J Am Oil Chem Soc (2011) 88:925–929
DOI 10.1007/s11746-011-1762-7

ORIGINAL PAPER

Influence of Polydimethylsiloxane on the Oxygen Concentration of Oils at Various Temperatures

Jose A. Gerde · Earl G. Hammond ·
Pamela J. White

Received: 30 August 2010 / Revised: 31 December 2010 / Accepted: 11 January 2011 / Published online: 11 February 2011

Abstract The effect of temperature on the oil oxygen concentration, tested in both soybean and olive oils with no added polydimethylsiloxane (PDMS), showed that the oxygen concentration increased with temperature to approximately 100 °C. Above 100 °C, the oxygen concentration abruptly decreased. This change was attributed to the balance between the rates of oxygen uptake and consumption by oil oxidation, which favored oxygen consumption over uptake at temperatures above 100 °C. The addition of 100 ppb PDMS to soybean oil, enough to form a continuous layer over the surface of the oil, reduced the oxygen concentration when compared to a soybean oil control containing no added PDMS at temperatures ranging from 93 to 180 °C; thus suggesting an oxygen barrier effect of PDMS. The accumulation of PDMS at the air–oil interface in soybean oil held at 180 °C was determined by comparing the oil's internal temperature and the apparent surface temperature. A decrease in the apparent surface temperature while the oil was held at a constant internal temperature was attributed to a change in the emissivity of the surface as a consequence of the accumulation of PDMS in the air–oil interface. The presence of PDMS at the air–oil interface was confirmed for 100 ppm of PDMS, a concentration greater than the concentration necessary to form a monolayer of PDMS on the oil surface.

Keywords Oxygen concentration · Polydimethylsiloxane · Soybean oil · Oil surface temperature

J. A. Gerde · E. G. Hammond · P. J. White (✉)
Department of Food Science and Human Nutrition,
Iowa State University, E262 Lagomarcino Hall,
Ames, IA 50011-1060, USA
e-mail: pjwhite@iastate.edu

Introduction

Oxidative reactions can bring about cooking oil degradation especially at frying temperatures (~180 °C) and in polyunsaturated oils. Oxygen concentration in the oil is a very important factor in this degradation. Oxygen solubility in oils is reported to increase with increasing temperatures between ambient temperatures and 100 °C [1, 2], but information on the solubility of oxygen in vegetable oils is fairly limited. Values previously reported include 0.055 mg/g for soybean oil at 20 °C [3] and 0.035 mg/g for olive oil at 25 °C [4].

Polydimethylsiloxane (PDMS), a silicon-based polymer extensively used in industrial frying as an anti-foaming agent at very low concentrations, has a powerful protective effect on oil oxidation [5]. The mechanism of protection, although extensively studied, is not well understood. The viscosity and solubility of the PDMS both affect the extent of oil oxidation. PDMS with a viscosity greater than 20 cSt prevented fat oxidation better than low-viscosity PDMS, and PDMS modified with fatty acids to make it more fat-soluble was less effective than unmodified PDMS [6]. The protective effect also has been associated with the accumulation of PDMS in the air–oil interface, and a PDMS concentration of 0.05–0.06 μg/cm^2 or more is required [7]. Inhibitions of convection currents [7, 8] or oxygen transfer to the oil have been proposed as mechanisms for the beneficial effect of PDMS on frying oils [7]. The influence of PDMS on the oxygen concentration in an oil previously was studied by Kusaka et al. [9]; however, this study measured oxygen by desorbing the gases from the oil with a stream of He at 105 °C followed by gas chromatography with thermal conductivity detection and did not reveal the influence of PDMS on oxygen concentration at typical frying temperatures. PDMS accumulation on the surface of an oil has been demonstrated [10], but the impact of surface area coverage as a mechanism for its effectiveness has not been determined. The objectives of the current study were to determine the effects of temperature and 100 ppb PDMS on the oxygen concentration in soybean and olive oils on the oxygen concentration between 93 and 180 °C using an oxygen electrode.

Experimental Procedures

Oil Heating

Refined, bleached, and deodorized soybean oil with citric acid added (Golden Chef, Archer Daniels Midland Company, Decatur, IL) and refined commercial olive oil were obtained at a local grocery store. The oils (200 g) were heated in a 100 × 50 mm crystallizing dish (Pyrex, Corning Inc., Corning, NY) at selected temperatures at a surface to volume ratio of 0.36 cm^{-1}. A solution of 100 ppm of PDMS (Dow Corning 200, 350 cSt, Dow Corning Co., Midland, MI) was prepared and appropriate amounts were applied to the crystallizing dishes and the solvent was evaporated before the addition of the oil.

Oxygen Concentration Measurement

The oxygen concentration was measured using an YSI Model 53 Biological Oxygen Monitor (Yellow Springs Instrument Co. Inc., Yellow Springs, OH) connected to an experimental apparatus (Fig. 1). The oil in the experiment flowed continuously into the measuring apparatus through a 55-cm long and 2-mm i.d. stainless-steel tube connected to the oil. Before entering the measuring chamber the oil was cooled to 20 °C by passage though a thermostat-controlled water bath. The measuring chamber was connected to a peristaltic pump (Masterflex, Cole-Parmer Instrument Co., Chicago, IL) that controlled the oil flow rate at 2 mL/min. After the oil in the vessel reached a selected temperature, it was equilibrated for 10 min before the oxygen concentration was measured. After equilibration, the oil was pumped for 4 min before the oxygen concentration was observed. After measurements at each temperature, the oil removed was returned to the heating vessel.

To study the effect of temperature on the oxygen concentration of oils, the oxygen analyzer was calibrated at 70% of its measuring scale with air-saturated soybean oil at 20 °C. Air-saturated soybean oil and olive oil at 20 °C were heated to selected temperatures.

To study the effect of 100 ppb PDMS, an amount sufficient to form a multilayer on the oil surface, on the oxygen concentration, soybean oils containing 100 ppb PDMS and no PDMS were heated at various temperatures. For this experiment, the oxygen analyzer was calibrated at 100%, rather than at 70% as noted for the previous experiment, with air-saturated soybean oil at 20 °C, and the oils were heated to the desired temperatures. Oil aliquots were taken from the surface of the oil and from the bottom of the oil at selected temperatures ranging from 93 to

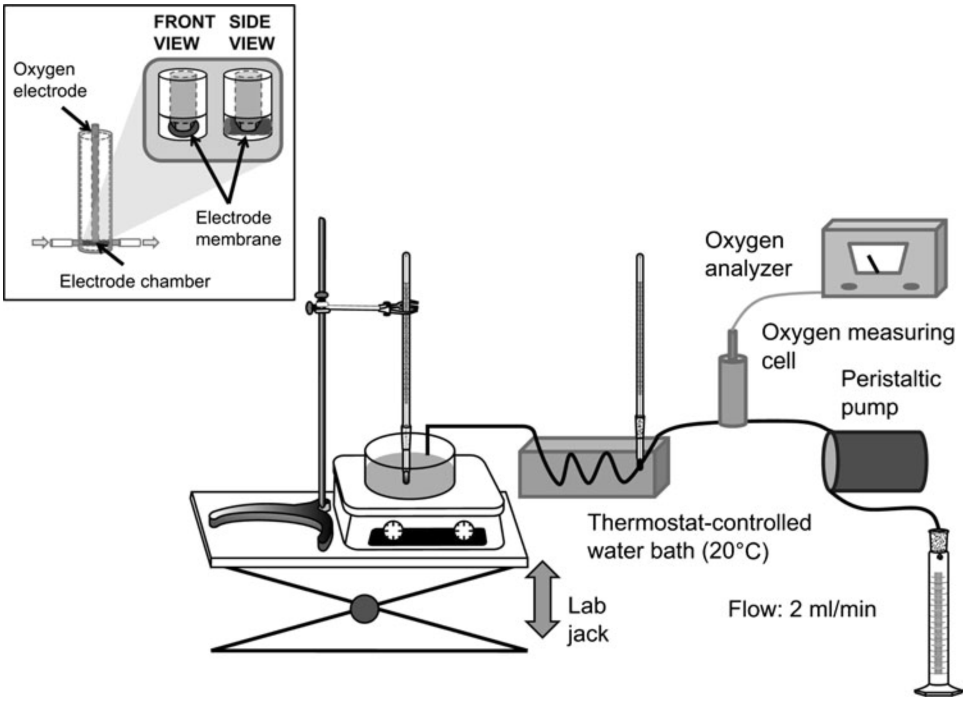

Fig. 1 Scheme of the apparatus used to measure the oxygen concentration in oil at various temperatures. The lab jack was adjusted to take oil aliquots from the surface or the bottom of the oil

180 °C and the oxygen percentage saturation relative to pure soybean oil at 20 °C measured.

Surface Temperature Determination

A Traceable Infrared Thermometer (Control Company, Friendswood, TX) was used to monitor the apparent surface temperature of the oils. The IR thermometer was installed 16 cm above the oil surface. The temperature inside the bulk oil was measured by using a glass thermometer tested at 100 °C in boiling water and at 180 °C in soybean oil versus other glass thermometers to confirm the accuracy of the measured temperature. Soybean oils treated with 5, 10, 25, 50, and 100 ppb of PDMS and a control without PDMS were heated to an internal temperature of 180 °C. After reaching 180 °C the oil was stirred with the thermometer, and after 1 min, the apparent temperature of the surface of the oil was measured by using the infrared thermometer.

The minimum effective concentration of PDMS was calculated to be 0.05–0.06 μg/cm^2 by Freeman et al. [7]. Assuming a monomer cross-section area of 20–25 Å^2 [11] and assuming all the PDMS to be in the air–oil interface, the PDMS concentration necessary to form a monolayer is

$$\mathrm{PDMS}_{\mathrm{concentration}} = \frac{\mathrm{Area}_{\mathrm{container}} \times \mathrm{mw}_{\mathrm{monomer}}}{\mathrm{Area}_{\mathrm{monomer}} \times N_{\mathrm{A}} \times \mathrm{mass}_{\mathrm{oil}}} \quad (1)$$

where $\mathrm{mw}_{\mathrm{monomer}}$ is 7.41×10^{10} ng/mol, the area of the container was 7.85×10^{17} Å^2, the area of the monomer was 20 Å^2, oil mass was 200 g, N_{A} is Avogadro's number, and the result is expressed in ppb. In the vessel used, the PDMS concentration necessary to form a monomolecular layer was estimated to be 25 ppb.

Statistical Analysis

Treatments (PDMS concentrations and oil types) were run in duplicate. Measurements were made in duplicate and averaged. Means were analyzed by ANOVA using PROC MIXED from SAS Institute Inc. (Cary, NC). Comparisons were performed by contrasts using the Tukey adjustment for multiple comparisons [12]. The level of significance was set at $P \leq 0.05$ unless otherwise indicated.

Results and Discussion

Influence of Temperature on the Oil Oxygen Concentration

The oxygen concentration increased in soybean oil for temperatures below 112 °C, in agreement with previously reported results [1, 2]. Above 112 °C, the oxygen concentration abruptly decreased, presumably as a result of an increase in the reaction of oxygen and the unsaturated fatty acids in the oil (Fig. 2). For olive oil, the oxygen concentration reached a maximum at 78 °C. Above this temperature, the oxygen concentration slowly decreased with increasing temperatures until the temperature reached 112 °C. Above 112 °C, the oxygen concentration fell abruptly, showing a behavior similar to that of soybean oil (Fig. 2).

The differences in apparent oxygen concentration between soybean oil and olive oil between 93 and 112 °C may result from the olive oil containing a greater variety of antioxidants and plant constituents missing in the more rigorously refined soybean oil. One would expect the fatty acid composition of the olive oil to be more stable than that of the soybean oil. But for both oils, the oxygen solubility increased with increased temperature until a certain point, after which it dropped. Above 112 °C dissolved oxygen in the oil was being used up in oxidation reactions much more quickly than it could be replenished by diffusion into the oil.

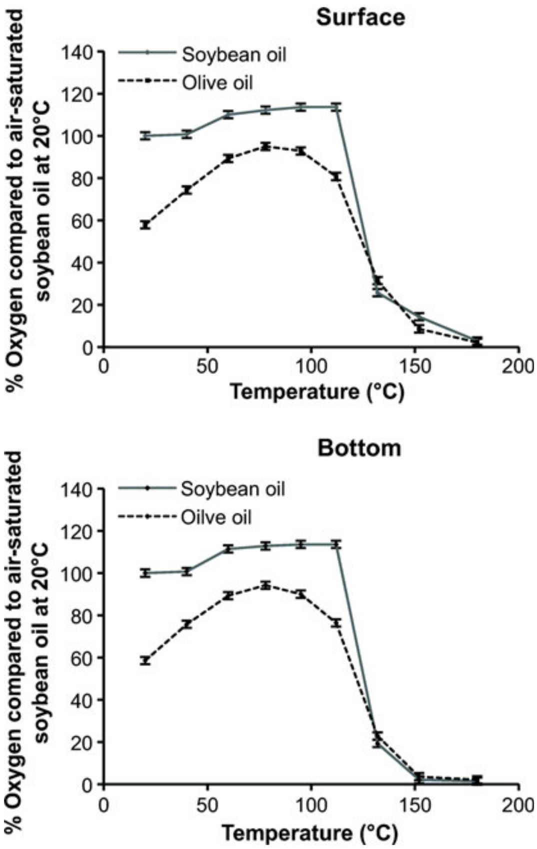

Fig. 2 Percentages of oxygen in soybean and olive oils at selected temperatures for samples collected near the top and bottom of the oil. 100% represents the solubility of the oxygen in the oils at 20 °C. *Bars* around each data point indicate standard error of the mean for all data points

Influence of PDMS on the Oil Oxygen Concentration

In general, the oxygen concentration decreased with increased temperatures in both the surface and bottom aliquots. For temperatures ranging from 93 °C to about 130 °C, the oxygen concentration for the oil treated with 100 ppb PDMS oil was less than that for the untreated control. The same trend continued at temperatures greater than 130 °C, especially for surface aliquots; however, because of the low oxygen concentrations the differences were not statistically significant (Fig. 3). This reduction in oxygen concentration with the addition of PDMS strongly suggests that PDMS acted as a barrier to oxygenation of the oil. This reduction in the oxygen concentration is likely responsible for the protective effect of PDMS in frying oil. In a previous study, a 4% decrease in atmospheric pressure had a 50% impact in the reduction of oil deterioration, presumably because of the drop in oxygen concentration [13].

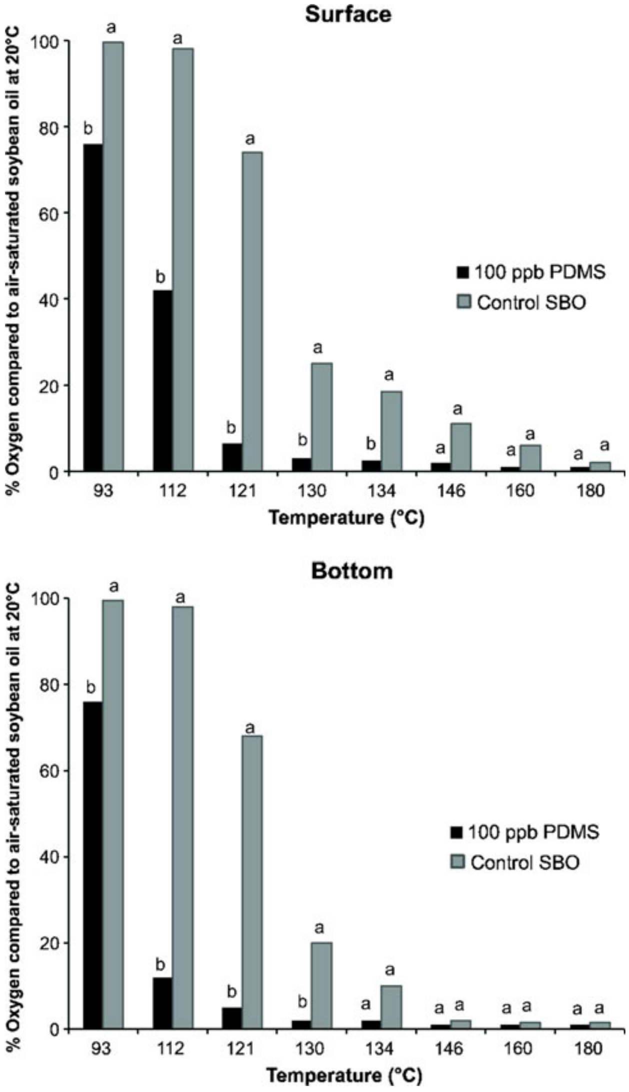

Fig. 3 Percentages oxygen saturation of soybean oil containing 100 ppb PDMS and a control soybean oil containing no added PDMS at selected temperatures collected near the top and bottom of the oil. *Different letters* within a temperature denote significant differences

At 112 °C, the oxygen concentration on the surface in the PDMS-treated oil was greater than in the bottom of the vessel (Fig. 3). For the other treatments, no differences between surface and bottom aliquots were detected.

Oil Surface Temperature

Table 1 shows the mean values of the core and surface temperatures for the various treatments. The apparent surface temperatures for PDMS treatments greater than the monolayer concentration were significantly lower than the temperature in the core of the oil by about 10 °C. It was previously suggested that such differences between surface and core temperatures resulted from convective currents being inhibited by the PDMS and resulting in a decrease in surface temperature [14]. Intuitively, the presence of a 10 °C difference between the surface and the bulk oil would seem very difficult to maintain. The output of infrared thermometers is dependent on the distance between the measured object and the thermometer, the temperature of the object, and the emissivity of the object. The emissivity of an object is dependent on the material making up the surface, surface characteristics such as smoothness or roughness, the wavelength being measured, and the actual temperature [15]. In this case, the change in apparent surface temperature, as read with the infrared thermometer, may not be caused by a real change in temperature but by a change in emissivity of the surface. For the 50- and 100-ppb PDMS treatments, the amounts of PDMS were enough to form two and four monomolecular layers, respectively, of the polymer on the oil, if all the PDMS was on the surface. The accumulation of PDMS on the air–oil interface may have changed the optical characteristics of the interface, which was translated as a seemingly lower surface temperature. Thus, for 100-ppb PDMS the observed apparent surface temperature was less than for 50-ppb PDMS, possibly meaning that the amount

Table 1 Internal and apparent surface temperatures of oil containing selected concentrations of PDMS

PDMS concentration (ppb)	0	5	10	25	50	100
Apparent surface temperature (°C)	183^a	183^a	181^a	181^a	174^b	170^c
Internal temperature (°C)	180^a	180^a	180^a	180^a	180^a	180^a

Different superscripts within the table denote a significant statistical difference of PDMS on the air–oil interface was greater for the 100 ppb treatment.

Internal and apparent surface temperatures in pure PDMS at 180 °C also were measured. In this case, the variability of the surface temperature measurements was very high, and the mean readings tended to be higher than the internal PDMS temperature. The variability of the surface temperature began at about 130–150 °C (data not shown), which is the temperature at which the PDMS begins to decompose according to the label of the manufacturer. These findings suggest that the change in apparent surface temperature is caused not only by the PDMS on the surface, but also by its interaction with the soybean oil and the formation of PDMS degradation products that also may accumulate on the air–oil interface.

Conclusions

For both soybean and olive oils, the oxygen concentration increased with increasing temperature until a certain point where it abruptly decreased. At this point, autoxidation reactions rapidly consumed the oxygen, thus decreasing its concentration.

The PDMS accumulated in the air–oil interface as demonstrated by a difference in the internal and apparent surface temperatures of the oil, a difference probably caused by a change in the emissivity of the oil surface. At temperatures above 93 °C, PDMS-treated soybean oil had a lower oxygen concentration than a control soybean oil with no added PDMS. Thus, PDMS accumulation on the surface of the oil decreased the uptake of oxygen from the oil. This decrease in oxygen uptake could account for the protective effect of PDMS in frying oils.

Acknowledgments The research was funded by a Special Grant from the United States Department of Agriculture (USDA) through the Nutrition and Wellness Research Center (NWRC) at Iowa State University (Project No. 20083411519372).

References

1. Hilder MH (1997) Oil storage, transport, and handling. In: Gunstone FD, Padley FB (eds) Lipid technologies and applications. Marcel Dekker, New York, pp 169–198
2. Swern D (1964) Physical properties of fats and oils. In: Swern D (ed) Bailey's industrial oil and fat products, 3rd edn. Wiley, New York, pp 97–144
3. Hintze F, Becker K, Heiss R (1965) Löslichkeit un diffusion von sauerstoff in lebensmitteln. Fette Seifen Anstrichmittel 67:419–430
4. Battino R, Evans FD, Danforth WF (1968) The solubilities of seven gases in olive oil with reference to theories of transport through the cell membrane. J Am Oil Chem Soc 45:830–833
5. Márquez-Ruiz G, Velasco J, Dobarganes MC (2004) Effectiveness of dimethylpolysiloxane during deep frying. Eur J Lipid Sci Technol 106:752–758
6. Kusaka H, Katsumasa H, Tsurumizu A, Ohta S (1984) On functions of silicone oil in frying oil. III. Protective effects of various silicone oils on the thermal deterioration of unsaturated oils and preventive effect of silicon oil (DMPS) on the thermal deterioration of various oils. J Jpn Oil Chem Soc 33:349–355
7. Freeman IP, Padley FB, Sheppard WL (1973) Use of silicones in frying oils. J Am Oil Chem Soc 50:101–103
8. Kusaka H, Nagano S, Ohta S (1985) On functions of silicone oil in frying oil. V. Influence of silicone oil on convection of frying oils. J Jpn Oil Chem Soc 34:187–190
9. Kusaka H, Kiyama K, Saita H, Koike S, Ohta S (1986) Functions of silicone oil in frying oil. VI. Effects of silicone oil on water and dissolved gas content in frying oils. J Jpn Oil Chem Soc 35:467–471
10. Ohta S, Kusaka H, Tokue K, Takaoka K (1987) Functions of silicone oil in frying oil. VIII. Investigation of the surface conditions on the frying oils containing silicone oil by infrared ATR spectrometry and photoacoustic spectrometer. J Jpn Oil Chem Soc 36:480–486
11. Ellison AH, Zisman WA (1956) Surface activity at the organic liquid/air interface. J Phys Chem 60:416–421
12. Littel RC, Stroup WW, Freund RJ (2002) SAS for linear models, 4th edn. SAS Institute, Cary
13. Totani N (2006) A small reduction in atmospheric oxygen decreases thermal deterioration of oil during frying. J Oleo Sci 55:135–141
14. Ohta S, Shimizu Y, Kinigawa M, Tosaki K, Tottori Y (1990) On functions of silicone oil in frying oil. X. Restudying on the previous presumptions. J Jpn Oil Chem Soc 39:23–28
15. Magison EC (1990) Temperature measurement in industry. Instrument Society of America, Research Triangle Park