineering, Department of Food Technology, State University of Campinas, Campinas, SP, Brazil.*

Abstract

The search for alternative materials to structure edible oils, needed to ensure sensorial qualities expected by consumers, lead to the research of the use of already approved food materials such as vegetable waxes, monoacylglycerols and phytosterols as structurants, with the objective of reduce the content of saturated and trans fatty acids at lipid based food products. Due to nutritional recommendations or regulatory establishments the use of saturated and trans fatty acids had been questioned at the past few years. An ideal structurant should be non toxic, effective at low concentrations and ideally already considered as a food product, considering these proposes the vegetable waxes are nowadays one of the best available options. Although many advances at the understanding of the behavior of organogels had been developed at recent years, especially for the organogelation processes and microstructure of such materials, the industrial application of organogels as fat replacement is at the present moment just a possibility.

Keywords: vegetable waxes, organogelation, shearing, industrial application.

Introduction

Fats are food materials of high technological and nutritional relevance, are important sources of energy, while fatty acids are essential nutrients for the proper functioning of the human body (Gurr and Harwood, 2002). In addition to its importance as food, lipids are responsible for physical characteristics of several food products due to the presence of a highly

---

Email addresses: `julio.fea@gmail.com` (Julio Cesar Barbosa Rocha), `daniel@fea.unicamp.br` (Daniel Barrera-Arellano)

organized crystalline microstructure (Rye et al., 2005). This means that although lipids are essentially an energy source, they have an importante role as solvent for vitamins and sterols, that are hormone precursors, contribute for palatability, aroma (Gurr and Harwood, 1996), consistency and melting behavior of foods. Fats can also be used as heat transfer fluid during frying and can also change the stability and shelf life of food products (Young, 1985).

The need to improve sensorial characteristics and the availability of natural sources of saturated fats lead to the production of modified vegetable fats, the mostly used were the partially hydrogenated fats that present high amounts of trans and also saturated fatty acids. Such components are considered responsible for increasing the risk of coronary diseases, as extensively reported at literature (Hu et al., 1999; Oomen et al., 2001; Noakes and Clifton, 1998).

With the information of the health implication of the presence of trans fatty acids, the presence of such components had been reduced increasing the use of fats with saturated fatty acids (as a replacement for the need of crystalline fats). Regulatory agencies are creating laws to regulate the amount of trans fatty acids that if does not prohibit its use, make it difficult to keep a clean labeling. At 2015 FDA established that partially hydrogenated oils (PHOs), that are the main source for trans fat acids, are not generally recognized as safe (GRAS) and a three year compliance period is being provided to the industry stop using it and adequate food products to the new regulation (FDA, 2015a) such modification of laws and the improvement of the consumer awareness are making trans fat acids virtually prohibited.

As a consequence the search for new technological processes to produce fats for industrial application had been though taking in consideration the maintenance of low cost, reduced amounts of saturated and trans fatty acids and of course physical and sensorial properties.

One of the most used processes is insteresterification which consists of a rearrangement of the fatty acids at the triacylglycerol, without changing the fatty acids profile (Sreenivasan, 1978; Anderson, 2005), the process uses a hard fat that is commonly a fully hydrogenated vegetable oil or a fractionated fat and a liquid oil as raw materials (Pokorný and Schmidt, 2011). The non specific interesterification reaction lead to random migration of fatty acids

(Yang et al., 2005).

Even though the interesterification produce trans free fats, if the used raw materials does not present such fat acids, there are questioning of the negative health implications of increasing the amount of saturated fatty acids at the sn-2 position at the glycerol (Hunter, 2001; Christophe, 2005; Karupaiah and Sundram, 2007; Berry, 2009). To reduce the such effect one of the alternatives is to use enzymatic interesterification that allows to use sterospecific enzymes keeping the sn-2 fatty acids at their natural positioning (Senanayake and Shahidi, 2005).

The technological importance of fats is associated with its physical behavior, the present technology needs to use saturated or trans fatty acids due to their ability to form organized networks (Narine and Marangoni, 1999), so the development of a new technology aiming the reduction of those components is needed.

Many lipids present a distinguish rheological behavior, presenting semisolid properties which means acting as both solids and liquids, making the crystalline network even more important, because it makes the material self-sustaining but also allows it to flow once under mechanical stress (Chrysan, 2005).

Organogels that are also called oleogels if the immobilized phase is an edible oil, are by definition a mixture that presents a continuous liquid phase immobilized by a tridimentional network of a structurant. Such material present mechanical spectra similar to hydrogels (Rogers et al., 2007) presenting both elastic and viscous properties. At the present moment organogels are serious candidates to be used as a replacement for chemically modified fats (by hydrogenation or interesterification), especially because no change of the triacylglycerol structure are done, keeping the stereospecific position and also the fatty acid composition of the continuous phase (Karupaiah and Sundram, 2007).

Rheological behavior of wax organogels show that they have a gel like behavior (Rocha et al., 2013; Lupi et al., 2014; Doan et al., 2015; Mert and Demirkesen, 2016), although each structurant presented some differences at frequency sweeps. The profile was typical for gels presenting a G' higher than G" and a constant tanδ (Lupi et al., 2014).

The knowledge of organogels behavior is increasing each day, a quick search using google scholar shows 258 articles using the keyword organogel at the title from 2012 to 2017 the same search for oleogel brought 23 results, the same search using the time period of 2007 to 2012 brough 148 articles for organogel and 8 results for oleogel at the same 5 year period. Although there are plenty of information a wide comprehension of the behavior of such materials is needed once each one of them is mainly focused at specific points of several structurant materials.

Organogel structuration

Organogels have already been described as viscoelastic materials where a liquid organic solvent is immobilized, sustained by a tridimentional self-sustaining structurant network (Dassanayake et al., 2009). Most of organogels are very simple to be made, consisting of dispersing the structurant using a liquid phase at a temperature above the melting point of the material and cooling up to room temperature (Patel and Dewettinck, 2016). The process had been presented by several authors and for several materials such as 12-hydroxystearic acid (Rogers et al., 2009b), monoacylglycerols (Murdan et al., 1999), vegetable waxes (Morales-Rueda et al., 2009b; Hwang et al., 2011; Dassanayake et al., 2012; Rocha et al., 2013) and other materials such as phytosterols, cholesterol and sorbitan esters (Bot and Agterof, 2006; Pernetti et al., 2007b) with no relevant differences.

The formed structure is presented at several different ways once there are many different organic components acting as structurants, the most important structures are solids dispersed at a continuous liquid phase (small inert particles, crystallized solids or droplets) or specific mechanisms (commonly observed at low mass structurants) (Hughes et al., 2009).

Although the structuring mechanism had not been totally elucidated, there are evidences of the formation of a self-assembled fibrillar network (SAFiN), with a d spacing similar to the observed for TAG structuring although with a different organization (Zhang and Weiss, 2015). The presence of fibrils that are needle like crystals had been observed at polarized light microscopy by Co and Marangoni (2012), for 12-hydroxystearic acid organogels and needle like crystals were reported by Rocha et al. (2013) for candelilla and sugarcane wax organogels. The formation of the needle like crystals had been elucidated and explained by Abdallah et al. (2000) as presented at Figure 1.

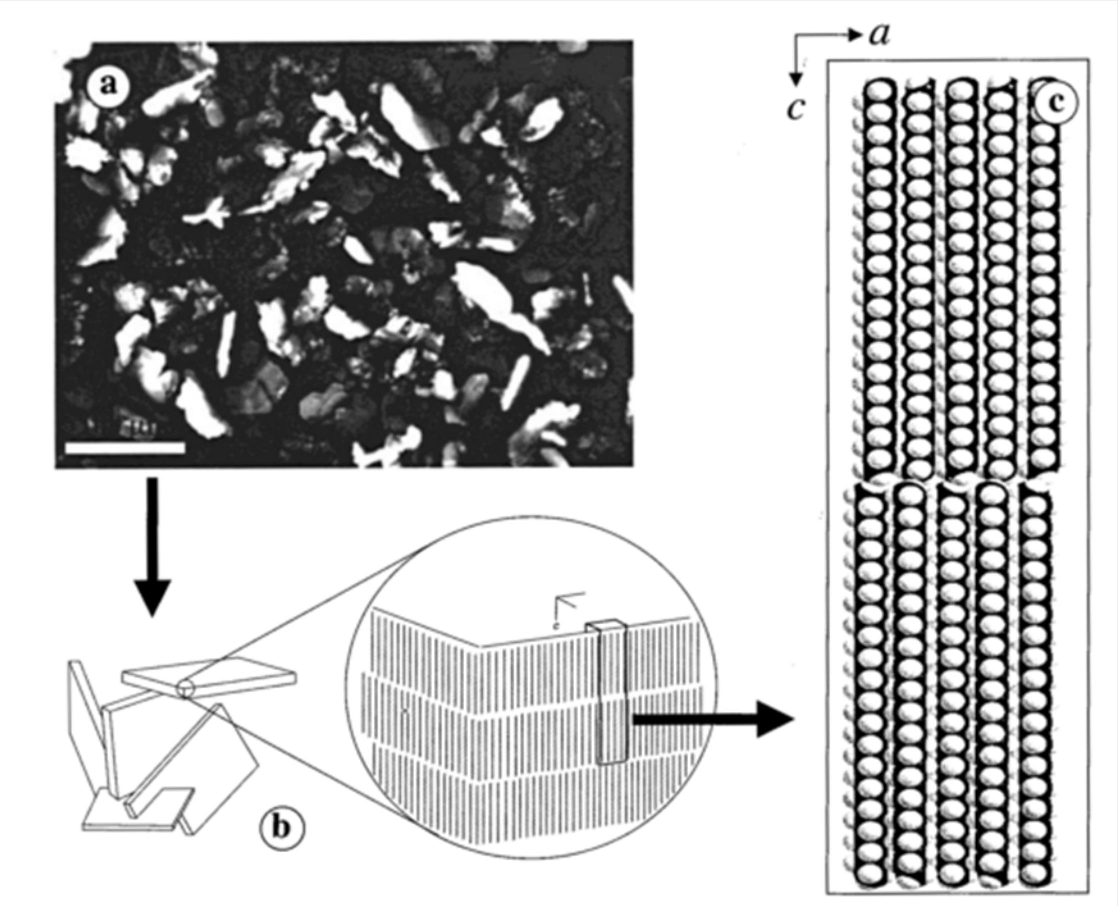

Figure 1: Optical micrograph of a 4% C36/1-octanol gel viewed through crossed polars (a), a cartoon representation of the microplatelets in (a) showing the orientations of the long molecular axes of C36 molecules (b), and the molecular packing of C36 in its BO12b phase viewed from the b-axis (c). The distance bar in (a) is 100 m. Reproduced from Abdallah et al. (2000).

More recently the presence of platellet like structures was observed for vegetable waxes (ricebran and sunflower waxes) (Blake and Marangoni, 2015a) as shown at Figure 2, similar to observed for mineral waxes by (Miyazaki and Marangoni, 2014), at both cases the material present the ability to immobilize liquids.

Size and shape of the structure are directly correlated with the mechanical properties of the obtained organogel (Pernetti et al., 2007a) and it interesting to consider that at two

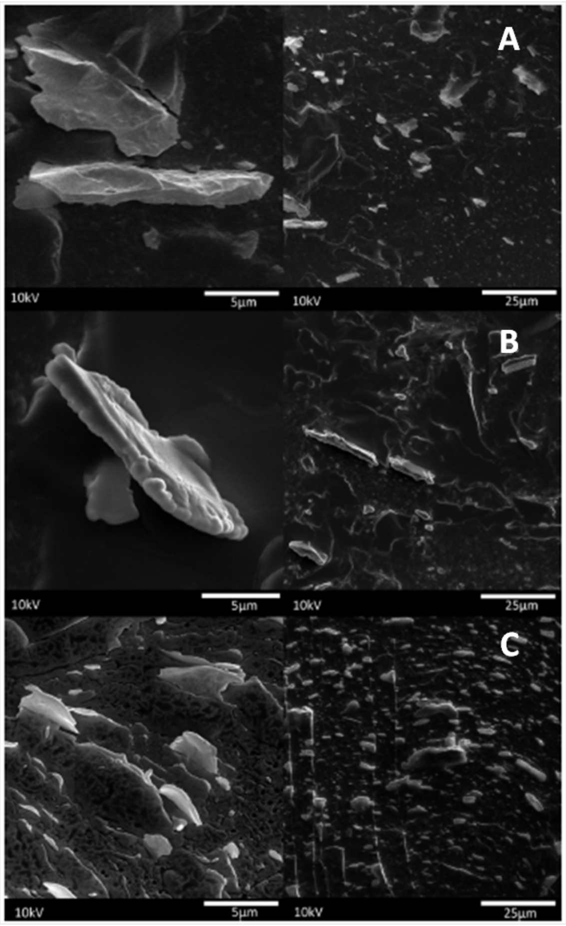

Figure 2: Platelet like structures observed for vegetable waxes (Blake and Marangoni, 2015a).

dimensional polarized light microscopy; the platelets will actually be seen as a needle like crystal. At Figure 3 the representation of an wax organogel is shown with a real micrograph from a sugarcane wax organogel obtained by Rocha et al. (2013), it is interesting to note the organization of the network as oriented needle like crystals or platelets.

Mallia and Weiss (2015), discussed a model for organogelation and formation of the SAFiNs as presented at Figure 4. The model is relevant because it consider that organogel formation should be due to thermal events described as the thermal reversibility, but also the lost of organization due to mechanical shear, such event is important once the material could be formed and destroyed using both ways.

Several materials had already been studied as structurants such as 12-hydroxystearic

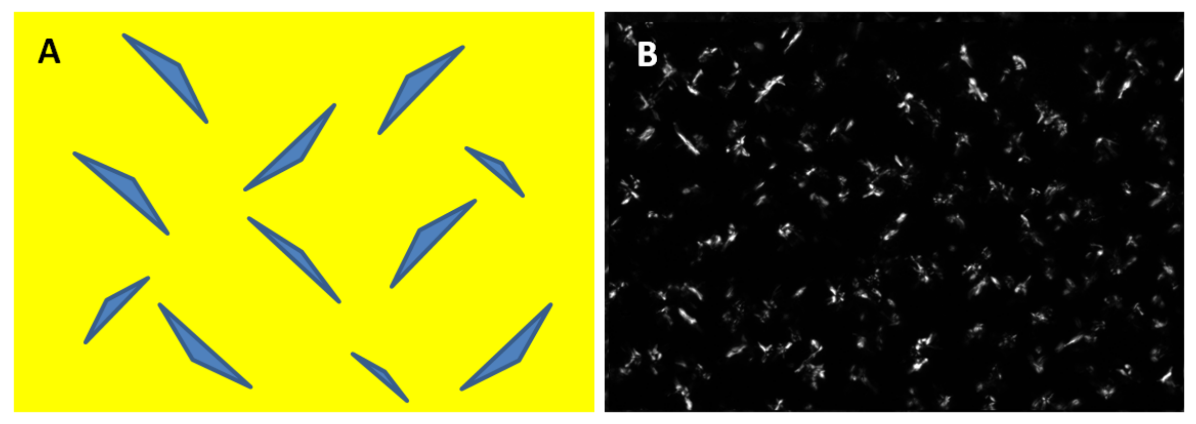

Figure 3: (A) representation of an organogel structuration, (B) actual micrograph of candelilla wax organogel 4% (w/w).

acid (Rogers et al., 2009b), phytosterols (Bot and Agterof, 2006), lecithins (Scartazzini and Luisi, 1988), mono and diacylglycerols (Batte et al., 2007), mixtures of lecithin with sorbitan esters (Murdan et al., 1999), fatty acids and alcohols (Schaink et al., 2007) and wax and wax esters (Toro-Vazquez et al., 2007; Dassanayake et al., 2009; Rocha et al., 2013), there were also studies with combinations of structuring agents such as candelilla wax added of tripalmitin (Toro-Vazquez et al., 2009), other components had also been studied such as cholesterol (Bot and Agterof, 2006; Almeida and Bahia, 2006) and ethylcellulose (Gravelle et al., 2012).

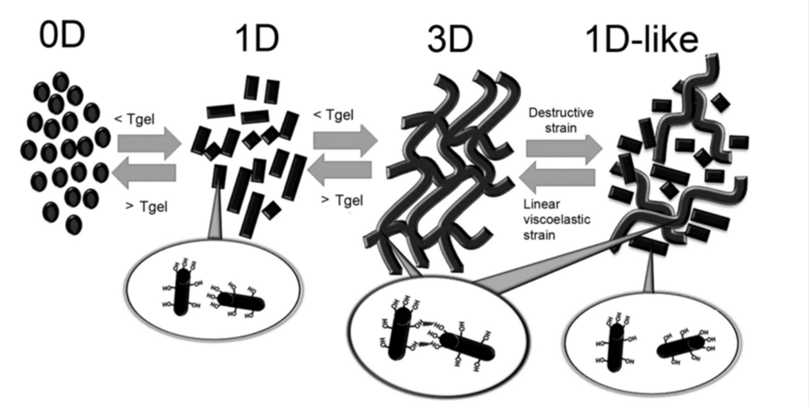

Figure 4: Proposed mechanism for formation and destruction of fibrilar networks (Mallia and Weiss, 2015).

Also the interaction of the continuous phase and the structurant is indeed very important, Toro-Vazquez et al. (2009) used tripalmitin (as cited before) and the change of composition modified the rheological behavior and should be easily confused as interaction of two solid materials (tripalmitin and the wax) that co-crystallize or act as seeding material, but changing from a liquid oil to another liquid oil, or materials that are not crystalline at room temperature, there are also modifications of the rheological behavior. The most studied continuous phases are canola, safflower, sunflower and soybean oils, but other materials such as olive and hazelnut oils have also been studied.

Organogels were produced with sunflower wax using oilve oil as continuous phase and presented different mechanical properties as compared with soybean oil organogels at the same conditions (Hwang et al., 2014) . The authors observed that olive oil presented lower firmness compared to other vegetable oils and that soybean and grapeseed oil presented the highest firmness values, the fatty acid composition of soybean and grapeseed oils that achieved similar values presented some similarities (specially at the amount of linoleic acid), but the major similarity was the amount of polar compounds, that should explain the physical behavior, a comparison of the firmness together with the amount of polar compounds is presented at Table 1, also at the table it is presented tha Unsaturated/Saturated ratio that are very similar to soybean and olive oils, but different from grapeseed. The amount of polar compounds of 5% make the organogels harder, probably due to physical interactions and composition of the sunflower wax. The results should be different for waxes from different sources so the selection of a structurant needs also to take in consideration the continuous phase in which the material will be used.

For food application an ideal structurant should be low cost, food grade and effective at low concentrations, the most promising as food grade products are fatty acids, monoacylglycerols, fatty alcohols, mixtures of fatty acids and fatty alcohols, mixtures of phytosterols and oryzanols, sorbitan monosterarate, waxes and mixtures of lecithin and sorbitan tristearate (Hughes et al., 2009). Even though a variety of materials presented the ability to form organogels, and have already proved their capacity as structurants with several studies evaluating the ideal conditions to form organogels, just a few are at the present moment ready available. Waxes, specially candelilla, present a great potential and at the momment

Table 1: Comparison of the firmness of organogels (3, 5 and 7%) of sunflower wax with different oils. Adapted from Hwang et al. (2014).

	Unsat/Sat (Ratio)	Polar compounds (%)	Firmness (N)		
			3%	5%	7%
Soybean	5.3	4.94	2.98	7.72	10.46
Almond	11.7	5.57	2.9	5.2	9.04
Canola	13.3	2.28	2.51	5.47	9.82
Corn	6.4	4.67	2.4	4.66	8.65
Flaxseed	9.7	6.82	1.71	3.81	8.42
Grape seed	8.2	4.95	2.5	5.16	10.5
Olive	5,0	3.01	1.28	3.86	6.43
Peanut	5,0	4.04	2.59	4.28	8.41
Pumpkin seed	5,0	6.93	2.49	5.17	9.38
Safflower	10.4	1.5	3.25	6.11	9.57
Sesame	5.2	4.81	2.38	5.18	9.18
Sunflower	9.8	3.14	1.79	4.55	7.88

it is the most studied material (Toro-Vazquez et al., 2007) with ricebran and carnauba waxes (Dassanayake et al., 2009) and some other vegetable waxes such as sugarcane (Rocha et al., 2013) sunflower (Hwang et al., 2011) and animal waxes such as beeswax (Ylmaz and Öütcü, 2014) and shellac (Patel et al., 2014). These material, specially candelilla and carnauba are already approved as food additives (FDA, 2015b), so it makes easier to make these materials as organogelators at least while new materials are not approved as food additives.

Wax organogels

Based on present studies it is known that several vegetable waxes present the ability to form organogels, one of the most studied waxes is candelilla, and it is probably the first studied wax to produce organogels with the objective of a fat replacer (Toro-Vazquez et al., 2007), the organogels produced with candelilla wax had been studied for several years and had been used almost as a standard benchmark at several studies due to the large amount of information available, good stability and high availability of the wax (Dassanayake et al., 2009; Hwang et al., 2011; Rocha et al., 2013).

Thermal reversibility is one of the most important characteristics of fats, any replacement material should have the same properties. For organogels the most important observed thermal event is the formation of the gel (gellation). A wax such as candelilla have a high melting point around 64°C (Toro-Vazquez et al., 2007), once it is melted and mixed with the liquid oil, the thermogram presents just one exothermic crystallization peak and it happens at a lower temperature, around 43°C (Alvarez-Mitre et al., 2012). The presence of just one peak for crystallization shows that the wax is not crystallizing at its usual crystalline form and then forming an organogels, such temperature is treated as gellation temperature and although the structuring does not modify the chemical composition of the structured material, it modifies its physical properties (Daniel and Rajasekharan, 2003), at the present moment no evidences of change of polymorphic forms have been reported.

Usually a second peak at lower temperature is also present, the first peak is easily associated to gellation, the second peak is associated to the crystallization of the TAG from the oil (Toro-Vazquez et al., 2007), similar thermal behavior was observed for candelilla wax, sugarcane wax (Rocha et al., 2013), rice bran wax (Dassanayake et al., 2009) and sunflower wax (Hwang et al., 2011) organogels. Other studies involving animal waxes such as beeswax (Pérez-Monterroza et al., 2014; Ylmaz and Öütcü, 2014) and shellac wax (Hwang et al., 2011) to form organogels also observed the same behavior.

One of the main evidences that the first exothermic peak is related to the formation of organogel network is that the observed thermal phenomena, happens at a similar temperature to the one observed for changes of the rheological properties during a cooling ramp, it was observed for organogel of candelilla (Toro-Vazquez et al., 2007), ricebran (Dassanayake et al., 2012), carnauba (Dassanayake et al., 2009), sugarcane (Rocha et al., 2013) and sunflower (Blake et al., 2014) waxes. The peaks as observed by the cited authors presented temperatures that were lower than the original wax crystallization temperature, but the peak shape were indeed similar to the observed for pure waxes, for example; ricebran and sunflower waxes presented just one peak as pure wax and as organogels the two peaks observed for carnauba and candelilla pure waxes were also observed for the organogels as observed by Blake et al. (2014), once the peak shape is related to the number of components or purity of a material as observed by Campos (2005), the maintenance of the peak profile indicates that all components of the waxes are behaving like one structurant agent and not just some components of them.

Morales-Rueda et al. (2009a), measured the rheological behavior of a candelilla wax organogel and compared to a pure dotriacontane (C32) a pure alkane to represent one of the major components of the wax, the authors measured G' and it was lower for C32 so the interaction of wax components is relevant for their ability to form organogels.

Also the reduction of the crystallization temperature (comparing the original wax and organogels), had not yet showed any modification of the microstructure, the measured d-spacing using x-ray diffraction for pure ricebran wax was the same as observed at the organogels (7.4nm) (Dassanayake et al., 2012), for other materials such as pure fat acids and fatty alcohols a change of the d-spacing measured at lengths higher than 8 were observed (Schaink et al., 2007), as the modifications of the microcrystalline structure was observed for candelilla by Toro-Vazquez et al. (2007) suggested the modification of the structure as the result of annealing.

The amount of energy needed to form an organogel network were measured and makes it possible to perform some comparison. For candelilla wax organogels at 3% (w/w), it was measured as ranging from 2 to 3.5J/g depending on the cooling rate (Toro-Vazquez et al., 2007), the same material at 4% (w/w) was measured by Rocha et al. (2013), with results slightly higher (4.83J/g) the author also measured the enthalpy variation for sugarcane organogels at 4% (w/w) that achieved a value of 1.96J/g using 10°C/min as cooling rate. A literature it is also possible to find results for sunflower organogels as 6.11J/g and beeswax as 2.4J/g both samples at 3% (w/w) (Ylmaz and Öütcü, 2014), such amount of energy is very low, if compared with a fat for example, making it clear that organogels need less energy to be formed, but also that need less energy to be melted, making them less thermal resistant then the equivalent fat.

The structure as discussed before is usually the same for wax organogels, with needle like/platelet crystals forming an organized network, although there are indeed several differences among waxes. Comparing the micrographs it is possible to observe that candelilla organogels have smaller crystal as observed by Morales-Rueda et al. (2009a) although the authors did not measured the crystal sizes, it is possible to compare the materials due to the presence of a scale bar, sugarcane wax organogels presented larger crystals, with sizes close to 5μm (Rocha et al., 2013), sunflower and carnauba waxes presented even larger crystals achieving sizes close to 50μm as observed by Blake et al. (2014) and better shown by Wang et al. (2016). The sizes observed to ricebran wax organogels were also close to 50μm (Dassanayake et al., 2012) and beeswax had also shown larger crystals when compared to candelilla organogels (Doan et al., 2015).

Crystal sizes were related to mechanical behavior usually with smaller crystals leading to organogels with higher G' (Blake et al., 2014) and a higher G' is related to materials with higher mechanical resistance.

Industrial processing and organogels

Although organogels are announced as the fat of the future (Rogers et al., 2009a), the industrial usage of such technology is limited. The main concerns about it include the oily mouthfeel and texture modifications due to change of rheological properties (Rogers et al., 2014), oxidative stability and also stability due to recrystallization of waxes (Patel and Dewettinck, 2016).

Organogel rheological properties are different from fats; while fats behave like newtonian fluids, organogels are thixotropic fluids, usually with the presence of stress overshoot (Rocha et al., 2013), the gel like behavior that justify the use of the name organogel is observed as a higher storage modulus (G') compared with loss modulus (G") (Patel et al., 2015; Steffe, 1996). Also industrial processing of fat based products usually include the use of high shear processes, for example margarine production using high shear to assure β' crystallization and improvement of spreadability (Alexandersen, 2005; Garcia et al., 2013), knowing that organogels are thixotropic materials (Rocha et al., 2013; Patel et al., 2015) the use of high shear processes is indeed a concern, so a better understanding of mechanical behavior of organogels during industrial processes is needed, thixotropicity is a concern especially due to recovery of rheological properties, according to Weiss (2014) and Mallia and Weiss (2015).

The study of how shear affects the rheological behavior were performed for monoacylglycerol organogels, presenting results that are conclusive that high shear damages organogel structure reducing oil binding due to the formation of small crystal clusters with weak interaction among each other (da Pieve et al., 2010). On the other side the use of a shear at 47 and 55°C at a rate of 300 and 75s^{-1} respectively increased the measured G' (Ojijo et al., 2004) meaning a harder organogel, problably due to a better organization of the network with shear at temperatures above gellation temperature.

For candelilla wax organogels the effect of shear showed that the use of high shear up to the gellation temperature, measured as 52°C using DSC, increased organogel mechanical resistance and network organization while the use of constant shear during crystallization (from 90 to 5°C), damaged the network structure reducing G' and complex viscosity (η^*) as mesured by Alvarez-Mitre et al. (2012). The effect of shear had also been studied for ricebran, candelilla and sunflower waxes, using a constant shear of 50s^{-1} and two cooling rates. The authors observed that shear reduced oil binding for candelilla and sunflower organogels, but improved oil binding capacity for ricebran wax organogels (Blake and Marangoni, 2015b). The application of shear at organogels and its effect have not been completed elucidated, although it is undoubtly clear that high constant shear breaks the organogel fibrillar network, there are also evidence that the use of controlled shear up to gellation temperature can improve organogel mechanical properties.

Another alternative is the use of organogel emulsions as suggested by several authors (Murdan et al., 1999; Bot et al., 2009, 2011; Toro-Vazquez et al., 2013; Patel et al., 2015), the main objective of the emulsification of organogels is to increase the mechanical resistance, as consequence modifying the food at such materials are used as ingredient (Rogers et al., 2014). An impact of the use of organogel emulsions is the change of the oily appearance and waxy mouthfeel of pure organogels (Zetzl and Marangoni, 2014), even though according to Chrysan (2005) with less than 3.5% of solids, the waxy mouthfeel should be reduced, the possibility of increasing the mechanical resistance by emulsification is an interesting alternative to be considered.

Food application of Organogels

Potential food application for organogels had not been widely explored, at the present moment some products had been developed at laboratory or pilot scales.

An ice-cream was developed using an organogel instead of milk fat, the product used high oleic sunflower oil (HOSO) and ricebran wax at 10% (w/w) (Zulim Botega et al., 2013), the mechanical properties of an ice-cream are highly dependent of the fat crystals so the presence of crystalline fat is unquestionable. The authors were able to make a product that was compared with a milk fat ice-cream and also a pure HOSO product. Considering the technological behavior the product obtained with organogels achieved a higher overrun, making it a pleasant product to look at, but not all of the technological properties were satisfactory for an ice-cream, but indoubitly there is a lot of potential for such application.

A margarine was develop by Hwang et al. (2013) using soybean oil as continuous phase and candelilla, sunflower or ricebran waxes as structurant. At the studied conditions, the authors observed some phase separation for the product obtained using candelilla wax. Even though the organogel produced using ricebran wax presented good behavior as organogel it did not achieve the desired consistency after margarine production, these formulation presented no phase separation, sunflower wax organogel was the sample that achieved better parameters for consistency and stability after margarine production. The margarines produced using 2 and 6% sunflower wax organogels presented similar consistency as for 18 to 30% hydrogenated fat commercial product, the minimum value as for a spreadable product was achieved using 2% sunflower wax organogel. Although the authors had a partial success, it is needed to take in consideration the high shear used on margarine production, and also the literature observations for organogel behavior under these situation, making it important to reevaluate the margarine processing process to reduce the use of shear under the crystallization temperature, once as observed by Alvarez-Mitre et al. (2012), the use of high shear at temperatures bellow the gellation temperature cause a rupture of the fibrillar network.

Ylmaz and Öütcü (2014) developed a spreadable product from hazelnut oil using beeswax and monoacylglycerol (MAG) as structuring material at the concentrations of 3, 7 and 10%. Beeswax and the studied MAG presented a good ability to form organogels, with no visible oil exsudation. As expected with the increase of the amount of the structurant, solid fat content (SFC) achieved 8.52% at 20°C, thermal properties were measured and the melting peak was observed from 41.86 to 50.77°C for beeswax organogels and from 37.72 to 52.68°C for MAG organogels, the increase of the measured temperatures followed the increase of the amount of structuring agent. The samples were stored for 90 days and hardness was measured with no difference during storage time. Even though the materials were softer than commercial fats, the spread presented a purchase intention higher than 50% (Ylmaz et al., 2015). In a similar way olive oil was strucutred using carnauba wax and MAG (ÖuTcu and Ylmaz, 2014), with good consumer acceptance and stability.

Patel et al. (2014) used sunflower oil and shellac wax to produce a fat base for emulsions, a replacement fat for chocolate spread and as shortening for cakes. The authors achieved emulsions with 60% water without the use of an emulsifier due to stabilization of water droplets at the solid interphase of crystallized shellac wax. The chocolate paste was produced using total replacement of palm oil and partial (27%), both materials presented good applicability and stability during 4 weeks at 30°C. The use of a 20% water emulsion to make cakes presented equivalent performance compared to a commercial baking margarine, making it possible to state that shellac wax presented a good potential as structuring material.

Mert and Demirkesen (2016) produced organogels using canola oil and candelila wax at 3 and 6%, the organogels were used as replacement fat for cookies. The cookies were made using pure canola oil, organogels, a commercial fat or a mixture of a commercial fat and organogel at the ratios 30:70 and 40:60. Cookies made with total replacement of fat for organogels presented a more similar texture to those produced using the commercial shortening compared to pure oil cookies. Even though the organogels products were no similar to those made using shortening, the authors observed that the fat added organogels were more shear sensible. Jang et al. (2015) also developed cookies using canola oil and candelilla wax organogels at 3 and 6%. At the study the authors observed that organogel samples presented a lower thermal resistance and the cookie dough presented lower G' and G" compared to shortening samples. The calculated values for satured fatty acids were reduced using organogel from 52.8 to 8%, even though cookies were softer, they presented a good consumer acceptance. Cookies were also developed by Ylmaz et al. (2015), using hazelnut oil strucutred with sunflower or beeswax at 5%, they used a CBS as commercial shortening. Sensory analysis using hedonic scale compared with instrumental texture lead to similar products.

A meat spreadable paste was also produced using organogels (Lupi et al., 2014). The authors used vegetable oil (sunflower and olive) and a mixture of MAG and polycosanols (a mixture of long chain alcohols), the structurant was presented at 0.1 up to 0.5% at the final product (0.5 and 2.5% of the lipid phase). A commercial product was used as comparison and a commercial meat base was used for each one of the formulations. The authors aimed to achieve the stabilization of a fat and meat oily suspension. Rheological measurement showed that polycosanol was better for stabilization of the system at lower concentrations, being effective even at the studied lowest concentrations and making a product with properties similar to the commercial sample. Even though MAG did not present the same ability to form organogels it samples were also stable, so it should be possible to choose the desired structurant aiming a characteristic at the final product.

A cream cheese was produced by Bemer et al. (2016) using ethylcellulose and ricebran wax organogels at 10% for both materials, the continuous phase was soybean and high oleic soybean oils. As part of the process the organogel components were added as ingredients instead of a fully crystallized organogel, four samples were made, two using ricebran wax and two with ethylcellulose. The authors compared the organogels samples to commercial cream cheese samples (regular and fat free). Organogel cream cheeses, presented a reduction of 25% of lipids compared to regular commercial sample. Hardness and spreadability were equivalent for all samples and adhesiveness were similar for ricebran wax cream cheese compared to commercial product. Microstructure were similar among commercial and organogel cream cheeses showing a viable substitution af fat for organogels at the product.

Conclusions

As observed during the review the use of waxes as structurant for lipids has been considered and studied for some time, considering the objective of reduce saturated and trans fatty acids, with no loss at physical properties.

The ideal material for production of organogels should be safe for ingestion, effective at low concentrations, form thermo-reversible gels and also be cost-effective. There are just few materials that can combine all these characteristics and waxes are one of them.

A concern about the change of lipid strucutring from TAG to organogelation is related to the use of shear, the use of intense shear is an important part of technological processes, many lipid materials such as margarine use high shear processes. As observed organogels fibrillar networks can be destroyed by shear, making the organgels lose their ability to be self-sustained, it is observed at literature that high shear lead to breakage of the network (da Pieve et al., 2010). The use of shear can also be used at organogel production to improve the strucutre, if its is not yet totally gellated as observed by (Alvarez-Mitre et al., 2012), such behavior should be an issue if we consider that at the present moment industrial processes are made using high shear processes. The alternative is to evaluate existing processes and manage to adequate them to the properties of the new materials.

The margarines produced by Hwang et al. (2013) with stability issues are the confirmation that high shear after crystallization even with the formation of an emulsion can lead to breakage of the fibrillar network.

Another relevant point is the oxidative stability, industrial fats made with saturated fat acids are more stable than liquid vegetable oils, the reviewed documents showed that oil structuring lead to an increase of the oxidative stability, the mechanism should be explained by immobilization that reduces oxygen permeation at the liquid oil. The behavior was observed by Da Pieve et al. (2011); Öütcü et al. (2015), specially for highly unsaturated oils such as fish oils, so if the material won't be as stable as a saturated fat, it will be at least more stable than a product made with pure oil.

The use of pure oils limits the applicability of organogels to a few products such as spreadable fats, so the combination of liquid oils with low *trans* fats is being presented as a possibility to modify the behavior of an organogel and also reduce the amount of saturated fatty acids. These mixed system composed of a liquid oil, a solid fat and an organogelator have not been studied, Toro-Vazquez et al. (2009) studied the addition of a trisaturated TAG (tripalmitin), the effect of saturated TAG was also observed by Mert and Demirkesen (2016) that used blends of fat and organogels to produce cookies with good results. Of course with the use of organogel and fats, saturated fatty acid reduction should not be so extensive, a 20% reduction for example, is a number that should be considered.

With so many advances at the past few years it is unquestionable the importance of alternative technologies to structure liquid oils, based on this scenario organogels are one of the most studied and with a great potential for food application even though it has been already observed that the material is not a direct fat replacement specially because of its rheological and thermal behavior.

References

David J. Abdallah, Scott a. Sirchio, and Richard G. Weiss. Hexatriacontane Organogels. The First Determination of the Conformation and Molecular Packing of a Low-Molecular-Mass Organogelator in Its Gelled State. *Langmuir*, 16(20):7558–7561, oct 2000. ISSN 0743-7463. doi: 10.1021/la000730k. URL `http://pubs.acs.org/doi/abs/10.1021/la000730k`.

Klaus A Alexandersen. Margarine Processing Plants and Equipment. In Fereidoon Shahidi, editor, *Bailey's Industrial Oil and Fat Products*, chapter 12, pages 459–532. John Wiley & Sons Inc., 6th edition, 2005.

Isabel F Almeida and M Fernanda Bahia. Evaluation of the physical stability of two oleogels. *International journal of pharmaceutics*, 327(1-2):73–7, dec 2006. ISSN 0378-5173. doi: 10.1016/j.ijpharm.2006.07.036. URL `http://www.ncbi.nlm.nih.gov/pubmed/16996708`.

F.M. Alvarez-Mitre, J.a. Morales-Rueda, E. Dibildox-Alvarado, M.a. Charó-Alonso, and Jorge F. Toro-Vazquez. Shearing as a variable to engineer the rheology of candelilla wax organogels. *Food Research International*, 49(1):580–587, nov 2012. ISSN 09639969. doi: 10.1016/j.foodres.2012.08.025. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996912003341`.

Dan Anderson. A Primer on Oils Processing Technology. In Fereidoon Shahidi, editor, *Bailey's Industrial Oil and Fat Products*, chapter 1, page 56. John Wiley & Sons Inc., 6th editio edition, 2005.

H Batte, A Wright, J Rush, S Idziak, and A. G. Marangoni. Effect of processing conditions on the structure of monostearinoilwater gels. *Food Research International*, 40 (8):982–988, oct 2007. ISSN 09639969. doi: 10.1016/j.foodres.2007.05.001. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996907000804`.

Hanna L. Bemer, Melissa Limbaugh, Erica D. Cramer, W. James Harper, and Farnaz Maleky. Vegetable organogels incorporation in cream cheese products. *Food Research International*, 85:67–75, 2016. ISSN 09639969. doi: 10.1016/j.foodres.2016.04.016. URL `http://dx.doi.org/10.1016/j.foodres.2016.04.016`.

Sarah E E Berry. Triacylglycerol structure and interesterification of palmitic and stearic acid-rich fats: an overview and implications for cardiovascular disease. *Nutrition research reviews*, 22(1):3–17, jun 2009. ISSN 1475-2700. doi: 10.1017/S0954422409369267. URL `http://www.ncbi.nlm.nih.gov/pubmed/19442321`.

Alexia I. Blake and Alejandro G. Marangoni. The Effect of Shear on the Microstructure and Oil Binding Capacity of Wax Crystal Networks. *Food Biophysics*, 2015a. ISSN 1557-1858. doi: 10.1007/s11483-015-9398-z. URL `http://link.springer.com/10.1007/s11483-015-9398-z`.

Alexia I. Blake and Alejandro G. Marangoni. Plant wax crystals display platelet-like morphology. *Food Structure*, 3:30–34, 2015b. ISSN 22133291. doi: 10.1016/j.foostr.2015.01.001. URL `http://linkinghub.elsevier.com/retrieve/pii/S2213329115000027`.

Alexia I. Blake, Edmund D. Co, and Alejandro G. Marangoni. Structure and Physical Properties of Plant Wax Crystal Networks and Their Relationship to Oil Binding Capacity. *Journal of the American Oil Chemists' Society*, 91(6):885–903, feb 2014. ISSN 0003-021X. doi: 10.1007/s11746-014-2435-0. URL `http://link.springer.com/10.1007/s11746-014-2435-0`.

Arjen Bot and Wim G M Agterof. Structuring of Edible Oils by Mixtures of γ -Oryzanol with β -Sitosterol or Related Phytosterols. *Journal of the American Oil Chemists' Society*, 83(6):513–521, 2006.

Arjen Bot, Yvonne S J Veldhuizen, Ruud den Adel, and Eli C. Roijers. Non-TAG structuring of edible oils and emulsions. *Food Hydrocolloids*, 23(4):1184–1189, 2009. ISSN 0268005X. doi: 10.1016/j.foodhyd.2008.06.009. URL `http://dx.doi.org/10.1016/j.foodhyd.2008.06.009`.

Arjen Bot, Ruud den Adel, Christos Regkos, Hassan Sawalha, Paul Venema, and Eckhard Fl??ter. Structuring in ??-sitosterol+??-oryzanol-based emulsion gels during various stages of a temperature cycle. *Food Hydrocolloids*, 25(4):639–646, 2011. ISSN 0268005X. doi: 10.1016/j.foodhyd.2010.07.026. URL `http://dx.doi.org/10.1016/j.foodhyd.2010.07.026`.

Rodrigo Campos. Experimental Methodology. In *Fat Crystal Networks*, volume 41, chapter 9, pages 267–348. Marcel Dekker, sep 2005. doi: 10.1590/S1516-93322005000300015. URL `http://www.scielo.br/scielo.php?script=sci`$_{a}rttextpid = S1516 - 93322005000300015$.

Armand B Christophe. Structural Effects on Absorption, Metabolism and Health Effects of Lipids. In Fereidoon Shahidi, editor, *Bailey's Industrial Oil and Fat Products*, chapter 16, pages 535–553. John Wiley & Sons Inc., 6th edition, 2005.

Michael M Chrysan. Margarines and Spreads. In Fereidoon Shahidi, editor, *Bailey's Industrial Oil and Fat Products*, chapter 2, pages 33–82. John Wiley & Sons Inc., 6th edition, 2005.

Edmund Daniel Co and Alejandro G. Marangoni. Organogels: An Alternative Edible Oil-Structuring Method. *Journal of the American Oil Chemists' Society*, 89(5):749–780, may 2012. ISSN 0003-021X. doi: 10.1007/s11746-012-2049-3. URL `http://link.springer.com/10.1007/s11746-012-2049-3`.

Sara da Pieve, Sonia Calligaris, Edmund Co, Maria C. Nicoli, and Alejandro G. Marangoni. Shear Nanostructuring of monoglyceride organogels. *Food Biophysics*, 5(3):211–217, 2010. ISSN 15571858. doi: 10.1007/s11483-010-9162-3.

Sara Da Pieve, Sonia Calligaris, Agnese Panozzo, Gianmichele Arrighetti, and Maria Cristina Nicoli. Effect of monoglyceride organogel structure on cod liver oil stability. *Food Research International*, 44(9):2978–2983, nov 2011. ISSN 09639969. doi: 10.1016/j.foodres.2011.07.011. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996911004510`.

Jaiyanth Daniel and Ram Rajasekharan. Organogelation of plant oils and hydrocarbons by long-chain saturated FA, fatty alcohols, wax esters, and dicarboxylic acids. *Journal of the American Oil Chemists' Society*, 80(5):417–421, may 2003. ISSN 0003-021X. doi: 10.1007/s11746-003-0714-0. URL `http://www.springerlink.com/index/10.1007/s11746-003-0714-0`.

Lakmali Samuditha K. Dassanayake, Dharma R. Kodali, S. Ueno, and K. Sato. Physical Properties of Rice Bran Wax in Bulk and Organogels. *Journal of the American Oil Chemists' Society*, 86(12):1163–1173, sep 2009. ISSN 0003-021X. doi: 10.1007/s11746-009-1464-6. URL `http://www.springerlink.com/index/10.1007/s11746-009-1464-6`.

Lakmali Samuditha K Dassanayake, Dharma R Kodali, Satoru Ueno, and Kiyotaka Sato. Crystallization kinetics of organogels prepared by rice bran wax and vegetable oils. *Journal of oleo science*, 61(1):1–9, jan 2012. ISSN 1347-3352. URL `http://www.ncbi.nlm.nih.gov/pubmed/22188800`.

Chi Diem Doan, Davy Van de Walle, Koen Dewettinck, and Ashok R. Patel. Evaluating the Oil-Gelling Properties of Natural Waxes in Rice Bran Oil: Rheological, Thermal, and Microstructural Study. *Journal of the American Oil Chemists' Society*, 92(6):801–811, 2015. ISSN 0003-021X. doi: 10.1007/s11746-015-2645-0. URL `http://link.springer.com/10.1007/s11746-015-2645-0`.

FDA. FDA Cuts Trans Fat in Processed Foods, 2015a. URL `http://www.fda.gov/ForConsumers/ConsumerUpdates/ucm372915.htm`.

FDA. Everything Added to Food in the United States (EAFUS), 2015b. URL `http://www.accessdata.fda.gov/scripts/fcn/fcnNavigation.cfm?rpt=eafusListing`.

Rita Kássia Almeida Garcia, Kelly Moreira Gandra, and Daniel Barrera-Arellano. Development of a zero trans margarine from soybean-based interesterified fats formulated using artificial neural networks. *Grasas y Aceites*, 64(5):521–530, oct 2013. ISSN 1988-4214. doi: 10.3989/gya.049113. URL `http://grasasyaceites.revistas.csic.es/index.php/grasasyaceites/article/view/1458/1465`.

Andrew J. Gravelle, Shai Barbut, and Alejandro G. Marangoni. Ethylcellulose oleogels: Manufacturing considerations and effects of oil oxidation. *Food Research International*, 48(2):578–583, oct 2012. ISSN 09639969. doi: 10.1016/j.foodres.2012.05.020. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996912001834`.

MI Gurr and JL Harwood. *Lipid Biochemistry: An Introduction*. Chapman & Hall, 4th edition, 1996.

MI Gurr and JL Harwood. *Lipid biochemistry*. Blackwell Science, 5th edition, 2002. ISBN 0-632-05409-3. URL `http://onlinelibrary.wiley.com/doi/10.1002/9780470774366.fmatter/summary`.

Frank B Hu, Meir J Stampfer, Joann E Manson, Alberto Ascherio, Graham A Colditz, Frank E Speizer, Charles H Hennekens, and Walter C Willett. Dietary saturated fats and their food sources in relation to the risk of coronary heart disease in women 1 3. *American Journal of Clinical Nutrition*, 1999.

Naomi E. Hughes, A. G. Marangoni, Amanda J. Wright, Michael a. Rogers, and James W.E. Rush. Potential food applications of edible oil organogels. *Trends in Food Science & Technology*, 20(10):470–480, oct 2009. ISSN 09242244. doi: 10.1016/j.tifs.2009.06.002. URL `http://linkinghub.elsevier.com/retrieve/pii/S0924224409002040`.

J E Hunter. Studies on effects of dietary fatty acids as related to their position on triglycerides. *Lipids*, 36 (7):655–68, jul 2001. ISSN 0024-4201. URL `http://www.ncbi.nlm.nih.gov/pubmed/11521963`.

Hong-Sik Hwang, Sanghoon Kim, Mukti Singh, Jill K. Winkler-Moser, and Sean X. Liu. Organogel Formation of Soybean Oil with Waxes. *Journal of the American Oil Chemists' Society*, 89(4):639–647, oct 2011. ISSN 0003-021X. doi: 10.1007/s11746-011-1953-2. URL `http://link.springer.com/10.1007/s11746-011-1953-2`.

Hong-Sik Hwang, Mukti Singh, Erica L. Bakota, Jill K. Winkler-Moser, Sanghoon Kim, and Sean X. Liu. Margarine from Organogels of Plant Wax and Soybean Oil. *Journal of the American Oil Chemists' Society*, 90(11):1705–1712, aug 2013. ISSN 0003-021X. doi: 10.1007/s11746-013-2315-z. URL `http://link.springer.com/10.1007/s11746-013-2315-z`.

Hong Sik Hwang, Mukti Singh, Jill K. Winkler-Moser, Erica L. Bakota, and Sean X. Liu. Preparation of margarines from organogels of sunflower wax and vegetable oils. *Journal of Food Science*, 79(10): C1926–C1932, 2014. ISSN 17503841. doi: 10.1111/1750-3841.12596.

Areum Jang, Woosung Bae, Hong-Sik Hwang, Hyeon Gyu Lee, and Suyong Lee. Evaluation of canola oil oleogels with candelilla wax as an alternative to shortening in baked goods. *Food Chemistry*, 187(4):525–529, nov 2015. ISSN 03088146. doi: 10.1016/j.foodchem.2015.04.110. URL `http://dx.doi.org/10.1016/j.foodres.20`.

Tilakavati Karupaiah and Kalyana Sundram. Effects of stereospecific positioning of fatty acids in triacylglycerol structures in native and randomized fats: a review of their nutritional implications. *Nutrition & metabolism*, 4:16, jan 2007. ISSN 1743-7075. doi: 10.1186/1743-7075-4-16. URL `http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=1947992`.

Francesca R. Lupi, Domenico Gabriele, Lucia Seta, Noemi Baldino, and Bruno de Cindio. Rheological design of stabilized meat sauces for industrial uses. *European Journal of Lipid Science and Technology*, 116(12): 1734–1744, 2014. ISSN 14389312. doi: 10.1002/ejlt.201400286.

V. Ajay Mallia and Richard G. Weiss. Structural bases for mechano-responsive properties in molecular gels of (R)-12-hydroxy-N-(ω-hydroxyalkyl)octadecanamides. Rates of formation and responses to destructive strain. *Soft Matter*, in press:5010–5022, 2015. ISSN 1744-683X. doi: 10.1039/C5SM00353A. URL `http://xlink.rsc.org/?DOI=C5SM00353A`.

Behic Mert and Ilkem Demirkesen. Evaluation of highly unsaturated oleogels as shortening replacer in a short dough product. *LWT - Food Science and Technology*, 68:477–484, 2016. ISSN 00236438. doi: 10.1016/j.lwt.2015.12.063. URL `http://linkinghub.elsevier.com/retrieve/pii/S0023643815304205`.

Yukihiro Miyazaki and Alejandro G Marangoni. Structural-mechanical model of wax crystal networksa mesoscale cellular solid approach. *Materials Research Express*, 1(2):025101, 2014. ISSN 2053-1591. doi: 10.1088/2053-1591/1/2/025101. URL `http://stacks.iop.org/2053-1591/1/i=2/a=025101`.

Juan a. Morales-Rueda, Elena Dibildox-Alvarado, Miriam a. Charó-Alonso, and Jorge F. Toro-Vazquez. Rheological Properties of Candelilla Wax and Dotriacontane Organogels Measured with a True-Gap System. *Journal of the American Oil Chemists' Society*, 86(8):765–772, jun 2009a. ISSN 0003-021X. doi: 10.1007/s11746-009-1414-3. URL `http://www.springerlink.com/index/10.1007/s11746-009-1414-3`.

Juan a. Morales-Rueda, Elena Dibildox-Alvarado, Miriam a. Charó-Alonso, Richard G. Weiss, and Jorge F. Toro-Vazquez. Thermo-mechanical properties of candelilla wax and dotriacontane organogels in safflower oil. *European Journal of Lipid Science and Technology*, 111(2):207–215, feb 2009b. ISSN 14387697. doi: 10.1002/ejlt.200810174. URL `http://doi.wiley.com/10.1002/ejlt.200810174`.

Sudaxshina Murdan, Benedicte Van Den Bergh, Gregory Gregoriadis, and Alexander T. Florence. Water-in-sorbitan monostearate organogels (water-in-oil gels). *Journal of Pharmaceutical Sciences*, 88(6):615–619, 1999. ISSN 00223549. doi: 10.1021/js980343j.

S. S. Narine and A. G. Marangoni. Relating structure of fat crystal networks to mechanical properties : a review. *Food Research International*, 32, 1999.

M Noakes and P M Clifton. Oil blends containing partially hydrogenated or interesterified fats: differential effects on plasma lipids. *The American journal of clinical nutrition*, 68(2):242–7, aug 1998. ISSN 0002-9165. URL `http://www.ncbi.nlm.nih.gov/pubmed/9701179`.

Nelson K O Ojijo, Ishak Neeman, Shaul Eger, and Eyal Shimoni. Effects of monoglyceride content, cooling rate and shear on the rheological properties of olive oil/monoglyceride gel networks. *Journal of the Science of Food and Agriculture*, 84(12):1585–1593, 2004. ISSN 00225142. doi: 10.1002/jsfa.1831.

Claudia M Oomen, Marga C Ocké, Edith J M Feskens, Frans J Kok, and Daan Kromhout. Association between trans fatty acid intake and 10-year risk of coronary heart disease in the Zutphen Elderly Study : a prospective population-based study. 357:746–751, 2001.

Mustafa Öütcü, Nazan Arifolu, and Emin Ylmaz. Preparation and Characterization of Virgin Olive Oil-Beeswax Oleogel Emulsion Products. *Journal of the American Oil Chemists' Society*, 92(4):459–471, apr 2015. ISSN 0003-021X. doi: 10.1007/s11746-015-2615-6. URL `http://link.springer.com/10.1007/s11746-015-2615-6`.

M ÖuTcu and E Ylmaz. Oleogels of virgin olive oil with carnauba wax and monoglyceride as spreadable products. *Grasas y Aceites*, 65(3):1–11, 2014. ISSN 19884214. doi: 10.3989/gya.0349141. URL `http://grasasyaceites.revistas.csic.es/index.php/grasasyaceites/article/viewArticle/1505`.

Ashok R. Patel and Koen Dewettinck. Edible oil structuring: an overview and recent updates. *Food Funct.*, 7(1):20–29, 2016. ISSN 2042-6496. doi: 10.1039/C5FO01006C. URL `http://xlink.rsc.org/?DOI=C5FO01006C`.

Ashok R. Patel, Nick Cludts, Mohd Dona Bin Sintang, Benny Lewille, Ans Lesaffer, and Koen Dewettinck. Polysaccharide-based oleogels prepared with an emulsion-templated approach. *ChemPhysChem*, 15(16): 3435–3439, 2014. ISSN 14397641. doi: 10.1002/cphc.201402473.

Ashok R. Patel, Mehrnoosh Babaahmadi, Ans Lesaffer, and Koen Dewettinck. Rheological Profiling of Organogels Prepared at Critical Gelling Concentrations of Natural Waxes in a Triacylglycerol Solvent. *Journal of Agricultural and Food Chemistry*, 63(19):4862–4869, 2015. ISSN 0021-8561. doi: 10.1021/acs.jafc.5b01548. URL `http://pubs.acs.org/doi/abs/10.1021/acs.jafc.5b01548`.

Ezequiel J. Pérez-Monterroza, Carlos J. Márquez-Cardozo, and Héctor J. Ciro-Velásquez. Rheological behavior of avocado (Persea americana Mill, cv. Hass) oleogels considering the combined effect of structuring agents. *LWT - Food Science and Technology*, 59(2):673–679, 2014. ISSN 00236438. doi: 10.1016/j.lwt.2014.07.020. URL `http://www.sciencedirect.com/science/article/pii/S0023643814004514`.

Mimma Pernetti, K van Malssen, D Kalnin, and E Floter. Structuring edible oil with lecithin and sorbitan tri-stearate. *Food Hydrocolloids*, 21(5-6):855–861, jul 2007a. ISSN 0268005X. doi: 10.1016/j.foodhyd.2006.10.023. URL `http://linkinghub.elsevier.com/retrieve/pii/S0268005X06002499`.

Mimma Pernetti, Kees F. van Malssen, Eckhard Flöter, and Arjen Bot. Structuring of edible oils by alternatives to crystalline fat. *Current Opinion in Colloid & Interface Science*, 12(4-5):221–231, oct 2007b. ISSN 13590294. doi: 10.1016/j.cocis.2007.07.002. URL `http://linkinghub.elsevier.com/retrieve/pii/S1359029407000659`.

Jan Pokorný and Stefan Schmidt. Plant Lipids and Oils. In A. Kolakowska, editor, *Chemical, Biological, and Functional Aspects of Food Lipids*, chapter 14, pages 249 – 269. Taylor and Francis, LLC, Boca Raton, Florida, 2nd edition, jul 2011. ISBN 978-1-4398-0238-0. URL `http://www.crcnetbase.com/isbn/9781439802380`.

Julio Cesar Barbosa Rocha, Julice Dutra Lopes, Maria Cristina Nucci Mascarenhas, Daniel Barrera Arellano, Lizielle Maria Ricardo Guerreiro, and Rosiane Lopes da Cunha. Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil. *Food Research International*, 50(1):318–323, jan 2013. ISSN 09639969. doi: 10.1016/j.foodres.2012.10.043. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996912004541`.

Michael A. Rogers, Alexandra K. Smith, Amanda J. Wright, and A. G. Marangoni. A Novel Cryo-SEM Technique for Imaging Vegetable Oil Based Organogels. *Journal of the American Oil Chemists' Society*, 84(10):899–906, sep 2007. ISSN 0003-021X. doi: 10.1007/s11746-007-1122-9. URL `http://www.springerlink.com/index/10.1007/s11746-007-1122-9`.

Michael A. Rogers, A. J. Wright, and A. G. Marangoni. Oil organogels: the fat of the future? *Soft Matter*, 5 (8):1594, 2009a. ISSN 1744-683X. doi: 10.1039/b822008p. URL `http://xlink.rsc.org/?DOI=b822008p`.

Michael A. Rogers, A. J. Wright, and A. G. Marangoni. Corrigendum to Nanostructuring fiber morphology and solvent inclusions in 12-hydroxystearic acid/canola oil organogels [Current Opinion in Colloid & Interface Science 14(1) (2009) 3342]. *Current Opinion in Colloid & Interface Science*, 14(3):223, jun 2009b. ISSN 13590294. doi: 10.1016/j.cocis.2009.02.003. URL `http://linkinghub.elsevier.com/retrieve/pii/S1359029409000132`.

Michael a. Rogers, Tara Strober, Arjen Bot, Jorge F. Toro-Vazquez, Terri Stortz, and Alejandro G. Marangoni. Edible oleogels in molecular gastronomy. *International Journal of Gastronomy and Food Science*, pages 1–10, may 2014. ISSN 1878450X. doi: 10.1016/j.ijgfs.2014.05.001. URL `http://linkinghub.elsevier.com/retrieve/pii/S1878450X14000043`.

G. G. Rye, J. W. Litwinenko, and A. G. Marangoni. Fat Crystal Networks. In Fereideon Shahidi, editor, *Bailey's Industrial Oil and Fat Products*. John Wiley & Sons Inc., 2005.

Roger Scartazzini and Pier Luigi Luisi. Organogels from lecithins. *The Journal of Physical Chemistry*, 92(3):829–833, feb 1988. ISSN 0022-3654. doi: 10.1021/j100314a047. URL `http://pubs.acs.org/doi/abs/10.1021/j100314a047`.

H Schaink, K Vanmalssen, S Morgadoalves, D Kalnin, and E Vanderlinden. Crystal network for edible oil organogels: Possibilities and limitations of the fatty acid and fatty alcohol systems. *Food Research International*, 40(9):1185–1193, nov 2007. ISSN 09639969. doi: 10.1016/j.foodres.2007.06.013. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996907001202`.

SPJ Senanayake and Fereidoon Shahidi. Modification of fats and oils via chemical and enzymatic methods. In Fereidoon Shahidi, editor, *Bailey's Industrial Oil and Fat Products*, chapter 17, pages 555–584. Wiley Online Library, 6th edition, 2005. URL `http://onlinelibrary.wiley.com/doi/10.1002/047167849X.bio062/full`.

B. Sreenivasan. Interesterification of fats in margarine: effect on blood lipids, blood enzymes, and hemostasis parameters. *Journal of the American Oil Chemists' Society*, 55(11):796–805, aug 1978. ISSN 0954-3007. URL `http://www.ncbi.nlm.nih.gov/pubmed/19442321`.

James F. Steffe. *Rheological methods in food process engineering*, volume 23. Freeman Press, 2nd edition, 1996. ISBN 0-9632036-1-4. doi: 10.1016/0260-8774(94)90090-6. URL `http://linkinghub.elsevier.com/retrieve/pii/0260877494900906`.

Jorge F. Toro-Vazquez, J. a. Morales-Rueda, E. Dibildox-Alvarado, M. Charó-Alonso, M. Alonzo-Macias, and M. M. González-Chávez. Thermal and Textural Properties of Organogels Developed by Candelilla Wax in Safflower Oil. *Journal of the American Oil Chemists' Society*, 84(11):989–1000, oct 2007. ISSN 0003-021X. doi: 10.1007/s11746-007-1139-0. URL `http://www.springerlink.com/index/10.1007/s11746-007-1139-0`.

Jorge F. Toro-Vazquez, Maritza Alonzo-Macias, Elena Dibildox-Alvarado, and Miriam a. Charó-Alonso. The Effect of Tripalmitin Crystallization on the Thermomechanical Properties of Candelilla Wax Organogels. *Food Biophysics*, 4(3):199–212, jun 2009. ISSN 1557-1858. doi: 10.1007/s11483-009-9118-7. URL `http://www.springerlink.com/index/10.1007/s11483-009-9118-7`.

Jorge F. Toro-Vazquez, Rosalba Mauricio-Pérez, Marco Martín González-Chávez, Mayra Sánchez-Becerril, José de Jesús Ornelas-Paz, and Jaime David Pérez-Martínez. Physical properties of organogels and water in oil emulsions structured by mixtures of candelilla wax and monoglycerides. *Food Research International*, 54(2):1360–1368, 2013. ISSN 09639969. doi: 10.1016/j.foodres.2013.09.046. URL `http://dx.doi.org/10.1016/j.foodres.2013.09.046`.

Fan C Wang, Andrew J Gravelle, Alexia I Blake, and Alejandro G Marangoni. Novel trans fat replacement strategies. *Current Opinion in Food Science*, 7: 27–34, 2016. ISSN 22147993. doi: 10.1016/j.cofs.2015.08.006. URL `http://linkinghub.elsevier.com/retrieve/pii/S221479931500106X`.

Richard G Weiss. The Past, Present, and Future of Molecular Gels. What Is the Status of the Field, and Where Is It Going? *Journal of the American Chemical Society*, may 2014. ISSN 1520-5126. doi: 10.1021/ja503363v. URL `http://www.ncbi.nlm.nih.gov/pubmed/24836858`.

Tiankui Yang, Maj-Britt Fruekilde, and Xuebing Xu. Suppression of acyl migration in enzymatic production of structured lipids through temperature programming. *Food Chemistry*, 92(1):101–107, 2005.

F.V.K. Young. Interchangeability of fats and oils. In *Journal of the American Oil Chemists' Society*, volume 62, pages 372–376. Springer, 1985. URL `http://www.springerlink.com/index/U62310V588484P20.pdf`.

Emin Ylmaz and Mustafa Öütcü. Comparative Analysis of Olive Oil Organogels Containing Beeswax and Sunflower Wax with Breakfast Margarine. *Journal of Food Science*, 79(9):E1732–E1738, 2014. ISSN 00221147. doi: 10.1111/1750-3841.12561. URL `http://doi.wiley.com/10.1111/1750-3841.12561`.

Emin Ylmaz, Mustafa Öütcü, and Yonca Karagül Yüceer. Physical Properties, Volatiles Compositions and Sensory Descriptions of the Aromatized Hazelnut Oil-Wax Organogels. *Journal of Food Science*, 80(9):S2035–S2044, sep 2015. ISSN 00221147. doi: 10.1111/1750-3841.12992. URL `http://doi.wiley.com/10.1111/1750-3841.12992`.

Alexander K. Zetzl and Alejandro G. Marangoni. Structured Emulsions and Edible Oleogels as Solutions to Trans Fat. In *Trans Fats Replacement Solutions*, number March, pages 215–243. Elsevier, 2014. ISBN 9781630670337. doi: 10.1016/B978-0-9830791-5-6.50015-0. URL `http://linkinghub.elsevier.com/retrieve/pii/B9780983079156500150`.

Mohan Zhang and Richard G. Weiss. Self-Assembled Networks and Molecular Gels Derived from Long-Chain, NaturallyOccurring Fatty Acids. *Journal of the Brazilian Chemical Society*, 00(00):1–17, 2015.

Daniele C Zulim Botega, Alejandro G Marangoni, Alexandra K Smith, and H Douglas Goff. The potential application of rice bran wax oleogel to replace solid fat and enhance unsaturated fat content in ice cream. *Journal of food science*, 78(9):C1334–9, sep 2013. ISSN 1750-3841. doi: 10.1111/1750-3841.12175. URL `http://www.ncbi.nlm.nih.gov/pubmed/24024686`.

Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil

Rocha, J. C. B., Lopes, J. D., Mascarenhas, M. C. N., Arellano, D. B., Guerreiro, L. M. R., da Cunha, R. L. (2013).

Food Research International, 50(1), 318–323. http://doi.org/10.1016/j.foodres.2012.10.043

Food Research International 50 (2013) 318–323

Contents lists available at SciVerse ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil

Julio Cesar Barbosa Rocha [a,*], Julice Dutra Lopes [a], Maria Cristina Nucci Mascarenhas [a], Daniel Barrera Arellano [a], Lizielle Maria Ricardo Guerreiro [b], Rosiane Lopes da Cunha [b]

[a] *University of Campinas (UNICAMP), Faculty of Food Engineer — Department of Food Technology, Brazil*
[b] *University of Campinas (UNICAMP), Faculty of Food Engineer — Department of Food Engineer, Brazil*

ARTICLE INFO

Article history:
Received 8 March 2012
Accepted 18 October 2012

Keywords:
Organogels
Sugarcane wax
Candelilla wax
Crystal morphology
Rheology

ABSTRACT

Sugarcane wax (SCW) was used to produce organogels and their properties were compared to candelilla wax (CLW) organogels a well known material for this purpose at concentrations of 1 to 4% (w/w). An empirical phase diagram showed that both waxes can form organogels with soybean oil as immobilized phase, SCW organogels were formed at higher concentration and at lower temperatures. The thermal behavior for SCW and CLW was similar, especially during crystallization (T_{Onset} and T_{Peak} of 42 °C and 41 °C respectively) differing only on enthalpy (1.957 and 4.829 J/g respectively), meaning that SCW organogels need less energy to form a network; the melting behavior showed that SCW organogels also need less energy to melt and that both materials presented two melting peaks one of the break of the network and melting of waxes. Rheological behavior presented similar behavior, but with higher values of complex modulus for CLW organogels. In the same way CLW gels showed larger mechanical resistance on compression/extrusion. Micrographs of organogels showed a more organized network present on CLW organogel than SCW organogels that showed larger crystals comparing to CLW organogels. The difference on the microstructure observed explains the difference on the mechanical behavior of organogels formed with both materials.

1. Introduction

Organogels can be defined as an organic liquid entrapped within a thermo-reversible, three-dimensional gel network. The self-assembly gel network is formed by a component at a relatively low concentration and organic liquid solvents (as benzene, hexane, etc) or liquid oils (Hughes, Marangoni, Wright, Rogers, & Rush, 2009).

Among the components that have the ability to form organogels only a few of them are interesting for food applications. These components can be separated as Low Mass Organogelators (LMOG) and Polymeric Organogelators. The most important LMOG are triacylglycerols, diacylglycerols, monoacylglycerols, fatty acids, fatty alcohols, waxy esters, sorbitan monostearate, fatty acid + fatty alcohols, lecithin + sorbitan tristearate and phytosterols + γ-oryzanol (Pernetti, van Malssen, Flöter, & Bot, 2007).

Wax is a common term used as a reference for mixtures of long chain nonpolar compounds, including hydrocarbons, waxy esters, sterol esters, ketones, aldehydes, fatty alcohols, fatty acids and sterols. The waxes can be classified as naturals or synthetics. Waxes are naturally present on the surface of plants and they have the function to protect them from the loss of water and attack from insects (Parish, Boos, & Li, 2002). Natural waxes are approved as food ingredients or additives according to FDA (FDA, 2012).

Candelilla wax (CLW) is a wax derived from the leaves of a small shrub native to northern Mexico and the southwestern United States. It is used in the cosmetic industry as a component of lip balms and lotion bars, and in the paint industry to manufacture varnishes. Additionally, CLW can be used as a substitute for carnauba wax and beeswax in different food systems (Toro-Vazquez et al., 2007). Sugarcane wax (SCW) is a component obtained from the filter cake of sugar and ethanol production from sugarcane (*Saccharum officinarum*). It is extracted using hexane (Vieira, & Barrera-Arellano, 2002) and clarified and purified (Barrera-Arellano & Botega, 2007).

Sugarcane wax presents a high potential for industrial use due to its high production potential in Brazil, that leads to a low cost and physical properties as shown in Table 1, that are very similar to some commercial waxes such as candelilla.

There are some studies using waxes as organogelators with candelilla wax (Toro-Vazquez et al., 2007), rice bran wax and carnauba wax (Dassanayake, Kodali, Ueno, & Sato, 2009), but to our knowledge there are no studies using sugarcane wax to produce organogels. The main objective of this study was to evaluate the ability of sugarcane wax to form organogels at different concentrations and temperatures, and also compare its rheological and thermal properties with the already studied organogel of candelilla wax.

---

[*] Corresponding author. Tel.: +55 19 32891186.
E-mail address: juliofea@gmail.com (J.C.B. Rocha).

0963-9969/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.foodres.2012.10.043

Table 1
Properties of candelilla wax (CLW) and sugar cane wax (SCW).

Property	CLW[a]	SCW[b]
Melting point (°C)	67–79	77.6–80.0
Acidity value (mg KOH/g)	12–22	17.9–18.5
Iodine value	14–27	19.9–20.1
Saponification value (mg KOH/g)	35–87	140.9–141.1

[a] Tada et al. (2007) and Tulloch (1973).
[b] Lopes (2010).

2. Material and Methods

2.1. Material and sample preparation

Refined, bleached and deodorized soybean oil (Cargill Alimentos S.A., Mairinque, SP, Brazil) was purchased from the local market and candelilla wax (CLW) was obtained from Frank B. Ross Co. Inc. (Jersey City, NJ, USA). Clarified and purified sugarcane wax (SCW) was kindly donated by Usina São Francisco (Sertãozinho, SP, Brazil). Chemical composition and physico-chemical properties of CLW and SCW are presented at Tables 1 and 2.

Samples were prepared firstly by heating soybean oil up to 80 °C under stirring and sugarcane or candelilla solid wax was slowly added (0.5, 1, 2, 3 and 4% w/w) and mixed up to its complete dissolution. After complete dissolution, the mixture was kept under agitation without heating for 3 min. The samples were stored at 20 °C for 24 h to form gel and kept at this temperature up to perform the analyses.

2.2. Qualitative phase diagrams

Phase diagrams were constructed using organogels prepared with both waxes at different concentrations, 0.5, 1, 2, 3 and 4% (w/w) as described on previous item on 12×2 cm tubes containing 10 mL and after crystallization for 24 h at 20 °C, stored at temperatures of 5, 10, 15, 20, 25, 30 and 35 °C for more 24 h. After that, the tubes were tilted and the self-standing ability of the samples was assessed visually and depending on the appearance of the samples was described as gel or liquid.

Materials that did not flow were named as *gel*, materials that slowly flowed were named as *thickened liquid* and the materials that immediately flowed were named as *liquid*.

2.3. Crystallization and melting behavior of organogels

The crystallization and melting thermograms were determined by differential scanning calorimetry (DSC) using a TA Instruments model Q2000 (TA Instruments, New Castle, DE, USA). Samples of organogels (10 mg) with 4% (w/w) of wax were placed in aluminum hermetic pans and weighted. The samples were heated at 100 °C and maintained at this temperature for 15 min before the samples were cooled to −40 °C at 10 °C/min. Samples were kept at this temperature for 30 min and then again heated to 100 °C at 10 °C/min.

Table 2
Chemical composition of candelilla wax (CLW) and sugar cane wax (SCW).

Acids and alcohols	Fatty acid (wt.%)		Fatty alcohol (wt.%)	
	CLW[a]	SCW[b]	CLW[a]	SCW[b]
16:0	2.0	22.5	–	–
18:3	–	3.3	–	–
18:1 e 18:2	–	7.1	–	–
18:0	1.0	3.9	–	–
20:0	12.0	1.6	–	–
22:0	4.0	2.1	5.0	–
24:0	1.0	4.1	–	3.2
26:0	1.0	2.9	3.0	10.4
28:0	7.0	24.8	9.0	58.5
29:0	–	2.0		0.8
30:0	32.0	10.1	65.0	15.6
32:0	33.0	5.4	15.0	7.6
34:0	7.0	5.3	3.0	1.0

[a] Tada et al. (2007) and Tulloch (1973).
[b] Lopes (2010).

The thermal parameters (T_{Onset}, T_{Endset}, T_{Peak}, ΔH) were calculated for the cooling (crystallization) and heating (melting) sweeps using Universal Analysis software (TA Instruments, New Castle, DE, USA).

3. Experimental

3.1. Rheological properties

The rheological analyses were performed using a Physica MCR 301 (Anton Paar, Graz, Austria) rheometer. A sandblasted rough plate geometry of 5 cm wide, with a roughness of 5–7 μm, with a gap of 200 μm was used for organogels. Temperature was controlled at 5 and 25 °C for flow curves and mechanical spectrum measurements. All determinations were done in triplicate.

3.1.1. Flow curves

Flow curves were obtained using shear rate ranging from 0 to 300 s^{-1} at 5 or 25 °C. The organogels were submitted to three shear rate sweeps (up–down–up) in order to eliminate thixotropy and rheological models were fitted to data obtained in steady state. In addition, apparent viscosity was evaluated at different temperatures between 5 and 85 °C, using a fixed shear rate of 100 s^{-1}, which is commonly associated with food process conditions.

The Power-law model used to fit the behavior of non-Newtonian fluids is defined by the equation $\sigma = k\ (\dot{\gamma})^n$, σ is shear stress (Pa) and $(\dot{\gamma})$ is shear rate (1/s).

3.1.2. Oscillatory rheometry

Heating–cooling sweeps were performed between 5 and 90 °C at 1 °C/min with a fixed frequency of 1 Hz to evaluate the gel formation process. Changes in the slope of complex modulus (G^*) as a function of temperature were evaluated from the derivation of the data using the Savitzky and Golay filter (Savitzky & Golay, 1964) in order to better visualize the thermal transitions. After gel formation frequency sweeps were done from 0.01 to 10 Hz with 1% deformation at 5 and 25 °C. All measurements were performed within the linear viscoelasticity domain.

3.1.3. Hardness (compression/extrusion)

Hardness of SCW and CLW organogels (2 and 4%w/w) were evaluated by compression/extrusion measurements using a texture analyzer Stable Micro Systems model TA-XT2i (Godalming — UK) using a head cross speed of 1.0 mm/s. The gels were conditioned in glass recipients (35 mm internal diameter and 22 mm high) and compressed using an acrylic cylinder (25 mm diameter and 35 mm high) up to 15 mm height at the temperature of 20 °C.

3.2. Polarized light microscopy

Micrographs of organogels (4%w/w) were obtained under polarized light microscope Olympus System Microscope model BX 50 (Olympus America Inc., Center Valley, PA, USA) equipped with a digital camera model Olympus EX300 (Olympus America Inc., Center Valley, PA, USA). The samples were conditioned at 20 °C and observed using the same temperature. The pictures obtained were evaluated using the software Image Pro-Plus 7.0.1 for Windows by Media Cybernetics (Bethesda, MD, USA).

3.3. Statistical analysis

The results were evaluated by analysis of variance (ANOVA) and significant differences ($p<0.05$) between the treatments were determined by Tukey test. Statistical analysis was performed using the software Statistica (Data Analysis Software system, StatSoft, Inc, Tulsa — USA) version 7.0.

4. Results and discussion

4.1. Qualitative phase diagram

Phase diagram (Fig. 1) shows that CLW can form gels at lower concentration and at higher temperatures (up to 35 °C), when compared to SCW. Both waxes formed organogels at 4% but only CLW could form self sustained gels at 35 °C; the results for CLW gels were similar to those presented on literature (Morales-Rueda, Dibildox-Alvarado, Charó-Alonso, Weiss, & Toro-Vazquez, 2009).

This behavior could be explained by chemical composition of waxes as shown in Table 2. CLW presented 65% of C30:0 and C32:0 fatty acids while SCW showed nearly 50% of C16:0 and C28:0. Fatty alcohol composition presented the same behavior once CLW showed prevailing C30:0 and SCW mostly C28:0.

These results indicate that a higher concentration of SCW than CLW is needed to produce at same temperature an organogel with similar visual characteristics. Thus the systems with a wax concentration of 4%w/w were evaluated, once after crystallization at 20 °C both samples presented self supported organogels at 25 °C.

4.2. Differential scanning calorimetry (DSC)

Thermal properties of SCW and CLW organogels, presented in Fig. 2A, B and Table 3, show that both waxes presented similar crystallization temperatures (T_{Onset}, T_{Peak} and T_{Endset}), which are similar with the thermal behavior observed by (Morales-Rueda et al., 2009) for CLW organogel.

However two peaks were observed on the melting thermograms as shown on Fig. 2B, these results suggest that two different phenomena are occurring. The first peaks on the right side of Fig. 2B, started close to 32 °C (T_{Onset}) and finished between 51 and 53 °C for both waxes (T_{Endset}); the second peak ranged from 58.52 °C (T_{Onset}) to 75.47 °C (T_{Endset}) for SCW while the CLW melting temperature values occurred between 61.98 °C (T_{Onset}) and 77.31 °C (T_{Endset}) (Table 3). The properties were similar for both waxes except T_{Onset} for CLW organogel, but it was similar to what is observed on literature (Toro-Vazquez et al., 2007).

The crystallization enthalpy of CLW was considerably higher than SCW organogel as shown in Table 3. The sum of melting enthalpy of both melting peaks for each organogel was considerably higher for CLW than SCW (2.843 and 1.625 J/g respectively) showing that the energy needed to melt CLW organogel was higher than needed for SCW organogel, evidencing that CLW organogel has higher resistance to temperature changes than SCW organogel.

The enthalpy needed to crystallize both materials was higher than needed to melt them, 1.957 and 1.625 J/g for SCW and 4.829 and 2.843 J/g for CLW respectively; this hysteresis should be explained by the heat of dissolution of waxes during the heating process (Abdallah, Lu, & Weiss, 1999), as reported by the author the increase of temperature leads to a breakage of the network and the dissolution of the solid material as an exothermic might suppress the visualization of the endothermic melting event.

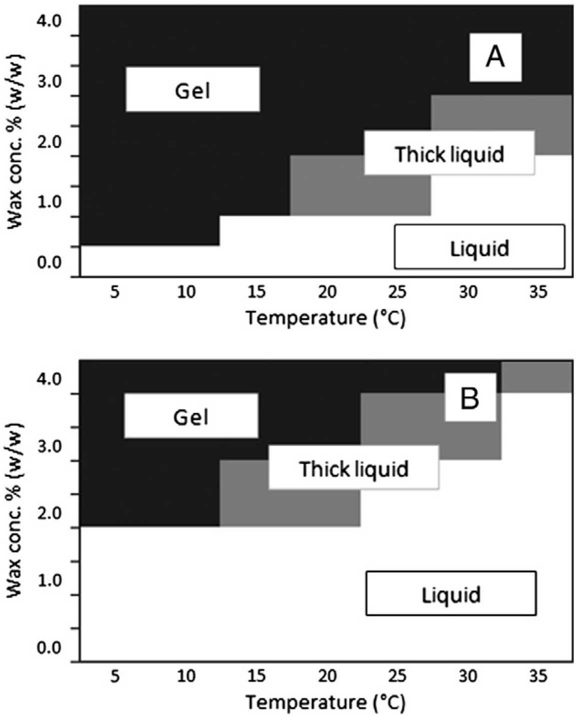

Fig. 1. Phase diagram for different wax concentration organogels at different temperatures (A) candelilla wax (B) sugarcane wax. Gel (i.e., self-standing gel), thick liquid (i.e., liquid was visibly thickened, but self-standing gel was not observed), and liquid (i.e., no thickening or gelation observed).

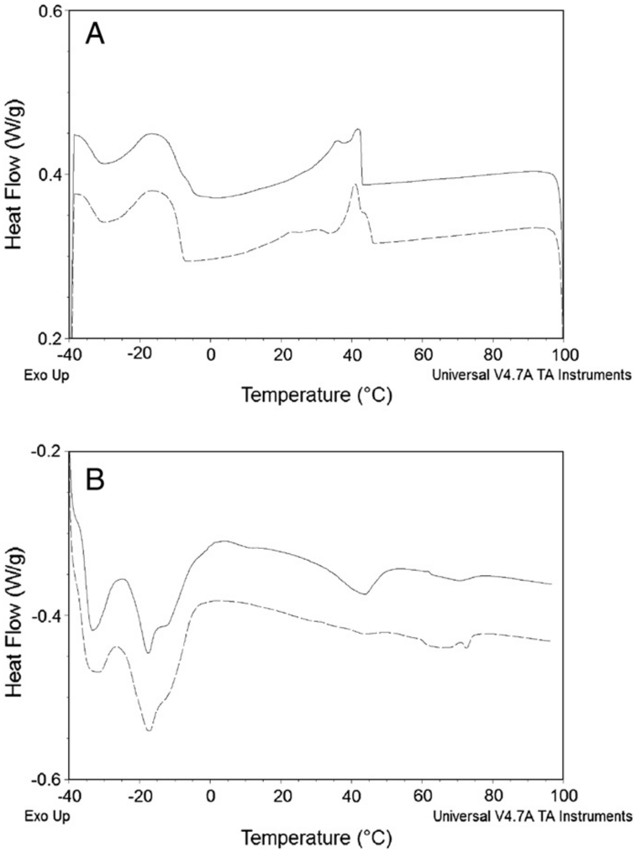

Fig. 2. Thermograms for SCW and CLW organogels at 4% (w/w) (A) crystallization, (B) melting, full lines, CLW organogel and dashed lines, SCW organogel.

Table 3
Thermal properties of SCW and CLW organogels at 4% (w/w).

Sample		T_{Onset} (°C)	T_{Peak} (°C)	T_{Endset} (°C)	ΔH (J/g)
SCW 4% (crystallization)		43.70	40.98	34.83	1.96
SCW 4% (melting)	Peak 1	31.92	43.14	51.39	0.37
	Peak 2	58.52	72.57	75.46	1.26
CLW 4% (crystallization)		42.95	41.6	14.51	4.83
CLW 4% (melting)	Peak 1	31.84	43.64	53.30	2.38
	Peak 2	61.98	70.15	77.31	0.46

4.3. Rheological measurements

4.3.1. Temperature sweeps

Fig. 3 shows rheological properties during heating and cooling cycle for CLW or SCW (4% w/w) organogels, which showed thermoreversibility.

During heating G^* values slightly decreased with the increase of temperature from 30 °C, but a more pronounced decrease was observed between 35–45 °C and 65–75 °C. The complex modulus values (G^*) (Fig. 3A) of CLW were higher than SCW organogels at temperatures below 45 °C. Above 70 °C curves shown in Fig. 3, presented a similar behavior, probably because of the complete melting of the organogel network as also observed on the thermal properties (Table 3). Melting temperatures were estimated from rheological measurements using Savitzky and Golay filter on inflection point, presenting values of 43.1 °C for SCW and 42.1 °C for CLW organogels. These values were similar to the first peak values observed on DSC (Table 3), showing that the first peak observed for thermal analysis is related to the breakage of the organogel network. Another melting temperature was estimated being 64. 1 °C for both organogels. The fat crystallizations in different polymorphic crystalline forms can be explained by the slope changes in G^* curves (Lupi et al., 2012).

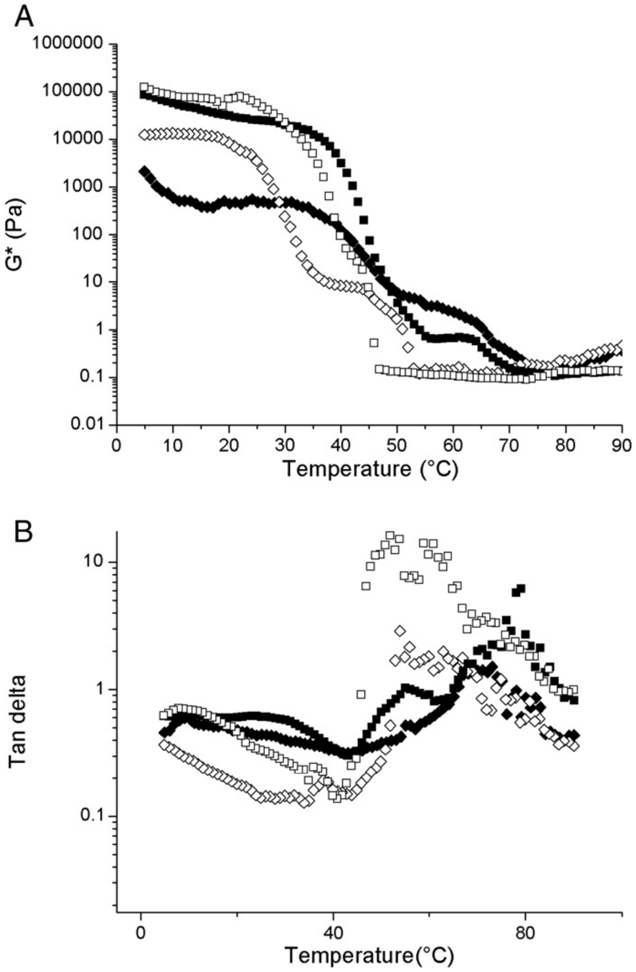

Fig. 3. Temperature sweep for SCW and CLW organogels at 4% (w/w), at 1 °C/min. ◆: SCW: ■ CLW; full symbols – heating; empty symbols – cooling. (A) Complex modulus and (B) tan delta.

Fig. 3B shows loss tangent curves for both samples. At low temperatures (<40 °C), the tangent was lower than 1, indicating that the values of G' higher than G''. At even higher temperatures, with crystals melting, the tangent values returned to be smaller than 1.

During cooling G^* values increased with temperature decrease, a result of the crystallization and reorganization of the organogel network. Crystallization temperatures were also estimated as 48.5 °C and 52.9 °C for CLW and SCW, respectively, being 5–10 °C higher than the ones determined for melting (Fig. 3A). In this range was also observed the G'–G'' crossover ($\tan = 1$), which could be also used as a simple criterion for gel point. Gelation temperature relates to the crystallization phenomena and the crystal aggregation in clusters (Lupi et al., 2012). When molten system is cooled, fat crystals in the α format are obtained and their size and number increase with decreasing temperature. Furthermore, during the cooling process, potential transitions ($\alpha \rightarrow \beta'$ polymorphic transformation) and aggregations occur forming a three-dimensional crystalline network (Wastra et al., 2001).

The similarity among DSC and temperature sweep values, specially T_{Peak} during melting for both wax organogels and melting temperatures measured using rheology was almost the same, indicating that the thermal phenomena are in fact correlated with rheological behavior.

4.3.2. Isothermal rheological measurements: mechanical spectra and flow curves

Fig. 4 shows the average results for mechanical spectra of organogels formed with SCW and CLW at 5 or 25 °C. The values of G' were higher than G'' and considered to be independent of frequency, which are characteristic of gels. However G' and G'' values for CLW organogel were significantly higher than the observed for SCW organogel. According to Fig. 4, organogels structured with the same wax showed a small difference between the observed values of G' and G'' at 5 and 25 °C, but this difference could not be considered significant (Tukey HSD $p<0.05$).

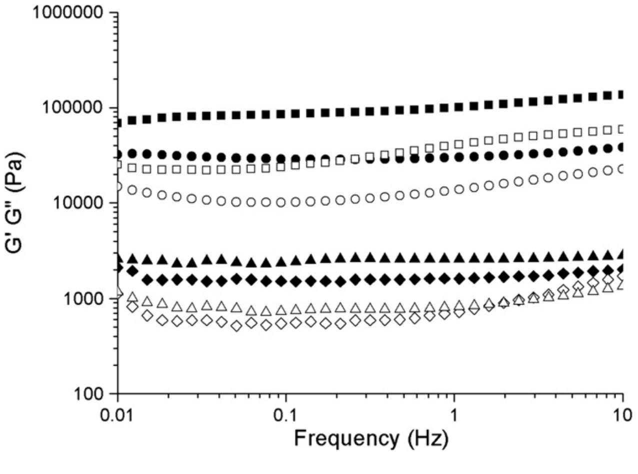

Fig. 4. Mechanical spectra of SCW and CLW organogels at 4% (w/w) at different temperatures. ◆: SCW T5, ▲: SCW T25; ■: CLW T5, ●: CLW T25; T5 – 5 °C and T25 – 25 °C; full symbols – G'; empty symbols – G''.

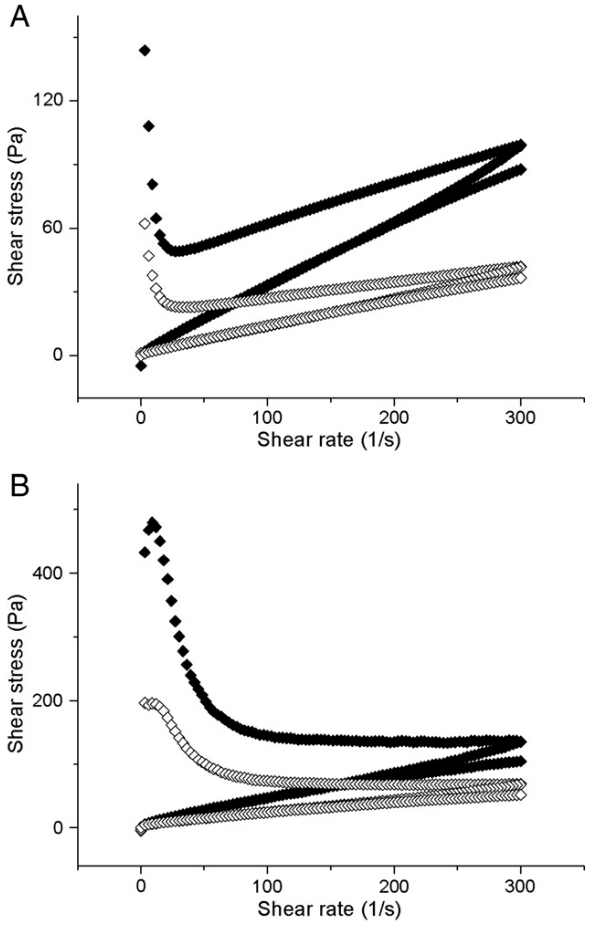

Fig. 5. Flow curves of organogels 4% (w/w) developed with (A) SCW and (B) CLW. Temperatures of 5 °C (◆) and 25 °C (◊).

Fig. 5A and B shows the flow curves of the SCW (A) and CLW (B) organogels at 5 or 25 °C, which showed that both materials presented thixotropy. Thixotropy can be estimated from the difference between the areas below the curves (hysteresis) during increase (S1 — transient) and decrease (S2 — steady state) (Sato & Cunha, 2007; Steffe, 1996). This measurement can be used as a qualitative comparison among the organogels. Table 4 shows that CLW organogel presented a higher hysteresis when compared to SCW organogels. Besides the time dependent behavior, it is possible to observe that both organogels presented *stress overshoot* (Fig. 5A and B). The fast increase and decrease of shear stress at low shear rates is a consequence of a structure network breaking (Perrechil, Santana, Fasolin, Silva, & Cunha, 2010; Riscardo, Moros, Franco, & Gallegos, 2005). The overshoot for CLW organogels at 5 and 25 °C was 479 Pa at 9.1 s^{-1} and 196 Pa at 3 s^{-1} respectively. For SCW organogels the values were considerably lower (144 Pa and 62.2 at 3 s^{-1} at 5 and 25 °C, respectively).

Power-law model for S2 curves (steady state) was fitted to both organogels and the rheological parameters (flow index **n** and consistency index **k**) were estimated with great adjustment as shown in Table 5. As seen in Table 5 the flow index values for SCW organogel were slightly higher than 0.8 independent of the temperature. However, CLW organogel showed higher pseudoplasticity (lower **n**), consistency index and viscosity than SCW organogel, which is characteristic of a more complex and dense network.

Table 4
Thixotropy estimation for candelilla wax and sugarcane wax organogels.

	SCW		CLW	
	T5	T25	T5	T25
Area S1 (Pa/s)	22.244	9.682	53.328	25.113
Area S2 (Pa/s)	13.960	5.947	19.463	8.985
Hysteresis	8.840	3.735	33.865	16.128

Table 5
Estimated Power-law parameters and apparent viscosity at 10, 50 and 100 s^{-1} for candelilla wax and sugarcane wax organogels.

		n	k (Pa s^n)	R^2	η_{10} (Pa s)	η_{50} (Pa s)	η_{100} (Pa s)
SCW	T5	0.867 ± 0.000	0.633 ± 0.000	0.999	0.476	0.354	0.332
	T25	0.846 ± 0.000	0.296 ± 0.001	0.999	0.206	0.152	0.140
CLW	T5	0.711 ± 0.014	1.852 ± 0.318	0.998	1.023	0.554	0.470
	T25	0.671 ± 0.014	1.124 ± 0.057	0.999	0.681	0.300	0.241

Table 6
Maximum force of sugarcane (SCW) and candelilla (CLW) waxes organogels.

	Maximum force (N)*
CLW (2%)	1.75^{b} ± 0.10
SCW (2%)	0.10^{c} ± 0.05
CLW (4%)	14.60^{a} ± 1.15
SCW (4%)	1.65^{b} ± 0.77

* Same letters at the same column indicate that there is no statistical difference ($p<0.05$).

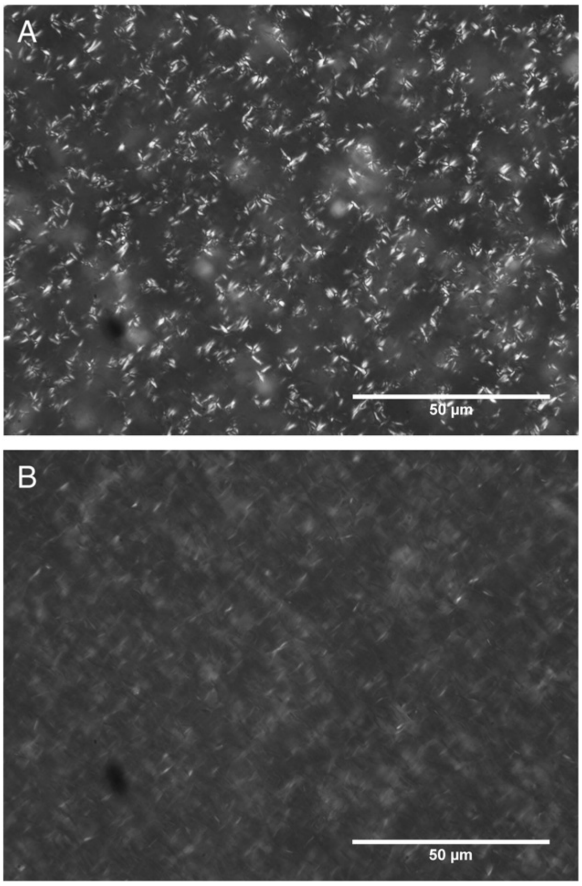

Fig. 6. Polarized light microphotographs, at a magnification of 1000×, (A) SCW and (B) CLW organogels at 4% (w/w).

4.3.3. Hardness

Based on the analysis of compression–extrusion measurements, it can be seen that the organogel formed using 4% w/w of CLW showed a much higher mechanical resistance than organogels obtained with SCW (14.6 and 1.7 N maximum force, respectively). Organogels obtained using SCW at 4% showed almost the same hardness with that of CLW at 2% as seen in Table 6.

The higher maximum force shown for CLW organogels on hardness analysis together with higher values observed on rotational rheological measurements are evidences of a more dense and complex network.

4.4. Polarized light microscopy

Polarized light microphotographs of the sugar cane wax and candelilla wax organogels are shown in Fig. 6A and B. Micrographs show that the crystal network formed in the CLW organogel is tighter (Fig. 6B) and more evenly distributed compared with the crystals of the SCW organogel network (Fig. 6A). The structure presented by CLW organogel (with smaller crystals) is an indication of stronger intermolecular interactions, which might explain the higher hardness and complex modulus, when compared to the SCW organogel at the same concentration.

5. Conclusion

The studied organogelators presented the ability to form organogels at the crystallization conditions (20 °C). The thermal behavior observed using DSC analysis showed that the materials had low thermal resistance. Rheological properties measured using rotational rheology and compression–extrusion analysis showed that CLW organogels were harder and presented higher mechanical resistance under shear. The network observed on the polarized light microscopy was similar for both materials but candelilla wax organogel presented a more organized and tighter network explaining the higher mechanical and thermal resistance of CW organogels. The use of a higher amount of sugarcane wax is needed to obtain an organogel with similar hardness than candelilla wax at the same temperature. The similarities among both organogelators were responsible for both of them produce organogels at the studied conditions, but also the chemical composition that is somewhat different, especially on the chain length of fatty acids and alcohols, affects the interaction of the organogelator and the liquid continuous phase (soybean oil) that causes the changes on the network that leads to the physical differences on organogels.

Acknowledgments

The authors thank the National Council for Scientific and Technological Development (CNPq), Coordination for Improvement of Personnel of Superior Level (CAPES), and Brazilian Society of Oils and Fats (SBOG) for scholarships.

References

Abdallah, D. J., Lu, L., & Weiss, R. G. (1999). Thermoreversible organogels from alkane gelators with one heteroatom. *Chemistry of Materials*, *11*(10), 2907–2911. http://dx.doi.org/10.1021/cm9902826.

Barrera-Arellano, D., & Botega, D. C. Z. (2007). *Processo de Clarificação de Cera de Cana de Açúcar.*

Dassanayake, L. S. K., Kodali, D. R., Ueno, S., & Sato, K. (2009). Physical properties of rice bran wax in bulk and organogels. *Journal of the American Oil Chemists' Society*, *86*(12), 1163–1173. http://dx.doi.org/10.1007/s11746-009-1464-6.

FDA (2012). Everything added to food in the United States (EAFUS). Retrieved January 30, 2012, from http://www.accessdata.fda.gov/scripts/fcn/fcnNavigation.cfm?rpt=eafusListing

Hughes, N. E., Marangoni, A. G., Wright, A. J., Rogers, M. A., & Rush, J. W. E. (2009). Potential food applications of edible oil organogels. *Trends in Food Science & Technology*, *20*(10), 470–480. http://dx.doi.org/10.1016/j.tifs.2009.06.002 (Elsevier Ltd.).

Lopes, J. D. (2010). *Master Thesis — Simplified process to production of concentrated long chain fatty acids from sugar cane wax* (*Saccharum officinarum* L.). Universidade Estadual de Campinas.

Lupi, F. R., Gabriele, D., Facciolo, D., Baldino, N., Seta, L., & de Cindio, B. (2012). Effect of organogelator and fat source on rheological properties of olive oil-based organogels. *Food Research International*, *46*, 177–184. http://dx.doi.org/10.1016/j.foodres.2011.11.029 (Elsevier Ltd.).

Morales-Rueda, J. A., Dibildox-Alvarado, E., Charó-Alonso, M. A., Weiss, R. G., & Toro-Vazquez, J. F. (2009). Thermo-mechanical properties of candelilla wax and dotriacontane organogels in safflower oil. *European Journal of Lipid Science and Technology*, *111*(2), 207–215. http://dx.doi.org/10.1002/ejlt.200810174.

Parish, E. J., Boos, T. L., & Li, S. (2002). The chemistry of waxes and sterols. In C. C. Akoh, & D. B. Min (Eds.), *Food lipids — Chemistry, nutrition, and biotechnology* (pp. 30). CRC Press LLC. http://dx.doi.org/10.1201/9780203908815.ch4.

Pernetti, M., van Malssen, K. F., Flöter, E., & Bot, A. (2007). Structuring of edible oils by alternatives to crystalline fat. *Current Opinion in Colloid & Interface Science*, *12*(4–5), 221–231. http://dx.doi.org/10.1016/j.cocis.2007.07.002.

Perrechil, F. A., Santana, R. C., Fasolin, L. H., Silva, C. A. S., & Cunha, R. L. (2010). Rheological and structural evaluations of commercial Italian salad dressings. *Ciência e Tecnologia de Alimentos*, *2009*(003636), 477–482.

Riscardo, M. A., Moros, J. E., Franco, J. M., & Gallegos, C. (2005). Rheological characterisation of salad-dressing-type emulsions stabilised by egg yolk/sucrose distearate blends. *European Food Research and Technology*, *220*(3–4), 380–388. http://dx.doi.org/10.1007/s00217-004-1052-9.

Sato, A. C. K., & Cunha, R. L. (2007). Influence of temperature on the rheological behavior of jaboticaba pulp. *Ciência e Tecnologia de Alimentos*, *27*(4), 890–896.

Savitzky, A., & Golay, M. J. E. (1964). Smoothing and differentiation of data by simplified least squares procedures. *Analytical Chemistry*, *36*(8), 1627–1639. http://dx.doi.org/10.1021/ac60214a047.

Steffe, J. F. (1996). *Rheological methods in food process engineering. Journal of Food Engineering, Vol. 23.* (pp. 418): Freeman Press. http://dx.doi.org/10.1016/0260-8774(94)90090-6.

Tada, A., Matsuda, A., Sugimoto, N., Yamagata, K., Yamazaki, T., & Tanamoto, K. (2007). *Analysis of constituents of ester-type gum bases used as natural food additives* (pp. 179–185).

Toro-Vazquez, J. F., Morales-Rueda, J. A., Dibildox-Alvarado, E., Charó-Alonso, M., Alonzo-Macias, M., & González-Chávez, M. M. (2007). Thermal and textural properties of organogels developed by candelilla wax in safflower oil. *Journal of the American Oil Chemists' Society*, *84*(11), 989–1000. http://dx.doi.org/10.1007/s11746-007-1139-0.

Tulloch, A. P. (1973). Comparison of some commercial waxes by gas liquid. *Journal of American Oil Chemistry Society*, *50*, 367–371.

Vieira, T. M. F. de S., & Barrera-Arellano, D. (2002). *Brazilian Patent* (PI0205153-2) *Processo de obtenção de cera de torta de filtração de cana de açucar.*

Wastra, P., Kloek, W., van Vliet, T., In Sato K. & Garti N. (Eds). *Crystallization Processes in Fats and Lipid Systems*. CRC Press LLC, 2001.

Comparative study of soybean oil organogels structured with sugarcane, candelilla and carnauba waxes

Julio Cesar Barbosa Rocha, Daniel Consul Kassaerdjan, Kamila Ferreira Chaves, Daniel Barrera-Arellano.

Artigo a ser submetido para o periódico *International Food Research Journal.*

Comparative study of soybean oil organogels structured with sugarcane, candelilla and carnauba waxes

Julio Cesar Barbosa Rocha[1], Daniel Consul Kassardjan[a], Kamila Ferreira Chaves[a], Daniel Barrera-Arellano[a]

[a]*Faculty of Food Engineering, Department of Food Technology, State University of Campinas, Campinas, SP, Brazil.*

Abstract

Waxy organogels are being studied as a fat replacement, specially due to no increase at the saturated fatty acids (SFA) amount. Candelilla wax (CLW) had been studied while sugarcane (SCW) and carnauba (CRW) waxes have some information about their organogelation ability. The objective of the present study was to compare soybean oil (SO) organogels at different concentrations (1, 2, 3 and 4% w/w) and crystallization conditions (5 and 25°C) to evaluate their stability, oxidative stability, thermal and rheological behavior and microstructure. All CLW and SCW organogels were stable, CRW organogels were stable above 2% (w/w) at 5°C and 3% (w/w) at 25°C. Oxidative stability increased with organogelation and thermal behavior showed that they are low stability gel. Measurements of apparent viscosity, G' and G" increased during cooling and organogelation temperatures were consistent with thermal analysis, the amount of organogelator increased viscosity and hardness. CLW organogels were harder than SCW and CRW. Oscillatory rheometry showed higher G' values for CLW, while CRW and SCW presented lower values, frequency sweeps showed that they behave like gels, sheared organogels behaved the same way. Microstructure observation showed that crystal sizes were different, CLW and SCW organogels presented similar sizes while CRW crystals were larger.

Keywords: waxy organogels, sugarcane wax, candelilla wax, carnauba wax, physical properties.

---

[*] I am corresponding author

Email addresses: `julio.fea@gmail.com` (Julio Cesar Barbosa Rocha), `daniel@fea.unicamp.br`

Preprint submitted to International Food Research Journal *March 2, 2017*

1. Introduction

The search for alternatives to saturated fats, lead the scientific community to the study of different structuring materials, such as the edible low mass organogelators (LMOG) used to produce organogels (Pernetti et al., 2007b).

Defined as a system where two phases coexist, a solid organogelator and an immobilized continuous phase that is an organic solvent (Abdallah et al., 1999), the potential shown by such materials as solid fat replacements resulted in several studies using different organogelators such as hydroxylated fatty acids (Rogers et al., 2008), phytosterols (Bot and Agterof, 2006), lecithin (Pernetti et al., 2007a) and vegetable waxes such as candelilla, ricebran, sunflower and sugarcane (Toro-Vazquez et al., 2007; Dassanayake et al., 2009; Hwang et al., 2011; Rocha et al., 2013).

Thermal behavior of organogels had been studied showing that organogelation is a thermal phenomena that is different from crystallization, allthough it presents a exothermic peak it happens at different temperatures compared to pure organogelators crystallization (Dassanayake et al., 2009; Jeong et al., 2007; Rocha et al., 2013; Toro-Vazquez et al., 2007).

The measurements of rheological properties (Lescanne et al., 2004; Lupi et al., 2012; Morales-Rueda et al., 2009a; Terech et al., 2000), showed that organogels are different from tryacilglycerol structured lipids, specially because they are non-newtonian fluids, presenting thixotropic behavior (Rocha et al., 2013) and a gel like profile at frequency sweeps with a G' higher than G" and no frequency dependency (Steffe, 1996). The microstructure observation (Blake and Marangoni, 2015a; Tang and Marangoni, 2006; Wang et al., 2006) showed that such materials are formed by tridimentional networks that present the ability to self sustain (Rocha et al., 2013).

One concern about the reduction of saturated fatty acids is the oxidative stability at future application of organogels as fats in food products so a better understanding of how organogelation affects the oxidation of a liquid fat is relevant. At the present moment there are no information about wax organogels effect at oxidative stability, but monoacylglicerols

---

(Daniel Barrera-Arellano)

had been studied with some oxidative improvements for fish oil (Calligaris et al., 2011), which is an oils with very low stability.

Organogels are one of the most promising fat alternatives, being called "the fat for the future" by Rogers et al. (2007). The study of food applications for wax organogels had been reported for several products such as margarine (Hwang et al., 2013), ice cream (Zulim Botega et al., 2013) and spreadable fats (Ylmaz and Öütcü, 2015).

One concern is about the implications of shear, at the present moment the behavior of organogels is uncertain, even though some information implicate loss of structure (da Pieve et al., 2010) for monoacylglycerol organogels but also an increase of rheological behavior using shear up to organogelation temperature (Alvarez-Mitre et al., 2012).

The objective of this study was to evaluate the formation of soybean oil organogels with the vegetable waxes candelilla (CLW), carnauba (CRW) and sugarcane (SCW), their thermal physical behavior and the effect at the oxidative stability, comparing the non structured oil against the gelated material at different storage conditions and the rheological behavior of organogels produced using static crystallization and shear up to gelation temperature.

2. Material and Methods

2.1. Material

The following materials were used: sugarcane wax (SCW) (Usina Sao Francisco, Brazil), candelilla wax (CLW) (Multiceras, Mexico), carnauba wax (CRW) (Pontes Industria de Ceras, Brazil), bleached and deodorized soybean oil (SO) (ADM, Brazil). Fatty acid composition for SO was C16:0 (12%), C18:0 (4%), C18:1 (19%), C18:2 (59%), C18:3 (7%) and was determined by GC analysis on an Agilent 6850 GC (Palo Alto, CA, USA) with a DB-23 Agilent (50% cyanopropyl - methylpolysiloxane, length 60m, int. diameter: 0.25mm, 0.25m thick film). Esterification according to Hartmann and Lago (1973) and quantification according to Ce 1-62 (AOCS, 2004).

2.2. Organogel preparation

Organogels were prepared heating soybean oil up to 80°C under constant agitation, the waxes were added to the system and kept under agitation until complete dissolution (visually assessed), after complete dissolution the material was agitated for more 3 minutes to assure homogeneity. All samples were crystallized under controlled temperature up to the moment of analysis (Rocha et al., 2013).

2.3. Methods

2.3.1. Organogel qualitative stability

Organogel samples were crystallized under 5 or 25°C for 24 hours and then stored for 7 days at 25°C. The samples were then visually evaluated to its stability, the evaluation consisted in observe any phase separation and formation of a solid gel or thick liquid using a tilt test (Rocha et al., 2013).

2.3.2. Accelerated Oxidative stability using Rancimat

A 5g sample of each organogel sample was weighted on glass tubes according to AOCS 12b-92 (AOCS, 2004). The samples were then conditioned at 110°C with forced air intake at 10ml/min. The induction time was measured as the inflection point of the electric conductivity curves using a 893 Biodiesel Rancimat (Metrohm, Herisau, Switzerland). All samples were measured as triplicates.

2.3.3. Peroxide value

Organogel samples (5g) were evaluated for peroxide value (PV) according to AOCS Cd 8b-90 (AOCS, 2004) method changing the solvent used for peroxide extraction to a 3:2 solution of acetic acid:chloroform. All samples were measured as triplicates.

2.3.4. Crystallization and Melting Behavior of Organogels

The crystallization and melting thermograms were determined by differential scanning calorimetry (DSC) using a TA Instruments model Q2000 (TA Instruments, New Castle, DE, USA), the instruments heat capacity response was calibrated using sapphire and heat flow response was calibrated with indium. Samples of organogels (10mg) with 4% (w/w) of wax were placed in aluminum hermetic pans and weighted. The samples were heated at 100°C and maintained at this temperature for 15 minutes before the samples were cooled to -40°C at 10°C/min. Samples were kept at this temperature for 30 minutes and then again heated to 100°C at 10°C/min (Rocha et al., 2013). The thermal parameters ($T_{Onset}, T_{Endset}, T_{Peak}, \Delta H$) were calculated for cooling (crystallization) and heating (melting) sweeps using Universal Analysis software (TA Instruments, New Castle, DE, USA). All samples were measured as triplicates.

2.3.5. Hardness

Hardness of organogels were evaluated by compression/extrusion measurements, for all samples that formed an organgel, using a texture analyzer Stable Micro Systems model TA-XT2i (Godalming UK) using a head cross speed of 1.0 mm/s. The gels were conditioned in glass recipients (35mm internal diameter and 22mm high) and compressed using an acrylic cylinder (25mm diameter and 35mm high) up to 15mm height at the temperature of 20°C.

2.3.6. Rheological measurements

2.3.7. Apparent viscosity

As a simple evaluation of the modification of mechanical behavior a determination of the change at the viscosity during sample cooling was made using a rotational viscometer DVI+ (Brookfield, EUA). The samples were conditioned inside a controlled temperature cell and cooled from 80 to 15°C and the viscosity measurements made at each 5°C, using a LV#2 spindle for non-newtonian fluids and a fixed rotational speed of 20 RPM resulting at a shearing rate of 5 s^{-1} calculated accordingly to the equation bellow (Steffe, 1996).

$$\gamma' = \frac{(2\omega Rc^2 Rb^2)}{(x^2(Rc^2 - Rb^2))}$$

Where:

Rc = 2.23 cm (cell radius)

Rb = 0.93 cm (spindle radius)

x = 0.93 cm (radius where shearing is calculated), considered as the limit of the spindle radius

ω = rotational speed at rad/s

2.3.8. Oscilatory rheometry

Oscilatory rheometry were performed using a Physica MCR 301 (Anton Paar, Graz, Austria) rheometer. A sandblasted rough plate geometry of 5 cm wide, with a roughness of 5 7 μm and a gap of 200 μm was used for organogels and temperature was controlled using a Peltier system (Rocha et al., 2013).

A cooling sweep were performed between 90 to 15°C at 10°C/min using a fixed frequency of 1 Hz to evaluate the gel formation process. Changes at storage (G) and loss (G) as a function of temperature were evaluated. After gel formation frequency sweeps were done from 0.1 to 10 Hz with 1% deformation at 15°C, for sheared crystallization a constant shear of $300s^{-1}$ was used from 90 up to 60°C and than a static crystallization was performed using a fixed frequency of 1 Hz as static crystallization analysis. All measurements were performed within the linear viscoelasticity domain and as triplicates.

The value of $300s^{-1}$ was used to represent a stirring or pipe flowing process, ranging from 100 up to $10^3 s^{-1}$ according to (Steffe, 1996).

2.3.9. Polarized light microsopy (PLM)

Micrographs of organogels (4%w/w) were obtained under polarized light microscope Olympus System Microscope model BX 53 (Olympus America Inc. Center Valley, USA) equipped with a digital camera model Olympus DP73 (Olympus America Inc. Center Valley, USA). Crystallized samples were melted and a droplet put over a glass slide, the slide was heated and a coverslip put over the sample for better spread (Campos, 2005). The samples were then crystallized at 5 or 25°C for 24 hours prior to observation at 25°C using a Linkam PE120 system (Linkam, UK). All images acquired and adjusted using cellSens Standard 1.7.1. software (Olympus, USA).

A fractal dimension analysis using Image J software 1.50i (National Institutes of Health, USA) were performed to measure the D using polarized light micrographs. The images were also used to measure the ratio among solid crystals (white pixels) and liquid (black pixels) the resulting value was called solid crystal density (SC%) and it was calculated according to the equation bellow.

$$SC\% = \frac{(\text{number of white pixels})}{(\text{total amount of pixels})} * 100$$

2.3.10. Statistical analysis

The obtained results were evaluated by Tukey test using STATISTICA 7.0 software (Statisoft Inc., USA).

3. Results

3.1. Organogel qualitative stability

After 24 hours crystallization it was possible to observe which material presented structuring capacity for all organogels obtained at 5 and 25°C.

At Table 1, the organogel samples after 24 hours are presented as positive (+) or negative (-) for organogelation. At the third day the samples were observed and CRW organogels lost their structure at 25°C (3%) and at 5°C (2%), no separation was observed but the sample started to flow. All other samples kept the same after the 7 days observation period. CRW did not form stable organogels at lower concentration, that is coherent with the information at the literature (Dassanayake et al., 2009), although sometimes waxes from different sources bring different results.

Not all SCW organogels were stable at studied conditions, all samples that were successfully gelated at the first 24 hours stayed stable up to the seventh day while CLW produced stable organogels at all concentrations and temperatures. As previously reported at literature candelilla has a great ability to form stable organogels at different concentrations (Dassanayake et al., 2009; Morales-Rueda et al., 2009b; Toro-Vazquez et al., 2009).

Table 1: Structuring capacity of waxes with soybean oil after 24 hours.

	SCW		CRW		CLW	
Wax concentration	5°C	25°C	5°C	25°C	5°C	25°C
1%	-	-	-	-	+	+
2%	+	-	+	-	+	+
3%	+	+	+	+	+	+
4%	+	+	+	+	+	+

3.2. Oxidative stability of organogels

Evaluation of oxidative stability of organogel samples at environment conditions for a real time oxidative stability evaluation. At the beginning of the experiment all raw materials were evaluated to its oxidative condition, measuring peroxide value that were all the same as 3.3 meq/kg.

The Rancimat analysis was used to evaluate the accelerated stability for all samples, resulting at a induction time of 4.7, 4.6 and 5.2 hours for the soybean oil, CRW and CLW organogels respectively, while SCW organogel presented a very low stability under 1 hour. The induction time is directly correlated with shelf-life (Farhoosh, 2007), such low stability observed at the SCW organogel is probably due to the presence of secondary oxidation components in SCW, that accelerated the oxidation of soybean oil, once peroxide value for all waxes, including sugarcane, were measured and were lower than 2 meq/kg.

Low temperature oxidation stability was evaluated using peroxide value, for that purpose, samples were kept under controlled temperature of 25°C, until the measured peroxide value was higher than 10 meq/kg.

The measured peroxide value is presented at Figure 1 along the time, SO, CRW and CLW samples kept the same peroxide levels up to 15 weeks, SCW organogel as observed during the Rancimat analysis presented a very low oxidative stability, increasing peroxide value to 14.2 after 3 weeks and 23.4 meq/kg after 6.5 weeks, after that period SCW organogel was not evaluated once that sample was completed oxidated.

After 15 weeks, peroxide value for SO increased to 6.7 meq/kg while CLW and CRW

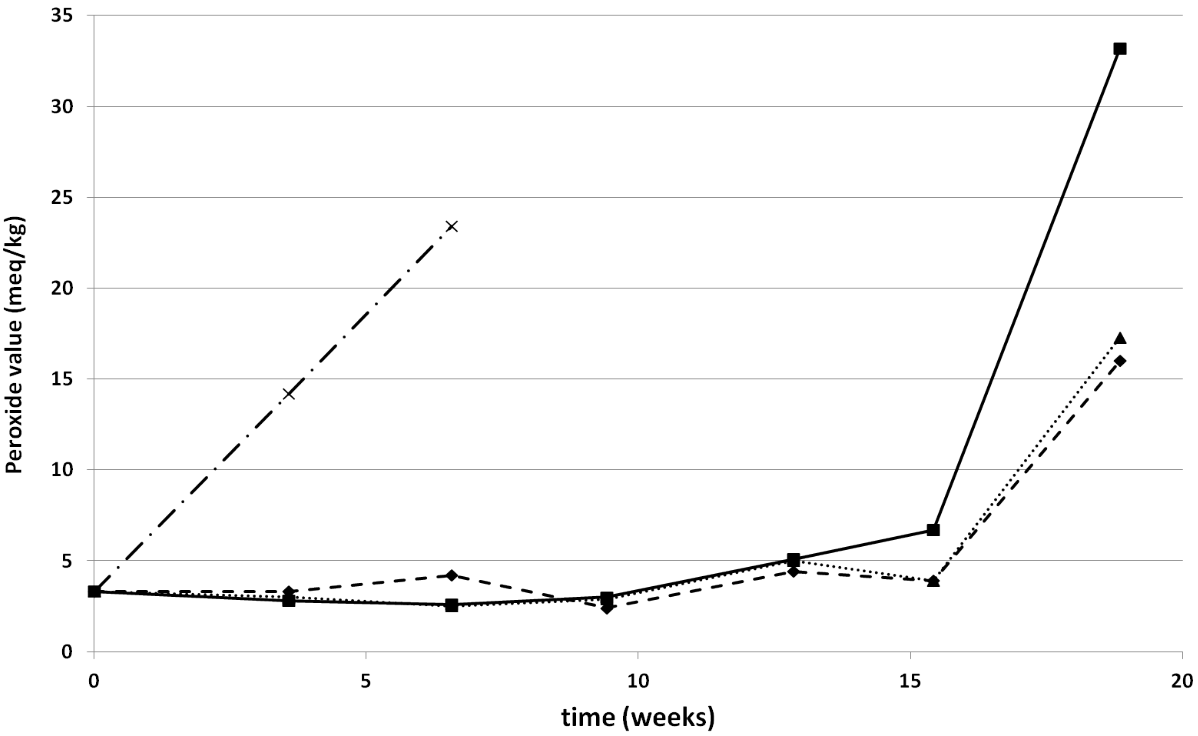

Figure 1: Peroxide value measurements. ■ (SO) and organogels; • (CLW); × (SCW) and ▲ (CRW) organogels.

organogels achieved 3.9 meq/kg. No statistical difference was observed using Tukey test ($p < 0.05$), at week 19 CLW and CRW organogels achieved 16.0 and 17.3 meq/kg respectively while pure SO reached 33.1 meq/kg, the measurements were statistically different within SO and organogels samples. Such results indicate that the organogelation increased the oxidative stability of SO similar to observed to fish oil (Kodali, 2010; Calligaris et al., 2011), due to physical immobilization that reduces oxygen transport to inside of the structured oil, the mechanism is directly related to material viscosity and it was reported by Paraskevopoulou et al. (2006) for polysaccharide systems. Once oxidative stability is one of the concerns about the replacement of saturated fats for organogels, so the observation that organogelation improves it is relevant to assure product shelf-life.

3.3. Crystallization and Melting Behavior of Organogels

Thermal behavior of organogelators as shown at Table 2, allows to compare with literature information to verify the material quality and also compare their behavior. Pure wax thermal properties were similar to reported at literature for SCW (Flaherty, 1971; Vieira and Barrera-Arellano, 2002), CRW and CLW (Flaherty, 1971). Thermal properties of organogels are presented at Table 3.

Table 2: Thermal properties of pure SCW, CRW and CLW.[1]

Crystallization			
	SCW	CRW	CLW
T_{Onset}(°C)	64.937^c	81.107^a	$65.790\ ^b$
T_{Peak}(°C)	63.727^b	76.850^a	60.937^c
T_{Endset}(°C)	41.557^b	57.893^a	44.263^b
ΔH(J/g)	87.477^c	161.733^a	133.067^b
Melting			
	SCW	CRW	CLW
T_{Onset}(°C)	41.997^c	65.843^a	49.260^b
T_{Peak}(°C)	63.663^c	84.493^a	67.357^b
T_{Endset}(°C)	83.243^b	91.403^a	76.863^c
ΔH(J/g)	97.100^c	160.300^a	130.600^b

[1]same letter at the same line mean no statistical difference ($p<0.05$).

The first observation is that with concentrations bellow 4% (w/w) the evaluation of thermal transition peaks are compromised at the used equipment due to the small amount of measured enthalpy variation. Observing the peak transitions, it is possible to verify that SCW and CLW presented similar peak width with TOnset of 44.573 and 42.933°C, TEndset of 6.887 and 6.727°C and TPeak of 32.483 and 33.127°C for SCW and CLW respectively while the same parameters for CRW were 56.227, 36.150 and 53.737°C, showing a narrower peak that leads to the questioning that CRW is gelling faster than other organogelators.

A closer observation of the enthalpy variation (ΔH), allows to note that compared to the

Table 3: Thermal properties of organogels 4% (w/w), SCW, CRW and CLW.[1]

Cristallization			
	SCW	CRW	CLW
$T_{Onset}(^\circ C)$	44.573^b	56.227^a	42.933^c
$T_{Peak}(^\circ C)$	32.483^b	53.737^a	33.127^b
$T_{Endset}(^\circ C)$	6.887^b	36.150^a	6.727^b
$\Delta H (J/g)$	2.523^c	7.689^a	5.004^b
Melting			
	SCW	CRW	CLW
$T_{Onset}(^\circ C)$	50.510^a	37.000^b	38.623^b
$T_{Peak}(^\circ C)$	66.580^a	47.913^b	46.757^c
$T_{Endset}(^\circ C)$	82.590^a	57.193^b	57.917^b
$\Delta H (J/g)$	0.786^a	0.153^b	0.789^a
$T_{Onset}(^\circ C)$	-	62.563^a	60.327^a
$T_{Peak}(^\circ C)$	-	76.197^a	66.803^b
$T_{Endset}(^\circ C)$	-	93.367^a	74.350^b
$\Delta H (J/g)$	-	3.601^a	0.038^b

[1] same letter at the same line mean no statistical difference ($p<0.05$).

original organogelators, ΔH for organogels is somewhat similar to the 4% (w/w) of structrant used. Calculating 4% of the energy needed to melt pure waxes, the calculated as expected energy for SCW was 3.5 J/g and was measured as 2.523 J/g, for CRW was also similar 6.5 and 7.689 J/g (calculated and measured respectively) and for CLW 5.3 J/g as expected and 5.004 J/g as measured, the difference of the measured energy and the calculated as 4% of the organogelator energy is probably due to modifications of the crystal structure to a different polymorph.

A reduction of the ΔH should be related to a less stable form, while an increase is usually associated with the modification to a less stable polymorph (Himawan et al., 2006), based on that evidence it is possible to assume that SCW formed such less stable polymorph while

CRW formed a more stable and CLW probably kept the original wax polymorphism, but only with a x-ray diffraction analysis such statement should be confirmed.

If CLW and SCW presented more similar behavior for crystallization, the same cannot be saw during melting, since SCW melting peak started at higher temperature (50.51°C), and there is no evidence of two melting peaks as observed for CLW and CRW samples. Comparing only the lower temperature peaks for all samples it is possible to observe that low energy is needed to break the organogel ranging from 0.153 J/g for CRW up to 0.789 J/g for CLW, while the second observed peak is similar to the melting peak observed for pure wax, so it could be explained as the melting of the organogelator. The presence of hysteresis among crystallization and melting ΔH is observed and is related to recrystallization phenomena (Abdallah and Weiss, 2000; Rocha et al., 2013), and was observed for all samples.

3.4. Hardness

Hardness was evaluated for all stable organogels and the maximum force is reported at Table 4 for samples crystallized at 5 and 25°C.

Hardness increased with the amount of wax, the samples crystallized, meaning, that more wax brought higher hardness. Organogels crystallized at lower temperature (5°C) were harder than those crystallized at 25°C. Based on that it is possible to conclude that the higher thermodynamic driving force brought by the lower temperature and consequently the faster crystallization, lead to a more organized network (Himawan et al., 2006). Although for CRW organogels the hardness increase was not so pronounced, SCW 4% (w/w) organogels at 5°C was 4.5 times harder than the same material crystallized at 25°C the CLW organogels were harder than all organogels obtained with other organogelators and more stable as observed during stability and hardness analysis and the material crystallized at lower temperature 5°C were also harder, evidenced for 3% (w/w) samples.

Another interesting point to evaluate is that although CRW organgels presented a higher ΔH and organogelation temperature, organogels were not harder than SCW organogels obtained at the same conditions, meaning that the higher thermal resistance is not related to higher mechanical resistance.

Table 4: Maximum Force (N) for SO organogels using SCW, CLW and CRW.[1]

Organogel	5°C	25°C
SCW1%	n.a.	n.a.
SCW2%	0.22^d	n.a.
SCW3%	0.69^d	n.a.
SCW4%	1.77^d	0.40^c
CRW1%	n.a.	n.a.
CRW2%	n.a.	n.a.
CRW3%	0.11^d	n.a.
CRW4%	0.24^d	0.16^c
CLW1%	0.55^d	0.12^c
CLW2%	5.38^c	1.29^c
CLW3%	14.55^b	8.58^b
CLW4%	21.31^a	19.42^a

[1] same letter at the same column mean no statistical difference ($p<0.05$)

n.a. = not evaluated

For 5°C samples, SCW organogels presented statistical difference for 3 and 4% samples, for CRW organogels, no statistical difference was observed, probably because the materials were very soft, but the statistical difference was observed for all concentrations of CLW organogels. At 25°C just one sample (4%) were measured for SCW and CRW, and the consistent increase of hardness as observed at 5°C for CLW organogels is present, even though no statistical difference was observed for CLW 1% and 2%, it should probably be due to intrinsic variance of the method.

The measured forces are similar to those from literature using similar method (Rocha et al., 2013), and as observed for comparison of CRW and CLW with ricebran wax, although different method was used, CLW organogels were harder than the obtained with CRW at the same concentration (Dassanayake et al., 2009).

3.5. Rheological measurements

Apparent viscosity

Measurements of apparent viscosity were made each 5°C during cooling and are presented bellow at Figure 2, only the samples that were stable during stability evaluation were considered for this analysis, such measurement was used to measure the mouthfeel of fluid and semi-fluid foods (Steffe, 1996), or the perception of thickness of a food product.

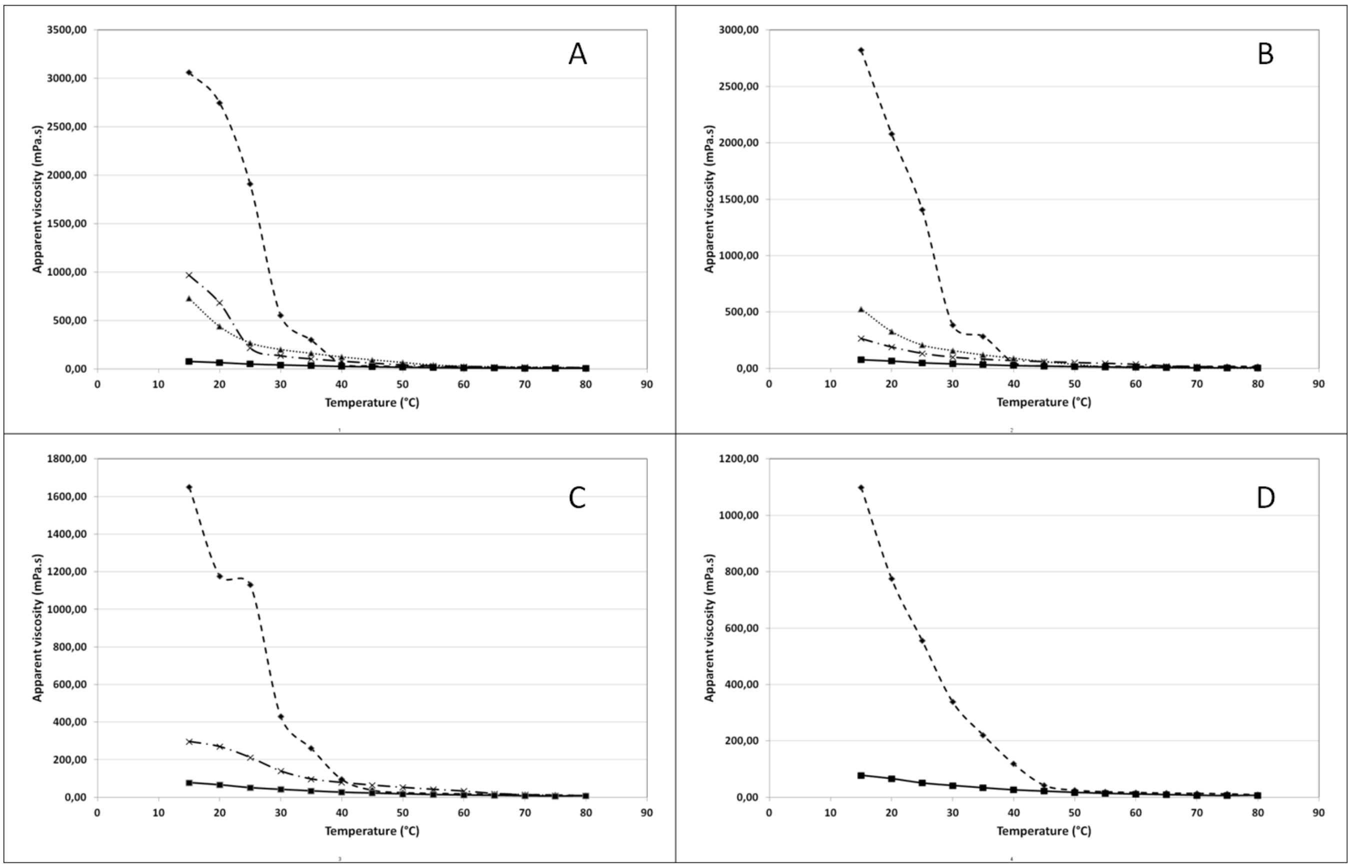

Figure 2: Apparent viscosity; ■ (SO) and organogels; ♦ (CLW), x (SCW) and ▲ (CRW) organogels. (A) 4% (w/w), (B) 3% (w/w), (C) 2% (w/w) and (D) 1% (w/w).

At Figure 2 the 4% (w/w) organogels are presented, CRW and SCW organogels presented similar behavior up to 15°C and that SCW organogel presented a higher viscosity compared to CRW. CLW organogels, even presenting lower values at temperatures above 35°C presented the highest values for apparent viscosity at lower temperatures.

Organogels at 3% (w/w) (Figure 2B) and 2% (Figure 2C), show that at both concentrations at temperatures below 35°C, CLW organogels presented a higher increase of viscosity than SCW and CRW, even though at temperatures higher than 40°C the measured viscosity were very similar, a indication of the material organogelation. The reported behavior, allows to conclude that the organogelation for CLW is happening at a lower temperature; compared to SCW; but at lower temperatures (15°C) CLW organogels viscosities were much higher than those produced with SCW. Comparing the 1% (w/w) CLW organogel with SO (Figure 2D), it is observed that at temperatures below 50°C the viscosity starts to diferentiate from the pure oil, although it was not yet completed structured.

The temperatures in wich the wax organogels viscosity started to diferentiate from pure SO, shows the organogelation temperature, and they are very similar to those observed at DSC analysis, CLW 4% (w/w) organogel presented a temperature close to 40°C, and verifying DSC analysis we have a T_{Onset} for crystallization 40.5°C, so the DSC analysis and the apparent viscosity presented the same events, apparent viscosity was used by Dassanayake (Dassanayake et al., 2009) at similar conditions for CLW organogels.

As reported by Steffe (1996), apparent viscosity above 60 can be related to human perception of thickness of a material, so observing the ramps, at temperatures bellow 30°C, only SCW at 2% did not achieve that value, meaning that all organogels would present a mouthfeel of a thick product, differing from an oil.

3.6. Oscillatory rheometry

Cooling ramps as presented at Figure 3A, showed a behavior similar to measured through apparent viscosity, with an increase of storage (G') and loss modulus (G") within the same temperature range. For CRW organogels the organogelation temperature was higher than observed for CLW and SCW organogels with the modification of rheological behavior staring at 61°C, which is higher than the measured temperature using DSC, so the rheological change is happening before the thermal event could be measured, probably a thickening before the crystallization of the organogelator could be measured.

For SCW organogel, an increase of G' and G" was measured at 46°C, at DSC a thermal event was observed at 44°C as an exothermic peak, the temperatures were similar to observed previously at literature (Rocha et al., 2013) but the achieved values for G' and G" were lower than observed for CRW and CLW organogels at the same concentration even though it formed organogels at lower concentrations compared to CRW.

Also a second change at concavity of G' and G" curves was observed for SCW organogels, the first as described started at 46°C and a second at 21°C, the change of rheological behavior has no presence of thermal event, meaning that no crystallization or change of polymorphism is happening, even though the reason has not been explained it should be due to an organization of the self-assembly tridimensional structure.

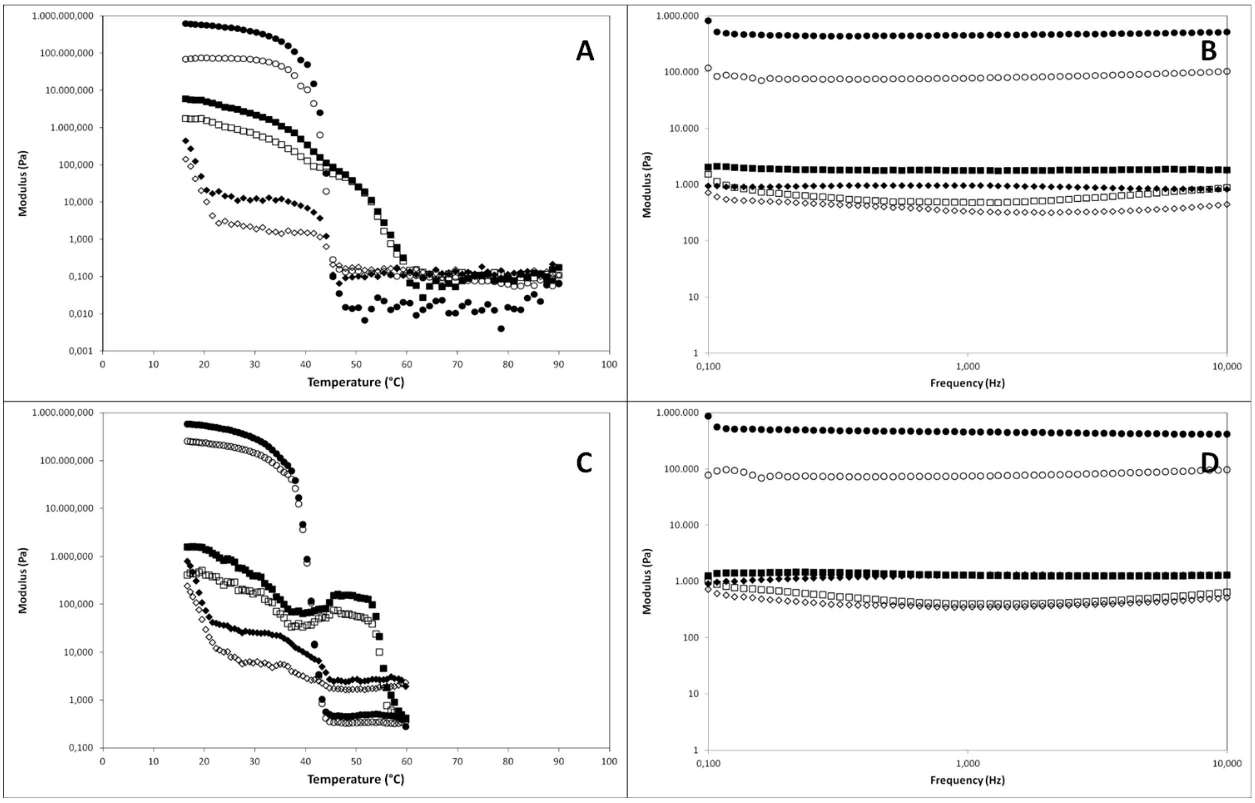

Figure 3: Static Crystallizaton (A) Cooling ramp 10°C/min; (B) Frequency sweeps, $300s^{-1}$ (C) Cooling ramp 10°C/min; (D) Frequency sweeps. ♦: SCW; ■: CRW; •: CLW; full symbols- G; empty symbols- G.

The observed organogelation temperature for CLW organogel were similar to SCW, which is compatible with the measured DSC thermal event (43°C) the measured temperature is in accordance to observed by Alvarez-Mitre (Alvarez-Mitre et al., 2012), with the rheological event happening at 46°C. The obtained G and G were higher than observed for SCW and CLW organogels at lower temperatures and as expected all organogel samples presented similar behavior above the organogelation temperature.

Frequency sweeps (Figure 3B) showed that all three organogels presented a gel like behavior with G' higher than G" and also that the material properties are not dependent of frequency. Modulus (G' and G") are related as tan(δ) and for the studied cases such value is practically constant with frequency, showing a solid-like behavior at all studied conditions (Steffe, 1996).

The obtained results for sheared organogels up to 60°C as presented in Figure 3C and 3D, showed that the behavior was the same as observed at static crystallization, even though some changes at the cooling ramp is observed, specially for CRW organogel at temperatures from 60 to 40°C, the measured G' and G" at 15°C was the same and also the frequency sweeps behavior.

The sheared organogelation shows that organogels could be used as fat replacement at industrial processes using shear if the temperature is higher than organogelation temperature as reported by Alvarez-Mitre (Alvarez-Mitre et al., 2012).

3.7. Organogels Microstructure using PLM

Polarized light microscopy was used to study the microstructure of the waxy organogels, at Figure 4 the 4% (w/w) organogels of SCW, CRW and CLW are shown with two different static crystallization temperatures (5 and 25°C), the observation were made at 25°C after 24 hours static crystallization.

Figure 4A and 4B, show small crystals of CLW organogels at 4% (w/w) at 5 and 25°C respectively; the crystals measuring an average of 3.66 ± 0.74μm for 5°C and 4.00 ± 0.68μm for 25°C, with no significant difference among them ($p>0.05$). SCW organogel at 4% (w/w) shown at Figure 4C and 4D, crystallized at 5 and 25°C respectively and measured 4.38 ± 0.59μm for 5°C and 3.57 ± 0.58μm for 25°C, for SCW organogels, crystal sizes were considered different (p¿0.05). Finally measurements of CRW organogels at 4% (w/w) shown at Figure 4E and 4F, crystallized at 5 and 25°C respectively, the crystals measured 9.63 ±

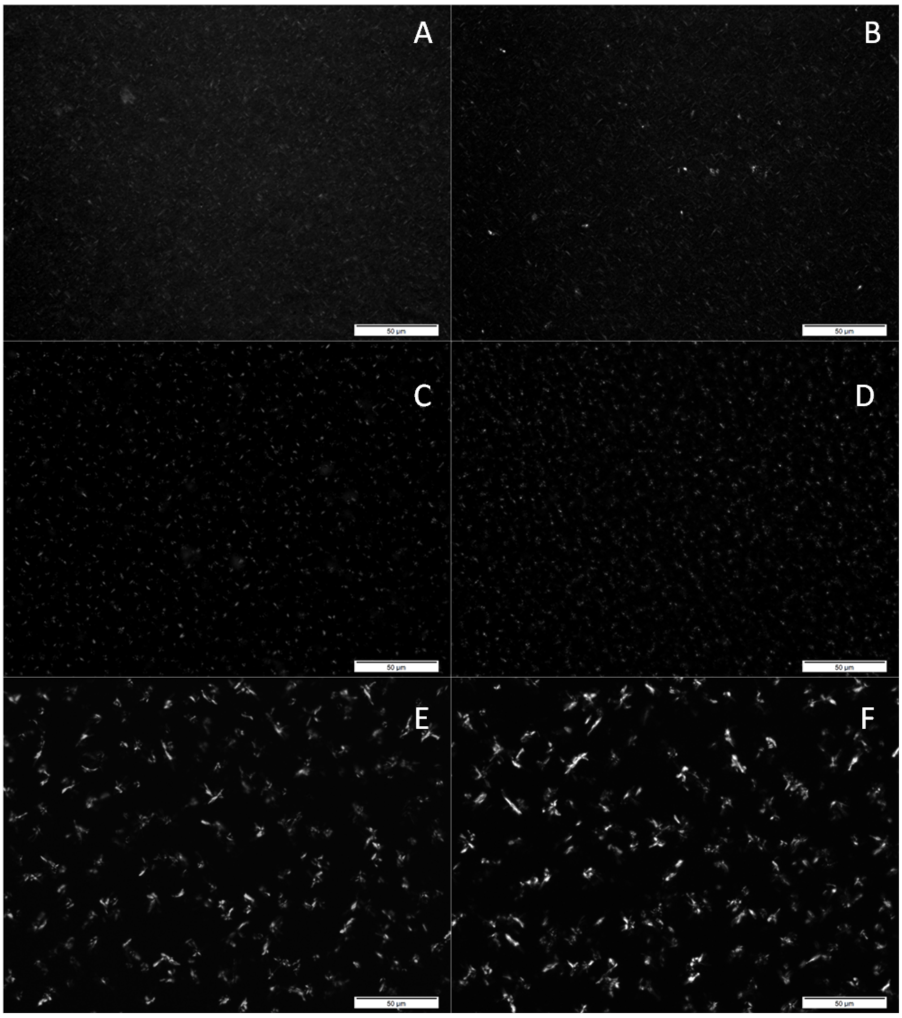

Figure 4: Organogel 4% (w/w) micrographs; (A) CLW 5°C, (B) CLW 25°C, (C) SCW 5°C, (D) SCW 25°C, (E) CRW 5°C, (F) CRW 25°C. Scale bar 50μm

.

1.96μm for 5°C and 10.61 ± 3.64μm for 25°C, with no significant difference among them ($p>0.05$).

The crystal sizes is usually related to an organized network, for fats larger crystals lead to more brittle material, while smaller particles are usually related to form plastic fats (DeMan and DeMan, 2002). Although organogels of liquid oils are fat systems, their behavior has been reported as different, if we consider that the particle sizes measured are ranging from 3.5 up to 10.6μm similar to plastic fats (DeMan and DeMan, 2002), it is in fact expected that wax organogels present plasticity but for those materials there are also thixotropy.

As related to hardness, it is easy to associate smaller crystals with higher values of hardness, for the studied materials, the higher values for hardness also presented smaller crystals, even though the relation is not direct as observed by Narine and Marangoni (2002), meaning that even though crystal sizes were not so different comparing SCW and CLW organogels at 4%, the organization of the network should be different as described by Toro-Vazquez et al. (2013), the optical microscopy does not allow to observe the different interaction among the organogelator crystal, even though they appear similar in size.

Fractal dimension (D) was measured using polarized light microscopy micrographs (Narine and Marangoni, 1999). CLW organogels presented a value of 1.96, CRW organogels measured as 1.45 and SCW 1.25. Measured value for CLW organogel was similar to observed at literature for 5% organogels (Blake and Marangoni, 2015b), although D value for SCW organogel was lower than measured for CRW organogels N value was lower for CRW, making it clear that there are more crystals from CLW and SCW while CRW has less and larger crystals. Narine and Marangoni (2002) presented a relation among D value and mechanical behavior, meaning that lower values for D should also be related to softer materials.

The measured SC% showed that CRW and SCW presented 3.0 and 3.7% respectively of white pixels against 27.0% of CLW organogels, the measured values for CRW and SCW were close to the amount of added wax while CLW presented a much higher value, such result should be explained due to the network density, as result of small crystals and network homogeneity. No difference at different temperatures was observed for these evaluations ($p>0.05$).

4. Conclusions

The studied organogelators formed organogels at some of the observed conditions, CRW needed higher amounts of wax to produce organogels at the studied conditions (static crystallization at 5 and 25°C). The oxidative stability increased with organogelation, but the presence of a pro-oxidant at SCW caused an increase of oxidation speed for that organogel, but the results achieve for CRW and CLW are consistent and statiscally relevant. Thermal analysis showed the formation of just one organogelation peak, so the materials are organogels, and the melting ΔH is correlated with material low thermal stabilty. Rheological measurements showed that CLW organogels presented higher hardness, viscosity, G' and G", for CRW and SCW organogels the values obtained for hardness were different with higher value for SCW, but CRW presented higher G' and G" at cooling ramp and similar behavior was observed for both samples at frequency sweeps. The results were similar to sheared or static crystallized organogels. Micrographs showed that CLW presented smaller and more organized network while CRW presented larger crystals and lower crystallinity (measured as white pixels).A chemical interaction of the organogelator and the liquid phase explain how obtained organogels are different among each other and that the organogelation should not considered as a simple crystallization process.

The observation of these organogels showed that some of their characteristics allow them to be a possible food applicable material, specially if we consider that they can be sheared at appropriate conditions.

References

David J. Abdallah and Richard G. Weiss. n -Alkanes Gel n -Alkanes (and Many Other Organic Liquids). *Langmuir*, 16(2):352–355, jan 2000. ISSN 0743-7463. doi: 10.1021/la990795r. URL `http://pubs.acs.org/doi/abs/10.1021/la990795r`.

David J Abdallah, Liangde Lu, and Richard G Weiss. Thermoreversible Organogels from Alkane Gelators with One Heteroatom. *Chemistry of Materials*, 11(10):2907–2911, 1999. ISSN 08974756. doi: 10.1021/cm9902826. URL `http://pubs.acs.org/doi/abs/10.1021/cm9902826`.

F.M. Alvarez-Mitre, J.a. Morales-Rueda, E. Dibildox-Alvarado, M.a. Charó-Alonso, and Jorge F. Toro-Vazquez. Shearing as a variable to engineer the rheology of candelilla wax organogels. *Food Research International*, 49(1):580–587, nov 2012. ISSN 09639969. doi: 10.1016/j.foodres.2012.08.025. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996912003341`.

AOCS. *Official methods and recommended practices of the American Oil Chemists Society.* AOCS Press, Champaign, IL, 5 edition, 2004.

Alexia I. Blake and Alejandro G. Marangoni. The Effect of Shear on the Microstructure and Oil Binding

Capacity of Wax Crystal Networks. *Food Biophysics*, 2015a. ISSN 1557-1858. doi: 10.1007/s11483-015-9398-z. URL `http://link.springer.com/10.1007/s11483-015-9398-z`.

Alexia I. Blake and Alejandro G. Marangoni. Plant wax crystals display platelet-like morphology. *Food Structure*, 3:30–34, 2015b. ISSN 22133291. doi: 10.1016/j.foostr.2015.01.001. URL `http://linkinghub.elsevier.com/retrieve/pii/S2213329115000027`.

Arjen Bot and Wim G M Agterof. Structuring of Edible Oils by Mixtures of γ -Oryzanol with β -Sitosterol or Related Phytosterols. *Journal of the American Oil Chemists' Society*, 83(6):513–521, 2006.

Sonia Calligaris, Sara Da Pieve, Agnese Panozzo, Gianmichele Arrighetti, and Maria Cristina Nicoli. Effect of monoglyceride organogel structure on cod liver oil stability. *Food Research International*, 44(9):2978–2983, nov 2011. ISSN 09639969. doi: 10.1016/j.foodres.2011.07.011. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996911004510`.

Rodrigo Campos. *Experimental Methodology*, volume 41. Marcel Dekker, sep 2005. doi: 10.1590/S1516-93322005000300015. URL `http://www.scielo.br/scielo.php?script=sci`$_{a}rttextpid = S1516 - 93322005000300015lng = ptnrm = isotlng = pt$.

Sara da Pieve, Sonia Calligaris, Edmund Co, Maria C. Nicoli, and Alejandro G. Marangoni. Shear Nanostructuring of monoglyceride organogels. *Food Biophysics*, 5(3):211–217, 2010. ISSN 15571858. doi: 10.1007/s11483-010-9162-3.

Lakmali Samuditha K. Dassanayake, Dharma R. Kodali, S. Ueno, and K. Sato. Physical Properties of Rice Bran Wax in Bulk and Organogels. *Journal of the American Oil Chemists' Society*, 86(12):1163–1173, sep 2009. ISSN 0003-021X. doi: 10.1007/s11746-009-1464-6. URL `http://www.springerlink.com/index/10.1007/s11746-009-1464-6`.

JM DeMan and Leny DeMan. Texture of fats. In A.G.Marangoni and S.S.Narine, editors, *Physical Properties of Lipids*, chapter 7, pages 191–215. Marcel Dekker, New York, 2002. URL `http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Texture+of+Fats#1` `http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Texture+of+fats#8`.

Reza Farhoosh. The Effect of Operational Parameters of the Rancimat Method on the Determination of the Oxidative Stability Measures and Shelf-Life Prediction of Soybean Oil. *Journal of the American Oil Chemists' Society*, 84(3):205–209, jan 2007. ISSN 0003-021X. doi: 10.1007/s11746-006-1030-4. URL `http://link.springer.com/10.1007/s11746-006-1030-4`.

B Flaherty. Characterisation of waxes by differential scanning calorimetry. *Journal of Applied Chemistry and Biotechnology*, 21:144–148, 1971. ISSN 1935-0554. doi: 10.1002/jctb.5020210507. URL `http://dx.doi.org/10.1002/jctb.5020210507`.

L. Hartmann and R. C. Lago. Rapid preparation of fatty acid methyl esters from lipids. *Laboratory Practices*, 22(8):475–476, 1973.

C Himawan, V M Starov, and a G F Stapley. Thermodynamic and kinetic aspects of fat crystallization. *Advances in colloid and interface science*, 122(1-3):3–33, sep 2006. ISSN 0001-8686. doi: 10.1016/j.cis.2006.06.016. URL `http://www.ncbi.nlm.nih.gov/pubmed/16904622`.

Hong-Sik Hwang, Sanghoon Kim, Mukti Singh, Jill K. Winkler-Moser, and Sean X. Liu. Organogel Formation of Soybean Oil with Waxes. *Journal of the American Oil Chemists' Society*, 89(4):639–647, oct 2011. ISSN 0003-021X. doi: 10.1007/s11746-011-1953-2. URL `http://link.springer.com/10.1007/s11746-011-1953-2`.

Hong-Sik Hwang, Mukti Singh, Erica L. Bakota, Jill K. Winkler-Moser, Sanghoon Kim, and Sean X. Liu. Margarine from Organogels of Plant Wax and Soybean Oil. *Journal of the American Oil Chemists' Society*, 90(11):1705–1712, aug 2013. ISSN 0003-021X. doi: 10.1007/s11746-013-2315-z. URL `http://link.springer.com/10.1007/s11746-013-2315-z`.

Y. Jeong, M.K. Joo, Y.S. Sohn, and B. Jeong. Reverse Thermal Organogel. *Advanced Materials*, 19(22):3947–3950, nov 2007. ISSN 09359648. doi: 10.1002/adma.200700149. URL `http://doi.wiley.com/10.1002/adma.200700149`.

Dharma R. Kodali. Stabilization of Long Chain Polyunsaturated Oils, 2010.

M Lescanne, P Grondin, A D'Aléo, F Fages, J L Pozzo, O Mondain Monval, P Reinheimer, a Colin, A Ale, A D'Aléo, F Fages, J L Pozzo, O Mondain Monval, P Reinheimer, a Colin, and A Ale. Thixotropic organogels based on a simple N-hydroxyalkyl amide: rheological and aging properties. *Langmuir : the ACS journal of surfaces and colloids*, 20:3032–3041, 2004. ISSN 0743-7463. doi: 10.1021/la035219g.

F.R. Lupi, D. Gabriele, D. Facciolo, N. Baldino, L. Seta, and B. de Cindio. Effect of organogelator and fat source on rheological properties of olive oil-based organogels. *Food Research International*, 46(1):177–184, apr 2012. ISSN 09639969. doi: 10.1016/j.foodres.2011.11.029. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996911006739`.

Juan a. Morales-Rueda, Elena Dibildox-Alvarado, Miriam a. Charó-Alonso, and Jorge F. Toro-Vazquez. Rheological Properties of Candelilla Wax and Dotriacontane Organogels Measured with a True-Gap System. *Journal of the American Oil Chemists' Society*, 86(8):765–772, jun 2009a. ISSN 0003-021X. doi: 10.1007/s11746-009-1414-3. URL `http://www.springerlink.com/index/10.1007/s11746-009-1414-3`.

Juan a. Morales-Rueda, Elena Dibildox-Alvarado, Miriam a. Charó-Alonso, Richard G. Weiss, and Jorge F. Toro-Vazquez. Thermo-mechanical properties of candelilla wax and dotriacontane organogels in safflower oil. *European Journal of Lipid Science and Technology*, 111(2):207–215, feb 2009b. ISSN 14387697. doi: 10.1002/ejlt.200810174. URL `http://doi.wiley.com/10.1002/ejlt.200810174`.

S. S. Narine and A. G. Marangoni. Relating structure of fat crystal networks to mechanical properties : a review. *Food Research International*, 32, 1999.

S. S. Narine and A. G. Marangoni. Structure and mechanical properties of fat crystal networks. *Advances in food and nutrition research*, 44:33–145, 2002. URL `http://www.sciencedirect.com/science/article/pii/S104345260244003X`.

D. Paraskevopoulou, D. Boskou, and A. Paraskevopoulou. Oxidative stability of olive oil-lemon juice salad dressings stabilized with polysaccharides. *Food Chemistry*, 101(3):1197–1204, 2006. ISSN 03088146. doi: 10.1016/j.foodchem.2006.03.022.

Mimma Pernetti, K van Malssen, D Kalnin, and E Floter. Structuring edible oil with lecithin and sorbitan tri-stearate. *Food Hydrocolloids*, 21(5-6):855–861, jul 2007a. ISSN 0268005X. doi: 10.1016/j.foodhyd.2006.10.023. URL `http://linkinghub.elsevier.com/retrieve/pii/S0268005X06002499`.

Mimma Pernetti, Kees F. van Malssen, Eckhard Flöter, and Arjen Bot. Structuring of edible oils by alternatives to crystalline fat. *Current Opinion in Colloid & Interface Science*, 12(4-5):221–231, oct 2007b. ISSN 13590294. doi: 10.1016/j.cocis.2007.07.002. URL `http://linkinghub.elsevier.com/retrieve/pii/S1359029407000659`.

Julio Cesar Barbosa Rocha, Julice Dutra Lopes, Maria Cristina Nucci Mascarenhas, Daniel Barrera Arellano, Lizielle Maria Ricardo Guerreiro, and Rosiane Lopes da Cunha. Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil. *Food Research International*, 50(1):318–323, jan 2013. ISSN 09639969. doi: 10.1016/j.foodres.2012.10.043. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996912004541`.

Michael A. Rogers, Alexandra K. Smith, Amanda J. Wright, and A. G. Marangoni. A Novel Cryo-SEM Technique for Imaging Vegetable OilBased Organogels. *Journal of the American Oil Chemists' Society*, 84(10):899–906, sep 2007. ISSN 0003-021X. doi: 10.1007/s11746-007-1122-9. URL `http://www.springerlink.com/index/10.1007/s11746-007-1122-9`.

Michael A. Rogers, A Wright, and A. G. Marangoni. Crystalline stability of self-assembled fibrillar networks of 12-hydroxystearic acid in edible oils. *Food Research International*, 41 (10):1026–1034, dec 2008. ISSN 09639969. doi: 10.1016/j.foodres.2008.07.012. URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996908001427`.

James F. Steffe. *Rheological methods in food process engineering*, volume 23. Freeman Press, 2nd edition, 1996. ISBN 0-9632036-1-4. doi: 10.1016/0260-8774(94)90090-6. URL `http://linkinghub.elsevier.com/retrieve/pii/0260877494900906`.

D. Tang and A. G. Marangoni. Quantitative study on the microstructure of colloidal fat crystal networks and fractal dimensions. *Advances in colloid and interface science*, 128-130:257–65, dec 2006. ISSN 0001-8686. doi: 10.1016/j.cis.2006.11.019. URL `http://www.ncbi.nlm.nih.gov/pubmed/17217908`.

P. Terech, D. Pasquier, V. Bordas, and C. Rossat. Rheological Properties and Structural Correlations in

Molecular Organogels. *Langmuir*, 16(10):4485–4494, may 2000. ISSN 0743-7463. doi: 10.1021/la991545d. URL `http://pubs.acs.org/doi/abs/10.1021/la991545d`.

Jorge F. Toro-Vazquez, J. a. Morales-Rueda, E. Dibildox-Alvarado, M. Charó-Alonso, M. Alonzo-Macias, and M. M. González-Chávez. Thermal and Textural Properties of Organogels Developed by Candelilla Wax in Safflower Oil. *Journal of the American Oil Chemists' Society*, 84(11):989–1000, oct 2007. ISSN 0003-021X. doi: 10.1007/s11746-007-1139-0. URL `http://www.springerlink.com/index/10.1007/s11746-007-1139-0`.

Jorge F. Toro-Vazquez, Maritza Alonzo-Macias, Elena Dibildox-Alvarado, and Miriam a. Charó-Alonso. The Effect of Tripalmitin Crystallization on the Thermomechanical Properties of Candelilla Wax Organogels. *Food Biophysics*, 4(3):199–212, jun 2009. ISSN 1557-1858. doi: 10.1007/s11483-009-9118-7. URL `http://www.springerlink.com/index/10.1007/s11483-009-9118-7`.

Jorge F. Toro-Vazquez, Juan Morales-Rueda, Adriana Torres-Martinez, Miriam a Charo-Alonso, V Ajay Mallia, and Richard G Weiss. Cooling Rate Effects on the Microstructure, Solid Content, and Rheological Properties of Organogels of Amides Derived from Stearic and (R)-12-Hydroxystearic Acid in Vegetable Oil. *Langmuir : the ACS journal of surfaces and colloids*, may 2013. ISSN 1520-5827. doi: 10.1021/la400809a. URL `http://www.ncbi.nlm.nih.gov/pubmed/23697446`.

Thais Maria Ferreira de Souza Vieira and Daniel Barrera-Arellano. Patente Brasileira PI0205153-2 - Processo de obtenção de cera de torta de filtração de cana de açucar, 2002.

Rongyao Wang, Xiang-Yang Liu, Junying Xiong, and Jingliang Li. Real-time observation of fiber network formation in molecular organogel: supersaturation-dependent microstructure and its related rheological property. *The journal of physical chemistry. B*, 110(14):7275–80, apr 2006. ISSN 1520-6106. doi: 10.1021/jp054531r. URL `http://www.ncbi.nlm.nih.gov/pubmed/16599498`.

Emin Ylmaz and Mustafa Öütcü. Oleogels as spreadable fat and butter alternatives: sensory description and consumer perception. *RSC Adv.*, 5(62):50259–50267, 2015. ISSN 2046-2069. doi: 10.1039/C5RA06689A. URL `http://xlink.rsc.org/?DOI=C5RA06689A`.

Daniele C Zulim Botega, Alejandro G Marangoni, Alexandra K Smith, and H Douglas Goff. The potential application of rice bran wax oleogel to replace solid fat and enhance unsaturated fat content in ice cream. *Journal of food science*, 78(9):C1334–9, sep 2013. ISSN 1750-3841. doi: 10.1111/1750-3841.12175. URL `http://www.ncbi.nlm.nih.gov/pubmed/24024686`.

Addition of a low trans fat to a soybean oil waxy organogel system: general properties

Julio Cesar Barbosa Rocha, Kamila Ferreira Chaves, Daniel Barrera-Arellano.

Artigo a ser submetido para o periódico *Journal of Food Science and Technology.*

Addition of a low trans fat to a soybean oil waxy organogel system: general properties

Julio Cesar Barbosa Rocha[a,b], Kamila Ferreira Chaves[a], Daniel Barrera-Arellano[a]

[a]*Faculty of Food Engineering, Department of Food Technology, State University of Campinas, Campinas, SP, Brazil.*
[b]*Federal Institute of Education, Science and Technology of Sao Paulo, Brazil.*

Abstract

The search for the next step at the fat technology take us to the research of organogel technology, at the present moment a better understanding of the behavior of such materials is needed. At the present study vegetable waxes: candelilla (CLW), carnauba (CRW) and sugarcane (SCW), were used to form organogels using as lipid phase a mixture of soybean oil (SO) and low trans fat (LTF) at 95:5, 85:15 and 75:25 (SO:LTF), qualitative stability for 7 days were assessed, thermal analysis at DSC, SFC using NMR, cooling ramps were measured using rheology and also crystallization with shear was performed , microstructure was observed using PLM. The SO:LTF blends were not stable at environment temperature and the addition of waxes stabilized some of the samples during 7 days, thermal behavior was measured for 4% (w/w) and showed that the increase on the amount of LTF increased the enthalpy variation needed for melting, but no change on the organogelation ΔH was observed, the SFC changed with the use of the LTF at the organogels the samples showed an increase on the SFC measurements, that ranged from 22 up to 50% for different waxes. Rheology showed that the use of LTF increased G' and G" for all samples and frequency sweep showed that the inclusion of 5% of LTF, for CLW organogels did not change the behavior for none LTF concentration, but CRW and SCW organogels suffered a modification of the gel like behavior making them frequency dependent with LTF at 15 and 25%. Microscopy showed how the materials changed with the increase of amount of crystals, decrease of crystal sizes and the organization of the microstructure as LTF amounts increase. The addition of LTF should be a possibility to increase the applications for organogels at food products.

Keywords: waxy organogels, soybean oil, candelilla wax, carnauba wax, sugarcane wax, commercial fat

---

Email addresses: `julio.fea@gmail.com` (Julio Cesar Barbosa Rocha), `daniel@fea.unicamp.br` (Daniel Barrera-Arellano)

Preprint submitted to Journal of Food Science and Technology *January 26, 2017*

1. Introduction

Organogels are viscoelastic materials made of an organogelator (structurant) and a continuous liquid phase. They are semi-solid systems, where a lipid phase is immobilized by a tridimentional self-sustaining network [1], the size and shape of the structure is directly related to the material physical behavior [2] interaction with the continuous phase. Several components can form organogels and include hydroxilated fatty acids, fatty acids, fatty alcohols, mixtures of fatty acids and fatty alcohols, mixtures of phytoesterols and oryzanols, sorbitan monostearate, waxes and mixtures of lecithin with sorbitan tristearate [3]. One of the most relevant characteristics which make organogels interesting is its potential to improve the physical behavior of an industrialized product, without increasing the amount of saturated fatty acids nor trans fatty acids, making it possible to develop products low sat keeping its sensory characteristics of texture and flavor [4].

The use of vegetable waxes to form organogels is technically viable and there are several studies evaluating their stability and ideal conditions to form them. Most commonly studied waxes are candelilla (CLW) [5], ricebran wax and carnauba (CRW) [1], sunflower wax [6] and sugarcane wax (SCW) [7].

The use of saturated fats are not commonly studied and its interaction with organogels is relevant once organogels produced only with liquid oils have limited application potential. The effect of the inclusion of saturated triacylglycerol (TAG) was studied [8, 9, 10] and it was possible to observe that TAG composition impacts the behavior of organogel strucutration. Fats structured by TAG had a unique behavior that is the target for organogel based fats.

At the present moment pure organogels had been studied as theoretical models and possible replacement for fats, but they are usually softer than fats and its thixotropic behavior [11, 12] is usually hard to be adapted to industrial processes. The behavior under shearing is being studied [8, 13], once the structure recover after shearing is slow. The effect of constant shear at organogels during crystallization showed an impact reducing material hardness [14], but the behavior changed as the shear stops before the organogelation resulting at organogel of higher quality [8].

At the present moment the use of fats added to organogels is not completed evaluated but some studies were performed [15, 16, 10], the main effect of the modification of continuous phase have not been yet explained the physical interaction among the materials due to polarity of samples is at the moment an acceptable explanation [17].

The application of organogels at fat based products, such as ice-cream [18], margarines [16] and spreadable fat [19] is being studied, it is possible to say that the development of organogel based products is advancing but there is still a lot of work to be developed.

At the present study, the objective is to evaluate the interactions among the vegetable waxes candelilla (CLW), carnauba (CRW) and sugarcane (SCW), with soybean oil:low trans fat (SO:LTF) blends, and how it should modify the stability, thermal behavior, SFC rheology, crystallization and microstructure of obtained organogels.

2. Materials and Methods

2.1. Materials

To the present study the following materials were used: sugarcane wax (Usina Sao Francisco, Brazil), candelilla wax (Multiceras, Mexico), carnauba wax (Pontes Industria de Ceras, Brazil), soybean oil (ADM, Brazil) and low trans vegetable fat LTF (Triangulo Alimentos, Brazil). Fatty acid composition for SO was C16:0 (12%), C18:0 (4%), C18:1 (19%), C18:2 (59%), C18:3 (7%) and LTF was C16:0 (39%), C18:0 (13%), C18:1 (25%), C18:1t (1%), C18:2 (20%), C18:3 (1%) and was determined by GC analysis on an Agilent 6850 GC (Palo Alto, CA, USA) with a DB-23 Agilent (50% cyanopropyl - methylpolysiloxane, length 60m, int. diameter: 0.25mm, 0.25μm thick film). Esterification according to Hartmann & Lago [20] and quantification according to AOCS Ce 1-62 [21].

2.2. Experimental procedure

2.2.1. Organogel preparation

All samples were prepared according to the following protocol: soybean oil was heated until 80°C under constant agitation, a solid wax and LTF was then added. The system was mixed until complete dissolution, after that the material was agitated for more 3 minutes to assure complete homogeneity. The samples were then cooled to a controlled temperature for 24 hour for gelation.

Organogel samples were formulated with: waxes sugarcane, carnauba and candelilla; wax concentration 1, 2, 3 and 4% (w/w); SO:LTF Ratio 95:5, 85:15 and 75:25 (w:w).

2.3. Methods

2.3.1. Organogel Visual Stability

Samples were visually assessed to its stability at 25°C for 7 days, to observe phase separation or oil exudation. A tilt test were performed according to Rocha et al.[7] to evaluate the formation of self-sustaining organogels.

2.3.2. Thermal behavior

The crystallization and melting curves were determined by DSC using a Q2000 (TA Instruments, USA), according to method AOCS Cj 1-94 (AOCS, 2004), with modifications, using a ramp of 10°C/min for melting and crystallization and a range of -40 to 80°C [7]. Heat capacity was calibrated using sapphire and heat flow using indium.

All thermograms were normalized based on the sample mass and evaluated using Universal Analisys software (TA Instruments, USA), to determine peak temperature (T_{Peak}), initial temperature (T_{Onset}) and final temperature (T_{Endset}) for melting and crystallization, the enthalpy variation were also measured. All temperatures were measured as °C and enthalpies as J/g. The measurements were performed as triplicates.

2.3.3. Solid fat content (SFC)

The organogel SFC was determined using a Bruker Minispeq Mq20 (Bruker- Optics, Inc., USA) nuclear magnetic resonance (NMR) according to method AOCS 16b-93 [21]. The samples were measured at the temperatures of 0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50°C, as triplicates, with an initial tempering (70°C for 1 hour and 0°C for 1 hour) and intervals of 30 minutes for temperature equilibrium and stabilization of crystalline forms. The measurements were performed as triplicates.

2.3.4. Organogels formation under controlled shear and temperature

A Physica MCR 301 (Anton Paar, Austria) rheometer was used with a sandblasted rough plate geometry of 5 cm wide, with a roughness of 5-7μm, with a gap of 200μm for organogel samples at 4% (w/w). Temperature was controlled using a Peltier system. A cooling sweep were performed between 90 to 15°C at 10°C/min using a fixed frequency of 1 Hz to evaluate the gel formation process as static crystallization, for sheared crystallization a constant shear of 300s-1 was used from 90 to 60°C and than a static crystallization was performed using a fixed frequency of 1 Hz as static crystallization analysis. Changes at storage (G) and loss (G) as a function of temperature were evaluated. After gel formation frequency sweeps were done from 0.1 to 10 Hz with 1% deformation at 15°C for all samples. All measurements were performed within the linear viscoelasticity domain. All analysis were performed as triplicates. The value of 300s-1 was used to represent a stirring or pipe flowing process, ranging from 100 up to $10^3 s^{-1}$ according to [22].

2.4. Polarized light microscopy (PLM)

Organogel morphology was evaluated using a Olympus BX-53 (Olympus, Japan), with a DP-73 camera (Olympus, Japan), using a controlled temperature Linkam PE120 system (Linkam, UK). All samples were melted at 80°C and put over a glass slide and covered with a glass coverslip. The set (slide + coverslip) was heated over a heating plate and crystallized at controlled temperature (5 and 25°C), according to Rocha et al.[7].

A fractal dimension analysis using Image J software 1.50i (National Institutes of Health, USA) were performed to measure the fractal dimension (D) using polarized light micrographs as described by Narine and Marangoni [23].

2.5. Statistical Analysis

The obtained results were evaluated by Tukey test using STATISTICA 7.0 software (Statisoft Inc., USA).

3. Results and Discussion

3.1. Organogel Stability

All prepared organogel samples were kept under controlled temperature for 7 days and visually assessed to check for a qualitative stability. The samples kept under 5°C for 7 days presented good stability, showing no phase separation during the evaluated period, but at

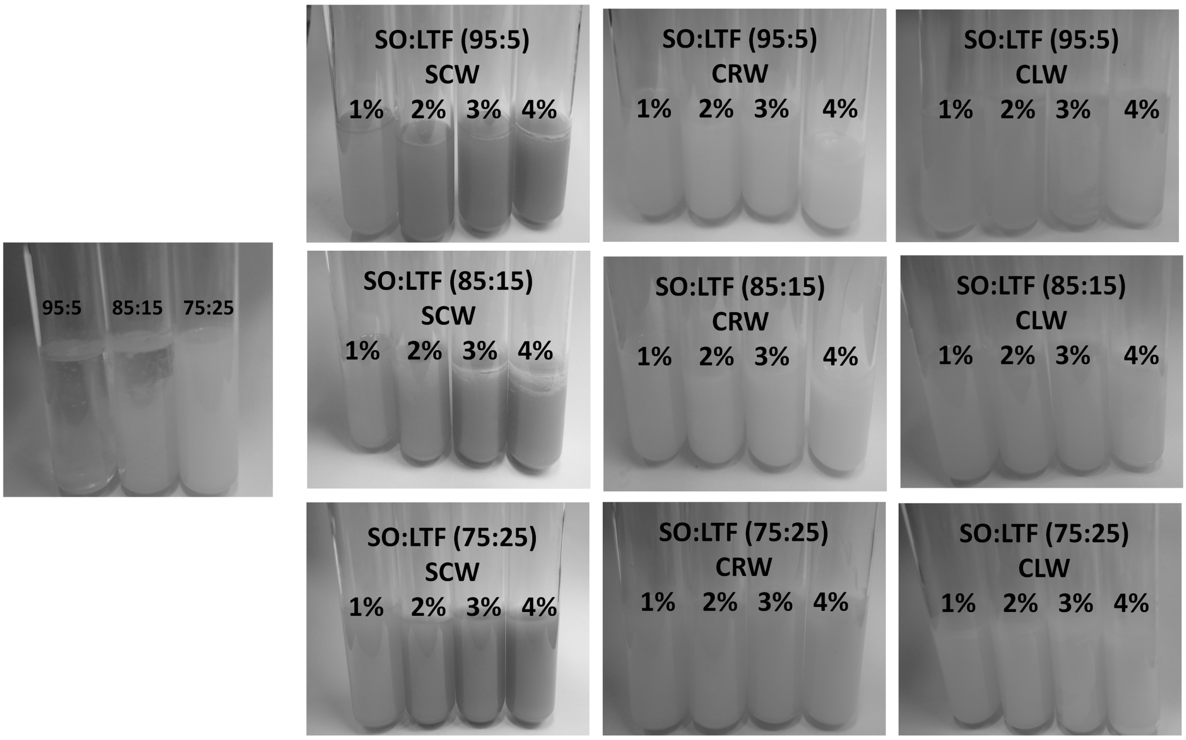

Figure 1: Wax organogels at different SO:LTF ratios and wax concentrations after 7 days at 25°C.

25°C after 7 days the samples without waxes (mixtures of SO and LTF), presented phase separation at the levels of 5 and 15%, as presented at Figure 1.

Organogel samples prepared with CLW presented a good stability at all concentrations, with no phase separation during the studied period, the samples obtained with CRW presented a different behavior, at lower concentrations (1 and 2% w/w), CRW was not able to stabilize the SO:LTF mixtures, but at 3 and 4% it was possible to observe no phase separation after 7 days, SCW organogels presented a behavior similar to CRW organogels, being not able to stabilize SO:LTF at all concentrations, but at 2% (w/w) it was able to maintain a unique phase for all SO:LTF mixtures and at the higher LTF concentration at the lipid phase at 1% (w/w) the material also kept an unique phase. The observed stability allow to say that organogelation improved the stability of SO:LTF mixtures.

3.2. Organogels thermal behavior

Once the samples present small amounts of organogelator (1 to 4% w/w), the thermal behavior could only be measured for the samples with higher concentrations (4% w/w) as presented at Table 1. No peak resolution was achieved using lower concentrations of waxes.

Comparing the values obtained for the thermal parameters it is possible to observe that the first observed peak (Peak 1)during crystallization as shown on Table 1 presented values for T_{Onset} that were not different from those observed at literature for CLW and SCW organogels [7, 5] with statistical differences among the T_{Onset}, $T_{Endnset}$ and ΔH for samples of different wax organogels. The first peak is the gellation peak, so it did not suffered no

Table 1: Thermal parameters of Soybean oil:low trans fat structured with vegetable waxes (4% w/w).[1]

		Cristallization			Melting		
Wax Type (SO:LTF) Ratio	Peak No.	T_{Onset} (°C)	T_{Endset} (°C)	ΔH (J/g)	T_{Onset} (°C)	T_{Endset} (°C)	ΔH (J/g)
SCW (95:5)	1	42.87^{d}	26.41^{e}	0.78^{h}	11.67^{i}	16.90^{j}	0.15^{j}
SCW (95:5)	2	8.40^{i}	-4.95^{k}	0.60^{h}	16.93^{h}	28.31^{g}	$0.49^{h,i,j}$
SCW (85:15)	1	45.22^{b}	30.34^{c}	$1.24^{e,f}$	-1.16^{h}	$18.29^{h,i}$	4.60^{c}
SCW (85:15)	2	18.04^{g}	3.24^{h}	$1.71^{e,f}$	$24.83^{d,e}$	36.83^{e}	$1.14^{f,g,h,i}$
SCW (75:25)	1	44.17^{c}	28.23^{d}	$1.18^{e,f,g}$	-5.79^{l}	18.74^{h}	4.58^{c}
SCW (75:25)	2	20.80^{f}	0.57^{i}	3.47^{c}	26.53^{c}	$40.00^{c,d}$	$1.88^{e,f}$
CRW (95:5)	1	58.32^{a}	$38.28^{a,b}$	5.53^{a}	10.87^{i}	17.05^{j}	0.18^{j}
CRW (95:5)	2	8.71^{i}	-4.87^{k}	0.58^{h}	17.02^{h}	28.48^{g}	$0.47^{h,i,j}$
CRW (85:15)	1	58.13^{a}	36.81^{b}	5.33^{a}	-1.52^{j}	17.18^{j}	$5.07^{b,c}$
CRW (85:15)	2	$17.36^{g,h}$	-1.80^{j}	2.52^{d}	23.75^{f}	37.27^{e}	$1.22^{f,g,h}$
CRW (75:25)	1	58.45^{a}	38.86^{a}	5.55^{a}	-6.70^{l}	18.58^{h}	$4.88^{b,c}$
CRW (75:25)	2	21.67^{e}	$1.94^{h,i}$	4.64^{b}	26.56^{c}	40.50^{c}	$2.54^{d,e}$
CLW (95:5)	1	43.79^{c}	$20.80^{f,g}$	4.6^{b}	11.86^{i}	19.05^{h}	0.31^{j}
CLW (95:5)	2	8.68^{i}	-5.2^{k}	$0.63^{g,h}$	19.02^{g}	29.84^{f}	$0.36^{i,j}$
CLW (95:5)	3				35.75^{b}	52.39^{a}	$1.34^{f,g}$
CLW (85:15)	1	$43.64^{d,c}$	19.17^{g}	4.67^{b}	-2.93^{k}	17.55^{j}	5.97^{a}
CLW (85:15)	2	$16.87^{g,h}$	-1.93^{j}	2.43^{d}	$24.24^{e,f}$	36.51^{e}	1.40^{f}
CLW (75:25)	1	43.83^{c}	21.31^{f}	4.69^{b}	-6.33^{l}	16.80^{j}	$5.49^{a,b}$
CLW (75:25)	2	20.56^{f}	0.50^{i}	4.33^{b}	$27.70^{c,d}$	39.16^{d}	2.89^{d}
CLW (75:25)	3				40.98^{a}	48.50^{b}	$0.58^{g,h,i,j}$

[1] Same letter at same column mean no statistical difference ($p>0.05$).

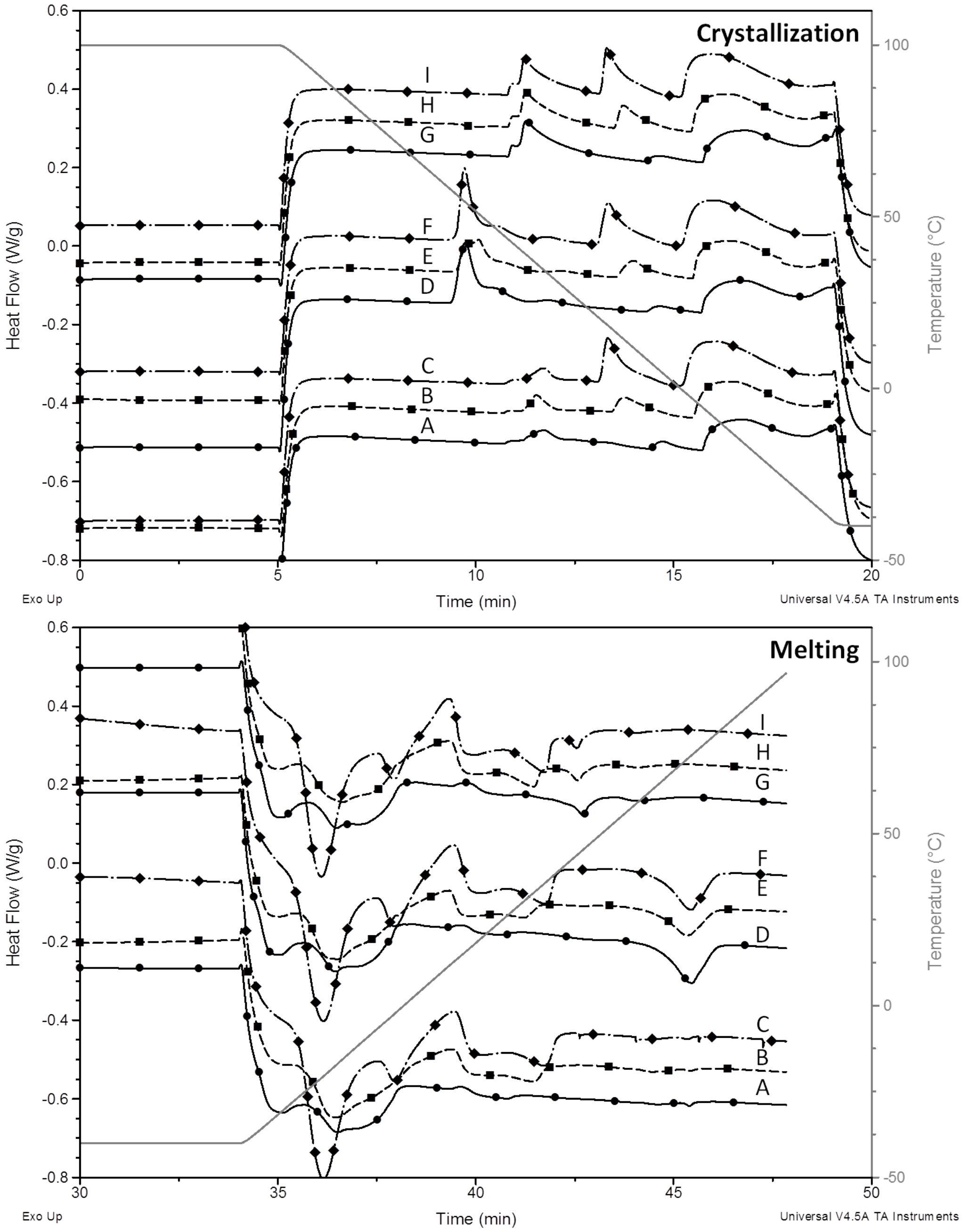

Figure 2: Thermograms for 4% (w/w) wax organogels at different SO:LTF ratios. (A) SCW 95:5, (B) SCW 85:15, (C) SCW 75:25; (D) CRW 95:5, (E) CRW 85:15, (F) CRW 75:25; (G) CLW 95:5, (H) CLW 85:15, (I) CLW 75:25. Top: Crystallization; Bottom: Melting. Temperature as grey line.

change of ΔH with the addition of LTF. The second crystallization peak (Peak 2) presented an increase of ΔH with the increase of the amount of LTF so it is the crystallization peak of that material, it is interesting to note that for the second peak no statistical differences was observed among the samples of 95:5 (SO:LTF) and different waxes, for all observed parameters, for the ratio 85:15 (SO:LTF) the observed T_{Onsed} was the same for all waxes but the same was not observed for T_{Endset}, with SCW presenting a narrower peak and lower ΔH, but those values presented no statistical difference for CRW and CLW organogel using 85:15 (SO:LTF) as continuous phase. For the higher concentration 75:25 (SO:LTF) no statistical difference was observed for T_{Onset} for CLW and SCW organogels, while for T_{Endset} the values were considered with no statistical difference, for ΔH, CRW and CLW also presented no statistical difference.

The melting, the behavior observed that the samples were similar, with the first peak (Peak 1) being the melting of the continuous phase and all three wax organogels at 95:5 (SO:LTF) presented values for T_{Onset}, T_{Endset} and ΔH that were statistically equivalent showing that such peak is related to the TAG phase and not the gel breakage. Considering the samples with 85:15 (SO:LTF) ratio, the values for T_{Onset}, T_{Endset} e ΔH were not statistically equivalent even though the values were indeed close. For 75:25 (SO:LTF) samples the values for T_{Onset} and ΔH were statistically equivalent for all waxes, only T_{Endset} presented similar values for SCW and CRW with a small diference for CLW organogels. The second peak (Peak 2) was observed at all samples and SO:LTF ratios. The samples with 95:5 (SO:LTF) presented similar values with SCW and CRW presenting no statistical difference for all thermal parameters, CLW organogel at the same ratio presented a slightly different value for T_{Onset} and T_{Endset} but similar value for ΔH. The second peak for 85:15 (SO:LTF) were presented no difference among the samples for all thermal parameters, the same behavior was observed for 75:25 (SO:LTF) samples but with SCW similar to CRW that was similar to CLW.

The presence of hysteresis has already been reported at literature [7] and it is usually realated to fusion and recrystallization of organogelator as described by Abdallah et al. [24].

Organogels from CRW presented a peak at temperatures higher than 60°C that were not discussed at the table, once it is only related to melting of CRW and not organogelation events. The peak can be seen at thermograms (Figure 2).

The sampes of same SO:LTF ratio presented same peaks at temperatures bellow 45°C showing that the organogel is formed and than the saturated TAG from LTF crystallizes, the values for ΔH presented at Table 1 also showed this behavior, but the peak shape is a characteristic of a chemical component [25], making the two information a evidence that those peaks are indeed the crystallization of saturated TAG.

3.3. Organogels solid fat content (SFC)

A NMR analysis of the organogel samples, allowed measuring the solid fraction of each sample during melting, from 0 to 50°C (considered as higher temperature once no sample presented peaks above this temperature at DSC during melting).

At Figure 3, the SFC for all organogels are presented. The increase on the amount of fat increased the SFC for the samples, as expected. Although an increase was expected, the observed value was higher than the expected, considering that all added wax will be completed solid, and measured as it. The effect was better observed at lower temperatures (0 and 10°C) and higher amounts of LTF (15 and 25% w/w). The behavior can be clearly

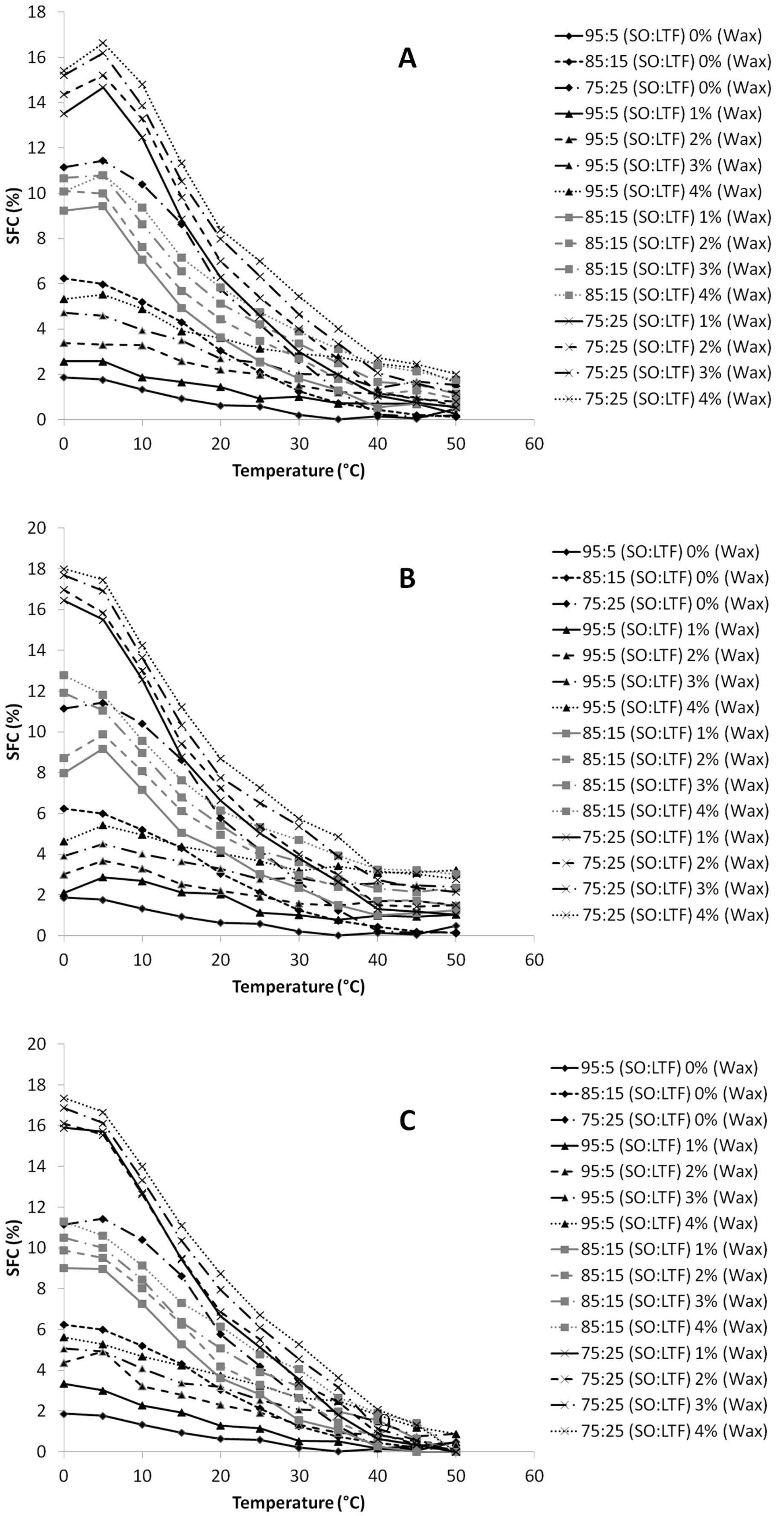

Figure 3: SFC profiles for 4% (A) SCW, (B) CRW and (C) CLW organogels.

observed for the sample with CLW 1% (w/w) and SO:LTF 75:25 (w:w) (Figure 3C) comparing with SO:LTF 75:25 (w:w) with no wax added (same SO:LTF ratio and addition of 1% w/w of CLW), the initial SFC content jumped from 11% to almost 16%, a change of 5 percentage points or 45% of the SFC, such behavior is way different of the expected increase of 1 percentage point as 1% w/w of solid was added.

The Figure 3B shows SFC for CRW organogels, and they present a similar behavior as observed for CLW organogels, including the increase of the SFC higher than the added solids for CRW samples, the higher increment was measured as 5.4 percentage points or 50%, from 11 to 16.5% for the sample with CRW 1% (w/w) and SO:LTF 75:25 compared with the same sample with no wax added.

At Figure 3A presentd the results obtained for SCW organogels and again the behavior is repeated, although with a smaller impact, for these samples the increase achieved 2.4 percentage points or 22%, from 11 to 13.4% for the sample with SCW 1% (w/w) and SO:LTF 75:25 compared with the same sample with no wax added, the results was similar to the other waxes.

The observed behavior was consistent for all samples, especially for the samples with higher amounts of LTF (higher amounts of saturated TAGs), showing that there is an interaction of the organogelator with the lipid continuous phase as reported by Abdallah [26]. The NMR analysis was previously used at the literature for oil and wax organogels [8, 5], at the studies the authors verified a reduction of the SFC due to the presence of a soluble fraction of the organogelator (the study used only CLW). The effect of the increase on the SFC was described by Toro-Vazquez [10], where the addition of 1% of tripalmitin on a 3% CLW organogel resulted on an increase of 1.5 percentage points for SFC at -5°C, although it presented a reduced effect and needed a lower temperature, the change of SFC was also observed.

3.4. Rheological measurements

Studied organogels were assessed to its rheological behavior. At Figure 4 the cooling ramps and frequency sweeps are presented using static crystallization. The cooling ramps showed that organogelation started for CLW organogels at temperatures similar for all LTF concentrations, similar to observed at DSC, the measured G' were similar to all LTF concentrations at 15°C, the frequency sweep showed that the material even with the higher addition of LTF kept the gel like behavior presenting G' higher than G" [22] and no frequency dependency.

The same observation for the organogels of CRW and SCW showed that although the increase of LTF resulted at a higher G' and G", as observed to CLW the organogelation temperature did not change, but the frequency sweep showed that the materials continued with a gel like bahvior (G' higher than G"), but it became frequency dependent. The frequency sweeps showed that for organogels of CLW, CRW and SCW the add of LTF produced an increase of G', such behavior is associated to a more plastic behavior [22]. The inclusion of LTF at the organogel system made CRW and SCW organogels became more sensitive to frequency variation, the change was not visible for 95:5 (SO:LTF) samples but for higher amounts of LTF (85:15 and 75:25) it was observed, it was also possible to

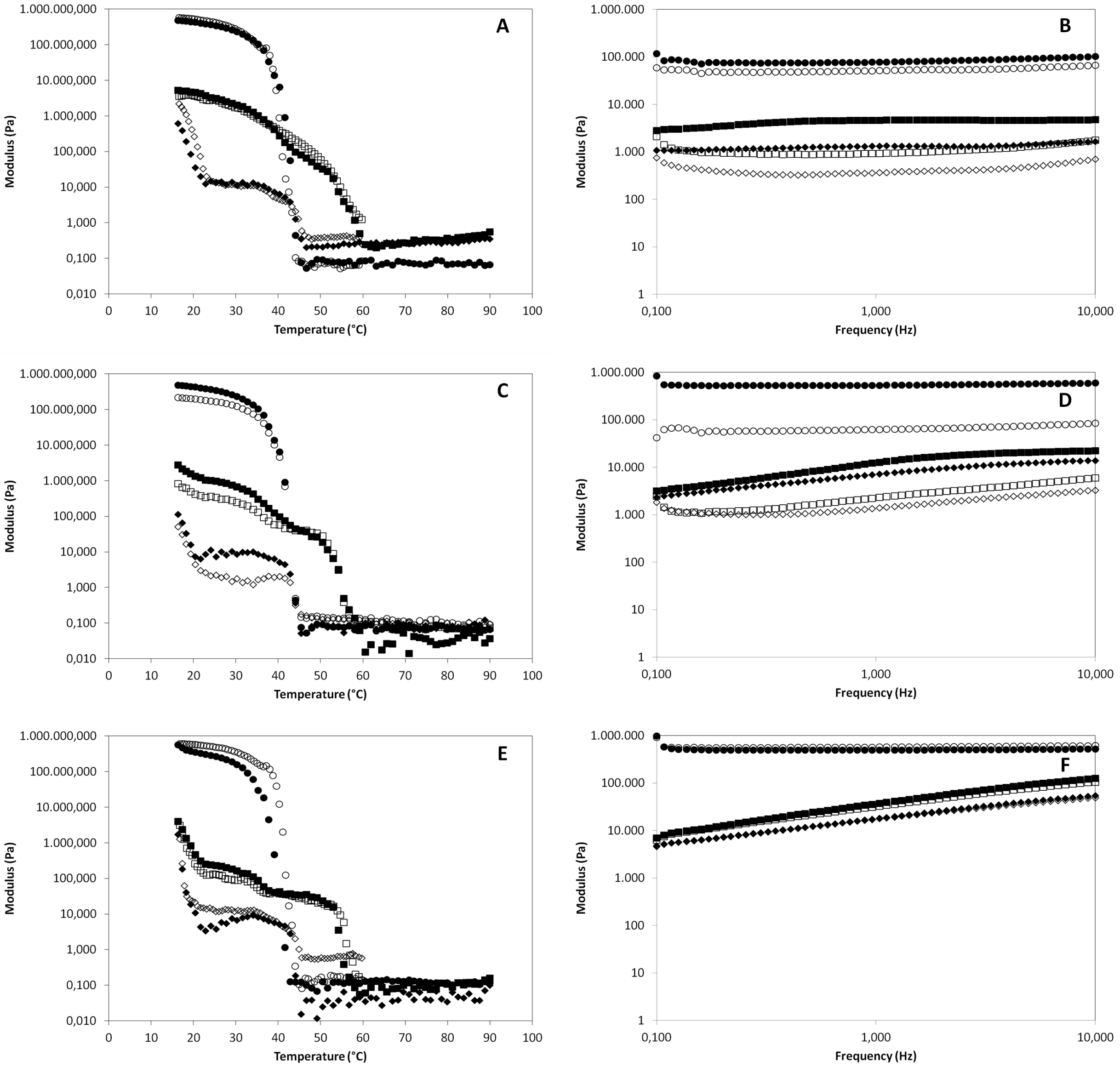

Figure 4: Rheology of static crystallized 4% (w/w) organogels ♦: SCW; •: CLW, ■: CRW; full symbols- G; empty symbols- G; (A) 95:5, (C) 85:15 and (E) 75:25 (SO:LTF) Cooling ramp 10°C/min; (B) 95:5, (D) 85:15 and (F) 75:25 (SO:LTF) Frequency sweeps.

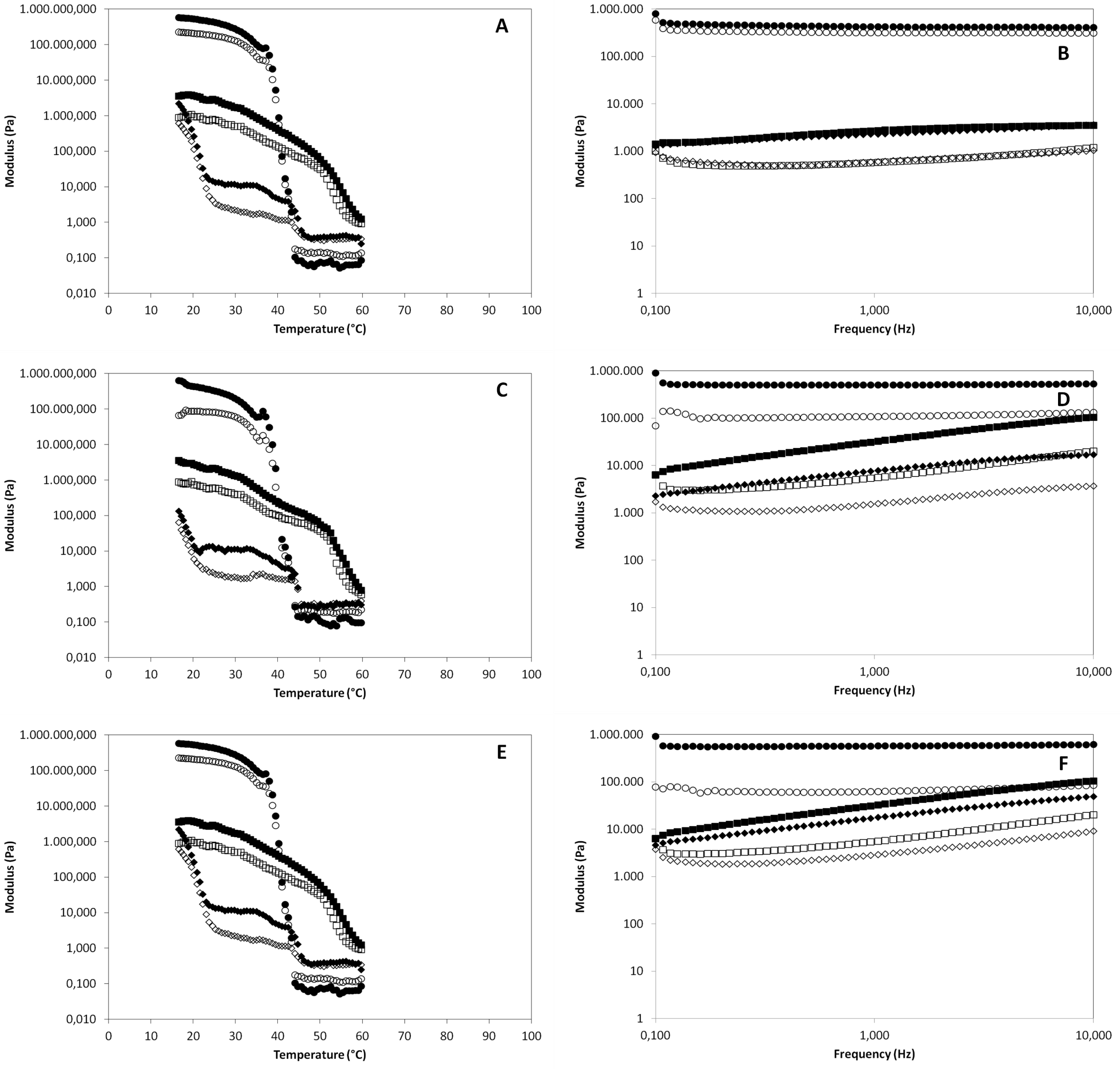

Figure 5: Rheology of sheared ($300s^{-1}$) 4% (w/w) organogels ♦: SCW; •: CLW, ■: CRW; full symbols- G; empty symbols- G; (A) 95:5, (C) 85:15 and (E) 75:25 (SO:LTF) Cooling ramp 10°C/min; (B) 95:5, (D) 85:15 and (F) 75:25 (SO:LTF) Frequency sweeps.

observe that the phase lag (δ) for all samples kept almost the same for all frequencies, the maintenance a constant δ makes the affirmative that the materials behave like gels stronger, once the moduli are increasing with the frequency there should be the possibility of the material behave like a mixture and at some moment G" became higher than G' [22]. The observation of the rheology makes it possible to say that the inclusion of different fats and oils in an organogel system can modify its rheological behavior specially due to interactions within the organogelator and the continuous phase as observed by Hwang et al.[17].

Sheared organogels as shown at Figure 5 presented a similar behavior as observed for static crystallized organogels. The results allow to conclude that at the shear rates of 300s^{-1}, the obtained organogels presented a similar behavior, meaning that shear at temperatures above 60°C did not modified the material. It is interesting to note that some increase of G' and G" was observed at temperatures above the organogelation temperature, but no difference was measured after complete gelation at 15°C. The results are similar to observed by Alvarez-Mitre et al. [8], where the use of shear at temperature above the organogelation did not cause a decrease of G' nor G".

3.5. Organogels microstructure using polarized light microscopy

Samples obtained with 4% (w/w) wax, were evaluated at 25°C to its structure using PLM. At Figure 6 the samples without waxes (SO and LTF mixtures) are shown, and it is possible to observe that with the increase on the amount of LTF the presence of fatty crystals were modified, for these samples the number and the size of the crystals were increased.

At the first line (identified as A, D, G and J), are presented samples A without wax, D CLW, G CRW and J SCW, all with SO:LTF ratio of 95:5 (w/w), it is possible to observe that CRW and SCW changed the organization of the material. Although it presented a better stability CLW did not present a good organization, being possible to observe LTF crystals outside of the network.

The samples with 85:15, SO:LTF ratio, presented at the second line (B, E, H and K), show much improved organization, being possible to observe an reduction of the crystal sizes comparing the first column (B) with the wax organogels (E, H and K) and also organization of such crystals as a network, the size of the crystals is usually related to the material firmness being a smaller crystal more resistant than a larger crystals (Hwang, Kim, Singh, Winkler-Moser, Liu, 2011) The same behavior was observed for the samples with 75:25, SO:LTF ratio, with the increase on the amount of wax, the crystal sizes decreased shown at Figure 6 (F, I and L), compared with the sample without wax (C), and again the size reduction is observed.

For a better comparison, crystals were measured using the micrographs just for 4% (w/w) organogels and 75:25 (SO:LTF); for CLW organogels a larger magnification (40x) was used and they measured as close to 3-5 μm needle like crystals and the initial material Figure 6C presented crystals ranging from 50 to 100 μm and different shapes (spherulites). For CRW samples, it was observed the change on crystal shape (from spherulites to organized needles) although it does no suffered a great size reduction (20-30 μm), for SCW organogel the crystals kept a similar shape as initial mixture (spherulites), but in much smaller size

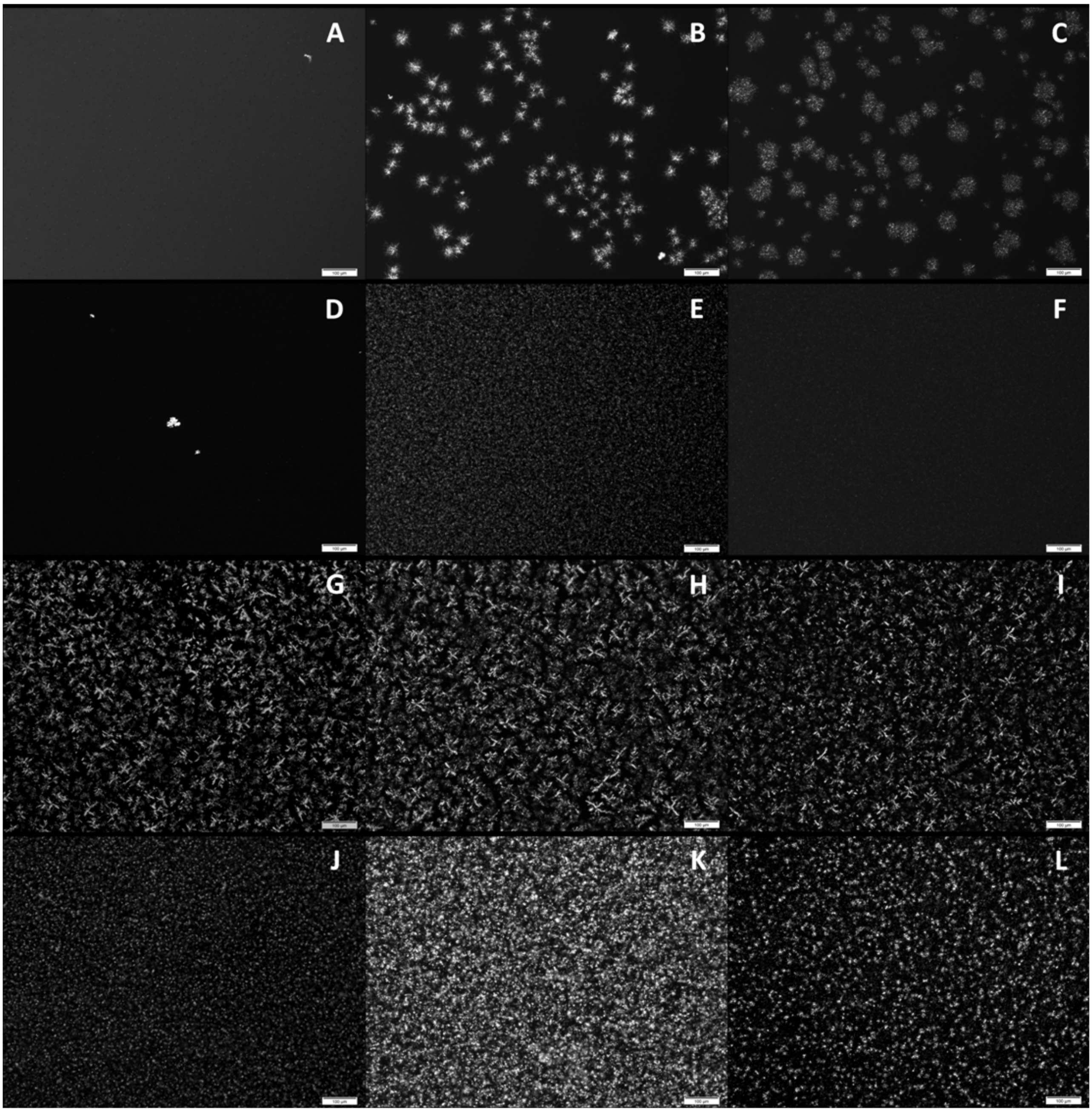

Figure 6: PLM of soybean oil:low trans fat:wax organogels (SO:LTF:Wax); (A) 95:5:0; (B) 85:15:0; (C) 75:25:0; (D) 95:5:4 (CLW); (E) 85:15:4 (CLW); (F) 75:25:4 (CLW); (G) 95:5:4 (CRW); (H) 85:15:4 (CRW); (I) 75:25:4 (CRW); (J) 95:5:4 (SCW); (K) 85:15:4 (SCW); (L) 75:25:4 (SCW);. Scale bar 100 μm.

(10-15 μm). The observed micrographs are coherent with observed at literature for these waxes [27, 28, 29, 30, 7, 5].

Fractal dimension measurements are presented at Table 2 and allow to observe that SO:LTF mixtures presented values that increased with 15% LTF and decreased with 25% LTF, such result is related to the crystal size and density the 25% LTF reduced crystal sizes but increased crystal density.

Table 2: Fractal dimension of wax organogels at 4% (w/w).[1]

SO:LTF	Waxes	D
95:5	no wax	0.74^d
85:15	no wax	1.55^b
75:25	no wax	1.30^b
95:5	4% CLW	0.72^d
85:15	4% CLW	1.27^c
75:25	4% CLW	1.82^a
95:5	4% CRW	1.34^c
85:15	4% CRW	1.32^c
75:25	4% CRW	1.24^c
95:5	4% SCW	1.22^c
85:15	4% SCW	1.50^b
75:25	4% SCW	1.35^d

[1] Same letter at same column mean no statistical difference (p>0.05).

The corelation of fractal dimension and macroscopic properties had been studied for some time, Narine and Marangoni [31] cited that there is a direct correlation to a higher D value and higher G', and it is possible to observe that the samples such as CLW 75:25 presented higher values and also the highest G' as measured using rheometry. Also the correlation is not direct once it depends of other factor such as the mass of the microstructure and the radius of the crystals, so even with similar D, CLW, SCW and CRW organogels did not present the same rheological behavior. Campos [25], used G' and the volume fraction (ϕ) as variables to calculate D, meaning that a similar fractal dimension will result at the same rheological properties.

Statistical analysis showed that CLW (75:25) organogel presented the highest value for D and that CLW (95:5) presented a similar value to the sample with no wax, at Figure 6 it is possible to observe the presence of a fat crystal separated from the network. All CRW samples, CLW (85:15), SCW (95:5) and SO:LTF (75:25) mixture with no wax added presented no statistical differences, the measured value for SCW (85:15) and the same mixture with no wax added also presented no statistical difference.

The addition of LTF changed the crystallization behavior of the organogels, suggesting an great relevance of the chemical interaction among organogelator and the continuous phase [32] making it clear that organogels are much more complex systems than just a fat blend. Also the amount of polar compounds as evaluated by Hwang et al. [17] showed that the physical and chemical interactions of continuous phase and structurant are much more relevant for rheological properties than previously expected.

4. Conclusions

The use of waxes stabilized mixtures of SO and LTF, the pure mixture of the components resulted at phase separation and the inclusion of waxes increased stability. The thermal behavior for organogelation suffered no modification with the use of LTF keeping organogelation temperature and H for all samples, for melting the H increased with the inclusion of LTF, making it possible to say that it increased thermal stability. The measurement of SFC showed that the use of waxes increased the SFC as expected, but with values that were higher than the added amount of solids from LTF and the respective wax. The rheological measurements showed that for all materials the rheological modification happened at the same temperature as thermal phenomena at DSC, the increase of the amount of LTF did not modified organogelation temperature and also the use of shear at temperatures above of the organogelation resulted at similar behavior compared with statically crystallized gels meaning that shear can be used with organogelated products. The microstructure allowed to see how the use of LTF changed the microstructure changing crystal sizes and distribution. These results suggest that the use of SO organogels added of LTF can improve the food application for such products, making it possible to use it at a wider range of products, even with the use of shear.

5. Acknowledgements

The authors thank Fundacao de Amparo a Pesquisa do Estado de Sao Paulo (FAPESP Process 2011-13591-1) for the funding of the present research and CNPq for Rocha, J. C. B. scholarship. The authors have declared no conflict of interest.

References

[1] L. S. K. Dassanayake, D. R. Kodali, S. Ueno, K. Sato, Physical Properties of Rice Bran Wax in Bulk and Organogels, Journal of the American Oil Chemists' Society 86 (12) (2009) 1163–1173. doi:10.1007/s11746-009-1464-6.
URL `http://www.springerlink.com/index/10.1007/s11746-009-1464-6`

[2] M. Pernetti, K. F. van Malssen, E. Flöter, A. Bot, Structuring of edible oils by alternatives to crystalline fat, Current Opinion in Colloid & Interface Science 12 (4-5) (2007) 221–231. doi:10.1016/j.cocis.2007.07.002.
URL `http://linkinghub.elsevier.com/retrieve/pii/S1359029407000659`

[3] M. A. Rogers, Novel structuring strategies for unsaturated fats Meeting the zero-trans, zero-saturated fat challenge: A review, Food Research International 42 (7) (2009) 747–753. doi:10.1016/j.foodres.2009.02.024.
URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996909000623`

[4] M. A. Rogers, A. J. Wright, A. G. Marangoni, Oil organogels: the fat of the future?, Soft Matter 5 (8) (2009) 1594. doi:10.1039/b822008p.
URL `http://xlink.rsc.org/?DOI=b822008p`

[5] J. F. Toro-Vazquez, J. a. Morales-Rueda, E. Dibildox-Alvarado, M. Charó-Alonso, M. Alonzo-Macias, M. M. González-Chávez, Thermal and Textural Properties of Organogels Developed by Candelilla Wax in Safflower Oil, Journal of the American Oil Chemists' Society 84 (11) (2007) 989–1000. doi:10.1007/s11746-007-1139-0.
URL `http://www.springerlink.com/index/10.1007/s11746-007-1139-0`

[6] E. Yilmaz, M. Ögütcü, Properties and Stability of Hazelnut Oil Organogels with Beeswax and Monoglyceride, Journal of the American Oil Chemists' Society 91 (6) (2014) 1007–1017. doi:10.1007/s11746-014-2434-1.
URL `http://link.springer.com/10.1007/s11746-014-2434-1`

[7] J. C. B. Rocha, J. D. Lopes, M. C. N. Mascarenhas, D. B. Arellano, L. M. R. Guerreiro, R. L. da Cunha, Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil, Food Research International 50 (1) (2013) 318–323. doi:10.1016/j.foodres.2012.10.043.
URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996912004541`

[8] F. Alvarez-Mitre, J. Morales-Rueda, E. Dibildox-Alvarado, M. Charó-Alonso, J. F. Toro-Vazquez, Shearing as a variable to engineer the rheology of candelilla wax organogels, Food Research International 49 (1) (2012) 580–587. doi:10.1016/j.foodres.2012.08.025.
URL `http://linkinghub.elsevier.com/retrieve/pii/S0963996912003341`

[9] J. Daniel, R. Rajasekharan, Organogelation of plant oils and hydrocarbons by long-chain saturated FA, fatty alcohols, wax esters, and dicarboxylic acids, Journal of the American Oil Chemists' Society 80 (5) (2003) 417–421. doi:10.1007/s11746-003-0714-0.
URL `http://www.springerlink.com/index/10.1007/s11746-003-0714-0`

[10] J. F. Toro-Vazquez, M. Alonzo-Macias, E. Dibildox-Alvarado, M. a. Charó-Alonso, The Effect of Tripalmitin Crystallization on the Thermomechanical Properties of Candelilla Wax Organogels, Food Biophysics 4 (3) (2009) 199–212. doi:10.1007/s11483-009-9118-7.
URL `http://www.springerlink.com/index/10.1007/s11483-009-9118-7`

[11] A. R. Patel, M. Babaahmadi, A. Lesaffer, K. Dewettinck, Rheological Profiling of Organogels Prepared at Critical Gelling Concentrations of Natural Waxes in a Triacylglycerol Solvent, Journal of Agricultural and Food Chemistry 63 (19) (2015) 4862–4869. doi:10.1021/acs.jafc.5b01548.
URL `http://pubs.acs.org/doi/abs/10.1021/acs.jafc.5b01548`

[12] J. F. Toro-Vazquez, R. Mauricio-Pérez, M. M. González-Chávez, M. Sánchez-Becerril, J. d. J. Ornelas-Paz, J. D. Pérez-Martínez, Physical properties of organogels and water in oil emulsions structured by mixtures of candelilla wax and monoglycerides, Food Research International 54 (2) (2013) 1360–1368. doi:10.1016/j.foodres.2013.09.046.
URL `http://dx.doi.org/10.1016/j.foodres.2013.09.046`

[13] A. I. Blake, A. G. Marangoni, The Effect of Shear on the Microstructure and Oil Binding Capacity of Wax Crystal Networks, Food Biophysicsdoi:10.1007/s11483-015-9398-z.
URL `http://link.springer.com/10.1007/s11483-015-9398-z`

[14] S. da Pieve, S. Calligaris, E. Co, M. C. Nicoli, A. G. Marangoni, Shear Nanostructuring of monoglyceride organogels, Food Biophysics 5 (3) (2010) 211–217. doi:10.1007/s11483-010-9162-3.

[15] A. I. Blake, E. D. Co, A. G. Marangoni, Structure and Physical Properties of Plant Wax Crystal Networks and Their Relationship to Oil Binding Capacity, Journal of the American Oil Chemists' Society 91 (6) (2014) 885–903. doi:10.1007/s11746-014-2435-0.
URL `http://link.springer.com/10.1007/s11746-014-2435-0`

[16] H.-S. Hwang, M. Singh, E. L. Bakota, J. K. Winkler-Moser, S. Kim, S. X. Liu, Margarine from Organogels of Plant Wax and Soybean Oil, Journal of the American Oil Chemists' Society 90 (11) (2013) 1705–1712. doi:10.1007/s11746-013-2315-z.
URL `http://link.springer.com/10.1007/s11746-013-2315-z`

[17] H. S. Hwang, M. Singh, J. K. Winkler-Moser, E. L. Bakota, S. X. Liu, Preparation of margarines from organogels of sunflower wax and vegetable oils, Journal of Food Science 79 (10) (2014) C1926–C1932. doi:10.1111/1750-3841.12596.

[18] D. C. Zulim Botega, A. G. Marangoni, A. K. Smith, H. D. Goff, The potential application of rice bran

wax oleogel to replace solid fat and enhance unsaturated fat content in ice cream., Journal of food science 78 (9) (2013) C1334–9. doi:10.1111/1750-3841.12175.
URL `http://www.ncbi.nlm.nih.gov/pubmed/24024686`

[19] E. Yilmaz, M. Ögütcü, Oleogels as spreadable fat and butter alternatives: sensory description and consumer perception, RSC Adv. 5 (62) (2015) 50259–50267. doi:10.1039/C5RA06689A.
URL `http://xlink.rsc.org/?DOI=C5RA06689A`

[20] L. Hartmann, R. C. Lago, Rapid preparation of fatty acid methyl esters from lipids, Laboratory Practices 22 (8) (1973) 475–476.

[21] AOCS, Official methods and recommended practices of the American Oil Chemists Society, 5th Edition, AOCS Press, Champaign, IL, 2004.

[22] J. F. Steffe, Rheological methods in food process engineering, 2nd Edition, Vol. 23, Freeman Press, 1996. doi:10.1016/0260-8774(94)90090-6.
URL `http://linkinghub.elsevier.com/retrieve/pii/0260877494900906`

[23] S. S. Narine, A. G. Marangoni, Relating structure of fat crystal networks to mechanical properties : a review, Food Research International 32.

[24] D. J. Abdallah, L. Lu, R. G. Weiss, Thermoreversible Organogels from Alkane Gelators with One Heteroatom, Chemistry of Materials 11 (10) (1999) 2907–2911. doi:10.1021/cm9902826.
URL `http://pubs.acs.org/doi/abs/10.1021/cm9902826`

[25] R. Campos, Experimental Methodology, in: Fat Crystal Networks, Vol. 41, Marcel Dekker, 2005, Ch. 9, pp. 267–348. doi:10.1590/S1516-93322005000300015.

[26] D. J. Abdallah, R. G. Weiss, n -Alkanes Gel n -Alkanes (and Many Other Organic Liquids), Langmuir 16 (2) (2000) 352–355. doi:10.1021/la990795r.
URL `http://pubs.acs.org/doi/abs/10.1021/la990795r`

[27] E. D. Co, A. G. Marangoni, Organogels: An Alternative Edible Oil-Structuring Method, Journal of the American Oil Chemists' Society 89 (5) (2012) 749–780. doi:10.1007/s11746-012-2049-3.
URL `http://link.springer.com/10.1007/s11746-012-2049-3`

[28] L. S. K. Dassanayake, D. R. Kodali, S. Ueno, K. Sato, Crystallization kinetics of organogels prepared by rice bran wax and vegetable oils., Journal of oleo science 61 (1) (2012) 1–9.
URL `http://www.ncbi.nlm.nih.gov/pubmed/22188800`

[29] H.-S. Hwang, S. Kim, M. Singh, J. K. Winkler-Moser, S. X. Liu, Organogel Formation of Soybean Oil with Waxes, Journal of the American Oil Chemists' Society 89 (4) (2011) 639–647. doi:10.1007/s11746-011-1953-2.
URL `http://link.springer.com/10.1007/s11746-011-1953-2`

[30] M. Lescanne, P. Grondin, A. D'Aléo, F. Fages, J. L. Pozzo, O. M. Monval, P. Reinheimer, a. Colin, A. Ale, A. D'Aléo, F. Fages, J. L. Pozzo, O. M. Monval, P. Reinheimer, a. Colin, A. Ale, Thixotropic organogels based on a simple N-hydroxyalkyl amide: rheological and aging properties., Langmuir : the ACS journal of surfaces and colloids 20 (2004) 3032–3041. doi:10.1021/la035219g.

[31] S. Narine, Marangoni, Fractal nature of fat crystal networks, Physical Review E 59 (2) (1999) 1908–1920.

[32] D. J. Abdallah, S. a. Sirchio, R. G. Weiss, Hexatriacontane Organogels. The First Determination of the Conformation and Molecular Packing of a Low-Molecular-Mass Organogelator in Its Gelled State, Langmuir 16 (20) (2000) 7558–7561. doi:10.1021/la000730k.
URL `http://pubs.acs.org/doi/abs/10.1021/la000730k`

Discussão geral

Após a estruturação dos organogéis com ceras de cana de açúcar, candelilla e carnaúba sob as temperaturas de 5 e 25°C em óleo de soja puro foi possível observar que a cera de carnaúba não forma organogéis estáveis em baixas concentrações (abaixo de 3%), resultado coerente com o existente na literatura para a formação de organogéis de cera de carnaúba (DASSANAYAKE et al., 2009), vale citar que ceras de origens distintas produzem organogéis diferentes.

Embora nem todos os organogéis de cera de cana de açúcar tenham sido formados nas concentrações e temperaturas analisadas, aqueles que se formaram no primeiro dia mantiveram-se estáveis até o sétimo dia. A cera de candelila se destacou por ter formado organogéis estáveis em todas as concentrações avaliadas, demonstrando ser, um agente estruturante muito efetivo sendo praticamente um padrão para comparação do comportamento de organogéis conforme observado na literatura (DOAN et al., 2015; HWANG et al., 2011; ROCHA et al., 2013).

Com a adição de gordura vegetal nos teores de 5, 15 e 25% nos organogéis também foi possível observar que a 5°C todas as amostras apresentaram estabilidade no período estudado, sem separação de fases, porém a 25°C as misturas de óleo mais gordura (sem a adição das ceras) apresentaram separação de fases, excetuando a amostra com 25% de gordura onde não houve separação visível. A amostra de gordura interesterificada apresentou teores de 53% e 1% para ácidos graxos saturados e *trans* respectivamente. Com base na avaliação da estabilidade foi possível concluir que a presença das ceras foi essencial para que as misturas formassem uma fase uniforme (vide a separação de fases observada no material sem ceras).

A estabilidade oxidativa dos organogéis foi semelhante a do óleo de soja sob as mesmas condições até o período de 15 semanas, sendo que apenas após esse período as amostras estruturadas com cera de candelila e carnaúba apresentaram índice de peróxidos mais elevado que o óleo puro sob as mesmas condições permitindo concluir que a imobilização do óleo melhorou a estabilidade oxidativa, como observado na literatura (KODALI, 2010). Esse efeito provavelmente se deve a uma menor permeação do oxigênio dentro do material devido à imobilização da fase lipídica.

O comportamento térmico dos organogéis foi semelhante para todas as amostras, apresentando um pico de cristalização referente à formação do gel, sem a cristalização evidente do estruturante. A adição de gordura não causou mudanças significativas nos valores de ΔH, para o fenômeno de formação do gel (primeiro pico de cristalização), porém um segundo pico referente à cristalização do TAG da gordura foi mensurado. Na fusão porém os valores de ΔH aumentaram com o aumento dos teores de gordura, esse aumento na variação da entalpia mostra que com a adição da gordura uma quantidade maior de energia foi necessária para desfazer a estrutura do organogel, ou seja o material se tornou mais resistente a fusão, nesse caso a fusão ainda ocorre em apenas um pico, mostrando que não é um simples mudança de hábito polimórfico e recristalização (SATO; UENO, 2005), mas um fenômeno de quebra da estrutura do organogel. O fato dos TAG estarem fundindo em momentos distintos foi especialmente visível nas amostras adicionadas de gordura interesterificada onde amostras usando ceras distintas apresentaram valores equivalentes para o primeiro pico de fusão.

Com a adição da gordura interesterificas aos organogéis, ocorreu um efeito do aumento do teor de sólidos, esse efeito foi previamente reportado por Toro-Vazquez et al. (2009), onde a adição de 1% de tripalmitina num organogel feito com cera de candelilla a 3% (m/m) resultou no aumento de 1,5 pontos percentuais no teor de sólidos a temperatura de -5°C, porém o efeito foi reduzido com o aumento da temperatura, esse comportamento apesar de não ser completamente elucidado, pode ser explicado pela mudança de comportamento da estrutura formada pelo estruturante em conjunto com a fase contínua. Não existem, até o momento, evidências de mudança de hábito polimórfico, porém a possibilidade de mudança organizacional como por exemplo anelamento, foi citada por Rogers, Wright e Marangoni (2009a), tal mudança poderia causar uma interferência entre os TAG permitindo um aumento na resposta do teor de sólidos.

A avaliação da dureza dos organogéis estruturados com as ceras de cana-de-açúcar, carnaúba e candelilla nas amostras sem adição de gordura e que formaram um organogel estável a 5 e 25°C permitiu observar que ocorreu um aumento da dureza com o aumento da concentração do material estruturante, resultado bastante coerente com o que se espera com o aumento de um agente estruturante (DASSANAYAKE et al., 2009; PATEL et al., 2015), mostrando que a dureza do material é influenciada diretamente pela concentração do estruturante. Os valores mensurados para as os organogéis de cera de candelila juntamente com a cera de cana-de-açúcar no primeiro artigo 14,60 e 1,65N respectivamente, foi semelhante ao observado para os géis de candelila e cana-de-açúcar nas mesmas concentrações, 19,42 e 0,40N respectivamente, com a carnaúba apresentando o valor mais baixos (0,16N) no segundo artigo, as variações nos valores são decorrentes de condições diferentes na temperatura de cristalização e análise.

Como a temperatura de cristalização foi associada a uma mudança no comportamento mecânico dos organogéis, foi possível observar que a baixa temperatura acelera o processo de formação da rede estruturante, aumentando a resistência mecânica dos organogéis. A análise dos valores permitiu observar também nos géis de ceras de cana de açúcar e carnaúba que o aumento da força máxima com o aumento da concentração não foi considerado estatisticamente siginificativo, o que ocorreu para os organogéis de cera de candelila.

A viscosidade aparente é uma análise para verificar o comportamento de um material sob condições de escoamento, sendo relevante para fins de comparação entre materiais (DASSANAYAKE; KODALI; UENO, 2011). Os organogéis estruturados com cera de candelila, mesmo apresentando menores valores de viscosidade em médias e altas temperaturas (acima de 35°C), apresentaram valores bem mais altos do que as outras duas ceras sob temperaturas mais baixas (15°C). O organogel estruturado pela cera de carnaúba apresentou menores valores de viscosidade sob temperaturas mais altas (acima de 40°C), porém o comportamento de viscosidade foi semelhante ao observado para o organogel de cana-de-açúcar na mesma concentração.

As temperaturas mensuradas para a mudança de comportamento reológico, foram similares às temperaturas do fenômeno térmico mensurado em DSC, o que comprova que o fenômeno térmico é de fato uma formação de gel que causa mudanças no comportamento reológico.

As medidas reológicas do comportamento dos organogéis de óleo de soja estruturados com as ceras estudadas, mostrou que o material formado de fato é um gel conforme os parâmetros de comportamento na varredura de frequências com G’ maiores que G"(STEFFE, 1996). Por outro lado a adição de gordura *low trans*, permitiu uma modificação no comportamento com incremento das medidas de G’ e G", o que aumenta as possibilidades de aplicação do material como substituto de gordura.

Apesar do discreto aumento dos valores de G’ e G", com o uso da gordura *low trans* nas proporções de 95:5, 85:15 e 75:25. Foi posível verificar que praticamente não houve diferença nas análises considerando apenas a varredura de temperatura.

Na varredura de frequências, os organogéis apresentaram valores de G’ superiores aos valores de G", uma evidência do comportamento de gel (STEFFE, 1996), além disso os valores de G’ e G"ficaram praticamente constantes, assim como o ângulo de fase (δ), porém esse comportamento foi diferente para os organogéis de carnaúba e cana-de-açúcar com adição de gordura interesterificada que se tornaram materiais com comportamento dependente da frequência, mais especificamente se tornaram menos viscosos com o aumento da frequência (MATUSZEK, 2003). Apesar da mundaça do comportamento, os organogéis de cana-de-açúcar e carnaúba também mantiveram o ângulo de fase (δ), praticamente constante.

As análises de morfologia permitiram verificar que que a adição de gordura, modificou amplamente o comportamento de cristalização dos materiais, sugerindo uma relação entre a composição química da fase imobilizada com o estruturante (ABDALLAH; WEISS, 2000; HWANG et al., 2014), que torna o organogel um sistema mais complexo que uma simples mistura. As dimensões dos cristais observadas para as amostras se mostrou variável, mas os organogéis de cera de candelila apresentaram cristais menores quando comparados com os cristais da cera de cana-de-açúcar e a cera de carnaúba apresentou os maiores cristais. O tamanho dos cristais se mostrou inversamente proporcional à resistência mecânica dos materiais, mostrando que uma rede mais organizada, com maior densidade de cristais, resulta em um material mais resistente (RYE; LITWINENKO; MARANGONI, 2005).

Quando comparamos o material sem adição de gordura com os organogéis com gordura, é possível observar como a microestrutura sofreu modificações. Com a adição da gordura vegetal, ela se tornou mais densa, porém mantendo características similares às do agente estruturante, em especial a redução do tamanho dos cristais de gordura, mostrando que existe uma uniformidade na cristalização do organogel e não simplesmente uma fase de cristais de TAGs dispersos na fase contínua dos organogéis.

Conclusões

Com base nos resultados obtidos para as diversas análises, é possível concluir que as ceras vegetais estudadas, apresentaram capacidade para formação de organogéis estáveis sob diferentes condições de temperatura e concentração e que a formação dos organogéis com as misturas de óleo de soja mais gordura apresentou a capacidade de estabilizar e modificar o comportamento térmico, perfil de sólidos e microestrutura dessas misturas.

A adição de ceras como agentes estruturantes quando em boas condições oxidativas, não apenas mantiveram a estabilidade oxidativa do óleo vegetal, como melhoraram a estabilidade, implicando um efeito positivo para o questionamento sobre a modificação da estabilidade oxidativa de produtos elaborados com óleos em substituição à gorduras.

O comportamento reológico dos materiais se manteve como gel mesmo comm a adição de gorduras *low trans* apesar de ocorrer uma mudança no comportamento mecânico, em especial o aumento da sensibilidade à mudanças de frequência, mas ainda assim se mantiveram como gel.

As ceras estudadas apresentaram comportamento distinto sendo a cera de candelila a que formou organogéis com maior resistência mecânica, porém à cera de carnauba apresenta um grande potencial devido ao grande volume produzido e a cera de cana-de-açúcar pelo potencial a ser desenvolvido considerando a produção atual da matéria-prima no Brasil. A escolha do agente estruturante dependerá não apenas do resultado de uma análise de dureza por exemplo, mas das características desejadas para a aplicação e à disponibilidade de matérias-primas.

Foi possível concluir ainda que os organogéis são uma alternativa às gorduras saturadas e que eles atendem à necessidade de estruturação usando pequenas quantidades dos estruturantes, permitindo então uma redução dos teores de ácidos graxos saturados em alimentos onde sejam aplicados como gorduras alternativas, mesmo que como substituto parcial das gorduras atualmente utilizadas.

Referências

ABDALLAH, D. J.; LU, L.; WEISS, R. G. Thermoreversible Organogels from Alkane Gelators with One Heteroatom. *Chemistry of Materials*, v. 11, n. 10, p. 2907–2911, 1999. ISSN 08974756. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/cm9902826>.

ABDALLAH, D. J.; SIRCHIO, S. a.; WEISS, R. G. Hexatriacontane Organogels. The First Determination of the Conformation and Molecular Packing of a Low-Molecular-Mass Organogelator in Its Gelled State. *Langmuir*, v. 16, n. 20, p. 7558–7561, oct 2000. ISSN 0743-7463. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/la000730k>.

ABDALLAH, D. J.; WEISS, R. G. n -Alkanes Gel n -Alkanes (and Many Other Organic Liquids). *Langmuir*, v. 16, n. 2, p. 352–355, jan 2000. ISSN 0743-7463. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/la990795r>.

ABIOVE. *Complexo Soja - Estatística Mensal Ano Safra 2010/11*. 2016. Disponível em: <http://www.abiove.org.br/site/index.php?page=estatisticaarea=NC0yLTE=>.

ALMEIDA, I. F.; BAHIA, M. F. Evaluation of the physical stability of two oleogels. *International journal of pharmaceutics*, v. 327, n. 1-2, p. 73–7, dec 2006. ISSN 0378-5173. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/16996708>.

ALVAREZ-MITRE, F. et al. Shearing as a variable to engineer the rheology of candelilla wax organogels. *Food Research International*, Elsevier Ltd, v. 49, n. 1, p. 580–587, nov 2012. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996912003341>.

ANVISA. *INSTRUÇÃO NORMATIVA Nº 49, DE 22 DE DEZEMBRO DE 2006*. 2006.

ANVISA. *Resolução RDC 54, DE 12 DE NOVEMBRO DE 2012*. 2012. 5 p.

AOCS. *Official methods and recommended practices of the American Oil Chemists Society*. 5. ed. Champaign, IL: AOCS Press, 2004.

BATTE, H. et al. Effect of processing conditions on the structure of monostearin–oil–water gels. *Food Research International*, v. 40, n. 8, p. 982–988, oct 2007. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996907000804>.

BEMER, H. L. et al. Vegetable organogels incorporation in cream cheese products. *Food Research International*, Elsevier B.V., v. 85, p. 67–75, 2016. ISSN 09639969. Disponível em: <http://dx.doi.org/10.1016/j.foodres.2016.04.016>.

BLAKE, A. I.; CO, E. D.; MARANGONI, A. G. Structure and Physical Properties of Plant Wax Crystal Networks and Their Relationship to Oil Binding Capacity. *Journal of the American Oil Chemists' Society*, v. 91, n. 6, p. 885–903, feb 2014. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007/s11746-014-2435-0>.

BLAKE, A. I.; MARANGONI, A. G. Plant wax crystals display platelet-like morphology. *Food Structure*, Elsevier Ltd., v. 3, p. 30–34, 2015. ISSN 22133291. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S2213329115000027>.

BLAKE, A. I.; MARANGONI, A. G. The Effect of Shear on the Microstructure and Oil Binding Capacity of Wax Crystal Networks. *Food Biophysics*, 2015. ISSN 1557-1858. Disponível em: <http://link.springer.com/10.1007/s11483-015-9398-z>.

BOT, A.; AGTEROF, W. G. M. Structuring of Edible Oils by Mixtures of γ -Oryzanol with β -Sitosterol or Related Phytosterols. *Journal of the American Oil Chemists' Society*, v. 83, n. 6, p. 513–521, 2006.

BOT, A. et al. Non-TAG structuring of edible oils and emulsions. *Food Hydrocolloids*, Elsevier Ltd, v. 23, n. 4, p. 1184–1189, 2009. ISSN 0268005X. Disponível em: <http://dx.doi.org/10.1016/j.foodhyd.2008.06.009>.

CAMPOS, R. Experimental Methodology. In: *Fat Crystal Networks*. Marcel Dekker, 2005. v. 41, n. 3, cap. 9, p. 267–348. Disponível em: <http://www.scielo.br/scielo-.php?script=sci_arttext\pid=S1516-93322005000300015\lng=pt\nrm>.

CHAVES, K. F. *PROCESSO SIMPLIFICADO DE FABRICAÇÃO DE MARGARINAS COM REDUZIDOS TEORES DE ÁCIDOS GRAXOS SATURADOS UTILIZANDO A TECNOLOGIA DE ESTRUTURAÇÃO DE ÓLEOS*. 75 p. Tese (Doutorado) — Universidade Estadual de Campinas, 2013.

CHRISTOPHE, A. B. Structural Effects on Absorption, Metabolism and Health Effects of Lipids. In: SHAHIDI, F. (Ed.). *Bailey's Industrial Oil and Fat Products*. 6th. ed. [S.l.]: John Wiley & Sons Inc., 2005. cap. 16, p. 535–553.

CHRYSAN, M. M. Margarines and Spreads. In: SHAHIDI, F. (Ed.). *Bailey's Industrial Oil and Fat Products*. 6th. ed. [S.l.]: John Wiley & Sons Inc., 2005. cap. 2, p. 33–82.

Da Pieve, S. et al. Effect of monoglyceride organogel structure on cod liver oil stability. *Food Research International*, Elsevier Ltd, v. 44, n. 9, p. 2978–2983, nov 2011. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii-/S0963996911004510>.

DANIEL, J.; RAJASEKHARAN, R. Organogelation of plant oils and hydrocarbons by long-chain saturated FA, fatty alcohols, wax esters, and dicarboxylic acids. *Journal of the American Oil Chemists' Society*, v. 80, n. 5, p. 417–421, may 2003. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10.1007/s11746-003-0714-0>.

DASSANAYAKE, L. S. K.; KODALI, D. R.; UENO, S. Formation of oleogels based on edible lipid materials. *Current Opinion in Colloid & Interface Science*, Elsevier Ltd, v. 16, n. 5, p. 432–439, oct 2011. ISSN 13590294. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S1359029411000756>.

DASSANAYAKE, L. S. K. et al. Physical Properties of Rice Bran Wax in Bulk and Organogels. *Journal of the American Oil Chemists' Society*, v. 86, n. 12, p. 1163–1173, sep 2009. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10-.1007/s11746-009-1464-6>.

DEMAN, J.; DEMAN, L. Texture of fats. In: A.G.MARANGONI; S.S.NARINE (Ed.). *Physical Properties of Lipids*. New York: Marcel Dekker, 2002. cap. 7, p. 191–215. Disponível em: <http://scholar.google.com-/scholar?hl=en\btnG=Search\q=intitle:Texture+of+Fats\1 http://scholar.google-.com/scholar?hl=en\btnG=Search\q=intitle:Te>.

DOAN, C. D. et al. Evaluating the Oil-Gelling Properties of Natural Waxes in Rice Bran Oil: Rheological, Thermal, and Microstructural Study. *Journal of the American Oil Chemists' Society*, Springer Berlin Heidelberg, v. 92, n. 6, p. 801–811, 2015. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007/s11746-015-2645-0>.

EFSA. Scientific Opinion on the safety evaluation of the substance poly (12-hydroxystearic acid) stearate , CAS No . 58128-22-6 for use in food contact materials 1. *EFSA Journal*, v. 8, n. 58128, p. 1–12, 2010.

FAO. *SORBITAN MONOSTEARATE.* 2000. 2 p. Disponível em: <http://www.fao.org/ag/agn/jecfa-additives/specs/Monograph1/Additive-434.pdf>.

FDA. *FDA Cuts Trans Fat in Processed Foods.* 2015. 1–2 p. Disponível em: <http://www.fda.gov/ForConsumers/ConsumerUpdates/ucm372915.htm>.

FDA. *FOOD FOR HUMAN CONSUMPTION (CONTINUED).* 2016. Disponível em: <http://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=178.3570>.

FLICKINGER, B.; HUTH, P. Dietary fats and oils: technologies for improving cardiovascular health. *Current atherosclerosis reports*, Springer, v. 6, n. 6, p. 468–476, 2004. Disponível em: <http://www.springerlink.com/index/G122Q7X878346708.pdf>.

GARCIA, R. d. K. d. A. Formulação de gorduras para aplicação em margarinas zero trans com redes neurais a partir de gorduras interesterificadas. p. 118, 2010.

GUINARD, J.-x.; MAZZUCCHELLI, R. The sensory perception of texture and mouthfeel. *Trends in Food Science & Technology*, v. 7, n. July, p. 213–219, 1996.

GURR, M.; HARWOOD, J. *Lipid Biochemistry: An Introduction.* 4th. ed. [S.l.]: Chapman & Hall, 1996. 162–243 p.

HAN, L.-J. et al. Rheological Properties of Organogels Developed by Sitosterol and Lecithin. *Food Research International*, Elsevier B.V., apr 2013. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996913002147>.

HIMAWAN, C.; STAROV, V. M.; STAPLEY, a. G. F. Thermodynamic and kinetic aspects of fat crystallization. *Advances in colloid and interface science*, v. 122, n. 1-3, p. 3–33, sep 2006. ISSN 0001-8686. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/16904622>.

HUGHES, N. E. et al. Potential food applications of edible oil organogels. *Trends in Food Science & Technology*, Elsevier Ltd, v. 20, n. 10, p. 470–480, oct 2009. ISSN 09242244. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0924224409002040>.

HUNTER, J. E. Studies on effects of dietary fatty acids as related to their position on triglycerides. *Lipids*, v. 36, n. 7, p. 655–68, jul 2001. ISSN 0024-4201. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/11521963>.

HWANG, H.-S. et al. Organogel Formation of Soybean Oil with Waxes. *Journal of the American Oil Chemists' Society*, v. 89, n. 4, p. 639–647, oct 2011. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007/s11746-011-1953-2>.

HWANG, H.-S. et al. Margarine from Organogels of Plant Wax and Soybean Oil. *Journal of the American Oil Chemists' Society*, v. 90, n. 11, p. 1705–1712, aug 2013. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007/s11746-013-2315-z>.

HWANG, H. S. et al. Preparation of margarines from organogels of sunflower wax and vegetable oils. *Journal of Food Science*, v. 79, n. 10, p. C1926–C1932, 2014. ISSN 17503841.

IBGE. *Prognóstico da Produção Agrícola Nacional, dos principais produtos, para safra 2017*. 2017. Disponível em: <http://www.ibge.gov.br/home/estatistica/indicadores-/agropecuaria/lspa/lspa_201612_1>.

JANG, A. et al. Evaluation of canola oil oleogels with candelilla wax as an alternative to shortening in baked goods. *Food Chemistry*, Elsevier Ltd, v. 187, n. 4, p. 525–529, nov 2015. ISSN 03088146. Disponível em: <http://www.scopus.com/inward/record-.url?eid=2-s2.0-84929206822\partnerID=40\md5=66b50062fe5bdd3516776fb9005fbfed https://www.jstage.jst.go.jp/article/jos/64/7/64_ess15053/_article http://xlink.rsc-.org/?DOI=C5FO01006C http://dx.doi.org/10.1016/>.

KARUPAIAH, T.; SUNDRAM, K. Effects of stereospecific positioning of fatty acids in triacylglycerol structures in native and randomized fats: a review of their nutritional implications. *Nutrition & metabolism*, v. 4, p. 16, jan 2007. ISSN 1743-7075. Disponível em: <http://www.pubmedcentral.nih.gov/articlerender-.fcgi?artid=1947992\tool=pmcentrez\rendertype=ab>.

KODALI, D. R. *Stabilization of Long Chain Polyunsaturated Oils*. 2010. 7 p.

LUPI, F. R. et al. Rheological design of stabilized meat sauces for industrial uses. *European Journal of Lipid Science and Technology*, v. 116, n. 12, p. 1734–1744, 2014. ISSN 14389312.

MALLIA, V. A.; BLAIR, D. L.; WEISS, R. G. Oscillatory Rheology and Surface Water Wave Effects on Crude Oil and Corn Oil Gels with (<i>R</i>)-12-Hydroxystearic Acid as Gelator. *Industrial & Engineering Chemistry Research*, v. 55, n. 4, p. 954–960, 2016. ISSN 0888-5885. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/acs.iecr-.5b04267>.

MALLIA, V. A.; WEISS, R. G. Structural bases for mechano-responsive properties in molecular gels of (R)-12-hydroxy-N-(ω-hydroxyalkyl)octadecanamides. Rates of formation and responses to destructive strain. *Soft Matter*, Royal Society of Chemistry, in press, p. 5010–5022, 2015. ISSN 1744-683X. Disponível em: <http://xlink.rsc.org-/?DOI=C5SM00353A>.

MATUSZEK, T. Rheological Properties of Lipids. In: *Chemical and Functional Properties of Food Lipids*. CRC, 2003. ISBN 978-1-4200-3199-7. Disponível em: <http://dx.doi.org/10.1201/9781420031997>.

MELO, C. A.; CHAVES, K. F.; BARRERA-ARELLANO, D. FORMULAÇÃO DE PASTA AMERICANA E GLACÊ COM BAIXO TEOR DE ÁCIDOS GRAXOS SATURADOS A PARTIR DA TECNOLOGIA DE ORGANOGÉIS. In: *SBOG 20 ANOS: NOVOS HORIZONTES PARA CIÊNCIA E TECNOLOGIA DE ÓLEOS E GORDURAS*. Florianópolis: [s.n.], 2013.

MERT, B.; DEMIRKESEN, I. Evaluation of highly unsaturated oleogels as shortening replacer in a short dough product. *LWT - Food Science and Technology*, Elsevier Ltd, v. 68, p. 477–484, 2016. ISSN 00236438. Disponível em: <http://linkinghub.elsevier.com-/retrieve/pii/S0023643815304205>.

MIYAZAKI, Y.; YOSHIDA, K.; MARANGONI, A. G. Online Only Supplement - Lecture Abstracts of the 9th Euro Fed Lipid Congress, Rotterdam 18-21 September 2011. *European Journal of Lipid Science and Technology*, v. 113, n. S1, p. 1–46, nov 2011. ISSN 14387697. Disponível em: <http://doi.wiley.com/10.1002/ejlt.201100363>.

MORALES-RUEDA, J. a. et al. Rheological Properties of Candelilla Wax and Dotriacontane Organogels Measured with a True-Gap System. *Journal of the American Oil Chemists' Society*, v. 86, n. 8, p. 765–772, jun 2009. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10.1007/s11746-009-1414-3>.

MURDAN, S.; GREGORIADIS, G.; FLORENCE, A. T. Novel sorbitan monostearate organogels. *Journal of Pharmaceutical Sciences*, v. 88, n. 6, p. 608–614, jun 1999. ISSN 00223549. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/10350496>.

NARINE, S. S.; MARANGONI, A. G. Relating structure of fat crystal networks to mechanical properties : a review. *Food Research International*, v. 32, 1999.

NARINE, S. S.; MARANGONI, A. G. Structure and mechanical properties of fat crystal networks. *Advances in food and nutrition research*, Elsevier, v. 44, p. 33–145, 2002. Disponível em: <http://www.sciencedirect.com/science/article/pii-/S104345260244003X>.

OEC. *OEC - Soybeans*. 2014. Disponível em: <http://atlas.media.mit.edu/en/profile-/hs92/1201/>.

OJIJO, N. K. O. et al. Effects of monoglyceride content, cooling rate and shear on the rheological properties of olive oil/monoglyceride gel networks. *Journal of the Science of Food and Agriculture*, v. 84, n. 12, p. 1585–1593, 2004. ISSN 00225142.

ÖğÜTCÜ, M.; ARIFOğLU, N.; YıLMAZ, E. Preparation and Characterization of Virgin Olive Oil-Beeswax Oleogel Emulsion Products. *Journal of the American Oil Chemists' Society*, v. 92, n. 4, p. 459–471, apr 2015. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007/s11746-015-2615-6>.

ÖUTCU, M.; YıLMAZ, E. Oleogels of virgin olive oil with carnauba wax and monoglyceride as spreadable products. *Grasas y Aceites*, v. 65, n. 3, p. 1–11, 2014. ISSN 19884214. Disponível em: <http://grasasyaceites.revistas.csic.es/index.php-/grasasyaceites/article/viewArticle/1505>.

PATEL, A. R. et al. Rheological Profiling of Organogels Prepared at Critical Gelling Concentrations of Natural Waxes in a Triacylglycerol Solvent. *Journal of Agricultural and Food Chemistry*, v. 63, n. 19, p. 4862–4869, 2015. ISSN 0021-8561. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/acs.jafc.5b01548>.

PATEL, A. R. et al. Polysaccharide-based oleogels prepared with an emulsion-templated approach. *ChemPhysChem*, v. 15, n. 16, p. 3435–3439, 2014. ISSN 14397641.

PATEL, A. R.; DEWETTINCK, K. Edible oil structuring: an overview and recent updates. *Food Funct.*, Royal Society of Chemistry, v. 7, n. 1, p. 20–29, 2016. ISSN 2042-6496. Disponível em: <http://xlink.rsc.org/?DOI=C5FO01006C>.

PERNETTI, M. et al. Structuring edible oil with lecithin and sorbitan tri-stearate. *Food Hydrocolloids*, v. 21, n. 5-6, p. 855–861, jul 2007. ISSN 0268005X. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0268005X06002499>.

PIEVE, S. da et al. Shear Nanostructuring of monoglyceride organogels. *Food Biophysics*, v. 5, n. 3, p. 211–217, 2010. ISSN 15571858.

POKORNÝ, J.; SCHMIDT, S. Plant Lipids and Oils. In: KOLAKOWSKA, A. (Ed.). *Chemical, Biological, and Functional Aspects of Food Lipids*. 2nd. ed. Boca Raton, Florida: Taylor and Francis, LLC, 2011. cap. 14, p. 249 – 269. ISBN 978-1-4398-0238-0. Disponível em: <http://www.crcnetbase.com/isbn/9781439802380>.

ROCHA, J. C. B. *Obtenção e caracterização de organogéis de óleo de soja preparados com cera de cana-de-açúcar e suas frações*. 109 p. — Universidade Estadual de Campinas, 2012.

ROCHA, J. C. B. et al. Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil. *Food Research International*, Elsevier Ltd, v. 50, n. 1, p. 318–323, jan 2013. ISSN 09639969. Disponível em: <http://linkinghub-.elsevier.com/retrieve/pii/S0963996912004541>.

ROGERS, M. A. Novel structuring strategies for unsaturated fats – Meeting the zero-trans, zero-saturated fat challenge: A review. *Food Research International*, Elsevier Ltd, v. 42, n. 7, p. 747–753, aug 2009. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996909000623>.

ROGERS, M. A. et al. A Novel Cryo-SEM Technique for Imaging Vegetable Oil Based Organogels. *Journal of the American Oil Chemists' Society*, v. 84, n. 10, p. 899–906, sep 2007. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10.1007-/s11746-007-1122-9>.

ROGERS, M. A.; WRIGHT, A.; MARANGONI, A. G. Crystalline stability of self-assembled fibrillar networks of 12-hydroxystearic acid in edible oils. *Food Research International*, Elsevier Ltd, v. 41, n. 10, p. 1026–1034, dec 2008. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996908001427>.

ROGERS, M. A.; WRIGHT, A. J.; MARANGONI, A. G. Corrigendum to "Nanostructuring fiber morphology and solvent inclusions in 12-hydroxystearic acid/canola oil organogels" [Current Opinion in Colloid & Interface Science 14(1) (2009) 33–42]. *Current Opinion in Colloid & Interface Science*, Elsevier Ltd, v. 14, n. 3, p. 223, jun 2009. ISSN 13590294. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii-/S1359029409000132>.

ROGERS, M. A.; WRIGHT, A. J.; MARANGONI, A. G. Nanostructuring fiber morphology and solvent inclusions in 12-hydroxystearic acid / canola oil organogels. *Current Opinion in Colloid & Interface Science*, Elsevier Ltd, v. 14, n. 1, p. 33–42, feb 2009. ISSN 13590294. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii-/S1359029408000149>.

ROGERS, M. A.; WRIGHT, A. J.; MARANGONI, A. G. Oil organogels: the fat of the future? *Soft Matter*, v. 5, n. 8, p. 1594, 2009. ISSN 1744-683X. Disponível em: <http://xlink.rsc.org/?DOI=b822008p>.

ROUSSEAU, D.; MARANGONI, A. G. The effects of interesterification on physical and sensory attributes of butterfat and butterfat-canola oil spreads. *Science And Technology*, v. 31, n. 5, 1999.

RYE, G. G.; LITWINENKO, J. W.; MARANGONI, A. G. Fat Crystal Networks. In: SHAHIDI, F. (Ed.). *Bailey's Industrial Oil and Fat Products*. [S.l.]: John Wiley & Sons Inc., 2005.

SATO, K.; UENO, S. Polymorphism in Fats and Oils. In: SHAHIDI, F. (Ed.). *Bailey's Industrial Oil and Fat Products*. 6th. ed. [S.l.]: John Wiley & Sons Inc., 2005. cap. 3, p. 77–120.

SCARTAZZINI, R.; LUISI, P. L. Organogels from lecithins. *The Journal of Physical Chemistry*, v. 92, n. 3, p. 829–833, feb 1988. ISSN 0022-3654. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/j100314a047>.

SCHAINK, H. et al. Crystal network for edible oil organogels: Possibilities and limitations of the fatty acid and fatty alcohol systems. *Food Research International*, v. 40, n. 9, p. 1185–1193, nov 2007. ISSN 09639969. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0963996907001202>.

SENANAYAKE, S.; SHAHIDI, F. Modification of fats and oils via chemical and enzymatic methods. In: Fereidoon Shahidi (Ed.). *Bailey's Industrial Oil and Fat Products*. 6th. ed. Wiley Online Library, 2005. cap. 17, p. 555–584. Disponível em: <http://onlinelibrary.wiley.com/doi/10.1002/047167849X.bio062/full>.

SENANAYAKE, S. N.; SHAHIDI, F. Dietary fat substitutes. In: SHAHIDI, F. (Ed.). *Bailey's Industrial Oil and Fat Products*. 6th. ed. John Wiley & Sons Inc., 2005. v. 14, n. 10, cap. 15, p. 503–533. Disponível em: <http://linkinghub.elsevier.com/retrieve/pii/S0271531705802398>.

SHAHIDI, F. *Bailey ' S Industrial Oil and Fat*. Hoboken, NJ: [s.n.], 2009. 2005–2006 p. ISBN 9786468600.

SHI, Y.; LIANG, B.; HARTEL, R. W. Crystal Morphology, Microstructure and Textural Properties of Model Lipid Systems. *J Am Chem. Soc.*, v. 82, n. 6, p. 399–408, 2005. Disponível em: <http://link.springer.com.proxy.lib.ohio-state.edu/article/10.1007/s11746-005-1084-3>.

SI, H. et al. Physical Properties of Soybean Oleogels and Oil Migration Evaluation in Model Praline System. *JAOCS, Journal of the American Oil Chemists' Society*, Springer Berlin Heidelberg, v. 93, n. 8, p. 1075–1084, 2016. ISSN 0003021X. Disponível em: <"http://dx.doi.org/10.1007/s11746-016-2846-1>.

SREENIVASAN, B. Interesterification of fats in margarine: effect on blood lipids, blood enzymes, and hemostasis parameters. *Journal of the American Oil Chemists' Society*, v. 55, n. 11, p. 796–805, aug 1978. ISSN 0954-3007. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/19442321>.

STEFFE, J. F. *Rheological methods in food process engineering.* 2nd. ed. Freeman Press, 1996. 418 p. ISSN 02608774. ISBN 0-9632036-1-4. Disponível em: <http://linkinghub-.elsevier.com/retrieve/pii/0260877494900906>.

STENDER, S.; DYERBERG, J. Influence of trans fatty acids on health. *Annals of nutrition & metabolism*, v. 48, n. 2, p. 61–6, jan 2004. ISSN 0250-6807. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/14679314>.

SUNDRAM, K.; KARUPAIAH, T.; HAYES, K. C. Stearic acid-rich interesterified fat and trans-rich fat raise the LDL/HDL ratio and plasma glucose relative to palm olein in humans. *Nutrition & metabolism*, v. 4, p. 3, jan 2007. ISSN 1743-7075. Disponível em: <http://www.pubmedcentral.nih.gov/articlerender-.fcgi?artid=1783656\tool=pmcentrez\rendertype=ab>.

TERECH, P. et al. Rheological Properties and Structural Correlations in Molecular Organogels. *Langmuir*, v. 16, n. 10, p. 4485–4494, may 2000. ISSN 0743-7463. Disponível em: <http://pubs.acs.org/doi/abs/10.1021/la991545d>.

TORO-VAZQUEZ, J. F. et al. The Effect of Tripalmitin Crystallization on the Thermomechanical Properties of Candelilla Wax Organogels. *Food Biophysics*, v. 4, n. 3, p. 199–212, jun 2009. ISSN 1557-1858. Disponível em: <http://www.springerlink.com-/index/10.1007/s11483-009-9118-7>.

TORO-VAZQUEZ, J. F. et al. Thermal and Textural Properties of Organogels Developed by Candelilla Wax in Safflower Oil. *Journal of the American Oil Chemists' Society*, v. 84, n. 11, p. 989–1000, oct 2007. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10.1007/s11746-007-1139-0>.

WILLIMANN, H. et al. Lecithin organogel as matrix for transdermal transport of drugs. *Journal of Pharmaceutical Sciences*, v. 81, n. 9, p. 871–874, 1992. ISSN 00223549.

WRIGHT, A. J.; MARANGONI, A. G. Time, Temperature, and Concentration Dependence of Ricinelaidic Acid–Canola Oil Organogelation. *Journal of the American Oil Chemists' Society*, v. 84, n. 1, p. 3–9, dec 2006. ISSN 0003-021X. Disponível em: <http://www.springerlink.com/index/10.1007/s11746-006-1012-6>.

WRIGHT, A. J. et al. Rheological Properties of Milkfat and Butter Concise Reviews in Food Science. *Journal of Food Science*, v. 66, n. 8, 2001.

YANG, T.; FRUEKILDE, M.-B.; XU, X. Suppression of acyl migration in enzymatic production of structured lipids through temperature programming. *Food Chemistry*, v. 92, n. 1, p. 101–107, 2005.

YOUNG, F. Interchangeability of fats and oils. In: *Journal of the American Oil Chemists' Society.* Springer, 1985. v. 62, n. 2, p. 372–376. Disponível em: <http://www.springerlink.com/index/U62310V588484P20.pdf>.

YıLMAZ, E.; ÖğÜTCÜ, M. Comparative Analysis of Olive Oil Organogels Containing Beeswax and Sunflower Wax with Breakfast Margarine. *Journal of Food Science*, v. 79, n. 9, p. E1732–E1738, 2014. ISSN 00221147. Disponível em: <http://doi.wiley.com/10-.1111/1750-3841.12561>.

YıLMAZ, E.; ÖğÜTCÜ, M. Properties and Stability of Hazelnut Oil Organogels with Beeswax and Monoglyceride. *Journal of the American Oil Chemists' Society*, v. 91, n. 6, p. 1007–1017, 2014. ISSN 0003-021X. Disponível em: <http://link.springer.com/10.1007-/s11746-014-2434-1>.

YıLMAZ, E.; ÖğÜTCÜ, M.; YÜCEER, Y. K. Physical Properties, Volatiles Compositions and Sensory Descriptions of the Aromatized Hazelnut Oil-Wax Organogels. *Journal of Food Science*, v. 80, n. 9, p. S2035–S2044, sep 2015. ISSN 00221147. Disponível em: <http://doi.wiley.com/10.1111/1750-3841.12992>.

ZHANG, M.; WEISS, R. G. Self-Assembled Networks and Molecular Gels Derived from Long-Chain, NaturallyOccurring Fatty Acids. *Journal of the Brazilian Chemical Society*, v. 00, n. 00, p. 1–17, 2015.

ZULIM BOTEGA, D. C. et al. The potential application of rice bran wax oleogel to replace solid fat and enhance unsaturated fat content in ice cream. *Journal of food science*, v. 78, n. 9, p. C1334–9, sep 2013. ISSN 1750-3841. Disponível em: <http://www.ncbi.nlm.nih.gov/pubmed/24024686>.

Autorizações para uso de imagens e documentos publicados.

ELSEVIER LICENSE TERMS AND CONDITIONS

Jan 17, 2017

This Agreement between Julio Rocha ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4030770993121
License date	Jan 16, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Food Research International
Licensed Content Title	Thermal and rheological properties of organogels formed by sugarcane or candelilla wax in soybean oil
Licensed Content Author	Julio Cesar Barbosa Rocha,Julice Dutra Lopes,Maria Cristina Nucci Mascarenhas,Daniel Barrera Arellano,Lizielle Maria Ricardo Guerreiro,Rosiane Lopes da Cunha
Licensed Content Date	January 2013
Licensed Content Volume Number	50
Licensed Content Issue Number	1
Licensed Content Pages	6
Start Page	318
End Page	323
Type of Use	reuse in a thesis/dissertation
Portion	full article
Format	both print and electronic
Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Order reference number	
Title of your thesis/dissertation	Obtention and characterization of organogels from soybean oil structured using vegetable waxes and interesterified fats through controlled crystallization conditions
Expected completion date	Feb 2017
Estimated size (number of pages)	160
Elsevier VAT number	GB 494 6272 12
Requestor Location	Julio Rocha R. Olga di Giorgio Geracci n. 190 Casa 12A Campinas, SP 13087546 Brazil Attn: Julio Rocha
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jan 17, 2017

This Agreement between Julio Rocha ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4031280899174
License date	Jan 17, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Current Opinion in Colloid & Interface Science
Licensed Content Title	Structuring of edible oils by alternatives to crystalline fat
Licensed Content Author	Mimma Pernetti,Kees F. van Malssen,Eckhard Flöter,Arjen Bot
Licensed Content Date	October 2007
Licensed Content Volume Number	12
Licensed Content Issue Number	4-5
Licensed Content Pages	11
Start Page	221
End Page	231
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	Yes
Number of languages	1
Languages	Portuguese
Order reference number	
Original figure numbers	Figure 1
Title of your thesis/dissertation	Obtention and characterization of organogels from soybean oil structured using vegetable waxes and interesterified fats through controlled crystallization conditions
Expected completion date	Feb 2017
Estimated size (number of pages)	160
Elsevier VAT number	GB 494 6272 12
Requestor Location	Julio Rocha R. Olga di Giorgio Geracci n. 190 Casa 12A Campinas, SP 13087546 Brazil Attn: Julio Rocha
Total	**0.00 USD**
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment

terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).
13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each

image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.
Authors can share their accepted author manuscript:

- immediately
    - via their non-commercial person homepage or blog
    - by updating a preprint in arXiv or RePEc with the accepted manuscript
    - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
    - directly by providing copies to their students or to research collaborators for their personal use
    - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
    - via non-commercial hosting platforms such as their institutional repository
    - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0. Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

SPRINGER LICENSE
TERMS AND CONDITIONS

Jan 30, 2017

This Agreement between Julio Rocha ("You") and Springer ("Springer") consists of your license details and the terms and conditions provided by Springer and Copyright Clearance Center.

License Number	4038860071413
License date	Jan 30, 2017
Licensed Content Publisher	Springer
Licensed Content Publication	Journal of the American Oil Chemists' Society
Licensed Content Title	Structure and Physical Properties of Plant Wax Crystal Networks and Their Relationship to Oil Binding Capacity
Licensed Content Author	Alexia I. Blake
Licensed Content Date	Jan 1, 2014
Licensed Content Volume Number	91
Licensed Content Issue Number	6
Type of Use	Thesis/Dissertation
Portion	Figures/tables/illustrations
Number of figures/tables/illustrations	1
Author of this Springer article	No
Order reference number	
Original figure numbers	Figure 2
Title of your thesis / dissertation	Obtention and characterization of organogels from soybean oil structured using vegetable waxes and interesterified fats through controlled crystallization conditions
Expected completion date	Feb 2017
Estimated size(pages)	160
Requestor Location	Julio Rocha R. Olga di Giorgio Geracci n. 190 Casa 12A Campinas, SP 13087546 Brazil Attn: Julio Rocha
Billing Type	Invoice
Billing Address	Julio Rocha R. Olga di Giorgio Geracci n. 190 Casa 12A Campinas, Brazil 13087546 Attn: Julio Rocha
Total	0.00 USD
Terms and Conditions	

Introduction
The publisher for this copyrighted material is Springer. By clicking "accept" in connection

with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

Limited License

With reference to your request to reuse material on which Springer controls the copyright, permission is granted for the use indicated in your enquiry under the following conditions:

- Licenses are for one-time use only with a maximum distribution equal to the number stated in your request.

- Springer material represents original material which does not carry references to other sources. If the material in question appears with a credit to another source, this permission is not valid and authorization has to be obtained from the original copyright holder.

- This permission

• is non-exclusive

• is only valid if no personal rights, trademarks, or competitive products are infringed.

• explicitly excludes the right for derivatives.

- Springer does not supply original artwork or content.

- According to the format which you have selected, the following conditions apply accordingly:

• **Print and Electronic:** This License include use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.

• **Print:** This License excludes use in electronic form.

• **Electronic:** This License only pertains to use in electronic form provided it is password protected, on intranet, or CD-Rom/DVD or E-book/E-journal. It may not be republished in electronic open access.

For any electronic use not mentioned, please contact Springer at permissions.springer@spi-global.com.

- Although Springer controls the copyright to the material and is entitled to negotiate on rights, this license is only valid subject to courtesy information to the author (address is given in the article/chapter).

- If you are an STM Signatory or your work will be published by an STM Signatory and you are requesting to reuse figures/tables/illustrations or single text extracts, permission is granted according to STM Permissions Guidelines: http://www.stm-assoc.org/permissions-guidelines/

For any electronic use not mentioned in the Guidelines, please contact Springer at permissions.springer@spi-global.com. If you request to reuse more content than stipulated in the STM Permissions Guidelines, you will be charged a permission fee for the excess content.

Permission is valid upon payment of the fee as indicated in the licensing process. If permission is granted free of charge on this occasion, that does not prejudice any rights we might have to charge for reproduction of our copyrighted material in the future.

-If your request is for reuse in a Thesis, permission is granted free of charge under the following conditions:

This license is valid for one-time use only for the purpose of defending your thesis and with a maximum of 100 extra copies in paper. If the thesis is going to be published, permission needs to be reobtained.

- includes use in an electronic form, provided it is an author-created version of the thesis on his/her own website and his/her university’s repository, including UMI (according to the definition on the Sherpa website: http://www.sherpa.ac.uk/romeo/);

- is subject to courtesy information to the co-author or corresponding author.

Geographic Rights: Scope

Licenses may be exercised anywhere in the world.

Altering/Modifying Material: Not Permitted

Figures, tables, and illustrations may be altered minimally to serve your work. You may not alter or modify text in any manner. Abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of the author(s).

Reservation of Rights

Springer reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction and (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

License Contingent on Payment

While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by Springer or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received by the date due, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and Springer reserves the right to take any and all action to protect its copyright in the materials.

Copyright Notice: Disclaimer

You must include the following copyright and permission notice in connection with any reproduction of the licensed material:

"Springer book/journal title, chapter/article title, volume, year of publication, page, name(s) of author(s), (original copyright notice as given in the publication in which the material was originally published) "With permission of Springer"

In case of use of a graph or illustration, the caption of the graph or illustration must be included, as it is indicated in the original publication.

Warranties: None

Springer makes no representations or warranties with respect to the licensed material and adopts on its own behalf the limitations and disclaimers established by CCC on its behalf in its Billing and Payment terms and conditions for this licensing transaction.

Indemnity

You hereby indemnify and agree to hold harmless Springer and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

No Transfer of License

This license is personal to you and may not be sublicensed, assigned, or transferred by you without Springer's written permission.

No Amendment Except in Writing

This license may not be amended except in a writing signed by both parties (or, in the case of Springer, by CCC on Springer's behalf).

Objection to Contrary Terms

Springer hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and Springer (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

Jurisdiction

All disputes that may arise in connection with this present License, or the breach thereof, shall be settled exclusively by arbitration, to be held in the Federal Republic of Germany, in accordance with German law.

Other conditions:

V 12AUG2015

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jan 30, 2017

This Agreement between Julio Rocha ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4038850745691
License date	Jan 30, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Trends in Food Science & Technology
Licensed Content Title	Potential food applications of edible oil organogels
Licensed Content Author	Naomi E. Hughes,Alejandro G. Marangoni,Amanda J. Wright,Michael A. Rogers,James W.E. Rush
Licensed Content Date	October 2009
Licensed Content Volume Number	20
Licensed Content Issue Number	10
Licensed Content Pages	11
Start Page	470
End Page	480
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	Figure 1
Title of your thesis/dissertation	Obtention and characterization of organogels from soybean oil structured using vegetable waxes and interesterified fats through controlled crystallization conditions
Expected completion date	Feb 2017
Estimated size (number of pages)	160
Elsevier VAT number	GB 494 6272 12
Requestor Location	Julio Rocha R. Olga di Giorgio Geracci n. 190 Casa 12A Campinas, SP 13087546 Brazil Attn: Julio Rocha
Total	0.00 USD

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0.

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

ROYAL SOCIETY OF CHEMISTRY LICENSE TERMS AND CONDITIONS

Jan 30, 2017

This Agreement between Julio Rocha ("You") and Royal Society of Chemistry ("Royal Society of Chemistry") consists of your license details and the terms and conditions provided by Royal Society of Chemistry and Copyright Clearance Center.

License Number	4038850646528
License date	Jan 30, 2017
Licensed Content Publisher	Royal Society of Chemistry
Licensed Content Publication	Soft Matter
Licensed Content Title	Structural bases for mechano-responsive properties in molecular gels of (R)-12-hydroxy-N-(ω-hydroxyalkyl)octadecanamides. Rates of formation and responses to destructive strain
Licensed Content Author	V. Ajay Mallia,Richard G. Weiss
Licensed Content Date	May 26, 2015
Licensed Content Volume Number	11
Licensed Content Issue Number	25
Type of Use	Thesis/Dissertation
Requestor type	academic/educational
Portion	figures/tables/images
Number of figures/tables/images	1
Format	print and electronic
Distribution quantity	1
Will you be translating?	no
Order reference number	
Title of the thesis/dissertation	Obtention and characterization of organogels from soybean oil structured using vegetable waxes and interesterified fats through controlled crystallization conditions
Expected completion date	Feb 2017
Estimated size	160
Requestor Location	Julio Rocha R. Olga di Giorgio Geracci n. 190 Casa 12A Campinas, SP 13087546 Brazil Attn: Julio Rocha
Billing Type	Invoice
Billing Address	Julio Rocha R. Olga di Giorgio Geracci n. 190 Casa 12A Campinas, Brazil 13087546 Attn: Julio Rocha
Total	0.00 USD
Terms and Conditions	

This License Agreement is between {Requestor Name} ("You") and The Royal Society of Chemistry ("RSC") provided by the Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by the Royal Society of Chemistry, and the payment terms and conditions.

RSC / TERMS AND CONDITIONS

INTRODUCTION

The publisher for this copyrighted material is The Royal Society of Chemistry. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by CCC, at the time that you opened your RightsLink account and that are available at any time at .

LICENSE GRANTED

The RSC hereby grants you a non-exclusive license to use the aforementioned material anywhere in the world subject to the terms and conditions indicated herein. Reproduction of the material is confined to the purpose and/or media for which permission is hereby given.

RESERVATION OF RIGHTS

The RSC reserves all rights not specifically granted in the combination of (i) the license details provided by your and accepted in the course of this licensing transaction; (ii) these terms and conditions; and (iii) CCC's Billing and Payment terms and conditions.

REVOCATION

The RSC reserves the right to revoke this license for any reason, including, but not limited to, advertising and promotional uses of RSC content, third party usage, and incorrect source figure attribution.

THIRD-PARTY MATERIAL DISCLAIMER

If part of the material to be used (for example, a figure) has appeared in the RSC publication with credit to another source, permission must also be sought from that source. If the other source is another RSC publication these details should be included in your RightsLink request. If the other source is a third party, permission must be obtained from the third party. The RSC disclaims any responsibility for the reproduction you make of items owned by a third party.

PAYMENT OF FEE

If the permission fee for the requested material is waived in this instance, please be advised that any future requests for the reproduction of RSC materials may attract a fee.

ACKNOWLEDGEMENT

The reproduction of the licensed material must be accompanied by the following acknowledgement:

Reproduced ("Adapted" or "in part") from {Reference Citation} (or Ref XX) with permission of The Royal Society of Chemistry.

If the licensed material is being reproduced from New Journal of Chemistry (NJC), Photochemical & Photobiological Sciences (PPS) or Physical Chemistry Chemical Physics (PCCP) you must include one of the following acknowledgements:

For figures originally published in NJC:

Reproduced ("Adapted" or "in part") from {Reference Citation} (or Ref XX) with permission of The Royal Society of Chemistry (RSC) on behalf of the European Society for Photobiology, the European Photochemistry Association and the RSC.

For figures originally published in PPS:

Reproduced ("Adapted" or "in part") from {Reference Citation} (or Ref XX) with permission of The Royal Society of Chemistry (RSC) on behalf of the Centre National de la Recherche Scientifique (CNRS) and the RSC.

For figures originally published in PCCP:

Reproduced ("Adapted" or "in part") from {Reference Citation} (or Ref XX) with permission of the PCCP Owner Societies.

HYPERTEXT LINKS

With any material which is being reproduced in electronic form, you must include a hypertext link to the original RSC article on the RSC's website. The recommended form for the hyperlink is http://dx.doi.org/10.1039/DOI suffix, for example in the link http://dx.doi.org/10.1039/b110420a the DOI suffix is 'b110420a'. To find the relevant DOI suffix for the RSC article in question, go to the Journals section of the website and locate the article in the list of papers for the volume and issue of your specific journal. You will find the DOI suffix quoted there.

LICENSE CONTINGENT ON PAYMENT

While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and the RSC reserves the right to take any and all action to protect its copyright in the materials.

WARRANTIES

The RSC makes no representations or warranties with respect to the licensed material.

INDEMNITY

You hereby indemnify and agree to hold harmless the RSC and the CCC, and their respective officers, directors, trustees, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this licence.

NO TRANSFER OF LICENSE

This license is personal to you or your publisher and may not be sublicensed, assigned, or transferred by you to any other person without the RSC's written permission.

NO AMENDMENT EXCEPT IN WRITING

This license may not be amended except in a writing signed by both parties (or, in the case of “Other Conditions, v1.2”, by CCC on the RSC's behalf).

OBJECTION TO CONTRARY TERMS

You hereby acknowledge and agree that these terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and the RSC (and CCC) concerning this licensing transaction, to the exclusion of all other terms and conditions, written or verbal, express or implied (including any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you). In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

JURISDICTION

This license transaction shall be governed by and construed in accordance with the laws of the District of Columbia. You hereby agree to submit to the jurisdiction of the courts located in the District of Columbia for purposes of resolving any disputes that may arise in connection with this licensing transaction.

LIMITED LICENSE

The following terms and conditions apply to specific license types:

Translation

This permission is granted for non-exclusive world English rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

Intranet

If the licensed material is being posted on an Intranet, the Intranet is to be password-protected and made available only to bona fide students or employees only. All content posted to the Intranet must maintain the copyright information line on the bottom of each image. You must also fully reference the material and include a hypertext link as specified above.

Copies of Whole Articles

All copies of whole articles must maintain, if available, the copyright information line on the bottom of each page.

Other Conditions
v1.2
Gratis licenses (referencing $0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.
If you would like to pay for this license now, please remit this license along with yourpayment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number {Invoice Number}.
Once you receive your invoice for this order, you may pay your invoice by credit card.
Please follow instructions provided at that time.
Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006
For suggestions or comments regarding this order, contact Rightslink Customer Support:
customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jan 30, 2017

This Agreement between Julio Rocha ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4038851108184
License date	Jan 30, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Current Opinion in Colloid & Interface Science
Licensed Content Title	Nanostructuring fiber morphology and solvent inclusions in 12-hydroxystearic acid / canola oil organogels
Licensed Content Author	Michael A. Rogers,Amanda J. Wright,Alejandro G. Marangoni
Licensed Content Date	February 2009
Licensed Content Volume Number	14
Licensed Content Issue Number	1
Licensed Content Pages	10
Start Page	33
End Page	42
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	Figure 12
Title of your thesis/dissertation	Obtention and characterization of organogels from soybean oil structured using vegetable waxes and interesterified fats through controlled crystallization conditions
Expected completion date	Feb 2017
Estimated size (number of pages)	160
Elsevier VAT number	GB 494 6272 12
Requestor Location	Julio Rocha R. Olga di Giorgio Geracci n. 190 Casa 12A Campinas, SP 13087546 Brazil Attn: Julio Rocha
Total	0.00 USD

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.
14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:
15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.
16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.
Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.
17. **For journal authors:** the following clauses are applicable in addition to the above:
Preprints:
A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).
Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).
If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.
Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions
You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.
Terms & Conditions applicable to all Open Access articles published with Elsevier:
Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.
The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.
If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.
Additional Terms & Conditions applicable to each Creative Commons user license:
CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.
CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.
CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0.
Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.
Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

ELSEVIER LICENSE
TERMS AND CONDITIONS

Jan 30, 2017

This Agreement between Julio Rocha ("You") and Elsevier ("Elsevier") consists of your license details and the terms and conditions provided by Elsevier and Copyright Clearance Center.

License Number	4038851241750
License date	Jan 30, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Food Structure
Licensed Content Title	Plant wax crystals display platelet-like morphology
Licensed Content Author	Alexia I. Blake,Alejandro G. Marangoni
Licensed Content Date	January 2015
Licensed Content Volume Number	3
Licensed Content Issue Number	n/a
Licensed Content Pages	5
Start Page	30
End Page	34
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	1
Format	both print and electronic
Are you the author of this Elsevier article?	No
Will you be translating?	No
Order reference number	
Original figure numbers	Figure 1
Title of your thesis/dissertation	Obtention and characterization of organogels from soybean oil structured using vegetable waxes and interesterified fats through controlled crystallization conditions
Expected completion date	Feb 2017
Estimated size (number of pages)	160
Elsevier VAT number	GB 494 6272 12
Requestor Location	Julio Rocha R. Olga di Giorgio Geracci n. 190 Casa 12A Campinas, SP 13087546 Brazil Attn: Julio Rocha
Total	0.00 USD

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at http://myaccount.copyright.com).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com). No modifications can be made to any Lancet figures/tables and they must be reproduced in full.
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.
9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.
10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.
11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.
12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation**: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article.

16. **Posting licensed content on any Website**: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at http://www.sciencedirect.com/science/journal/xxxxx or the Elsevier homepage for books at http://www.elsevier.com; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at http://www.elsevier.com . All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

17. **For journal authors:** the following clauses are applicable in addition to the above:

Preprints:

A preprint is an author's own write-up of research results and analysis, it has not been peer-reviewed, nor has it had any other value added to it by a publisher (such as formatting, copyright, technical enhancement etc.).

Authors can share their preprints anywhere at any time. Preprints should not be added to or enhanced in any way in order to appear more like, or to substitute for, the final versions of articles however authors can update their preprints on arXiv or RePEc with their Accepted Author Manuscript (see below).

If accepted for publication, we encourage authors to link from the preprint to their formal publication via its DOI. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help users to find, access, cite and use the best available version. Please note that Cell Press, The Lancet and some society-owned have different preprint policies. Information on these policies is available on the journal homepage.

Accepted Author Manuscripts: An accepted author manuscript is the manuscript of an article that has been accepted for publication and which typically includes author-incorporated changes suggested during submission, peer review and editor-author communications.

Authors can share their accepted author manuscript:

- immediately
  - via their non-commercial person homepage or blog
  - by updating a preprint in arXiv or RePEc with the accepted manuscript
  - via their research institute or institutional repository for internal institutional uses or as part of an invitation-only research collaboration work-group
  - directly by providing copies to their students or to research collaborators for their personal use
  - for private scholarly sharing as part of an invitation-only work group on commercial sites with which Elsevier has an agreement
- after the embargo period
  - via non-commercial hosting platforms such as their institutional repository
  - via commercial sites with which Elsevier has an agreement

In all cases accepted manuscripts should:

- link to the formal publication via its DOI
- bear a CC-BY-NC-ND license - this is easy to do
- if aggregated with other manuscripts, for example in a repository or other site, be shared in alignment with our hosting policy not be added to or enhanced in any way to appear more like, or to substitute for, the published journal article.

Published journal article (JPA): A published journal article (PJA) is the definitive final record of published research that appears or will appear in the journal and embodies all value-adding publishing activities including peer review co-ordination, copy-editing, formatting, (if relevant) pagination and online enrichment.
Policies for sharing publishing journal articles differ for subscription and gold open access articles:
Subscription Articles: If you are an author, please share a link to your article rather than the full-text. Millions of researchers have access to the formal publications on ScienceDirect, and so links will help your users to find, access, cite, and use the best available version.
Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.
If you are affiliated with a library that subscribes to ScienceDirect you have additional private sharing rights for others' research accessed under that agreement. This includes use for classroom teaching and internal training at the institution (including use in course packs and courseware programs), and inclusion of the article for grant funding purposes.
Gold Open Access Articles: May be shared according to the author-selected end-user license and should contain a CrossMark logo, the end user license, and a DOI link to the formal publication on ScienceDirect.
Please refer to Elsevier's posting policy for further information.
18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.
19. **Thesis/Dissertation**: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for Proquest/UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission. Theses and dissertations which contain embedded PJAs as part of the formal submission can be posted publicly by the awarding institution with DOI links back to the formal publications on ScienceDirect.

Elsevier Open Access Terms and Conditions

You can publish open access with Elsevier in hundreds of open access journals or in nearly 2000 established subscription journals that support open access publishing. Permitted third party re-use of these open access articles is defined by the author's choice of Creative Commons user license. See our open access license policy for more information.

Terms & Conditions applicable to all Open Access articles published with Elsevier:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation. If any changes have been made, such changes must be clearly indicated.

The author(s) must be appropriately credited and we ask that you include the end user license and a DOI link to the formal publication on ScienceDirect.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: The CC-BY license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article and to make commercial use of the Article (including reuse and/or resale of the Article by commercial entities), provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by/4.0.

CC BY NC SA: The CC BY-NC-SA license allows users to copy, to create extracts, abstracts and new works from the Article, to alter and revise the Article, provided this is not done for commercial purposes, and that the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, indicates if changes were made and the licensor is not represented as endorsing the use made of the work. Further, any new works must be made available on the same conditions. The full details of the license are available at http://creativecommons.org/licenses/by-nc-sa/4.0.

CC BY NC ND: The CC BY-NC-ND license allows users to copy and distribute the Article, provided this is not done for commercial purposes and further does not permit distribution of the Article if it is changed or edited in any way, and provided the user gives appropriate credit (with a link to the formal publication through the relevant DOI), provides a link to the license, and that the licensor is not represented as endorsing the use made of the work. The full details of the license are available at http://creativecommons.org/licenses/by-nc-nd/4.0.

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Associating advertising with the full text of the Article
- Charging fees for document delivery or access
- Article aggregation
- Systematic distribution via e-mail lists or share buttons

Posting or linking by commercial companies for use by customers of those companies.

20. **Other Conditions**:

v1.9

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.