Food Chemistry 242 (2018) 131–138

Contents lists available at ScienceDirect

Food Chemistry

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

Measurement and characterization of external oil in the fried waxy maize starch granules using ATR-FTIR and XRD

Long Chen[a,b], Yaoqi Tian[a,b], Binghua Sun[a], Canxin Cai[b], Rongrong Ma[b], Zhengyu Jin[a,b,*]

[a] State Key Laboratory of Food Science and Technology, Jiangnan University, 1800 Lihu Road, Wuxi 214122, China
[b] School of Food Science and Technology, Jiangnan University, 1800 Lihu Road, Wuxi 214122, China

ARTICLE INFO

Keywords:
Fried starchy samples
External oil content
ATR-FTIR
XRD
Quantitative analysis

Chemical compounds studied in this article[1]:
Starch (PubChem CID: 24836924)
Waxy starch (PubChem CID: 86278134)
Water (PubChem CID: 962)
Amylose (PubChem CID: 53477771)
Amylopectin (PubChem CID: 439207)
n-Hexane (PubChem CID: 8058)

ABSTRACT

Concerns regarding increased dietary oil uptake have prompted efforts to investigate the oil absorption and distribution in fried starchy foods. In the present study, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, together with a chloroform–methanol method, was used to analyze the external and internal oil contents in fried starchy samples. The micromorphology of fried starchy samples was further investigated using scanning electron microscope (SEM), polarized light microscope (PLM) and confocal laser scanning microscopy (CLSM). The results indicated that large amounts of oil were absorbed in or within waxy maize starch, but the majority of oil was located near the surface layer of the starch granules. After defatting, the internal oil was thoroughly removed, while a small amount of external oil remained. As evidenced by the changes of the crystalline characteristics with the help of X-ray diffraction (XRD), the interaction between starch and lipids on the surface was confirmed to form V-type complex compounds during frying at high moisture.

1. Introduction

As a traditional food processing method, frying is widely applied to produce various foods with unique texture, flavor, and appearance (Mellema, 2003; Saguy & Dana, 2003). Frying is characterized by rapid oil absorption along with water evaporation, which is caused by the severe heat and mass transfer during heating at high temperature (Dana & Saguy, 2006; Mellema, 2003). The high oil content in fried starchy foods is found to be associated with a high incidence of cardiovascular and cerebrovascular diseases (Saguy & Dana, 2003). Therefore, reducing oil uptake during frying and the subsequent cooling process have become a consensus among consumers, manufacturers, and regulators. Additionally, scientific studies to control and reduce the oil uptake have been performed. Some hydrocolloids, especially the thermo-gelling gums, have been incorporated with fried foods, and this has achieved good results in inhibiting oil absorption (Kim, Lim, Bae, Lee, & Lee, 2011; Marquez, Di Pierro, Esposito, Mariniello, & Porta, 2014; Varela & Fiszman, 2011). Moreover, the effective reduction of oil uptake can be realized by applying vacuum frying (Contardo, Parada, Leiva, & Bouchon, 2016; Yagua & Moreira, 2011) and appropriate pretreatments (Ignat, Manzocco, Brunton, Nicoli, & Lyng, 2015; Karizaki, Sahin, Sumnu, Mosavian, & Luca, 2013; Moyano & Pedreschi, 2006; Troncoso & Pedreschi, 2009).

These strategies for reducing oil absorption during frying are relied on the work which focus on the oil absorption mechanisms. Specifically, understanding of the relationship between the structural information and oil absorption properties (i.e. the oil distribution, oil migration during frying and cooling, and its possible interactions with food components) is important to develop niche-targeting strategies in food production. Therefore, a technique for the detection of oil in different depths of food samples is needed. The traditional method usually involves the stripping of samples step by step, and then the oil from each layer is extracted and calculated using a Soxhlet extractor or differential scanning calorimetry (Aguilera & Gloria, 1997). This procedure makes it possible to generate a rough tridimensional distribution pattern for oil at successive depths within samples, but the results are limited by samples heterogeneity, the extraction conditions, and possible interactions between oil and other components in the samples. Furthermore, the need for large amounts of organic solvents and the time-consuming procedures make the traditional method unsuitable for rapid and accurate analysis. Other techniques, including low-field nuclear magnetic resonance (LF-NMR) (Chen et al., 2017a), confocal

* Corresponding author at: State Key Laboratory of Food Science and Technology, Jiangnan University, 1800 Lihu Road, Wuxi 214122, China.
E-mail address: fpcenter@jiangnan.edu.cn (Z. Jin).
[1] Please note: Edible oil is not a specific chemical, it is the mixture of triglyceride and fatty acid. So oil will not have a specific record in PubChem.

http://dx.doi.org/10.1016/j.foodchem.2017.09.016
Received 21 April 2017; Received in revised form 3 August 2017; Accepted 4 September 2017
Available online 07 September 2017
0308-8146/

microscopy (Zhu, Zou, Shi, Zhao, & Huang, 2017), Raman spectroscopy (Dong, Wu, Chen, & Liu, 2017), and infrared microscopy (Bouchon, Hollins, Pearson, Pyle, & Tobin, 2001) have been used to detect or characterize the oil biomass, with both advantages and disadvantages for each method. For example, our previous work confirmed that LF-NMR analysis was a reliable method for the simultaneous determination of water and oil contents in fried starchy samples. However, the LF-NMR method only reflected the overall oil value of the samples and could not provide additional information regarding the distribution differences of the oil in the samples (Chen et al., 2017a).

Fourier transform infrared (FTIR) spectroscopy is a non-invasive, rapid, and powerful technique used to probe the molecular and conformational transitions in macromolecules (Xiao, Tong, & Lim, 2014). The development of attenuated total reflection (ATR) technique has facilitated and enlarged the application range of FTIR. In addition, ATR-FTIR has been proven to have superiority in noise-signal ratio, spectral resolution, sample treatment, and detection sensitivity (Touitou, Meidan, & Horwitz, 1998). ATR-FTIR has been successfully applied to quantify the trans fatty acids in deep frying oils (Bansal, Zhou, Tan, Neo, & Lo, 2009) and the anionic detergent content in milk (Jaiswal, Jha, Kaur, & Borah, 2017). Xiao et al. (2014) determined the film-forming process and mechanism of pullulan-based edible films associated with the water evaporation using ATR-FTIR and two-dimensional correlation spectroscopy. Taking into consideration the limited penetration depth of the infrared beam from the ATR accessory, ATR-FTIR could be potentially applied in the identification and quantification of chemical composition on material surface.

Therefore, the primary objective of the present work was to investigate the oil distribution in fried starchy samples by using ATR-FTIR and a chloroform–methanol extraction procedure. Furthermore, the different interactions between starch and oil in the external/internal sections of samples were verified using defatting and X-ray diffraction (XRD), and the micromorphology of fried starchy samples was observed using scanning electron microscope (SEM), polarized light microscope (PLM) and confocal laser scanning microscopy (CLSM). As glutinous starch was commonly used in fried starchy foods in Asian countries, waxy maize starch was selected as the research sample in the present study. The data could be useful for monitoring, evaluating, and modifying oil absorption in fried starchy foods.

2. Materials and methods

2.1. Materials

Waxy maize starch (WMS) with 12.52% moisture and 2.48% amylose was obtained from Suzhou Gaofeng Starch Technology Co., Ltd. (Jiangsu, China). Soybean oil was purchased from the local supermarket. Normal hexane (n-hexane) was of chromatographic grade and produced by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Enzymes, including α-amylase (EC 3.2.1.1, No. A4551, 1000 units/mg protein) and amyloglucosidase (EC 3.2.1.3, No. 10115, A7420, 55 units/mg protein), were purchased from Sigma-Aldrich Chemical Co., Ltd. (Shanghai, China). All other chemicals and reagents were of analytical grade unless otherwise stated.

2.2. Preparation of fried starchy samples

A starch–water-oil model system was used in the present work because starch was the primary material in the fried starchy foods. The fried WMS samples were prepared as follows. Firstly, the WMS was hydrated to different moisture contents (10%, 20%, 40%, and 80%) in sealing bags for 12 h for the purpose of moisture balance. After hydration, the WMS (5 g in dry basis) was equably dispersed into 100 mL of soybean oil at 20 °C with magnetic stirring for 10 min. Then, the starch-oil–water mixtures were heated at 180 °C in an oil bath for 20 min to mimic the frying procedure. A time of 20 min was selected after considering the equilibrium moisture of different samples and the constant temperature of soybean oil (Fig. S1). At this time, the simulated conditions of the present study came close to the actual frying conditions. Subsequently, hot fried samples were instantly isolated from hot oil to prevent secondary oil absorption during cooling (Mellema, 2003), and then filtered using vacuum filtration to remove uncombined oil. The solid materials on the filter-paper were collected and preserved in a brown vacuum bag for further testing and evaluation. Samples with initial moistures of 10%, 20%, and 40% remained as powder state after frying, while sample with an initial moisture of 80% turned into agglomeration when subjected to the same frying treatment.

2.3. Measurements of external and internal oil contents

2.3.1. Chloroform-methanol method

The total oil content in fried starchy samples was determined using chloroform–methanol extraction according to AOAC (1990) with some modifications. Briefly, 5 g of fried starchy samples was added into a 250 mL conical flask and dispersed in 40 mL of sodium acetate buffer (0.2 mol/L, $CaCl_2$ 1 mM, pH 5. 2). The suspension was equilibrated at 45 °C for 10 min, then 10 mL of the mixed enzyme solution (200 U/mL of α-amylase and 10 U/mL of amyloglucosidase) was added into the flask. Subsequently, the flasks were immersed in a shaking bath for enzymatic hydrolysis of starch at 45 °C for 90 min at 180 rpm. After hydrolysis, the hydrolysates were homogenized with 150 mL of 1:1 (v:v) chloroform–methanol solution to extract oil from the samples. The mixed solution was centrifuged, and the supernatant fluid was separated and dried to a constant weight. The total oil content was calculated by the following Eq. (1):

$$Oil_{Total} = \frac{m_e}{m_0} \quad (1)$$

where m_0 is the sample weight, and m_e is the oil content extracted from the sample, i.e. the weight of the supernatant after drying to a constant weight.

2.3.2. ATR-FTIR

ATR-FTIR was used to analyze the oil content around the surface of the fried starch granules on the basis of its limited detection distance (Mossoba, Milosevic, Milosevic, Kramer, & Azizian, 2007). Specifically, the infrared light merely penetrated to a depth of approximately 0.6–1.2 μm from the surface of the starch granules according to the Eq. (2):

$$dp = \frac{\lambda}{2\pi\eta_1[\sin^2\theta - (\eta_2/\eta_1)^2]^{1/2}} \quad (2)$$

where λ is the wavelength, η_1 is the refractive index of the ZnSe crystal, η_2 is the refractive index of the samples, and θ is the incidence angle of IR light. This penetration depth is much lower than the diameter of the WMS (Fig. S2), confirming the validity of the ATR-FTIR method in the external oil determination on the surface fraction of the fried starch granules.

An FTIR spectrometer (IS10, ThermoNicolet Inc., America) equipped with a 50 μL ATR accessory was used in the present study. Soybean oil of different concentrations or samples was homogeneously spread onto the surface of the ATR crystal, and the FTIR spectra were recorded from 600 to 4000 cm^{-1} at a resolution of 4 cm^{-1} by 32 scans. For each scanning, the spectrum was collected by subtracting the origin spectrum from the air background spectrum. Then, the obtained spectra were baseline-collected, and peak area for 1743 cm^{-1} was integrated between 1693 and 1793 cm^{-1}. The details for this calculation was shown in Fig. S3. Subsequently, a plot of peak area vs. oil concentration was used to generate the calibration curve for the ATR-FTIR method. Various concentrations of soybean oil were prepared by dissolving in *n*-hexane to generate calibration curves for the quantitative analysis of external oil contents near the surface of starch granules.