Polydimethylsiloxane Droplets Exhibit Extraordinarily High Antioxidative Effects in Deep-Frying

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Abstract: The addition of more than about 1 ppm polydimethylsiloxane (PDMS) into oil results in PDMS forming both a layer at the oil-air interface and droplets suspended in the oil. It is widely accepted that the extraordinarily strong and stable antioxidative effects of PDMS are due to the PDMS layer. However, the PDMS layer showed no antioxidative effects when canola oil did not contain droplets but rather was covered with a layer of PDMS, then subjected to heating under high agitation to mimic deep-frying. Furthermore, no antioxidative effect was exhibited by oil-soluble methylphenylsiloxane (PMPS) in canola oil or by PDMS in PDMS-soluble canola oil fatty acid ester during heating, suggesting that PDMS must be insoluble and droplets in oil in order for PDMS to exhibit an antioxidative effect during deep-frying. The zeta potential of PDMS droplets suspended in canola oil was very high and thus the negatively charged PDMS droplets should attract nearby low molecular weight compounds. It was suggested that this attraction disturbed the motion of oxygen molecules and prevented their attack against unsaturated fatty acid moiety. This would be the reason in the deep-frying why PDMS suppressed the oxidation reaction of oil. PDMS droplets also attracted volatile compounds (molecular weight below 125 Da) generated by heating canola oil. Thus, adding PDMS to oil after heating the oil resulted in the heated oil smelling less than heated oil without PDMS.

Key words: polydimethylsiloxane, zeta potential, droplet, antioxidative effect, volatile compounds, fatty acid isopropyl esters

1 INTRODUCTION

Polydimethylsiloxane (PDMS) is colorless, odorless, transparent, heat stable and viscous liquid. Freeman et al. reported that oil-insoluble PDMS showed extraordinarily strong and stable antioxidative effects when PDMS was added to sunflower seed oil and heated on a hot plate. This effect was due to the monolayer (0.05-0.06 μg/cm²) of PDMS at the air-oil interface. Marquez-Ruiz et al. summarized from the previous conclusions that addition of PDMS would be of particular interest in fried food shops where the fryers usually remain without food during significant periods of time, i.e., catering services, fast-food outlets, restaurants and others. Many commercial oils for frying food contain PDMS at ppm levels, because PDMS may degrade at high temperature and may be transferred to food fried in PDMS-containing oil.

PDMS at a level above about 1 ppm forms a layer at the oil-air interface as well as droplets suspended in oil. The addition of 100 ppb PDMS to soybean oil resulted in the formation of a PDMS layer on the oil; upon heating on a hot plate, the oxygen content of the oil was decreased because the PDMS layer inhibited the penetration of oxygen from air into the oil during oxidation of the oil. Canola oil was deoxygenated under reduced pressure, then samples with and without a surface layer of PDMS were allowed to stand at room temperature. No difference was observed in the rate of oxygen penetration and oxidation of the oil. In contrast, the oxygen content of non-deoxygenated oil covered with a layer of PDMS decreased due to oxidation of the oil when the samples were kept at 60°C in an oven, indicating that the PDMS layer inhibited oxygen in the air from penetrating the oil sufficiently to compensate for the amount of oxygen consumed by oxidation and thus oxidation of the oil was only slightly inhibited. Soybean oil treated with...
100-ppb PDMS and a control with no PDMS were heated at 180°C on a hot plate for 48 h without stirring. In the oil with PDMS, toxic 4-hydroxynonenal which was formed at the beginning of the heating period, increased very slowly during the first 32 h. This suggested that PDMS layer reduced oxygen transfer when the layer was kept during heating.

It is unclear if the PDMS monolayer is retained during deep-frying because foods generate bubbles vigorously during frying due to the release of water as steam. In addition, PDMS present above approximately 1 ppm in oil forms droplets suspended in the oil as described above. We confirmed PDMS droplets about 7 μm in diameter in oil prepared by adding a PDMS-hexane solution to canola oil, followed by evaporation of hexane under reduced pressure to provide 10 ppm PDMS in canola oil.

Ten-ppm PDMS-containing canola oil in a 4-L laminated steel canister was allowed to stand at room temperature for 1 week with the upper void volume replaced with nitrogen gas. Fifty-mL samples were taken gently from the surface, center, and bottom parts of the oil with pipets. The concentration of suspended PDMS droplets and dissolved oxygen in the oil decreased as the depth of the oil sample increased, indicating an interaction between the PDMS droplets and oxygen molecules. In addition, PDMS droplets are reported to gradually migrate to the surface of the oil.

During the oxidation of oil, radicals such as alkoxy radical preferentially remove hydrogen radicals from the double allyl position of a polyunsaturated fatty acid moiety of oil to generate lipid radicals. Triplet oxygen attacks these lipid radicals and the lipid peroxide radicals thus generated remove hydrogen radicals from another polyunsaturated fatty acid moiety to form lipid hydroperoxides; the lipid radicals thus generated initiate an oxidation chain reaction. Tocopherols in vegetable oils terminate the chain reaction by reacting with lipid peroxide radicals. We observed that the formation of hydrogen peroxides was inhibited under a high oxygen concentration in heated PDMS-containing canola oil compared to in heated canola oil without PDMS, and that the concentration of natural tocopherols decreased far more slowly in the PDMS-containing canola oil than in the canola oil without PDMS. PDMS therefore appears to disturb the reaction not between lipid peroxide radicals and tocopherols (because prior to the reaction much oxygen is consumed for the lipid peroxide radical formation) but between oxygen and lipid radicals. This interpretation of the observation described above will explain the antioxidative mechanism of PDMS. Gerde et al. concluded that PDMS had a protective effect on the rate of disappearance of 18:2 and tocopherols in PDMS-containing soybean oil if the PDMS concentration was equal or greater than the monolayer concentration, and that the tocopherol controlled oxidation at the beginning, but once their concentration dropped to a low value, the rate of 18:2 oxidation was controlled by the PDMS present. PDMS did not protect the thermal decomposition of tocopherol but reduced the involvement of tocopherols in the oxidation reaction which was inhibited drastically by PDMS.

However, it is unknown why there is an interaction between PDMS droplets and oxygen molecules in oil, and if the effect is due to a layer of PDMS or suspended droplets. The present study investigated the effects of oil-soluble polymethylphenylsiloxane (PMPS) in canola oil and of PDMS dissolved in canola oil fatty acid isopropyl ester. Next, canola oil not containing PDMS droplets but covered with a layer of PDMS was subjected to thermal treatment imitating deep-frying conditions. The particles in a colloidal suspension or emulsion usually carry an electrical charge. Sometimes the surface of the particles contains chemical groups that can ionize to produce a charged surface, and the surface itself preferentially absorbs ions of one sign of charge in preference to charge of the opposite sign. Zeta potential is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles, and is one of the fundamental parameters known to affect stability. The zeta potential of PDMS droplets was determined to demonstrate the interaction between PDMS droplets and oxygen molecules in oil. Additionally, it was shown that PDMS droplets attracted not only oxygen molecules, but also volatile compounds generated as oil decomposition products.

2 EXPERIMENTAL
2.1 Materials
Canola oil was a product of J-Oil Mills Ltd. (Tokyo, Japan). Polymethylsiloxane (PDMS, KF 96TM) and polymethylphenylsiloxane (PMPS, KF56TM) were purchased from Shin-Etsu Chemical Industry (Tokyo, Japan), and all solvents and reagents were from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Canola oil fatty acid isopropyl ester was synthesized. The synthetic procedure is described briefly as follows. Titanium (IV) isopropoxide was added dropwise to a mixture of canola oil and isopropyl alcohol, followed by agitation at room temperature. After 2 h, the esterification reaction was terminated by the addition of water. Tetrahydrofuran (THF) and 1N hydrochloric acid were added and the reaction mixture was stirred for 20 min, then the water phase was discarded. Hydrochloric acid (1N) was added again and the reaction mixture was stirred as before. The organic phase was washed with water, dried over sodium sulfate 10-hydrate, then THF was removed using a rotary evaporator. The progress of the reaction and product formation were monitored by NMR. The product was also analyzed by GC analysis using an
Agilent J&W column (column length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm, stationary phase DB-1). Canola oil fatty acid isopropyl ester was composed of 3.6% palmitic acid, 4.1% stearic acid, 60.7% oleic acid, 19.9% linoleic acid, 7.9% α-linolenic acid, and 3.8% other fatty acids.

2.2 Chemical properties

The peroxide value (PV) was determined according to the standard methods of the Japan Oil Chemists’ Society for the analysis of fats, oils, and related materials. A 4-mL oil sample was placed in a 15-mL test tube and heated to 50°C and the polar compound content (PC) was determined using a digital edible oil tester (testo270, Testo Japan, Yokohama, Japan).

2.3 Phase contrast microscopic observation

Canola oil and canola oil fatty acid isopropyl ester containing silicone oil were subjected to phase contrast microscopy using a CX41 System biological microscope (Olympus, Tokyo, Japan) equipped with a HDCE-20C USB digital camera (ASONE, Osaka, Japan)\(^7\).

2.4 Oxygen content determination

The oxygen content of the oils was determined using a DO/O2/temperature meter (UC-12-SOL; Central Science, Tokyo, Japan) equipped with a polarographic electrode\(^13,14\). The oxygen content reading (relative oxygen content) of canola oil saturated with oxygen by bubbling air at 25°C was set as 100%.

2.5 Thermal treatment of canola oil containing oil-soluble PMPS

Canola oil containing 10 ppm PMPS was confirmed by phase contrast microscopy not to contain PMPS droplets, then 1100 g of the oil was poured into a 2-L four-neck separable round-bottomed flask fitted with a stir bar, thermometer, and air pump delivering 110 mL/min of air into the headspace of the flask; air flow did not disturb the oil surface at all. One neck of the flask was left open as an outlet for the pump. Under stirring at 85 rpm, the oil was heated from room temperature to 180°C; the surface to volume ratio was 0.15 cm\(^{-1}\). Stirring was maintained for 5 h after the oil reached 180°C, then the oil was allowed to cool without stirring or aeration. At 180, 150, 100, 35°C and room temperature, enough sample was removed by pipetting through the open neck of the flask to completely fill a 50-mL brown vial. The vial was closed with a cap lined with heat-stable sealant so that no air was trapped in the vial. After cooling the oil samples to room temperature, the relative oxygen content, PV, and PC values were determined. The above thermal treatment was repeated using canola oil containing 10 ppm PDMS, and canola oil without any additive.

2.6 Thermal treatment of canola oil fatty acid isopropyl esters containing PDMS

Oil-insoluble PDMS dissolves in isopropyl myristate and isopropyl stearate\(^15\). Canola oil fatty acid isopropyl ester was synthesized as described in 2.1 and 10 ppm PDMS was added; phase contrast microscopy confirmed that there were no PDMS droplets in the oil.

Thermal treatment of the ester was conducted according to 2.5. Canola oil fatty acid isopropyl ester was heated in the same fashion as the control.

2.7 Thermal treatment of canola oil covered with a layer of PDMS and under high agitation

Freeman et al.\(^{11}\) reported that the effectiveness of PDMS was independent of the concentration of PDMS until the concentration fell below 0.05-0.06 μg/cm\(^2\) at the oil-air surface. The antioxidative effects of PDMS have been thus studied using more PDMS than is necessary to form a monolayer on the surface of the oil. First, the stir rate required to disperse an oil monolayer was determined using heat stable polypropylene pellets that float on the surface of heated oil. Next, to confirm if the antioxidative effect during deep-frying is due solely to the PDMS monolayer, concentrated PDMS-hexane solution (10 μL; 1 mg/mL hexane) was placed gently on the surface of 1100 g canola oil in a 2-L round bottom flask to achieve a PDMS concentration of 0.06 μg/cm\(^2\), then the oil was kept under 2 kPa to remove the hexane. After 24 h, the oil was heated at 180°C for 5 h with stirring at 200 rpm. At room temperature and at 180°C, sample was removed as described in 2.5 and the relative oxygen content, PV, and PC values were determined. The same thermal treatments were carried out with canola oil without any additive.

2.8 Zeta potential determination of PDMS

Shimadzu Techno-Research, Inc. (Kyoto, Japan) measured the zeta potential of PDMS. Canola oil containing 1000 ppm PDMS (1 mL) was poured into a universal dip cell and zeta potential was determined repeatedly at 25°C using a ZETA SIZER NANO ZS (Malvern, UK). The refractive index and dielectric constant of rapeseed oil reported in the literature were also used for canola oil. The viscosity of 1000 ppm PDMS-containing canola oil was determined using an A&D SV-10 viscometer (A&D Corp., Tokyo, Japan) and corrected for density.

2.9 Volatile compound determination by solid phase micro extraction

Canola oil containing 0, 1 or 10 ppm PDMS was heated at 180°C for 10 h, then subjected to a solid phase micro extraction-GC/MS method at J-Oil Mills, Inc. (Yokohama, Japan). In addition, canola oil containing a final concentration of 2000 ppm was generated by adding a PDMS hexane solution to canola oil, then removing the hexane at 2 kPa;
this mixture was then added to canola oil which had been heated at 180°C for 3 h, to generate a final concentration of 10 ppm PDMS. The volatile compounds were determined by Japan Food Research Laboratories (Osaka, Japan). Volatile compounds in the samples were collected using a GERSTEL MPS2 (GERSTEL K.K. Tokyo, Japan). Approximately 0.2 g samples were placed in 20 mL vials and heated at 60°C for 15 min with stirring at 300 rpm. After equilibration, the volatile compounds were trapped in an absorbent material (50/30 μm StableFlex DVB/Carboxen/PDMS, Sigma Aldrich Japan, Tokyo, Japan) for 30 min, then recovered from the absorbent material for 3 min. The released compounds were subjected to GC/MS (7890B/5977A, Agilent Technologies Japan, Ltd. Tokyo, Japan) using an InertCap Pure WAX column (60 m × 0.25 mm i.d.; GL Science, Tokyo, Japan), a column inlet temperature of 240°C, and a carrier gas (He) flow of 1.2 mL/min. The column was held at 60°C for 3 min, then heated at 5°C/min to 200°C. Ionization was performed using the EI method and the ion source temperature was 230°C. The peaks which were reduced in composition by the addition of PDMS were identified using authentic samples or by a library search. As references, the volatile compounds in canola oil heated at 180°C for 3 h, fresh canola oil and PDMS, were also determined.

2.10 Statistical analyses
All values for oxygen content, PV and PC are provided as mean ± SD and were analyzed using one-way analysis of variance with Dunnett’s multiple comparison post hoc test or Student’s t test. Results were considered significant at \( p < 0.05 \).

3 RESULT and DISCUSSION

3.1 Thermal treatment of canola oil containing oil-soluble PMPS
Heating canola oil containing heat-stable and oil-soluble PMPS resulted in drastic increases in the PV and PC levels, and in the oxygen content, similar to that observed for canola oil alone as shown in Figs. 1A and C. Figure 1B shows the antioxidative properties typical of PDMS, in which the PV and PC values stayed low at 180°C, and at lower temperature down to room temperature under high oxygen content conditions as well. It has been shown that the PDMS effect took place only at high temperature, but it worked at temperature between 20-100°C \(^{16-18}\). We therefore concluded that PMPS did not exhibit an antioxidative effect, in agreement with the report by Kusaka et al. \(^8\). In addition, Kusaka et al. did not observe an antioxidative effect in heat-stable and oil-soluble poly-α-methylstyrrene-siloxane (KF-410\(^{TM}\)) \(^8\), suggesting that oil-soluble silicones do not exhibit an antioxidative effect in oil.

Fig. 1 Relative oxygen content, peroxide value, and polar compound content of canola oil containing polymethylphenylsiloxane (A), polydimethylsiloxane (B), or canola oil (C) with no additive. All samples were heated at 180°C for 5 h. Values are expressed as mean ± SD. Values with non-common superscript letters differ significantly (\( p < 0.05 \)) by Dunnett’s multiple comparison post hoc test.

3.2 Thermal treatment of canola oil fatty acid isopropyl esters containing PDMS
Canola oil fatty acid isopropyl ester readily dissolved PDMS at room temperature, as confirmed by phase contrast microscopy. PDMS exhibited no antioxidative property during the heating of canola oil isopropyl ester, as shown by the absence of changes in oxygen content, PV and PC (Figs. 2A and B). Thus, PDMS that does not form either droplets or a surface layer does not exhibit antioxidant properties.
3.3 Thermal treatment of canola oil covered with a layer of PDMS and subjected to high agitation

Marquez-Ruiz et al.\textsuperscript{2} reported that PDMS showed the antioxidative effects when the oil surface was not disturbed by the presence of food and water evaporation during fryer stand-by times in non-continuous frying process. In the present study, a deep-frying model without foods was employed. \textbf{Figures 3A} and \textbf{B} show that oxidation proceeded vigorously under high agitation, regardless of the presence or absence of a PDMS layer. In both cases, the oxygen content remained low, and PV and PC increased to about 7 meq/kg and 14%, respectively, after heating at 180°C for 5 h, indicating that the PDMS layer did not function as an antioxidant in the present deep-frying model. Thus, we propose that PDMS droplets exhibit the antioxidative effects in the practical deep-frying, while a PDMS layer has the effect in oil heated without disturbance.

3.4 Zeta potential determination of PDMS\textsuperscript{19}

The zeta potential of PDMS was $-74 \pm 10.6$ mV, indicating that PDMS droplets attract positively charged molecules such as oxygen. The same result was obtained using canola oil containing 10 ppm PDMS.

Freeman et al.\textsuperscript{1} proposed several reasons why a PDMS layer at the oil-air interface showed antioxidative effects. One is that a PDMS layer inhibited convection currents at the surface of oil, although it is unknown if a several angstroms-thick PDMS layer can reduce heat radiation from oil. However, we suggest that countless PDMS droplets, which are stably scattered in oil due to the high negative charge, form a network and sustain a stable and rigid suspension in oil. Such a suspension decreases fluidity, thus...
inhibiting convection currents.

PDMS at a level above about 1 ppm forms a layer at the oil-air interface as well as droplets suspended in oil. It might be possible that the PDMS droplets accumulate on the oil surface forming a PDMS layer under elevated temperature. We heated canola oil containing more than 1 ppm PDMS at 180°C for some hours under stirring or without stirring, then allowed to stand at room temperature for cooling (without stirring). By the phase contrast microscopy the same PDMS droplets were observed in the resultant oils as in the oil before heating. In addition, 10-mL canola oil containing 1000 ppm PDMS, which turbidity due to PDMS droplets was visible to the naked eye, was heated in a 15-mL test tube. The turbidity was decreased at 180°C but observed clearly. Then the oil was allowed to cool at room temperature. The turbidity of the whole oil increased uniformly with cooling. The existence of droplets in 10 ppm PDMS-containing oil heated at 180°C is not confirmed yet. But droplets do not likely to disappear completely at elevated temperature even if the conversion between droplets and a layer could happen. If droplets would convert to a layer at the oil-air interface completely at elevated temperature, it is a question that the same-sized droplets regenerate from the layer during cooling without stirring. It seems reasonable that the droplets exist in the oil at 180°C.

### 3.5 Determination of volatile compounds

The amount of volatile compounds increased with time (Fig. 4) when canola oil was heated at 180°C, whereas volatiles did not increase in PDMS-containing canola oil regardless of the amount of PDMS added, indicating that the thermal deterioration of oil is effectively inhibited by PDMS. This result was easily expected as one of the antioxidative effects of PDMS.

Figure 5 shows chromatograms separating the volatile compounds of canola oil heated at 180°C for 3 h followed by the addition of PDMS. The numbers 1-7 indicate peaks that decreased in the content after the addition of PDMS. The peak due to hexane shown in Fig. 5B originates from the 2000 ppm PDMS-hexane solution used to prepare the sample. Figures 5C and D show the volatile compounds of original PDMS and fresh canola oil, respectively. Table 1 shows volatile compounds whose concentrations were reduced by the addition of PDMS and the reduction. The molecular weights of these compounds are below 125 Da. Above we suggested that PDMS droplets attract the volatile compounds and thus inhibit volatilization, and that the volatile compounds with the molecular weights more than 125 Da are too big for the PDMS droplets to attract. The results shown in Fig. 4 suggest that volatile compounds generated during the heating of PDMS-containing canola oil may be partially trapped by PDMS droplets.

**Conclusion**

A layer of PDMS on canola oil showed no antioxidative effect during thermal treatment imitating deep-frying (Fig. 3). In addition, foods easily incorporate PDMS during deep-frying. Therefore, only a layer of PDMS on the oil is not practical and will not prevent the thermal oxidation of frying oil. No antioxidative effect was observed using either PMPs dissolved in canola oil or by PDMS in PDMS-soluble canola oil fatty acid ester, suggesting that PDMS must be insoluble and droplets in oil in order for PDMS to exhibit an antioxidative effect during deep-frying. The zeta potentials of PDMS droplets suspended in canola oil were very high. Negatively charged PDMS droplets should attract nearby low molecular weight compounds. It is suggested that the strong attraction of PDMS droplets disturbed the motion of oxygen molecules and their attack against unsaturated fatty acid moiety, thus suppressing the oxidation reaction by PDMS. PDMS also attracted volatile compounds generated during heating canola oil and thus the addition of PDMS to oil after heating decreased the smell of the oil compared to oil treated the same way but without PDMS.

**Acknowledgement**

J-Oil Mills performed volatile compound determination of canola oil containing PDMS heated at 180°C for 10 h.
Fig. 5  Ion chromatograms of canola oil heated for 3 h (A), canola oil + 10 ppm PDMS added after heating (B), PDMS alone (C) and fresh canola oil (D).

Table 1  Decrease in the content of volatile compounds by the addition of PDMS.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Chemical structure</th>
<th>Area after heating</th>
<th>Area after addition of PDMS</th>
<th>Reduction of area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pentane</td>
<td>5313339 ± 159400</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>octane</td>
<td>209159240 ± 6274777</td>
<td>107487835 ± 3224635</td>
<td>0.514</td>
</tr>
<tr>
<td>3</td>
<td>pentanal</td>
<td>28279052 ± 848371</td>
<td>13598894 ± 407966</td>
<td>0.481</td>
</tr>
<tr>
<td>4</td>
<td>butylcyclopentane*</td>
<td>36642163 ± 1099264</td>
<td>31198387 ± 935951</td>
<td>0.851</td>
</tr>
<tr>
<td>5</td>
<td>hexanal</td>
<td>321201908 ± 9636057</td>
<td>199029405 ± 5970882</td>
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<tr>
<td>6</td>
<td>1-pentene-3-ol</td>
<td>94880013 ± 2846400</td>
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</tr>
<tr>
<td>7</td>
<td>1-pentanol</td>
<td>84313729 ± 2529411</td>
<td>59775071 ± 1793252</td>
<td>0.709</td>
</tr>
</tbody>
</table>

See Fig. 5 for peaks 1-7.  *by library search
Values with non-common superscript letters differ significantly ($p < 0.05$) by Student's $t$-test test.

J. Oleo Sci.
References


