ÖZET

OLEİK ASİT İÇERİĞİ YÜKSEK BİTKİSEL SIVI YAĞ KARIŞIM OLEOJELİNE BAL İLAVESİ İLE ÜRETİLEN YENİ BİR SÜRÜLEBİLİR KAHVALTILIK MARGARİN

Bu buluş, farklı jelleşme ajanları ile sıvı yağlardan doymuş ve trans yağ içeriği düşük katı yağların elde edilmesini mümkün kılan oleojelasyon yöntemi ile elde edilen oleojellerin içerisine bal katılarak üretilen sürülebilir kahvaltılık yağ elde edilmesi ile ilgilidir.

Lipit temelli materyallerin trans ve doymuş yağlardan oluşan koloidal yağ ağı yapıları yerine trans ve doymamışlık düzeylerini düşürmek veya tamamen ortadan kaldırmak için moleküler jeller yani düşük molekül ağırlıklı oleojel ajanları kullanılmaktadır. Oleojel üretiminde hemen hemen her çeşit bitkisel yağ kullanılabilmektedir. Jel ajanları geniş hacimdeki sıvıları çeşitli şekillerde (çubuk, tüp, lif ve trombosit) kendi içerisinde toplayarak hareketsiz hale getirebilmektedir. Buluşumuz, oleik asit içeriği yüksek bitkisel sıvı yağ karışım oleojeline bal ilave edilmek suretiyle üretilen kahvaltılık sürülebilir margarin ile ilgilidir.

İSTEMLER

1. Buluş, yağların katılaştırılmasında kullanılan yeni bir yöntem olan oleojelasyon işlemi ile elde edilen düşük katı yağ içeriğine sahip oleik asit içeriği yüksek bitkisel sıvı yağ karışım oleojeline bal katılarak elde edilen yeni hoş aromalı sürülebilir bir gıda ürünü olup; özelliği üretiminde hem doymuş yağ içeriği düşük oleojellerin kullanılması hem de hoş aromalı bal kullanılmasıdır.

2. İstem 1'e göre oleik asit içeriği yüksek bitkisel sıvı yağ karışım oleojeline bal ilavesi ile üretilen yeni bir sürülebilir kahvaltılık margarin olup özelliği; farklı jelleşme ajanları ile sıvı yağlardan doymuş ve trans yağ içeriği düşük katı yağların elde edilmesini mümkün kılan oleojelasyon tekniği ile üretilen sürülebilir kahvaltılık margarini içermesidir.

3. İstem 1'e göre oleik asit içeriği yüksek bitkisel sıvı yağ karışım oleojeline bal ilavesi ile üretilen yeni bir sürülebilir kahvaltılık margarin olup özelliği; %16 ila %40 arasında su miktarını içermesidir.

4. İstem 1 ve 2'ye göre oleik asit içeriği yüksek bitkisel sıvı yağ karışım oleojeline bal ilavesi ile üretilen yeni bir sürülebilir kahvaltılık margarin olup özelliği; başta carnauba vaksı bitkisel vakslar ile yüksek oleik asitli Ayçiçek yağı ağırlıklı,zeytin yağı,fındık yağı ve pamuk yağı karışımından üretilen bitkisel yağın 90^{o}C deki su banyosunda bekletilerek vaksın eritilmesi, daha sonra stabilizatörlerin su fazı içerisinde çözündürülürken emülgatörler, renk maddesi ve aroma maddelerinin yağ fazı içeriğinde çözündürülmesi, sonra su fazın yağın içerisine dökülerek ultrasyon işleminin uygulanması, oluşan homojen dağılımlı emülsiyonun tekrar ısıtılarak içerisine bal ilave edilip karışım oluşması, oluşan karışımın erimiş vaks karışımı üzerine dökülerek

karıştırılması ile oluşan oleomargarini içermesidir.

TARİFNAME

OLEİK ASİT İÇERİĞİ YÜKSEK BİTKİSEL SIVI YAĞ KARIŞIM OLEOJELİNE BAL İLAVESİ İLE ÜRETİLEN YENİ BİR SÜRÜLEBİLİR KAHVALTILIK MARGARİN

Buluşun ilgili olduğu teknik saha

Bu buluş, farklı jelleşme ajanları ile sıvı yağlardan, doymuş ve trans yağ içeriği düşük katı yağların elde edilmesini mümkün kılan oleojelasyon yöntemi ile elde edilen oleojellerin içerisine bal katılarak üretilen sürülebilir kahvaltılık yağ elde edilmesi ile ilgilidir.

Tekniğin bilinen durumu

Sıvı ve katı yağlar, uzun yıllardır gıdaların başta duyusal ve besleyici karakteristikleri olmak üzere birçok özelliğini geliştirmek için kullanılmaktadır. Katı yağlar sıvı yağların hidrojenasyon, interesterifikasyon ve fraksiyonlaması olmak üzere 3 farklı metot ile elde edilmektedir. Bu yöntemler ile elde edilen katı yağların içermiş oldukları doymuş ve trans yağ miktarlarının fazla olması hem üreticiyi hem de tüketiciyi farklı alternatiflere yönelmeye zorlamıştır. Son yıllarda yağların katılaştırılmasında kullanılmaya başlanılan oleojelasyon, geleneksel metotlara alternatif umut vaat eden bir teknoloji olma yolunda ilerleme kat etmektedir.

Sıvı ve katı yağlar gıda üretiminde, lezzet verici ve besleyici olarak uzun yıllar kullanılmaktadır. Sıvı yağlardan katı yağ üretiminde hem ülkemizde hem de dünyada kullanılan teknolojilerden birisi yağ hidrojenasyonudur. Ancak bu işlem esnasında yağ asitlerinin doymuş fraksiyonları üretilirken bir yandan da yoğun miktarda cis izomerlerden trans izomerlere dönüşüm de sağlanmaktadır. Son yıllarda yağların yapısı incelendiğinde sağlığa zararlı olduğu bilinmekte olan doymuş yağ asitlerinin yanı sıra trans yağ asitlerinin de sağlık üzerindeki olumsuz etkileri bilinmektedir. Sıvı yağların kısmi hidrojenasyonu sonucu elde edilen ve çoğunlukla yemeklik yağ, hazır yiyecekler ve unlu mamullerin üretiminde kullanılan margarin ve şorteninglerin bünyesinde yüksek miktarda trans yağ asidi bulunmaktadır. Yağların katılaştırılması sonucu elde edilen ürünlerin yapısında bulunan doymuş ve trans yağ asitleri HDL kolesterolü (iyi huylu) düşürürken LDL kolesterolü (kötü huylu) ise artırmaktadır.

Son yıllarda toplum sağılığını iyileştirmeye yönelik olarak tasarlanan gıda ürünleri ve bunların geliştirilmesine yönelik araştırmalar bütün dünyada yoğun olarak yürütülmektedir. Bunların başında da doymuş yağ ve trans oranı azaltılmış yağlar gelmektedir. Bu amaçla, sıvı yağlara farklı özellikteki organik ya da polimer jel ajanları (oleojelatör) katılarak yağa sürülebilir elastik bir yapı kazandırılması ile elde edilen ürünler olan oleojeller kullanılmaktadır.

Genel olarak katı yağların, likit yağlardan oksidatif stabilite açısından daha dayanıklı olduğu bilinmektedir. Gıda endüstrisi için trans içermeyen yağların üretilebilmesi her zaman istenen bir durumdur. Ancak bu durumu sağlama isterken her zaman ve kolay bulunabilme, istenen fonksiyonel özellikleri taşıma, ucuz olma, sağlık için risk taşımama ve gıda ürünlerinin fiziksel özelliklerini modifiye edebilme gibi özellikleri de sağlaması gerekmektedir. Bu ihtiyaç için ortaya çıkan en son alternatif teknoloji oleojellerdir. Gelişen teknolojinin yeni tekniklerinden biri olan oleojeller, üç boyutlu bir jel ağı içerisinde hapsedilmiş organik likit olarak da tanımlanmaktadır.

Oleojelasyon tekniği sıvı yağlardan doğal veya sentetik ajanlar ile doymuş yağ içeriği düşük ve trans yağ içermeyen katı yağların eldesini mümkün kılan yenilikçi bir yöntem olmaktadır. Oleojeller, bugüne kadar birçok gıda maddesinde yağ ikame maddesi olarak kullanılmış olup, olumlu sonuçlar alınmıştır. Bunların başında fırıncılık ürünleri, peynir, dondurma, salam ve sosis gibi hem ülkemizde hem de dünyada çokça tüketilen ürünler gelmektedir.

Ülkemizde yağlı tohum üretimimizin yaklaşık olarak %45 ini Ayçiçek tohumu oluşturmakta olup, yemeklik yağ olarak en çok tüketilen yağların başında da bu tohumlardan üretilen Ayçiçek yağı gelmektedir. Ayçiçek tohumundan elde edilen yağ, linoleik asitçe zengindir. Ayrıca son yıllarda Ayçiçek yağının içermiş olduğu linoleik asit miktarı düşürülerek oleik asit miktarı artırılmış ve yüksek oleik asitli ayçiçek yağı üretimine de başlamıştır. Yüksek oleik asitli ayçiçek yağı, içermiş olduğu oleik asitten dolayı zeytin yağına alternatif bir yağ olarak, ABD, Arjantin, Kanada ve Fransa da yüksek oranda tüketilmektedir. Söz konusu yağlı tohum bitkisi ülkemizde de TAGEM projesi kapsamında üretilmeye başlanmış bulunmaktadır. Yine zeytinyağı ve fındık yağı üretiminde de ülkemiz önemli bir yere sahiptir.

Dünya üzerinde üretimi yapılan başlıca arıcılık ürünü baldır. Bunun yanı sıra polen, arı sütü gibi arıcılık ürünleri de üretilmektedir. Ülkemiz bal üretiminde dünya genelinde Çin ve Arjantin den sonra 3. sırada gelmektedir. Bal çoğunluğunu karbonhidaratlar, aminoasitler, mineral maddeler ve bir takım tat ve aroma maddelerinin oluşturduğu bir gıda maddesidir. Balın şekerinin %80-90 civarını glukoz ve fruktoz oluşturmaktadır.

Buluşun çözümünü amaçladığı teknik problemler

Bu buluş, gıda sanayisinde hali hazırda ticari olarak üretilen doymuş ve trans yağ içeriği yüksek hidrojene yağlara ve doymuş yağ içeriği yüksek interifikasyon teknolojisi ile üretilen sürülebilir yağlara alternatif olabilecek nitelikte, tat, aroma ve koku bakımından daha iyi olan yeni bir yüksek oleik asit içeriğine sahip sürülebilir kahvaltılık yağ üretilmesi ile ilgilidir.

Oleojelasyon teknolojisi ile üretilen, formülasyonu ile tamamen sıvı, sağlıklı bitkisel yağlar (yüksek oranda yüksek oleik asitli ayçiçek yağı olmak üzere, fındık yağı, zeytin yağı ve pamuk yağı) ile sürülebilir yağ üretilmesi sağlanacaktır. İçeriğine ilave edilen bal ile istenen lezzet bileşenlerini bir araya getirerek, özellikle küçük yaştaki bireylerin de severek tüketebileceği bir ürün olma özelliği taşımaktadır.

Buluş, ülkemizin yüksek miktarda tüketmiş olduğu doymuş ve trans yağ içeriği yüksek hidrojene margarinlere alternatif olacağı için toplum sağlığı açısından olumlu katkılar sağlamasının yanı sıra ihracat potansiyeli yüksek katma değerli, yeni bir ürün olacağı için ülke ekonomimize de katkı sağlayacaktır.

Buluşun açıklaması

Formülasyonlar sulu ve susuz olarak belirlenmiştir. Sulu formülasyonların su miktarı ülkemizde üretimi yapılan margarin formülasyonundaki su miktarı olan %16 ile % 40 arasında belirlenmiştir. Ancak bu oran % 70'e kadar çıkabilir. Oleomargarinler hazırlanmadan önce başta carnauba vaksı olmak üzere bitkisel vakslar (erime sıcaklığı 84.5 °C) ve farklı oranlarda karışım halindeki bitkisel sıvı yağlar 90 °C deki su banyosuna konulmaktadır. Vaksın tamamen erimesi sağlanırken bir taraftan da yağın aynı sıcaklığa şartlanması sağlanır. Stabilizatöreler su fazı içerisinde çözündürülürken emülgatörler, renk maddesi ve aroma maddeleri de yağ fazı içerisinde çözündürülmektedir. Önce su fazı yağın içerisine dökülerek %100 güçte 10 dakika ultrason işlemi uygulanır. Bu işlemde su ve yağın homojen bir biçimde emülsiyon oluşturması amaçlanmaktadır. Daha sonra oluşan emülsiyon tekrar ısıtılır. Üzerine %5 ile % arasında değişebilen oranlarda bal ilave edilerek karıştırılır. Tamamen erimiş vaks karışımının üzerine dökülür ve iyice karıştırılır. Daha sonra oluşan ürün belli bir süre soğumaya bırakılarak nihai ürünün elde edilmesi sağlanmış olunur.

Buluş, oleojelasyon tekniği ile üretilen sürülebilir yağa bal ilavesi yapılarak yağın daha hoş aroma ve lezzete sahip olmasını sağlamaktadır.

Buluşun sanayiye uygulanma biçimi

Ballı oleomargarin, diğer birçok sürülebilir yağ ürünlerine göre daha kolay bir biçimde üretimi yapılabilmektedir. Ayrıca oleomargarin üretimi yaygınlaştıkça farklı bitkisel yağlardan özellikleri zenginleştirilmiş çeşitli oleomargarin ürünleri üretilmesi mümkün olacaktır.

Elde edilen bu ürün hem doymamış yağ asidi içeriği bakımından yüksek, insan sağlığı açısından önem arz eden oleik asitçe zengin hem de görünüş ve lezzet açısından da normal sürülebilir gıda ürünleri kadar albenisi olacağı için bu ürünün üretimi ve satışı hem besleyici hem de ticari yönden önem arz etmektedir.

T.C.
TÜRK PATENT VE MARKA KURUMU
Patent Dairesi Başkanlığı

Sayı : E-39616753-110-210764851 23.12.2021
Konu : Patent Yazısı - 2017/03522 Numaralı Başvuru

RÜŞTÜ GÜMÜŞ (ACAR FİKRİ MÜLKİYET VE YÖNETİM DAN. A.Ş.)

İlgi : 08/03/2017 tarihli, 2017/03522 numaralı başvurunuz.

İlgide kayıtlı başvuru ve buna ilişkin buluşun 6769 Sayılı Sınai Mülkiyet Kanununun 98 inci maddesinin ikinci fıkrası hükmüne göre incelenmesine ilişkin 1. Bildirim ilişikte gönderilmektedir.

Söz konusu başvurunuzla ilgili olarak anılan Kanunun 98 inci maddesinin dördüncü fıkrası ve ilgili Yönetmeliğin 103 üncü maddesinin ikinci fıkrası hükümleri uyarınca, 1. Bildirimde yer alan hususlara ilişkin görüşünüzün veya yapılacak değişikliklerin **tebliğ tarihinden itibaren üç ay içinde** Kurumumuza gönderilmesi gerekmektedir.

Anılan süre içinde görüş bildirilmemesi veya değişiklik yapılmaması halinde başvurunuz geri çekilmiş sayılacaktır.

İşbu yazıya konu talebi, Kurumumuzun Elektronik Başvuru Sistemi (epats.turkpatent.gov.tr) üzerinden, Benim Sayfam panelinde Başvuru Sonrası İşlemler menüsü altında yer alan "İnceleme Bildirimine Cevap Verme" işlemini seçerek gerçekleştirebilirsiniz.

Saygılarımla.

Batuhan ERTÜRK
Kurum Başkanı a.
Sınai Mülkiyet Uzmanı

EK: İncelemeye İlişkin Görüş

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İNCELEMEYE İLİŞKİN GÖRÜŞ

Başvuru No: **2017/03522**	Başvuru Tarihi: **08/03/2017**	(İlk) Rüçhan Tarihi **-----------**

Patent Sınıfı (IPC):

A23D 7/00

PATENTLENEBİLİRLİK ŞARTLARI İLE İLGİLİ AÇIKLAMALAR

Yenilik	EVET	İstem	1-4
	HAYIR	İstem	----
Buluş Basamağı	EVET	İstem	4
	HAYIR	İstem	1-3
Sanayiye Uygulanabilirlik	EVET	İstem	1-4
	HAYIR	İstem	----

DETAYLI GÖRÜŞLER

İlgili Dokümanlar

İncelemeye ilişkin görüş aşağıda belirtilenler esas alınarak hazırlanmıştır.

Tarifname 5 sayfa (31/01/2020 tarihli değişen nüsha)
İstem 4 adet (31/01/2020 tarihli değişen nüsha)
Başvuru sahibinin 31/01/2020 tarihli görüşleri

Aşağıdaki dokümanların başvuru ile ilgili olduğu düşünülmektedir:

D1: “Characterization of Hazelnut Oil Oleogels Prepared with Sunflower and Carnabua Waxes” International Journal of Food Properties

D2: US2015157038 A1

D3: https://www.youtube.com/watch?v=ik1XGouPhLg

DüzenlenmeTarihi: **23/12/2021**

TÜRK PATENT VE MARKA KURUMU Patent Dairesi Başkanlığı Hipodrom Cad. No:115 06330 Yenimahalle/ANKARA Tel: (312) 303 1182 Faks: (312) 303 1220	İncelemeyi Yapan Uzman: **Batuhan ERTÜRK**

Başvuru konusu buluş, farklı jelleşme ajanları ile sıvı yağlardan, doymuş ve trans yağ içeriği düşük katı yağların elde edilmesini mümkün kılan oleojelasyon yöntemi ile elde edilen oleojellerin içerisine bal katılarak üretilen sürülebilir kahvaltılık yağ elde edilmesi ile ilgilidir.

D2 dokümanı, İstem 1'de tanımlanan buluş konusunda tekniğin bilinen durumunu gösteren en yakın doküman olarak alınmıştır.

Patentlenebilirlik Şartları

Yenilik

Tekniğin bilinen durumunda, buluşa ait söz konusu özelliklerin tümünün bir arada olduğu bir doküman mevcut değildir.

Bu nedenle, D1 dokümanı göz önüne alındığında, buluş konusu istem 1 ve ona bağımlı olan 2-4 nolu istemler 6769 sayılı Sınai Mülkiyet Kanununun 83 üncü maddesinin birinci fıkrasına göre yenidir.

Buluş basamağı

D2 dokümanında bir yenilebilir oleojel hazırlamak için bir yöntem açıklanmaktadır. Başvuru sahibinin itirazında su içermediğinden bahsedilse de paragraf 35-36'da karışımın su içerdiği açıklanmaktadır. Tekniğin bilinen durumunda bulunan D3 dokümanında ise sürülebilir kahvaltılık margarin olan teremyağın bal aroması içerdiği açıklanmaktadır.

Başvuruya konu buluşun üretim yönteminde kullanılan su miktarının %16-%40 oranı arasında olmasının beklenmedik bir teknik katkısı bulunmadığından, D2 ve D3 dokümanları birlikte düşünüldüğünde, buluş konusu istem 1 ve ona bağımlı olan 2-3 nolu istemlerdeki yapılanma teknikte uzman bir kişi için aşikâr olarak kabul edileceğinden 1-3 nolu istemler buluş basamağı niteliğine sahip değildir.

İstem 4'te açıklanan işlem adımlarına ait teknik özellikler tekniğinin bilinen durumundaki dokümanlara bakılarak aşikâr bir biçimde çıkarılamamaktadır. Diğer bir ifadeyle tekniğin bilinen durumundaki dokümanlara göre teknikteki uzman kişinin bakış açısıyla, istem 4'le objektif teknik probleme çözüm olarak sunulan buluş konusu tekniğin bilinen durumundan kolaylıkla çıkarılabilecek bir çözüm değildir.

Bu nedenle istem 4 6769 sayılı Sınai Mülkiyet Kanununun 83 üncü maddesinin dördüncü fıkrasına göre buluş basamağı içermektedir.

Sanayiye uygulanabilirlik

Buluş konusu istem 1 ve ona bağlı olan 2-4 nolu istemler 6769 sayılı Sınai Mülkiyet Kanununun 83 üncü maddesinin altıncı fıkrasına göre sanayiye uygulanabilir niteliktedir.

T.C.
TÜRK PATENT VE MARKA KURUMU
Patent Dairesi Başkanlığı

Sayı : 39616753- 2017/03522 /
Konu : Patent

RÜŞTÜ GÜMÜŞ (ACAR FİKRİ MÜLKİYET VE YÖNETİM DAN. A.Ş.)
19 MAYIS MAH. AYTEKİN KOTİL CAD. NO:12/A ŞİŞLİ/İSTANBUL

İlgi: 08/03/2017 tarihli patent başvurunuz.

İlgide kayıtlı başvurunuzla ilgili olarak Kurumumuz tarafından düzenlenen tekniğin bilinen durumu konusundaki Araştırma Raporu ve Ekleri ilişikte gönderilmektedir.

6769 sayılı Sınai Mülkiyet Kanununun 98 inci maddesinin birinci fıkrası ve anılan Kanunun Uygulanmasına Dair Yönetmeliğin 102 nci maddesinin birinci fıkrası hükümleri uyarınca bildirim tarihinden itibaren üç ay içinde ücretinin de ödenerek inceleme talebinde bulunulması gerekmektedir. Aksi takdirde başvurunuz geri çekilmiş sayılacaktır.

Saygılarımla.

Batuhan ERTÜRK
Kurum Başkanı a.
Sınai Mülkiyet Uzmanı

Ek: Araştırma Raporu ve Ekleri

NOTLAR:

1- Türk Patent ve Marka Kurumunun sunduğu hizmetlere ilişkin ücretlerde, ödemenin yapıldığı tarih itibariyle yürürlükte olan Ücret Tebliğinin dikkate alınması gerekmektedir.

2- Başvurunun korunması için gerekli olan yıllık ücretler üçüncü yıldan başlamak üzere her yıl vadesinde ödenir. Vade tarihi, başvuru tarihine tekabül eden ay ve gündür. Yıllık ücretler, vadesinde ödenmediği takdirde ek ücretle birlikte vadeyi takip eden altı ay içinde de ödenebilir. Yıllık ücretlerin bu süre içinde de ödenmemesi halinde başvurular geçersiz sayılır.

Evrak bilgisine http://www.turkpatent.gov.tr adresinden, "mnvh39FAC08E" DYS No ve Evrak tarihinden erişebilirsiniz.

"e-imzalıdır"

Cevaplarda; ilgili yazının çıktığı daire, tarih ve sayının tam olarak yazılması rica olunur.

ARAŞTIRMA RAPORU

Başvuru Sahibi:
İSTANBUL SABAHATTİN ZAİM ÜNİVERSİTESİ

Başvuru No: 2017/03522	Başvuru Tarihi: 08/03/2017	(İlk) Rüçhan Tarihi -

Patent Sınıfı (IPC^8):
A23D 7/00 (2009.01)

GENEL GÖZLEMLER

Buluş Bütünlüğü

X Var (başvuru sadece bir buluş konusunu içermektedir)

... (başvuru birden çok buluş konusunu içermektedir) (Bakınız: Bölüm III)

Tarifname Takımı

X Rapor aşağıda belirtilen tarifname takımı esas alınarak düzenlenmiştir.

Tarifname	4 sayfa (Orijinal)
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“olegeol, honey, flusk, water, carnabua, wax, margarin, butter” ve bunların uygun kombinasyonları

C. İLGİLİ DOKÜMANLAR

Kategori	Dokümanlar	İlgili Olduğu İstem
X	“Characterization of Hazelnut Oil Oleogels Prepared with Sunflower and Carnabua Waxes” International Journal of Food Properties Mustafa Öğütücü, Emin Yılmaz 16 Nisan 2015 (16.04.2015)	1-2,4-5
X	US2015157038A1 (DOW GLOBAL TECHMOLOGIES LLC [US]) 11 Haziran 2015 (11.06.2015) Tüm Doküman	1-2,4-5
A	https://www.youtube.com/watch?v=ik1XGouPhLg 12 Mart 2009 (12.03.2009)	1-2,4-5

☐ İlgili Dokümanlar sonraki sayfadan devam etmektedir. ☐ Patent Ailesi Üyeleri ekine bakınız.

Kategorilerin Açıklaması:

“X”	Buluşun yeni olmadığını veya buluş basamağı içermediğini tek başına gösteren doküman	“E”	Başvuru tarihinde veya başvuru tarihinden sonra yayımlanan doküman
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ARAŞTIRMA RAPORU

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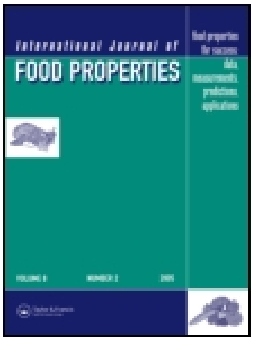
II. GÖRÜŞLER
• 3 numaralı istem ile sadece ulaşılmak istenen sonuç/sağlanan fayda korunmaya çalışıldığından bu istem istemlerden çıkartılmalıdır.



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Characterization of Hazelnut Oil Oleogels Prepared with Sunflower and Carnauba Waxes

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In this study, hazelnut oil oleogels prepared with sunflower wax and carnauba wax were analyzed and compared with a commercial shortening. Oil binding capacities of sunflower wax oleogels were higher than 99%, while carnauba wax had a maximum value of 97.6% for 10% addition level. At 3% addition level of carnauba wax, no gel developed. The crystal formation time of sunflower wax was shorter. Although the highest (8.5%) solid fat content was observed in the 10% carnauba wax containing oleogel (HC10) sample, it was 30.4% in the commercial shortening sample at 20°C. The peak melting temperature of commercial shortening was 52.3°C, and among all organogels, sunflower wax oleogel at 3% addition level had the closest value (58.4°C). The melting enthalpies of the oleogels ranged from 4.3 to 20.3 J/g, while it was 10.9 J/g for the commercial shortening sample. The firmness and stickiness values in the oleogel samples were lower than that of commercial shortening sample. On the other hand, there was no significant change of firmness and stickiness during storage, indicating good stability ($p \leq 0.001$). Especially the sunflower wax oleogels were very homogenous and smooth in structure. The polarized light microscopy pictures revealed needle-like crystals for sunflower wax and aggregate-like crystals for carnauba wax oleogels. The x-ray diffraction measurements of the crystals showed the β' types of the polymorphic structures. Furthermore, the oleogels were very stable against oxidation during the storage period. Hazelnut oil organogels prepared with sunflower wax can be good source material for shortening or margarine-like products.

Keywords: Oleogel, Hazelnut oil, Sunflower wax, Carnauba wax, X-ray diffraction, Storage.

INTRODUCTION

Edible oils naturally exist in solid, semi-solid or liquid state, and this physical state can determine their application areas in food products.[1,2] The physical state of oil depends on the chain length and saturation level of its fatty acids, *cis/trans* isomers content and the position of fatty acids in the glycerol. As versatile raw materials, the physical properties of liquid oils have been modified by some technological applications such as hydrogenation, fractionation, interesterification, blending,

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and crystallization. Although these present technologies are useful, they may have some disadvantages, such as increase in saturated and *trans* fatty acid content, expensive investment and higher operation cost.[1,3,4]

Oil structuring has been a technological challenge for many research efforts. Organogelation is based on a completely different approach than hydrogenation or fractionation.[2] Briefly, some small molecular weight organogelator agents are added into liquid oil and mixed, and the oil is entrapped within a thermo-reversible, 3-dimentional network created by the organogelators. Apparently there is no change in the fatty acid composition of the stock oil. For edible oils, sometimes the term "oleogel" is used to distinguish it from other organic phase gels. This technique is novel, easy to apply, relatively cheaper, and safer compared to hydrogenation. The most important challenge in organogelation researches is to find the most suitable organogelators. Oleogels are suggested for production of plastic fat stocks, nutraceutical encapsulation and delivery, controlled release of bioactives, production of creams and cookies, substitution in meat products and confectionary, minimizing oil migration in different processed foods, and others.[2,3,5,6]

Among others, natural waxes have been investigated for their organogelation properties in edible oils. Carnauba wax (CW) is produced from the leaves of Brazilian palm, *Copernicia prunifera*. It is usually more expensive than most of the other plant waxes.[2] In a study,[7] the organogel properties of rice bran wax, candelilla wax, and CW were compared. The melting temperature and enthalpy change of CW were determined to be 84°C and 137.6 J/g, respectively. It was shown that the minimum gel concentration for CW is 4%, and gelation time was 13.5 min. The hardness value of CW oleogels was the lowest among others. In that study, it was concluded that rice bran wax was the best as organogelators when compared with candelilla and CWs. Sunflower wax (SW) is produced from the seeds of *Helianthus annuus* plant.[2] The organogelation properties of SW with soybean oil were investigated. The minimum quantity required for gelation were determined for many plant waxes, animal waxes, and synthetic waxes in that study, but only SW organogels were studied extensively. It was determined that SW can produce gels at 0.5–10% concentration with 47–67°C melting point range, and as the wax content increased in the organogels, the melting temperatures, enthalpies, and firmnesses enhanced. The microphotographs of SW organogels were also provided.[8]

In this study, the oleogels of hazelnut oil (HO) prepared with CW and SW and their textural, structural, thermal, visual, and storage properties were examined in detail. Three different addition levels (3, 7, and 10%, w/w) of the waxes were also compared to find out the most suitable one as spreadable product. The oleogels produced in this study were also compared with a commercial shortening (CS) product to reveal the level of similarities. In addition, storage stability for texture and oxidation was monitored at both room and refrigerator temperatures for three months. Furthermore, the x-ray diffraction (XRD) data is provided for the oleogels developed. To our best knowledge, the literature is lacking for SW oleogels for XRD pattern data.

MATERIALS AND METHODS

Materials

Refined HO (Çotanak Oil Co., Ordu, Turkey) was purchased from marketplaces. The fatty acid composition of the oil (% weight) provided by the producer, as 0.03% myristic, 5.87% palmitic, 0.2% palmitoleic, 2.64% stearic, 82.7% oleic, 9.50% linoleic, 0.07% linolenic, 0.13% arachidic, and 0.02% behenic acids. SW (6607L) was purchased from KahlWax (Kahl GmbH & Co., Trittau, Germany). It is a yellowish solid pellet with soft/characteristic odor, with 0.85–1.05 g/cm^3 density at 20°C, having a melting range of 74–80°C, acid value of 2–8 mg KOH/g, saponification value of 80–96 mg KOH/g, peroxide value (PV) of 0 mval/kg. It is classified as free from dangerous chemicals according to Annex I to Directive 67/548/EEC. CW (5023) was also purchased from KahlWax (Kahl GmbH & Co., Trittau, Germany). It is a yellow to brown solid powder/flakes with faint odor, having density of 0.99–1.00 g/cm^3 at 20°C, with melting range of 78–88°C, acid value of 5–15 mg KOH/g, saponification value of 80–95 mg KOH/g. No dangerous materials were acknowledged and the wax was claimed as safe product.

Preparation of the Oleogels

The addition levels of waxes were 3, 7, and 10% as weight ratio. First HO and each of the SW and CW were placed into beakers and heated in a water bath at 90°C. When the waxes melted completely, and all are at the same temperature, the waxes were added into the oil and stirred vigorously for 5 min. Then this mixture was poured into sterile plastic cups (150 mL) and glass tubes with caps for subsequent analyses. The oleogels were formed at ambient temperature without any shear effect overnight. Finally, the planned analyses were performed for each sample. For the storage trial, the samples were stored at 20°C in a dark place, and at 4°C in a refrigerator for three months and analyzed periodically. The oleogel production was repeated twice, and all analyses within each production replicate were at least twice. In Fig. 1, the pictures of the HO oleogels are shown. Throughout this manuscript, the samples were abbreviated with codes: HO-hazelnut oil; SW-sunflower wax; CW-carnauba wax; CS-commercial shortening; HS3, HS7, and HS10-oleogels of HO at concentrations of 3, 7, and 10% SW; HC3, HC7, and HC10-oleogels of HO prepared with addition of CW in concentrations of 3, 7, and 10%.

Oil Binding Capacity (OBC)

The OBC method was adapted from Da Pieve et al.[9] First, 1 mL of the melted oleogel sample was put into previously weighed eppendorf tube (weight a) and conditioned in refrigerator for 1 h. Then the tube was weighed again (weight b). The tubes were centrifuged at 9167 g for 15 min at room temperature, and turned over onto a filter paper for drainage of released oil. Finally, the tubes were weighed (weight c) again and OBC was calculated by Eq. (1).

$$\text{OBC}\ (\%) = 100 - \text{Released Oil}\ (\%)\ \text{and Released Oil}\ (\%) = [(b-a)-(c-a)]/(b-a) \times 100 \tag{1}$$

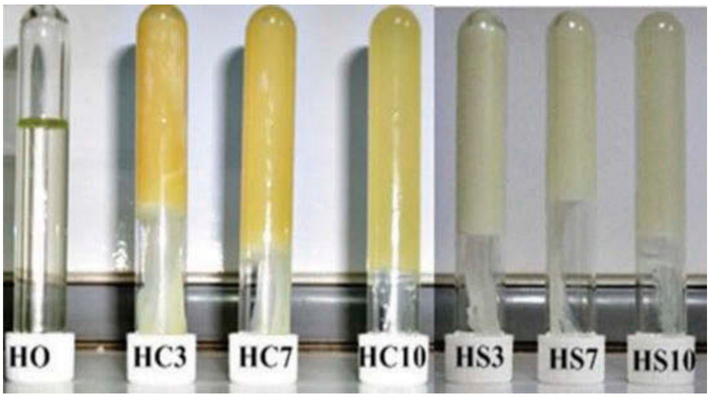


FIGURE 1 The hazelnut oil oleogels of CW and SW.

Crystal Formation Time (CFT)

The previously formed oleogel samples were first completely melted in water bath (90°C) and kept for 2 h for isothermal setting. Then they were taken out from the water bath to room temperature, and meantime chronometer was started. The CFT was recorded when the tubes turned 90° and no flow observed.[7]

Solid Fat Content (SFC)

The method of ISO 8292-2[10] was followed for the percent of SFC measurement. The analysis were carried out at 20 and 30°C with a Minispec Bruker NMR Analyzer mq20 (Bruker Optics, Inc., Billerica, MA, USA) calibrated with 0, 31, and 73.5% solid fat containing standard solutions.

Color Measurement

The color of the oleogel samples was measured with Minolta CR-400 colorimeter (Konica Minolta Sensing, Osaka, Japan). First, the instrument was calibrated with white tile, and then blink reading on an empty glass tube was done to set off the effects of tube. Finally, the color reading were accomplished on several different points of the glass tubes filled with the organogel samples, and the values of L, a^*, and b^* were recorded.[11]

Thermal Analysis

The thermal cycling technique of Dassanayake et al.[7] was adapted for this analysis. The thermal analysis was performed with a Perkin-Elmer 4000 Series differential scanning calorimeter (DSC; Groningen, The Netherlands). The instrument was calibrated with Indium and Zinc standards. First, the DSC was purged with nitrogen at 50 mL/min flow rate. Then the oleogel samples were weighed around 5–7 mg into aluminum pans and sealed hermetically. The temperature program was heating the samples from room temperature to 140°C by 10°C/min; then cooling to –20°C by 10°C/min rate and keeping for 3 min at that temperature for full crystal formation and finally heating again to 100°C by 5°C/min rate. The thermal parameters were calculated by Pyris 1 Manager Software on the instrument.

Instrumental Texture Analysis

The firmness and stickiness of the oleogels were measured with a Texture Analyzer TA-XT2i (Stable Microsystems, Surrey, UK) equipped with a custom-built block and 45° conic acrylic probe. The samples stored at room temperature (20°C) or refrigerator (4°C) were taken out and measured at that temperature to observe the effect of storage temperature. Texture was also monitored during 90 days storage to observe the effects of storage time. The penetration test was accomplished by penetrating the probe into 23 mm depth by 3.0 mm/s speed, and then pulling the probe out at 10 mm/s speed. The texture parameters were calculated by Texture Exponent v.6.1.1.0 software (Stable Microsystems).[12]

Crystal Morphology

The crystal morphology of the oleogels was observed at room temperature with an Olympus BX51 polarized light microscope (Olympus Optical Co., Ltd., Tokyo, Japan) equipped with a CCD color video camera (Canon Inc., Tokyo, Japan).[13]

XRD Analysis

The wide and small-angle XRD patterns of the oleogels were taken with a Rigaku D-Max Rint 2200 model XRD (Rigaku Int. Corp, Tokyo, Japan). The angular scans from 2.0° to 50° (2θ) were performed by $2°/\text{min}$ scan rate. A Cu source x-ray tube ($\lambda = 1.54056$ Å, 40 kV and 40 mA) and MDI Jade 7 software (Materials Data Inc, Livermore, USA) was used for the data analysis.

Oxidative Stability

During the 90 days storage at the two different temperatures, the oxidative stabilities of the samples were monitored by measuring the PV (Cd 8-53 method).[14]

Statistical Analysis

The duplicate measurements within each replicate of oleogel productions were performed for the samples and the results were represented as mean values with standard deviations. The data were analyzed by ANOVA and the multiple comparisons of the means accomplished by Tukey's test. Statistic analysis was performed with Minitab v.16.1.1.[15]

RESULTS AND DISCUSSION

Physico-Chemical Properties

The OBC, CFT, SFC and color values (L, a^*, and b^*) of the oleogel samples are shown in Table 1. Clearly, the oil binding capacities (OBC) of the CW oleogels at 3 and 7% addition levels were much lower than that of SW oleogels. No stable gels were observed for CW oleogels at 3% addition level, and the crystal formation periods were also longer. The results indicated that the 10% CW containing oleogel exhibited maximum SFC (8.5%) at 20°C, whereas at the same temperature CS had 30.4% SFC. The SFCs measured at 30°C were lower than that measured at 20°C. Co and Marangoni[2] have indicated that there was no change in the SFC of organogels, as one of the main advantages listed for organogelation. This situation is confirmed in this study as well. There was a proportional increase of SFC in the oleogels depending on the addition and saturation levels of the organogelators used. The instrumental color values of the oleogel samples showed similarity for a^* and b^* values with CS, while the level of brightness (L value) was somewhat different. The colors and appearances of the oleogels can be visualized from Fig. 1.

Thermal Properties

In any plastic fat product, crystallization and melting behaviors are essential components of its technological properties.[1] Hence, the thermal properties of the oleogel samples together with HO, SW, and CW are measured with DSC and from the thermograms (Fig. 2) the thermal parameters were calculated by the software and the results are presented in Table 2. The melting temperatures and enthalpies of the SW and CW oleogels were quite similar. On the other hand, the melting temperatures of SW containing oleogels were a little lower than that of CW containing oleogels. The melting peak temperatures of the CS was 52.3°C, and among the oleogel samples, 3% SW containing oleogel had the closest value (58.4°C) to that of the CS sample. As the level of added wax increased, the melting temperatures and enthalpies also increased, as expected.[2] The melting enthalpies of the oleogels were different from that of CS sample. The melting enthalpies increased as the level of added organogelators enhanced. The melting temperatures of SW and soybean oil organogels were reported to be between 47 and 65°C within 0.5–10% addition levels. At the same

TABLE 1

The oil binding capacity (OBC), crystal formation time (CFT), solid fat content (SFC), and color values (*L, a**, and *b**) of the oleogel samples

			% SFC				
Samples	*OBC (%)*	*CFT (min)*	*(20°C)*	*(35°C)*	L	a*	b*
HC3	39.8 ± 2.3A*a**	–	2.7 ± 0.03Af	2.6 ± 0.01Ad	42.9 ± 0.2Aa	−3.8 ± 0.07Aa	4.5 ± 0.6Ade
HC7	80.6 ± 5.6Ab	12.0 ± 1.0Aa	6.0 ± 0.2Ac	5.8 ± 0.2Ac	52.9 ± 0.4Ab	−4.9 ± 0.02Ab	11.05 ± 0.2Ab
HC10	97.7 ± 2.1Ac	8.5 ± 0.5Ab	8.5 ± 0.04Ab	8.2 ± 0.03Aa	56.4 ± 0.8Ab	−5.1 ± 0.01Ab	14.6 ± 0.6Aa
HS3	99.8 ± 0.1Bc	5.0 ± 0.0Bc	2.2 ± 0.01Af	2.2 ± 0.06Ad	53.4 ± 1.04Bb	−2.3 ± 0.2Bc	2.9 ± 0.3Be
HS7	99.8 ± 0.1Bc	4.0 ± 0.0Bc	4.9 ± 0.2Ae	5.1 ± 0.1Ac	64.7 ± 1.06Bc	−2.4 ± 0.2Bc	4.8 ± 0.3Bde
HS10	99.8 ± 0.1Bc	4.0 ± 0.0Bc	6.8 ± 0.06Ad	7.2 ± 0.2Ab	68.7 ± 0.5Bd	−2.6 ± 0.1Bc	5.5 ± 0.4Bd
CS	–	–	30.4 ± 0.2Ba	–	79.2 ± 0.6Ce	−3.2 ± 0.1Ba	7.7 ± 0.3Abc

*Capital letters compare the two waxes ($p \leq 0.001$);

**Small letters compare the addition levels of the waxes ($p \leq 0.001$).

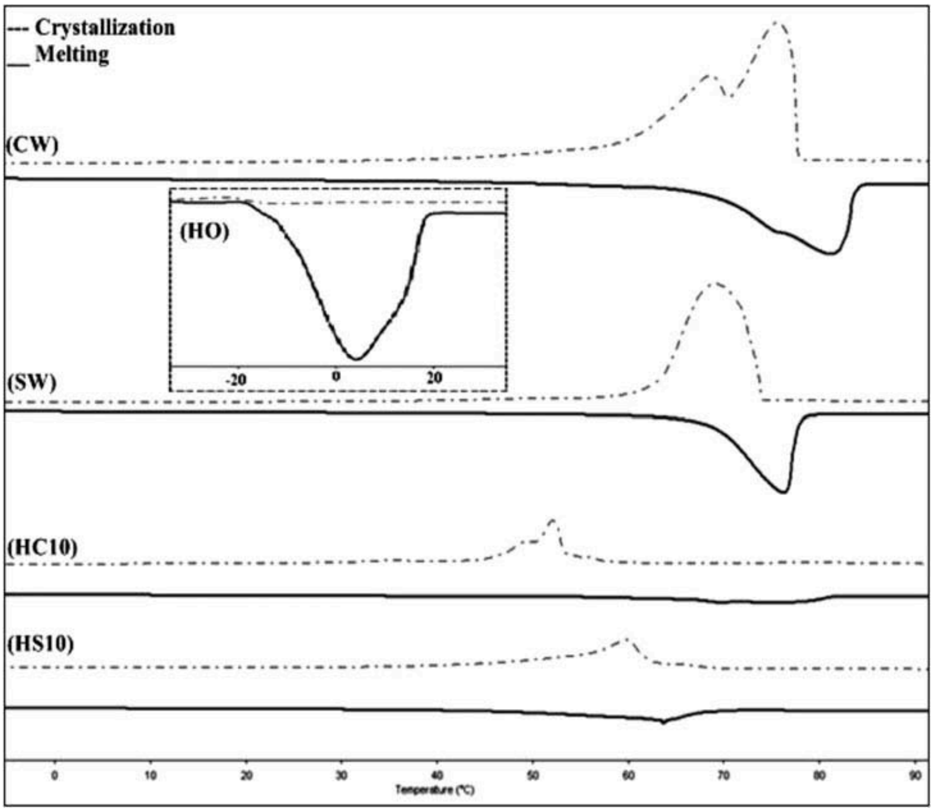


FIGURE 2 The DSC thermograms of hazelnut oil (HO), carnauba wax (CW), sunflower wax (SW), and the oleogel samples.

addition range, the enthalpy change of melting was reported between 0.2 and 15 J/g.[8] Hence, 3–7% SW containing HO can be suggested as an alternative source for shortening fat stock. CW oleogels had similar performance as long as only the thermal properties concerned. Dassanayake et al.[7] reported 84°C melting point and 137.6 J/g melting enthalpy for CW, and we measured 81.04°C melting point and 182.15 J/g melting enthalpy for the same wax. The differences can be attributed to the materials source and purity differences. It was concluded that rice bran wax was better than CW for organogel properties.[7] Similarly, we conclude that SW is better than CW regarding the oleogel properties.

Textural Properties and Storage Stability of the Oleogels

The textural properties of plastic fats are as important as thermal properties, and they define the spreadability, adhesion, and oil separation phenomena.[1] An example graph of the texture measurement is shown in Fig. 3. The firmness values measured for the oleogel samples are shown in Fig. 4. For both waxes, as the addition level increased, the firmness of corresponding oleogels increased proportionally ($p \leq 0.001$). At room temperature, the firmness values have mostly not changed during storage, but only the firmness value of 10% CW containing sample has increased. There was no significant difference between the samples ($p = 0.794$) for the two organogelators in terms of

TABLE 2
The thermal properties of the oleogel samples

	Crystallization			Melting		
Samples	*Onset$_c$ (°C)*	*Peak (Tc, °C)*	*H_c (J/g)*	*Onset$_m$ (°C)*	*Peak (Tm, °C)*	*H_m (J/g)*
HO	−19.4 ± 0.0f*	−22.5 ± 0.0g	−0.8 ± 0.0a	−16.7 ± 0.4c	−8.9 ± 0.4g	66.3 ± 5.5b
CW	77.9 ± 0.1a	75.04 ± 0.7a	−183.8 ± 5.6c	68.8 ± 0.2a	81.04 ± 0.1a	182.2 ± 7.09a
SW	74.04 ± 0.2ab	69.3 ± 0.2b	−197.4 ± 9.4c	68.8 ± 0.2a	76.3 ± 0.04b	199.7 ± 0.04a
CS	24.02 ± 0.1A**e	22.6 ± 0.02Af	−17.2 ± 0.3Aab	36.8 ± 0.7Ab	52.3 ± 0.0Af	10.9 ± 1.02Ac
HC3	47.9 ± 0.2Bd	45.8 ± 0.8Be	−4.2 ± 0.3Aab	61.7 ± 1.4Ba	67.7 ± 0.1Bc	4.3 ± 0.1Ac
HC7	52.4 ± 0.6Bcd	50.5 ± 0.2Bd	−11.3 ± 0.04Aab	63.8 ± 0.1Ba	69.3 ± 0.04Bc	11.5 ± 0.8Ac
HC10	54.8 ± 1.4Bcd	52.9 ± 0.8Bd	−15.3 ± 0.8Aab	64.3 ± 0.2Ba	75.1 ± 0.05Bb	15.1 ± 0.9Ac
HS3	60.8 ± 6.9Cbc	51.4 ± 0.5Cd	−7.2 ± 0.9Aab	45.07 ± 4.2Cb	58.4 ± 1.02Ce	7.9 ± 0.01Ac
HS7	60.1 ± 0.5Ccd	56.9 ± 0.04Cc	−11.3 ± 0.1Aab	46.3 ± 3.3Cb	61.2 ± 0.06Cd	12.07 ± 0.06Ac
HS10	62.4 ± 0.04Cbc	59.3 ± 0.6Cc	−17.5 ± 0.9Ab	62.03 ± 1.1Ca	62.6 ± 1.1Cd	20.3 ± 0.9Ac

*Small letters compare the ten different samples within a column ($p \leq 0.001$);

**Capital letters compare CS with CW and SW oleogel groups ($p \leq 0.001$).

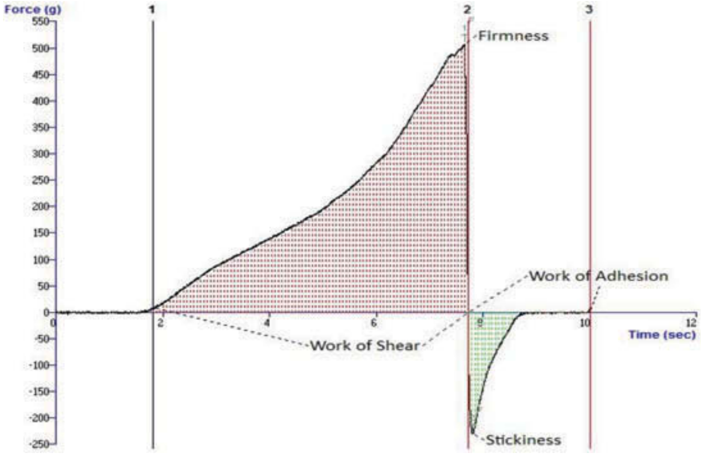
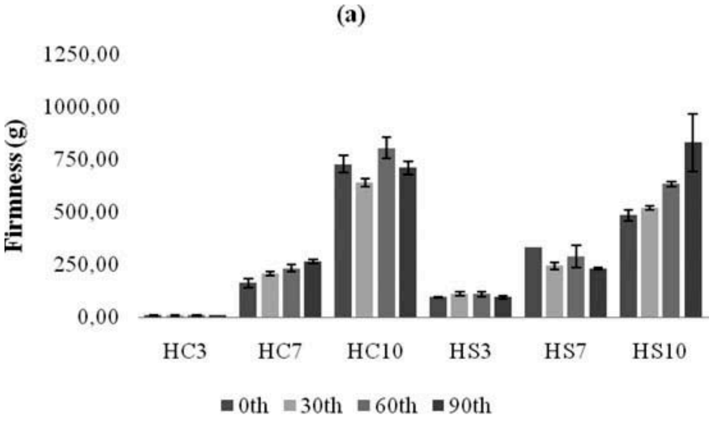


FIGURE 3 The texture measurement curve of hazelnut oil and SW (10%) oleogel.



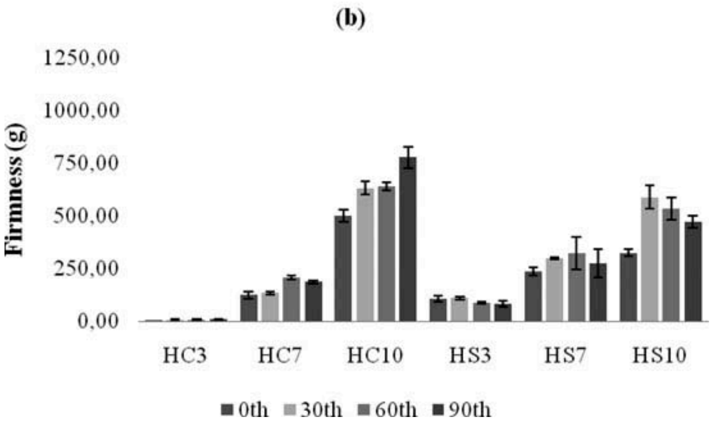


FIGURE 4 The firmness values of the oleogel samples; (a) 4°C (b) 20°C.

firmness values. Similarly, there was no significant difference of the firmness values for the samples stored at refrigerator or room temperature ($p = 0.469$). This situation is quite important for the reduction of cooling requirements. Oleogels are self-stable, thermoreversible and plastic products which do not require cooling systems.[2,3] The lowest firmness value among the samples was 6.9 g with 3% CW oleogel stored at 20°C at the beginning of storage, and the highest value was 831.8 g in 10% SW oleogel stored for 90 days at 4°C. The CS sample had the lowest firmness value (533.8 g) in sample stored at 20°C for 30 days, and the highest value (5824.8 g) in a sample stored at 4°C for 60 days. Clearly CS had higher firmness values, but the oleogel samples prepared with 10% organogelator had firmness values close to the values measured in the CS sample. In fact, all oleogel samples were very stable during storage and the perceptible firmness was almost the same as that of the CS sample. The stickiness or adhesion, the other very important textural parameters, was measured and the results are presented in Fig. 5. The stickiness values of CW oleogels were not significantly different ($p = 0.731$) from that of the corresponding SW oleogels at both storage temperatures. Similarly to firmness, storage at 4°C has yielded a little higher stickiness values for the two types of the oleogels ($p = 0.416$). As the added wax level increased, the stickiness was also enhanced ($p \leq 0.001$) for both types. Among all oleogels prepared, the lowest stickiness value was found as 7.2 g for 3% CW oleogel stored at 4°C for 90 days. The highest stickiness value was 343.3 g for 10% CW oleogel stored at 4°C for 0 days. The range of stickiness for CS samples was

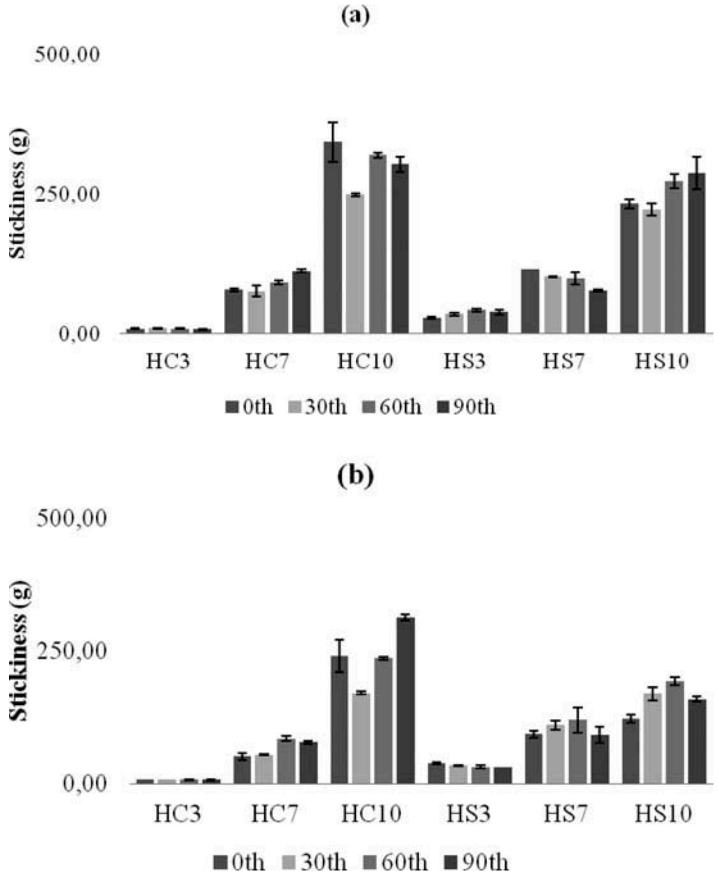


FIGURE 5 The stickiness values of the oleogel samples; (a) 4°C (b) 20°C.

from 274.06 g measured in a sample stored at 20°C for 0 day to 1917.4 g measured in another sample stored at 4°C for 90 days. The measured stickiness values of the CS were much higher than that of the oleogel samples. It was indicated that the correlation between hardness (firmness) and spreadability, and of cohesiveness and spreadability were higher, but correlation between adhesiveness and spreadability was lower among the analyzed table fats.[16] Hence, the evaluation of both firmness and stickiness together might be more meaningful for the estimation of spreadability of plastic fats. As stickiness of a plastic fat sample increases, more force is required to pull back the probe, indicating the possible difficulty of spreading.[12] In another study,[17] pistachio oil spreads were characterized. It was shown that firmness, adhesiveness, and compressibility of spreads were declined by added cocoa butter, whereas the same attributes were improved by xanthan gum additions. In a recent study,[18] margarines from organogels were prepared and firmness values were compared with themselves and with commercial spread and margarine products. It was indicated that SW organogels are more suitable than rice bran and candelilla wax organogels for margarine formulations as long as firmness considered, although they did not perform a sensory analysis.

Polarized Light Microscopy and XRD Patterns

The polarized light microscopy pictures of the oleogels are shown in Fig. 6. Since no true crystals were present in 3% CW sample, its picture is not presented. Although SW oleogels had needle-like crystal structures, CW oleogels seem rather more aggregate-like. A very similar optical micrograph of CW in olive oil is presented by Dassanayake et al.[7] They also suggested that CW organogels yield spherulitic structures and at 1% addition level, it is in a viscous sol state rather than an organogel structure. On the other hand, needle-like crystals in SW-soybean oil organogels[8] seem very similar to those viewed in this study. We have also taken the wide and small angle XRD patterns of the oleogel samples (Fig. 7 and Table 3). The XRD patterns of 10% CW and SW oleogels were very similar to each other. In fact, similar peaks in the CS sample are observed with much higher intensities. In addition to the common peaks, there was a distinct peak at around 14.06 Å in the CS sample which creates the main difference from the oleogels (Fig. 7). There are three common peaks at wide-angle region for both wax oleogels at around 2.99–3.73, 4.14–4.15, and 4.50–5.55 Å. Similar peaks at 0.372 and 0.413 nm were shown in olive oil and CW organogels.[7] Usually peaks at

FIGURE 6 The polarized light microscopy (PLM) pictures of the oleogel samples, HC7 (b) HC10 (c) HS3 (d) HS7 (e) HS10.

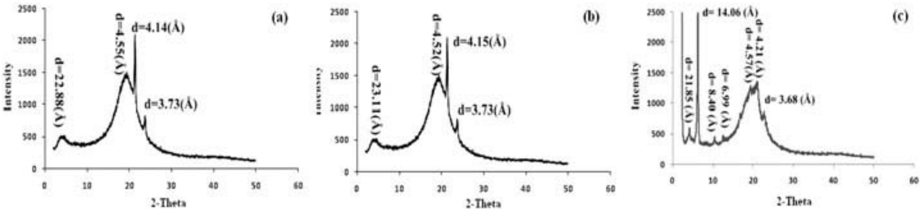


FIGURE 7 The x-ray diffraction patterns of the oleogel samples, (a) HC10 (b) HS10 (c) CS.

TABLE 3
The XRD measurement results of the oleogels samples

Samples	*2-Theta*	*d (Å)*
CW	4.83, 19.37, 21.53, 23.81, 30.02, 36.29, 40.49, 43.80	18.27, 4.57, 4.12, 3.73, 2.97, 2.47, 2.22, 2.06
SW	2.61, 3.93, 5.34, 19.32, 21.47, 23.87, 28.28, 29.93, 31.53, 36.13, 40.07, 41.98, 43.16, 43.85, 47.23, 52.89, 79.10	33.82, 22.46, 16.50, 4.58, 4.13, 3.72, 3.15, 2.98, 2.83, 2.48, 2.24, 2.15, 2.09, 2.06, 1.92, 1.72, 1.20
HC3	–	–
HC7	4.39, 19.56, 21.40, 23.82	20.08, 4.53, 4.14, 3.73
HC10	3.85, 19.47, 21.42, 23.78, 35.99	22.88, 4.55, 4.14, 3.73, 2.49
HS3	3.99, 19.67, 21.42, 23.82	22.07, 4.50, 4.14, 3.73
HS7	3.84, 19.69, 21.43, 23.80, 31.31	22.97, 4.50, 4.14, 3.73, 2.85
HS10	3.82, 19.58, 21.38, 23.77, 29.78, 40.14	23.11, 4.52, 4.15, 3.73, 2.99, 2.24
CS	2.22, 4.24, 6.38, 10.52, 12.64, 16.88, 19.54, 21.18, 22.89	39.75, 21.85, 14.06, 8.40, 6.99, 5.24, 4.57, 4.21, 3.68

that region indicate orthorhombic perpendicular subcell packing type crystals, and this type is found very similar to the β' crystals of margarines and spreads with smooth texture and better mouthfeel properties defined.[1,7] Although the crystal microphotographs were shown in the study of Hwang et al.,[8] the XRD patterns of SW organogels have not been investigated. This study provides the XRD patterns data of SW oleogels for the literature. SW oleogels had the very similar wide-angle region peaks and yielded very smooth and uniform crystalline network. Especially, SW containing oleogels were very stable during storage in terms of textural properties. As suggested previously for rice bran wax organogels[7] and SW organogels,[8] we also suggest that especially SW oleogels can be an alternative hard fat stock in some products formulations.

Oxidative Stability

The oxidative stability of the oleogel samples and CS sample were monitored during three months storage at room and refrigerator temperatures by the PV measurements, and the results are shown in Fig. 8. Generally at both storage temperatures for all samples, the increase in the PVs through the storage time was minimal. Also, the increase was much less in refrigerator stored samples ($p = 0.001$). Among all stored oleogel samples, the highest PV (0.6 meqgO_2/kg) was measured in 3% CW containing oleogel stored at 20°C for 90 days. At the same temperature (20°C), the PV for CS sample has reached its max value of 0.5 meqgO_2/kg after 90 days. These results indicate that HO oleogels are very stable in terms of oxidation. This might be due to the fatty acid composition (see materials section) and higher amounts of tocols and sterols found in HO.[19] The effect of mineral fortification on oxidative stability of reduced-fat spreads has shown that iron and copper added

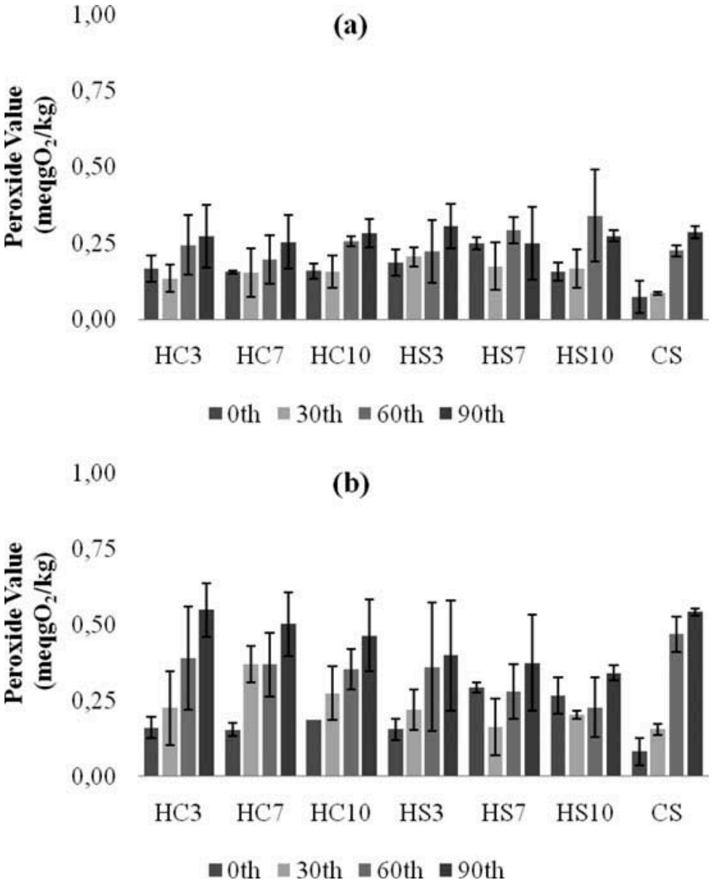


FIGURE 8 The peroxide values of the oleogel samples; (a) 4°C (b) 20°C.

samples were very susceptible to oxidation, whereas low level of zinc addition led to acceptable oxidative stability in the spreads developed.[20] In our study, there was no antioxidant or any other addition into the oleogels.

CONCLUSIONS

In this study, some important properties of the CW and SW containing oleogels of HO in comparison with a CS were determined. The SW oleogels were binding more liquid oil and forming the gel more quickly than that of the CW oleogels. The SFC of the oleogels were much lower than that of the CS sample. In general, the melting temperatures of the CW oleogels were higher than that of the SW oleogels. The melting temperature of 3% SW containing oleogel was the most similar one to the melting temperature of the CS sample. The firmness and stickiness values of the oleogels were fairly stable during the 90 days storage period. Both firmness and stickiness were a little higher in refrigerator stored oleogels than that of the room temperature stored samples. Compared to the CS, the measured texture values of the oleogels were lower. During the three months of storage, the textural and oxidative stabilities of SW oleogel samples were better than those of CW oleogels.

Overall, from the determined properties of the HO oleogels, it would be concluded that, these HO-SW oleogels can be used in the productions of shortenings or similar products with acceptable suitability.

NOMENCLATURE

HO-	hazelnut oil
CW-	carnauba wax
SW-	sunflower wax
CS-	commercial shortening
OBC-	oil binding capacity
CFT-	crystal formation time
SFC-	solid fat content
DSC-	differential scanning calorimetry
PV-	peroxide value
PLM-	polarized light microscopy
XRD-	x-ray diffraction

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(54) **METHOD OF PREPARING AN EDIBLE OLEOGEL**

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§ 371 (c)(1),
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CPC ***A23D 9/02*** (2013.01); ***A23L 1/0534*** (2013.01); *A23V 2002/00* (2013.01)

(57) **ABSTRACT**

A method of preparing an edible oleogel comprising combining an edible triacylglycerol oil or triacylglycerol fat and ethylcellulose in a weight ratio of from 99:1 to 80:20 to form a mixture, and heating and agitating the mixture at a temperature within the range of from 80 to 300° C. to form an oleogel, wherein the heating and agitating is conducted under an inert atmosphere; an oleogel obtainable by said method, its use to prepare food products and to food products comprising said oleogel.

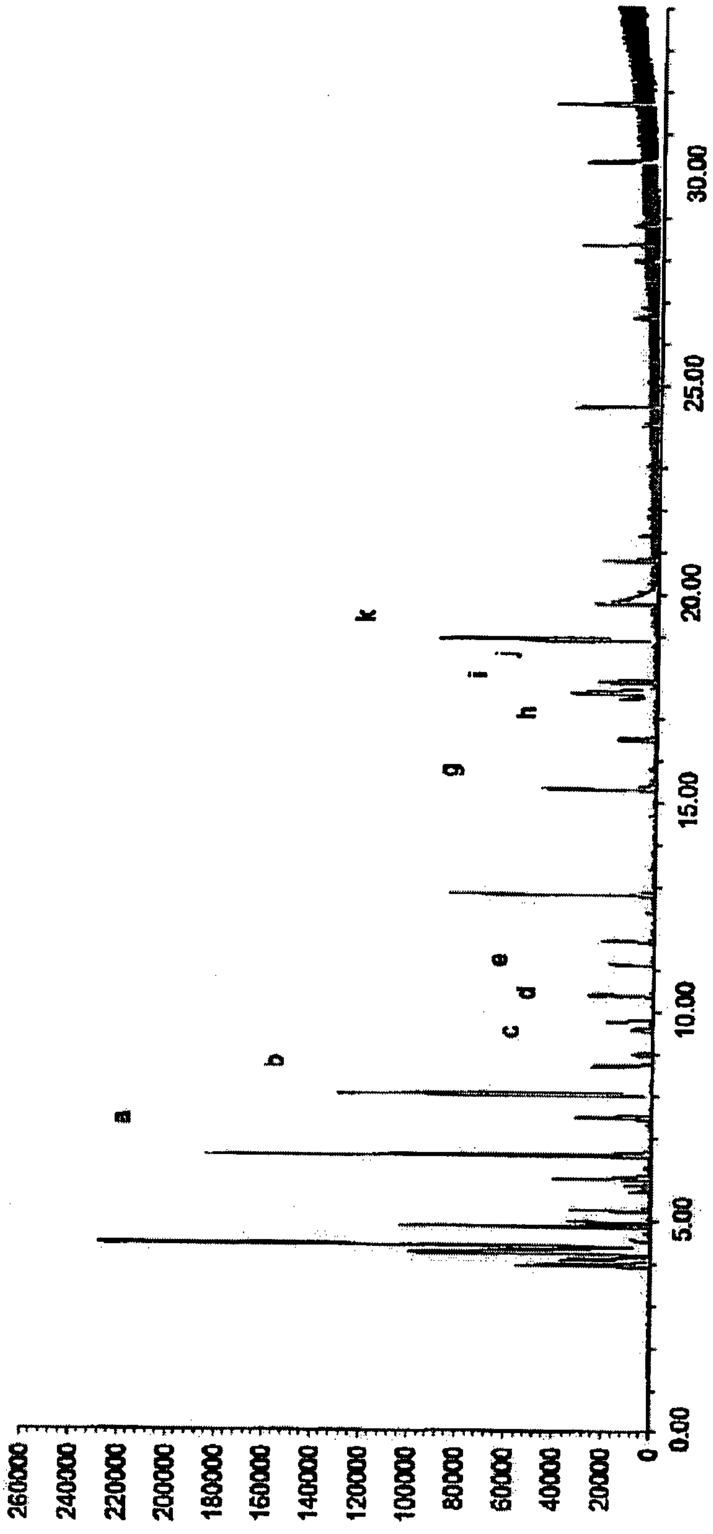
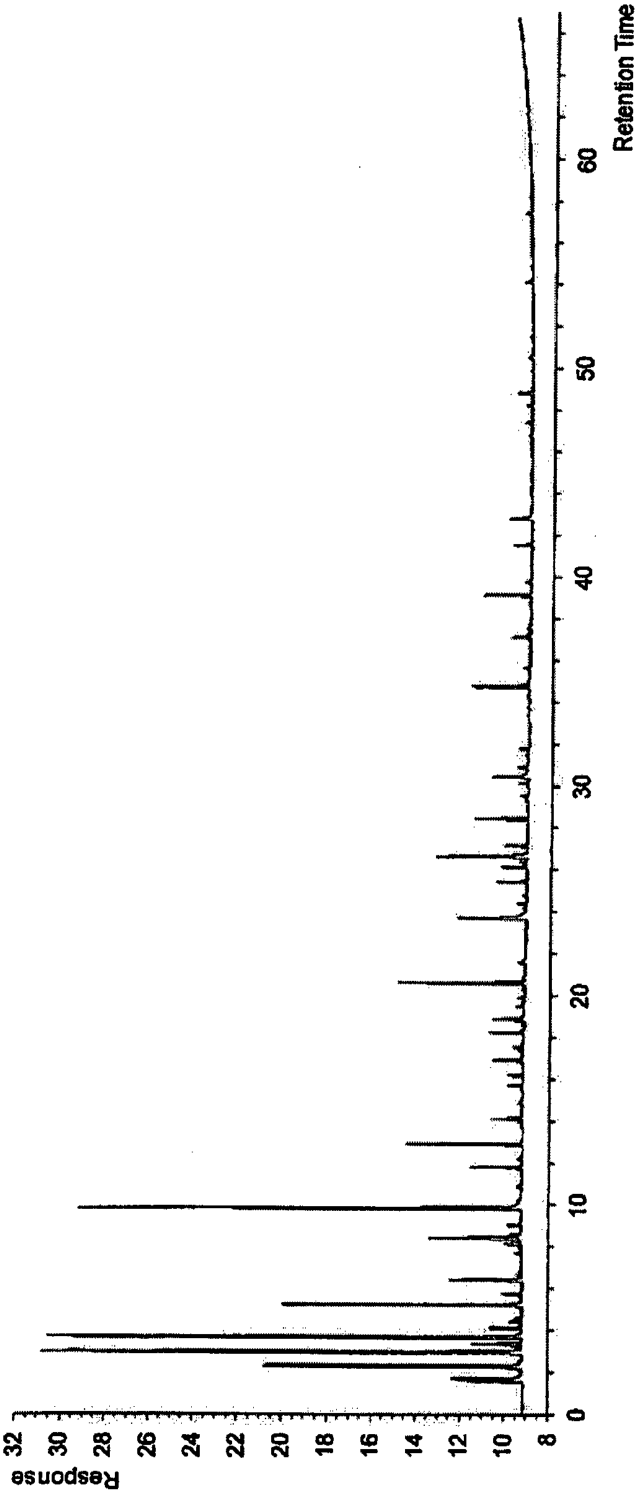


Fig. 1

RECTIFIED SHEET (RULE 91) ISA/EP


Response
32
30
28
26
24
22
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18
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12
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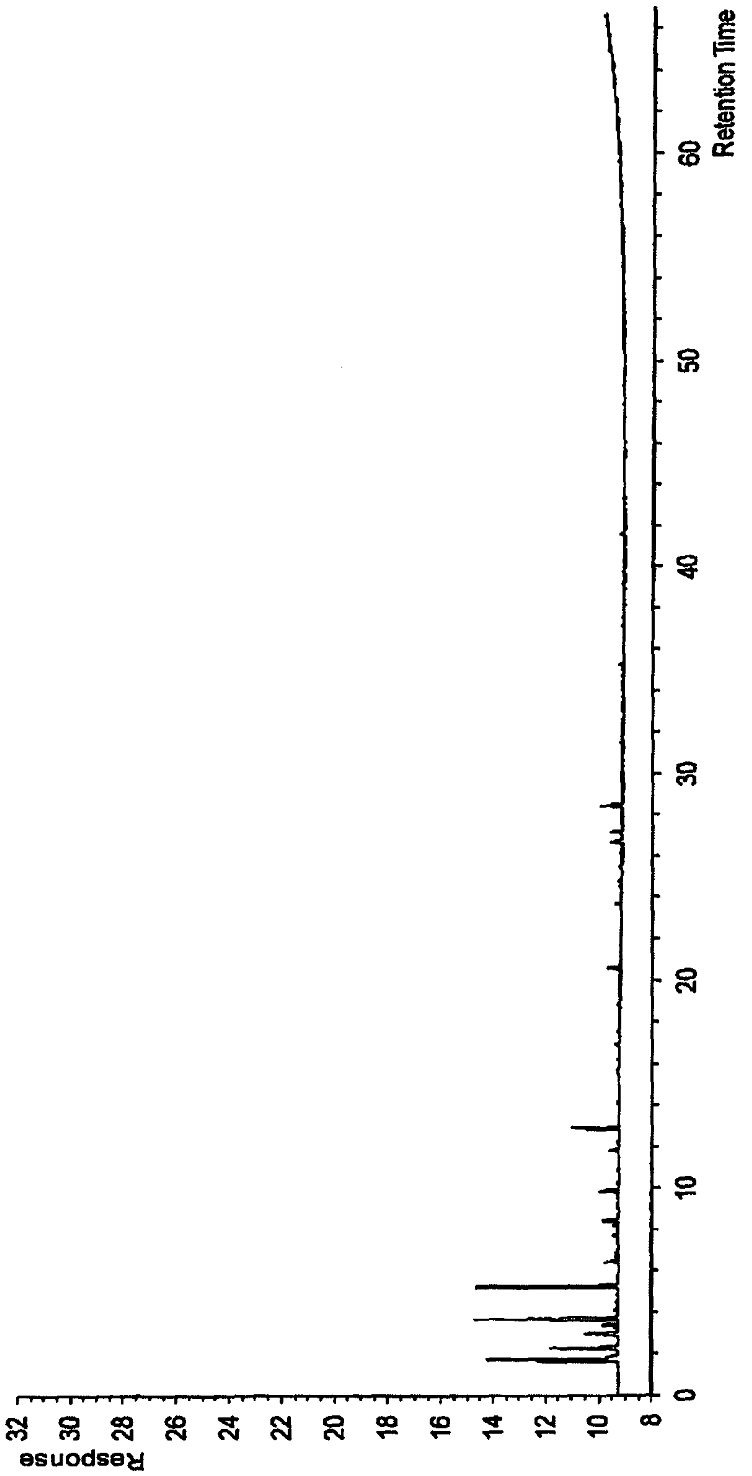
Retention Time

Fig. 2


Response
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60
Retention Time

Fig. 3

METHOD OF PREPARING AN EDIBLE OLEOGEL

[0001] The present invention relates to a method of preparing an edible oleogel comprising triacylglycerol oil or fat and ethylcellulose.

[0002] Structure in solid fat-containing food products is provided by the network of crystalline triacylglycerols. However, these triacylglycerols contain high levels of saturated fatty acids. Instead of using naturally highly saturated solid fats, oils comprising triacylglycerols having high levels of unsaturated fatty acids are also transformed to more solid products by hydrogenation or partial hydrogenation. “Trans fats” which are unsaturated fats with trans-isomer unavoidably emerge from partial hydrogenation of unsaturated oils. Research into the role fats and oils play in human health has indicated that consumption of saturated fatty acids, even more of trans fatty acids is associated with elevated cholesterol levels and cardiovascular diseases.

[0003] Therefore, it is desirable to develop healthier alternatives to triacylglycerols containing saturated or partially hydrogenated fatty acids. The demand for a healthy alternative to trans fats and saturated fats creates technological hurdles for the food manufacturing industry. It is difficult to eliminate trans and saturated fats from a food formulation where the goal is to transform a healthier unsaturated oil, which is liquid at room temperature to a fat, which is ‘solid’ at room temperature to enhance the texture and appearance of a food product.

[0004] In the food industry there have been many attempts to find alternative components that can provide the desired features of texture, structuring, stability and taste that are normally found in animal and vegetable fats or hydrogenated oils. One alternative, organogels (oleogels), have been recognized for their potential to be used to reduce oil migration in multi component foods and to act as an alternative to butter or margarine. Oleogels can be used to provide structure to edible oils thereby reducing the need for saturated and trans fatty acids.

[0005] U.S. Pat. No. 6,187,323 describes pharmaceutical and cosmetic compositions comprising a mixture of an oleogel and an aqueous gel. In the example a semisynthetic triglyceride is gelled with ethylcellulose in the presence of propylene glycol isostearate by stirring the components at 140° C. until a uniform oleogel is formed.

[0006] WO 2008/081175 describes compositions containing an active agent for cosmetic and pharmaceutical applications, similar to those of U.S. Pat. No. 6,187,323. The compositions are homogeneous mixtures (not emulsions) of an oil component with an aqueous component. In the example a synthetic oil is gelled with a combination of propylene glycol laurate, ethylcellulose and propylene glycol isostearate at ambient temperature prior to mixing with the aqueous component. The aqueous component is gelled with a conventional cosmetic gelling agent.

[0007] In “Influence of the concentration of a gelling agent and the types of surfactant on the rheological characteristics of oleogel” (Il farmaco 58 (2003) 1289-1294) M. A. RuíMartínez et al. report on oleogels comprising olive oil, ethylcellulose and a surfactant selected from Olivem 300, 700 and 900. The oleogels were prepared by stirring the components at 100° C. and are destined for topical use only.

[0008] U.S. Pat. No. 4,098,913 describes edible fat particles for incorporation into textured protein meat analog products. The edible fat products are made by gelling a triacylglyceride fat or oil with ethylcellulose. In the example partially hydrogenated cottonseed oil is mixed under rapid stirring with ethylcellulose at 180° C. The gelled fat is then added to the meat analog product. U.S. Pat. No. 4,098,913 is focused on a meat substitute having a meat-like texture. The problem of healthiness is not addressed and the partially hydrogenated oil used in the example does not avoid the presence of trans fatty acids and is thus undesirable in terms of healthiness.

[0009] WO 2010/143066 relates to an edible oleogel comprising an oil, ethylcellulose and a surfactant. It is describes that the oleogel is obtained by heating the ethylcellulose and the surfactant in oil up to a temperature above the glass transition temperature of the ethylcellulose with constant mixing. Suitably, the mixture is heated up to at least 130° C. to about 160° C. and after a few minutes a clear and very viscous solution is formed. Although WO 2010/143066 is not precise about the role of the surfactant and its teaching is in contrast to its two priority applications U.S. 61/213,480 and U.S. 61/213,738 the surfactant seems to act as a plasticizer. Its presence is mandatory and makes the essence of the invention described.

[0010] However, for many applications the addition of a surfactant to an edible product is to be avoided, for example because many surfactants are suspected to cause allergic reactions or other health and behavioral problems. Consumers tend to become more and more critical of additives to food products and often prefer a product containing as few non-natural ingredients as possible.

[0011] The problem underlying the present invention is to provide a new method of preparing a solid or semi-solid fat product comprising healthy unsaturated fatty acids which method does not necessitate the addition of a surfactant.

[0012] The problem is solved by a method of preparing an edible oleogel comprising:

[0013] combining an edible triacylglycerol oil or triacylglycerol fat and ethylcellulose in a weight ratio of from 99:1 to 80:20 to form a mixture, and

[0014] heating and agitating the mixture at a temperature within the range of from 80 to 300° C. to form an oleogel,

[0015] wherein the heating and agitating is conducted under an inert atmosphere.

[0016] The present invention is also directed to the oleogel obtainable by said method, its use to prepare food products and to food products comprising said oleogel.

[0017] Preparing the oleogel, the triacylglycerol oil or fat and ethylcellulose are employed in a weight ratio of from 99:1 to 80:20, preferably from 95:5 to 85:15, more preferably from 92:8 to 87:13, and most preferably in a weight ratio of about 90:10.

[0018] Typically, the oleogel comprises from 70 to 99% by weight, preferably from 75 to 95% by weight, more preferably from 80 to 92% by weight and most preferably from 85 to 90% by weight of the triacylglycerol oil or fat.

[0019] The triacylglycerol oil or fat can be a natural, synthetic or semi-synthetic oil or fat. In preferred embodiments it is a fat or oil of natural origin such as a vegetable or animal oil or vegetable or animal fat, typically the triacylglycerol is a vegetable oil or fat. The term triacylglycerol oil designates triacylglycerols that are liquid at 20° C. and atmospheric pressure (1013.25 hPa) whereas triacylglycerol fats are solid or semi-solid at 20° C. and atmospheric pressure (1013.25 hPa). The liquid nature of triacylglycerol oils is due to their higher content of healthier mono- or polyunsaturated fatty acids which prevent an arrangement in a crystalline structure. The oleogel of the present invention preferably contains triacylglycerol oil(s). In preferred embodiments the triacylglycerol(s) oils or fats for use in the present invention have a iodine value of at least 30, more preferably the oleogel contains triacylglycerol oil(s) having a iodine value of at least 70 and in certain embodiments of at least 80. The iodine value is determined according to method AOCS Official Method Cd 1-25 (Wijs method).

[0020] Exemplary triacylglycerol oils that can be employed in the inventive oleogel include canola oil, sunflower oil, corn oil, flaxseed oil, olive oil, soybean oil, safflower oil, peanut oil, grape seed oil, sesame oil, argan oil, rice brain oil, algal oil and echium oil. Exemplary triacylglycerol fats for use in the present invention are cocoa butter and palm oil. Examples of animal oils include squid oil and fish oils such as salmon oil and halibut oil. Mixtures of various triacylglycerol oils and fats (including mixtures of at least two different oils, mixtures of at least two different fats and mixtures of at least one oil and at least one fat) as well as fractions and mixtures of fractions of triacylglycerol oils and fats can also be employed. In most preferred embodiments the present oleogel contains at least one of canola oil olive oil, palm oil, cocoa butter, flaxseed oil and sunflower oil.

[0021] Preferably, the ethylcellulose for use in the present invention has a degree of substitution (DS) of from 2.40 to 3, preferably from 2.42 to 2.80, more preferably from 2.43 to 2.70, even more preferably from 2.44 to 2.65, still more preferably from 2.45 to 2.60, and most preferably from 2.46 to 2.57. In typical embodiments the ethylcellulose, including ethylcellulose having the preferred DS described before, has a 5% solution viscosity of from 3 to 110 mPa·s, preferably from 16 to 76 mPa·s, and more preferably from 18 to 50 mPa·s. The term "5% solution viscosity" refers to the viscosity of a 5% by weight solution of the ethylcellulose in a mixture of toluene/ethanol in a weight ratio of 80/20. The viscosity is determined at 25° C. in an Ubbelohde viscometer. A typical viscosity analysis is performed as follows: 57 g of a 80/20 w/w toluene/ethanol mixture are weighed into a dry 8-ounce bottle and 3 g (dry weight) of ethylcellulose are added. The bottle is placed on a mechanical shaker and shaken until all material goes into solution (approximately 20 min) The resulting solution is analyzed within 24 h of preparation. For viscosity measurement, the solution is filled in a Ubbelohde viscometer which is then placed in a water bath at 25° C. until the solution has equilibrated to 25° C. Following the instruction for the Ubbelohde viscometer the solution is sucked up through the calibration flow tube and then allowed to drain. The time of the flow between the upper and lower calibration mark is stopped and the viscosity is calculated according to the instruction taking into account the specific capillary used for the measurement.

[0022] The values of the 5% solution viscosities reflect the molecular weight of the ethylcellulose.

[0023] Exemplary ethylcelluloses that can be used in the method of the present invention include ETHOCEL™ Std. 4, ETHOCEL™ Std. 7, ETHOCEL™ Std. 10, ETHOCEL™ Std. 14, ETHOCEL™ Std. 20, and ETHOCEL™ Std. 45, all commercially available from The Dow Chemical Company, Midland, U.S.A. ETHOCEL™ Std. 20 (DS=2.46 to 2.57, 5% solution viscosity=18-22 mPa·s) and ETHOCEL™ Std. 45 (DS=2.46 to 2.57, 5% solution viscosity=41-49 mPa·s) are most preferred. Combinations of the exemplary ethylcelluloses can also be used.

[0024] In the inventive method the mixture comprising the triacylglycerol oil or fat and the ethylcellulose is heated and agitated, preferably stirred, at a temperature within the range of from 80 to 300° C., generally from 90 to 250° C., typically from 130 to 200° C., more typically from 140 to 170° C., even more typically from 143 to 160° C. Typical heating times (holding times) range from 1 to 120 min, preferably from 5 to 100 min, more preferably from 10 to 80 min, even more preferably from 20 to 60 min, and most preferably from 30 to 40 min until an oleogel is formed. It is known to the person skilled in the art that higher temperatures require only short holding times whereas lower temperatures require longer holding times. In some embodiments the mixture is heated and agitated at a temperature of from 140 to 200° C. for 20 to 90 min, such as at a temperature of from 145 to 160° C. for 30 to 60 min. The specific temperature and holding time depend on the type of ethylcellulose (i.e. its molecular weight) and the type of oil or fat. The stage of solubilization of the ethylcellulose in the triacylglycerol oil/fat is typically determined by feel with hand inspection. If the resulting oleogel has a grainy/sandy texture at about 23° C. then the ethylcellulose was not fully soluble. If the oleogel gel has a smooth texture at about 23° C. the ethylcellulose is considered soluble at the processing temperature.

[0025] It is essential for the present invention that heating and agitating is conducted under an inert atmosphere such as under an inert gas atmosphere or in ambient air under vacuum (reduced pressure). Examples of inert gases that may be used according to the present invention include nitrogen and noble gases such as for example argon. It is preferred to conduct the heating and agitating under a nitrogen gas atmosphere. Processing under an inert atmosphere is applied to reduce, preferably minimize and most preferably substantially exclude the presence of oxygen. In practice, the inert atmosphere may still contain minor amounts of oxygen. Typically, the inert atmosphere has an oxygen level of less than 90 g oxygen/m^3 of the atmosphere, preferably less than 50 g/m^3, more preferably less than 30 g/m^3, even more preferably less than 25 g/m^3 and most preferably less than 23 g/m^3. Vacuum conditions that may be applied are, for example, subpressures within the range of from 70 to 1 kPa, preferably from 30 to 2 kPa, and most preferably from 10 to 2.5 kPa.

[0026] Any technique to create an inert gas atmosphere may be applied in the present invention including continuously purging the system containing the mixture of triacylglycerol oil or fat and ethylcellulose with an inert gas such as nitrogen, e.g. with a continuous gas flow, in order to drive out air and ensure that air is not reintroduced into the system. It is also possible evacuate the system to remove the air before the inert gas is flown into the system. If an inert gas atmosphere is used the heating and agitating are typically conducted under ambient pressure such as at pressures within the range of from 900 to 1100 hPa, preferably from 950 to 1060 hPa. However, overpressures of up to 10,500 hPa could also be applied.

[0027] In preferred embodiments the triacylglycerol oil or fat and the ethylcellulose are combined by introducing them into the system such a reactor, e.g. a glass reactor. Typically, the mixture is already agitated and the system is purged with the inert gas, e.g. by flowing the inert gas such as nitrogen through the system, to create an inert atmosphere prior to heating and the inert gas purge is continued during heating up.

[0028] After heating and agitating the mixture under inert atmosphere at the temperatures described above the oleogel is preferably cooled, e.g. allowed to cool, typically to ambient temperature, for example to a temperature of less than 30° C. or to a temperature equal to or less than 25° C. or to a temperature of equal to or less than 23° C. or to a temperature of equal to or less than 20° C. It is preferred that the cooling is also conducted under an inert atmosphere such as under a nitrogen atmosphere. In preferred embodiments the inert gas purge, i.e. the inert gas flow through the system, is continued during cooling.

[0029] When the mixture is heated above the glass transition temperature of the ethylcellulose, the ethylcellulose is solubilized in the triacylglycerol oil or fat to create a three-dimensional, thermo-reversible gel network upon cooling. Due to the restricted mobility and migration of the oil/fat inside the polymer network, the present oleogels provide the solid-like properties of crystalline triacylglycerols without the high levels of saturated fatty acids. Replacing crystalline triacylglycerols with healthy oils/fats while retaining structural properties of solid fats is highly desirable for various food applications.

[0030] It has been observed that too low temperatures and/or insufficient holding times result in an unacceptable sandy texture of the resulting oleogel. It is believed that this is due to incomplete disentanglement of the ethylcellulose polymer molecules. Unfortunately, it has been further observed that the oil/fat comprising unsaturated fatty acids easily oxidize if held at such high temperatures of at least 80° C. or 90° C., or even at least 130° C. or 140° C. for the required holding times and rapidly become rancid, developing an unpleasant odor and flavor. According to the present invention the oleogels are manufactured under an inert atmosphere to prevent oxidation during solubilization. A significant reduction in the level of oxidation in oleogels that are manufactured by the inventive process is shown. No unpleasant odor or flavor is detected in various foods, when formulated with oleogels prepared according to the present method.

[0031] Although a stabilizer is not necessary to prepare the oleogel according to the present invention it may be added in certain embodiments to modify the properties of the oleogel such as to increase its firmness. Examples of stabilizers that may be used in the present method are food grade surfactants and emulsifiers such as polyoxyethylene sorbitan monooleate (Tween 80 or Polysorbate 80); polyoxyethylene sorbitan tristearate (Tween 65 or Polysorbate 65); polyoxyethylene sorbitan monostearate (Tween 60 or Polysorbate 60); sorbitan monooleate (SMO or Span 80); sorbitan monostearate (SMS or Span 60); glyceryl monooleate (GMO); glyceryl monostearate (GMS); glyceryl monopalmitate (GMP); polyglycerol esters such as polyglyceryl ester of lauric acid—polyglyceryl polylaurate (PGPL), polyglyceryl ester of stearic acid—polyglyeryl polystearate (PGPS), polyglyceryl ester of oleic acid—polyglyceryl polyoleate (PGPO) and polyglyceryl ester of ricinoleic acid—polyglyceryl polyricinoleate (PGPR); diglycerides; monoglycerides, such as succinylated monoglyceride, lactylated monoglyceride, acetylated monoglyceride, monoglyceride citrate, monoglyceride phosphate, stearyl monoglyceride citrate, and diacetyl-tartrate ester of monoglyceride; calcium stearoyl lactylate; sodium stearoyl lactylate; sucrose esters; lecithin; and triethyl citrate. If added, the stabilizer is preferably present in an amount resulting in a weight ratio of ethylcellulose/stabilizer of no more than 20:1. The typical range is a 8:1 to 1:8 w/w ethylcellulose-to-stabilizer ratio, such as for example a ratio of from 5:1 to 1:1.

[0032] In preferred embodiments the inventive oleogel does not contain any emulsifier or surfactant in addition to ethylcellulose, i.e. no emulsifier or surfactant is added during preparation.

[0033] The oleogel of the present invention may contain additional optional ingredients such as antioxidants to further reduce oxidation. As a matter of fact the antioxidants should be food grade; exemplary antioxidants for use herein include Butylated Hydroxyanisole (BHA), Butylated Hydroxytoluene (BHT), Tertiary Butyl Hydroquinone (TBHQ), ascorbic acid, sodium ascorbate, calcium ascorbate, β-carotene, tocopherols, chlorogenic acids, gallates and flavanols. If used, antioxidants are typically added in an amount of up to 10,000 ppm by weight, preferably within a range of from 50 to 1000 ppm by weight, and more preferably within a range of from 100 to 500 ppm by weight, based on the total amount of triacylglycerol oil(s) and fat(s).

[0034] The oleogels of the present invention are edible. They can be formulated into any food product requiring a structured solid-like or semi-solid like fat. Accordingly, in a further aspect, the present invention provides a food product comprising an oleogel according to the invention. The food product may be made by mixing food components with an oleogel according to the invention. The mixing may be performed with the oleogel in the gelled state, or with the oleogel composition in the molten state followed by cooling.

[0035] The term “food product” herein refers to edible products suitably also containing one or more additional ingredients such as selected from carbohydrates (e.g. sugars and starches), proteins, dietary fiber, water, flavoring agents such as salt, colorants, and vitamins. Typically, the food product contains at least about 1% by weight of the oleogel, for example at least about 5% by weight, at least about 10% by weight or at least about 15% by weight of the oleogel. In some embodiments the food product contains less than 95% by weight of the oleogel, for example less than about 90% by weight of the oleogel. Examples of food products that can be prepared by using the present oleogel include baked goods such as cookies and cakes; spreads such as margarine and chocolate spreads; chocolate and fillings.

[0036] In certain embodiments, the food product according to the present invention is a meat product. For example, a ground meat product such as hamburger meat, or a meat emulsion product such as bologna, mortadella, frankfurters, or other sausage products. Typically, the meat products of the invention comprise from 10 to 25% by weight of protein, from 5 to 35% by weight of fat (including oils and oleogels), and from 40 to 60% by weight of total water. Replacement of a fraction of the animal fat present in such products by oils, suitably vegetable oils, results in meat products having an unacceptably hard, chewy and/or gummy texture when cooked. However, replacement of a fraction of the animal fat by an oleogel according to the present invention has been found to result in meat products that do not exhibit these drawbacks.

[0037] Some embodiments of the invention will now be described in detail in the following examples wherein all parts and percentages are by weight unless otherwise specified.

EXAMPLES

Raw Materials

[0038]

Ingredient	Supplier
ETHOCEL ™ Std. 20 (ethylcellulose)	The Dow Chemical Company, Midland, MI, USA
ETHOCEL ™ Std. 45 (ethylcellulose)	The Dow Chemical Company, Midland, MI, USA.
Canola oil	Dow AgroSciences Indianapolis, IN, USA
Cocoa butter	ADM, Milwaukee, Wisconsin, USA
Flaxseed oil	Jedwards International Inc., Quincy, MA, USA
Sunflower oil	Jedwards International Inc., Quincy, MA, USA
Olive oil	Jedwards International Inc., Quincy, MA, USA
Tocopherol (W530066 - mixture of D-α, D-β, D-δ, and D-γ-tocopherols)	Sigma Aldrich, St Louis, MO, USA

Example 1

[0039] 75 g of ethylcellulose (ETHOCEL™ Std. 20) and 675 g of canola oil were weighed and placed in a glass reactor. While the ethylcellulose and the oil were being stirred nitrogen flowed through the reactor to remove air and create a nitrogen environment (oxygen level of less than 23 g/m^3) prior to heating. The mixture was heated to 150° C. while stirring at 200 rpm and held at that temperature for 60 min under continued stirring. At the end of the holding time, the resulting solution was allowed to cool to ambient temperature of about 25° C. Nitrogen was flowed through the reactor during the heating and cooling process to ensure oxygen would not be introduced to the system.

Comparative Example 2

[0040] In Comparative Example 2 the procedure of Example 1 was followed except that it was conducted under air, i.e. no nitrogen was flowed through the reactor.

Examples/Comparative Examples 3 to 15

[0041] In these examples the procedure of Example 1/Comparative Example 2 was followed except that ETHOCEL™ Std. 45 was used instead of ETHOCEL™ Std. 20 and the heating temperature was 160° C. for a holding time of 40 min. Different oils were employed instead of canola oil as reported in the table below. In Comparative Example 4 and Example 6 tocopherol was added to the reactor during heating up (at about 63° C.) as an antioxidant in an amount of 0.135 g to 750 g of the mixture of ETHOCEL™ Std. 45 and oil.

[0042] Example 7 was prepared under vacuum conditions by pulling a vacuum (15 inch Hg) on the glass reactor during stirring and prior to heating. After 5 min of agitation under vacuum, the mixture was heated up to 160° C. and the target temperature was held for 40 min. When allowing cooling down the reactor, vacuum was removed at about 80° C. and the reactor was inerted with nitrogen.

[0043] Test Results and Discussion

[0044] Headspace Gas Chromatography—Volatiles

[0045] Headspace GC/MS and GC/FID were used to identify and monitor the levels of volatiles in Example 1 and Comparative Example 2.

[0046] FIG. **1** is a GC/MS chromatogram of a 10/90 (w/w) mixture of ETHOCEL™ Std. 20 and canola oil after heating to 150° C. in sealed headspace vial for 60 min.

[0047] Several aldehydes and alcohols (volatiles) were identified as decomposition products of the oil as follows:

a: hexanal
b: 1-penten-ol
c: heptanal
d: hexenal
e: pentanol
f: heptenal
g: nonanal
h: 2-octenal
i: 1-octen-3-ol
j + k: heptadienal
l: decenal

[0048] Most of the identified compounds are recognized as oxidation products of vegetable oils and are often associated with odor and taste.

[0049] FIG. **2** is a GC-FID chromatogram of Comparative Example 2.

[0050] FIG. **3** is a GC-FID chromatogram of Example 1.

[0051] It is evident from the figures that the levels of volatiles were dramatically affected by the presence of air. For Example 1 according the present invention and conducted under an inert (nitrogen) environment the levels of volatiles were 10-25 fold lower than with an air environment (Comparative Example 2).

[0052] Peroxide and p-Anisidine Values

[0053] The oxidation process can be divided into two phases: In the first phase of the oxidation fatty acids react with oxygen to form odorless compounds such as peroxides while in the second phase peroxides degrade into various substances that are responsible for the rancid odor and smell. The peroxide value (PV) test can be used to determine the primary oxidation products while the p-anisidine test can be used for measuring the secondary products. The latter method determines the amount of aldehydes (principally 2-alkenals and 2,4-dienals) by reaction in an acetic solution of the aldehydic compounds and the p-anisidine. The PV and the p-anisidine value (p-AV) can be combined to evaluate the oxidation level of the oil samples: With the PV the oxidative the status of the product can be determined while with the p-AV the oxidative history of the product can be determined.

[0054] Peroxide and p-anisidine values of Examples/Comparative Examples 3 to 15 were determined and the p-anisidine values are reported in the table below. The peroxide values were determined by the acetic acid-chloroform method according to AOCS Official Method Cd 8-53, revised 1990 and updated 1992. The p-AV value is defined by convention as 100 times the optical density measured at 350 nm in a 1 cm cell of a solution containing 1.00 g of the oil/fat in a 100 ml mixture of chloroform and a solution of p-anisidine in glacial acetic acid according to AOCS Official Method Cd 18-90 (AOCS Official Method Cd 18-90 uses isooctane whereas herein chloroform is used because it is a good solvent for ethylcellulose). The peroxide values of the samples prepared both in air and nitrogen environments were close to zero. The low peroxide values suggest that the primary oxidation levels of the products were very low regardless of the environment they were prepared in.

[0055] The p-anisidine values of all the samples suggest some level of oxidative history in the samples. For most examples the p-anisidine values of the inventive oleogels prepared under nitrogen environment (Examples 5, 6, 7, 9 and 11) were at least 50% lower than of those prepared under air environment (Comparative Examples 3, 4, 8, and 10); for Examples 13 and 15 the p-anisidine values of the inventive oleogels were about 43 and 38% lower than of those prepared under air environment (Comparative Examples 12 and 14). These results show that the method according to the present invention decreases the oxidation significantly.

TABLE

p-Anisidine values of ethylcellulose/oil samples after heat treatment at 160° C./40 min

	Oil	Additive	Atmosphere	p-AV
Reference	Canola oil (plain oil, no heat treatment)			1.44
Comp. Ex. 3	Canola oil	—	air	13.69
Comp. Ex. 4	Canola oil	tocopherol	air	9.82
Example 5	Canola oil	—	nitrogen	2.79(1)
Example 6	Canola oil	tocopherol	nitrogen	2.48
Example 7	Canola oil	—	vacuum	3.95
Reference	Cocoa butter (plain oil, no heat treatment)			0.74
Comp. Ex. 8	Cocoa butter	—	air	6.13
Example 9	Cocoa butter	—	nitrogen	2.63
Reference	Flaxseed oil (plain oil, no heat treatment)			0.67
Comp. Ex. 10	Flaxseed oil	—	air	10.4
Example 11	Flaxseed oil	—	nitrogen	3.07
Reference	Sunflower oil (plain oil, no heat treatment)			6.84
Comp. Ex. 12	Sunflower oil	—	air	29
Example 13	Sunflower oil	—	nitrogen	16.4
Reference	Olive oil (plain oil, no heat treatment)			5.42
Comp. Ex. 14	Olive oil	—	air	12
Example 15	Olive oil	—	nitrogen	7.48

(1)average of three samples

1. A method of preparing an edible oleogel comprising:

combining an edible triacylglycerol oil or triacylglycerol fat and ethylcellulose in a weight ratio of from 99:1 to 80:20 to form a mixture, and

heating and agitating the mixture at a temperature within the range of from 130 to 200° C. for 10 to 80 min to form an oleogel,

wherein the heating and agitating is conducted under an inert atmosphere.

2. The method of claim **1** wherein the inert atmosphere is an inert gas atmosphere.

3. The method of claim **1** wherein the heating and agitating is conducted under an inert atmosphere containing less than 90 g/m^3 of oxygen.

4. The method of claim **1** further comprising cooling the oleogel, wherein the cooling is also conducted in the inert atmosphere.

5. The method of claim **1**, wherein the ethylcellulose has a degree of substitution of from 2.40 to 3.00.

6. The method of claim **1**, wherein the ethylcellulose has a 5% solution viscosity of from 3 to 110 mPa·s, measured as a 5% by weight solution of the ethylcellulose in a 80/20 (w/w) toluene/ethanol mixture at 25° C. in an Ubbelohde viscometer.

7. The method of claim **1**, wherein the edible triacylglycerol oil or triacylglycerol fat is of natural origin.

8. The method of claim **7**, wherein the edible triacylglycerol oil or triacylglycerol fat has a iodine value of at least 30.

9. The method of claim **1**, wherein the edible triacylglycerol oil is selected from canola oil, sunflower oil, corn oil, flaxseed oil, palm oil, olive oil, soybean oil, safflower oil, peanut oil, grape seed oil, sesame oil, argan oil, rice brain oil, algal oil, echium oil, squid oil, salmon oil, halibut oil, fractions and mixtures thereof.

10. The method of claim **1**, wherein the mixture is heated and agitated at a temperature of from 140 to 200° C. for 20 to 90 min.

11. An edible oleogel obtainable by the method of claim **1**.

12.-**13**. (canceled)

14. A food product comprising the oleogel of claim **11**.

15. The food product of claim **14**, wherein the food product is selected from baked goods; chocolate and fillings.

16. The method of claim **1** wherein the ethylcellulose has a 5% solution viscosity of from 16 to 76 mPa·s, measured as a 5% by weight solution of the ethylcellulose in a 80/20 (w/w) toluene/ethanol mixture at 25° C. in an Ubbelohde viscometer.

17. The method of claim **1** wherein the mixture is heated and agitated at a temperature of from 145 to 160° C. for 30 to 60 min.

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