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A Study on the Effect of Polydimethylsiloxane from the Viewpoint of Oxygen Content in Oil

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Abstract: It has been reported that polydimethylsiloxane (PDMS) inhibits oxygen dissolution into oil by forming a monolayer on the surface of the oil, thereby reducing thermal oxidation. In the present study, the distribution of PDMS was determined by the inductively coupled plasma atomic emission spectroscopy in standing PDMS-containing canola oil. PDMS did not disperse in the oil uniformly, but there was a tendency that the PDMS concentration decreased as the depth of oil increased, and the concentration of the bottom part was the lowest. When canola oil was covered with PDMS by dropping it gently on the surface of the oil and kept at 60℃, the oxygen content and oxidation of the oil were lower than those of the control canola oil. PDMS-containing canola oil and canola oil were heated with stirring from room temperature to 180℃, and then allowed to stand while cooling. Oxygen contents of both oils increased up to 120℃ then dropped abruptly. While cooling, oxygen contents sharply increased at 100℃ and approached the saturation content, although the increase for PDMS-containing canola oil was a little slow. Likewise, the thermal treatment of PDMS-containing canola oil and canola oil at 180℃ for 1 h under stirring was repeated 5 times with standing intervals for 2-3 days at room temperature. Oxidation of the former was less than that of the latter in spite of its high oxygen content. In conclusion, the oxygen content of oil with/without PDMS addition increased, but oxidation of PDMS-containing canola oil was inhibited both during heating and standing with intermittent heating. It was suggested that PDMS exerted its antioxidative effect regardless of whether it covered the oil or was dispersed in it.

Key words: polydimethylsiloxane, oxygen content, oxidation, intermittent heating, monolayer

1 INTRODUCTION

Polydimethylsiloxane (PDMS) has been known to have an antifoaming effect[1, 2] and inhibits decline of the smoke point of oil[3], and is combined with oil for commercial use in Japan on the level of some ppm. A surface activating molecule moves not to the liquid phase but to the surface layer when it is mixed with a solvent having a relatively weak intermolecular force, such as oil, under the condition that the difference of the forces between the solvent molecules and the surface activating molecules is greater than the mixing entropy. Thus, it is reported that heat-resistant PDMS mixed with oil moves to the oil surface and protects it from foaming[4].

In addition, J. B. Martin[5] found that 0.03 ppm of PDMS exhibited an antioxidative effect in heated oil at 190℃. Tocopherol is mixed in oil more than some thousand times as much as PDMS to provide this antioxidation property[6], but it is easily decomposed under thermal treatment[7, 8]. PDMS slightly decomposes under repeated thermal treatments, followed by volatilization, but the antioxidative effect is maintained very well in heated oil. This is the big reason why PDMS is added to heavy-duty oil as an antioxidant in addition to its safety.

Canola oil containing only 0.1 ppm PDMS looks slightly turbid, is lighter in touch, and absorbs into skin slower than canola oil. The smell of canola oil is reduced by the addition of PDMS. However, it is not easy even by analytical instruments to confirm if PDMS in oil in the ppb to ppm range is dispersed or dissolved due to its low solubility. Available PDMS is a polymer of dimethylsiloxane with a certain degree of polymerization. This makes our understanding more complicated.

Freeman *et al.*[9] reported that PDMS formed a monolayer on an oil surface and that oxygen in the air was inhibited from penetration and diffusion in oil, resulting in an antioxidative effect. However, when the oil surface is disturbed

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vigorously as in deep-frying, it is hard to imagine that PDMS in such a very small quantity maintains a monolayer on the surface of oil. Still the antioxidative effect on oil is consistent. In the present study, it is investigated whether PDMS existing only on the surface of canola oil[9] exhibits the antioxidative effect as has been believed since the latter half of the 20th century. As oils for commercial use contain PDMS on the level of some ppm, we studied with canola oil containing 10 ppm PDMS.

2 EXPERIMENTAL

2.1 Materials

PDMS KF-96ADF was purchased from Shin-etsu Chemical Industry, Tokyo, Japan. Canola oil was a product of J-Oil Mills, Inc., Yokohama, Japan. A PDMS-hexane solution was added to Canola oil, followed by desolvation under reduced pressure and bubbling with nitrogen gas to obtain an oxygen content of 0.67 v/v%. The 10-ppm PDMS-containing canola oil, thus obtained, was kept in a 4-L laminated steel canister until use. All solvents and reagents were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan.

2.2 Experimental design

Oil absorbs oxygen from air continuously. Oxygen dissolved in oil mainly attacks the unsaturated fatty acid moiety to cause oxidation. Once oxidation begins, some oxygen in the oil is consumed for the formation of peroxides, which are the primary oxidation products. The oxygen content in oil is a balance of oxygen being absorbed from air and that consumed for oxidation[10]. In the present study, oxygen content and specific gravity of canola oil and PDMS were measured at room temperature to determine the influence of oxygen penetration into oil on those specific gravities. Next, PDMS concentrations of three parts, surface, center, and bottom, of standing PDMS-containing canola oil were analyzed. In order to estimate the effect of PDMS localized on the surface of oil, canola oil, to which a trace amount of PDMS was spotted on the surface, was allowed to stand and the oxygen content, peroxide value (PV), and polar compound content (PC) were determined. The temperature factor of PDMS was investigated by heating PDMS-containing canola oil from room temperature to 180℃ once, and by heating at 180℃ for 1 h repeatedly with a 2-3 day interval between heatings (intermittent heating).

2.3 Methods for oil analyses

2.3.1 Chemical properties

PV and *p*-anisidine value (AnV) were determined according to the standard methods of the Japan Oil Chemists' Society for analysis of fats, oils, and related materials. A 4-mL oil sample was placed in a 15-mL test tube and heated to 50℃ to determine PC with a digital edible oil tester (testo270, Testo Japan, Yokohama, Japan).

2.3.2 Determination of oxygen content

The oxygen content of oil was determined by the following two methods. The gas chromatographic method for the detection of absolute amounts of oxygen (v/v%) employed a Chromatograph GC-8AIT, Shimadzu, Tokyo, Japan, equipped with a SUS column (diameter 3.0 mm × length 2.0 m) filled with molecular sieves 5A, 60/80 mesh; helium was flowed as a carrier gas at 39 mL/min; column temperature, 70℃; TCD temperature, 100℃. The amount of oil sample injected was 5 μL.

The second method employed a DO/O_2/Temp Meter, UC-12-SOL, Central Science, Tokyo, Japan, equipped with a polarographic electrode[10]. The oxygen content reading (relative oxygen content) of canola oil saturated with oxygen by bubbling air at 25℃ was set as 100%.

The saturated oxygen amount is 37.7 mg/kg oil under 0℃ and 1 atm[11]. According to the value, saturated oxygen content is given as 24.3 mL/L oil. In fact, oxygen-saturated oil which relative oxygen content is set as 100% by DO/O_2/Temp Meter showed the oxygen content of 2.4% by the gas chromatographic method described above.

2.3.3 Determination of specific gravity in canola oil and PDMS

Canola oil and PDMS-containing canola oil were bubbled with air and their specific gravities at 20℃ were determined by a Density-Specific Gravity Meter, DA-650, Kyoto Electronics Manufacturing Co. Ltd., Kyoto, Japan.

2.4 Determination of PDMS distribution in frying 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 PDMS contents of the samples were analyzed by the Japan Food Research Laboratories, Osaka, Japan. The method is described briefly as follows. The sample weighed in a tube was added to a saturated sodium chloride solution and diethyl ether and the mixture was shaken then centrifuged for 30 min. After centrifugation, the ether phase was isolated and the water phase was added to diethyl ether, shaken then centrifuged again. The first ether fraction was combined with the second, dried over sodium sulfate, and the solvent was removed by a rotary evaporator. The residue was dissolved in kerosene quantitatively. The silicone content was determined by inductively coupled plasma atomic emission spectroscopy 735-ES, Agilent Technology (RF output, 1400 W; plasma gas, 15 L/min (Ar); auxiliary gas, 1.5 L/min (Ar); carrier gas, 0.55 L/min (Ar); plasma observation direction, vertical; detection wavelength, 251.611 nm). A calibration curve was obtained by

processing standard solutions containing 0-5 ppm PDMS KF-96ADF using the same procedure as described above.

2.5 Change of relative oxygen content in canola oil and PDMS at room temperature

Canola oil and PDMS, 25 mL each, were separately poured into 50-mL brown glass vials (inner diameter 30 mm, height 77 mm) and allowed to stand at room temperature under 2.5 kPa for 60 h, and then under atmospheric pressure for 60 h. Relative oxygen content was determined at 25℃ by a DO/O_2/Temp Meter.

2.6 Autoxidation of canola oil with/without PDMS

Eight 200-mL beakers were gently filled with canola oil obtained from a newly opened bottle, 130 mL each, in such a manner that oil did not take in oxygen. With a micropipette, 13 μL (100 ppm) of PDMS was placed on the surface of the oil in four of the beakers: 13 μL was practically the minimum amount for the precise work. All the beakers were kept at 60℃ in an electric oven, FUW242P, ADVANTEC, Tokyo, Japan, and relative oxygen content at 25℃, PV, and PC were determined after 0, 3, 6, and 13 days.

Canola oil obtained from a newly opened bottle, 130 mL each, was poured into eight 200-mL beakers and maintained under reduced pressure at 2.5 kPa to decrease those oxygen contents down to 5%. Then, the same autoxidation experiment described above was also carried out at room temperature instead of at 60℃, and relative oxygen content at 25℃, PV, and PC were determined after 0, 3, 11, and 18 days.

2.7 Relative oxygen content change of heated then cooled oil containing PDMS

According to the procedure described in our previous paper[10], 10-ppm PDMS-containing canola oil, 1 kg, was poured into a 2-L four-necked separable round-bottomed flask fitted with a stir bar, thermometer, and air pump delivering 110 mL/min of air into the flask. One neck of the flask was left open as an outlet for the pump. Under stirring at 85 rpm, the canola oil was heated from room temperature to 180℃. The surface to volume ratio was 0.15. After the oil temperature reached 180℃, heating under stirring was stopped and the oil was allowed to stand until it reached room temperature. During the process, samples were collected at 25, 120, 150, 180, 150, 100, 60, and 25℃ by pipetting through the open neck of the flask and completely filling a 50-mL brown vial. As soon as the sample temperature decreased to 25℃, the relative oxygen content was measured by the DO/O_2/Temp Meter. The same experiment was carried out with canola oil and PDMS.

2.8 Intermittent heating of oil containing PDMS

Thermal treatment composed of heating from room temperature to 180℃, at 180℃ for 1 h, and standing at room temperature for 2-3 days was repeated 5 times with 10-ppm PDMS-containing canola oil. The procedure[10] was basically the same as that in section 2.7. Oil was sampled after the heating and standing (just before the next heating). Oxygen content was determined by gas chromatography. PV and AnV of the samples were also determined.

2.9 Statistical analyses

All values obtained for chemical properties, oxygen content, specific gravity, and PDMS distribution are revealed as mean ± SD and were analyzed using Student's *t* test or one-way analysis of variance with Dunnett's multiple comparison post hoc test. Results were considered significant at $p<0.05$.

3 RESULTS

3.1 Change of relative oxygen content in canola oil and PDMS at room temperature

As shown in **Fig. 1A**, the relative oxygen content in canola oil slowly decreased under reduced pressure, while that in PDMS quickly did. When the contents of canola oil and PDMS reached 5%, both were allowed to stand under atmospheric pressure. Canola oil and PDMS increased in relative oxygen content slowly and quickly, respectively (**Fig. 1B**).

3.2 Determination of PDMS distribution in frying oil

Table 1 shows the distribution of PDMS in standing PD-

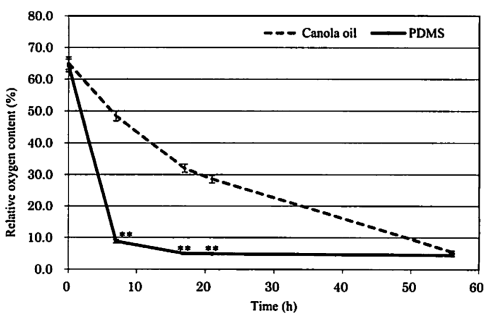

Fig. 1A Relative oxygen content of canola oil and PDMS kept under reduced pressure at 2.5 kPa. Oxygen content was determined by DO/O_2/Temp Meter. Values are expressed as mean ± SD. $^{**}p < 0.01$ significantly different from the corresponding value of canola oil by Student's *t* test. PDMS: polydimethylsiloxane.

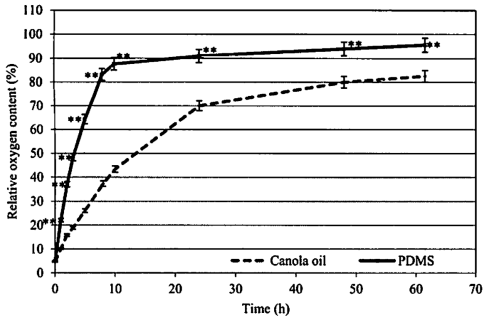

Fig. 1B Relative oxygen content of canola oil and PDMS allowed to stand under atmospheric pressure at 25℃. Oxygen content was determined by DO/O_2/Temp Meter. Values are expressed as mean ± SD. $^{**}p < 0.01$ significantly different from the corresponding value of canola oil by Student's *t* test. PDMS: polydimethylsiloxane.

Table 1 PDMS distribution (ppm) in frying oil.

containing 10-ppm PDMS.	
Surface	6.5 ± 0.7^a
Center	5.4 ± 0.6^a
Bottom	4.7 ± 0^b

PDMS: polydimethylsiloxane, Values are expressed as mean ± SD. The value with the non-common superscript letter differs significantly ($p < 0.05$) by Dunnett's multiple comparison post hoc test.

MS-containing canola oil. There was a tendency that the concentration of PDMS decreased as the depth of oil increased, and that in the bottom part was the lowest.

3.3 Determination of specific gravity in canola oil and PDMS

PDMS, most of which is not dissolved but dispersed in canola oil, had tendency toward moving up in the standing canola oil, although PDMS has greater specific gravity than canola oil does. It was our interest if the specific gravity of PDMS became smaller than that of canola oil with the increasing oxygen content. When oxygen contents of canola oil and PDMS increased, those specific gravities decreased concurrently (Table 2). However, the specific gravity of PDMS was always greater than that of canola oil. Considered together with the results described in section 3.2, it seems that PDMS is dispersed in canola oil without a strong influence of its specific gravity.

3.4 Autoxidation of canola oil covered with/without PDMS

When PDMS was applied to the center of the oil surface, rainbow-colored rings were observed on the surface, which then turned into an irregular pattern after 30 min. During the experiment, PDMS was observed on the surface of the oil.

At room temperature, the relative oxygen contents of canola and PDMS-containing oils were over 80% after 3 days, and stayed at a high level for 18 days (Fig. 2A). But, the color was not changed, and PVs (Fig. 2B) and PCs (Fig. 2C) increased a little under high oxygen content.

At 60℃, the color of the oil changed to yellow regardless of PDMS. The oxygen content of PDMS-containing canola oil was lower than that of canola oil (Fig. 2A). This fact seems to confirm that PDMS inhibits oxygen intake of canola oil at 60℃. PVs (Fig. 2B) and PCs (Fig. 2C) of canola oil were higher than those of PDMS-containing canola oil, respectively, and the antioxidative effect of PDMS was confirmed at 60℃.

3.5 Relative oxygen content change of heated then cooled oil containing PDMS

Figure 3A and Fig. 3B show the relative oxygen content changes in canola oil and PDMS-containing canola oil after heating and cooling, respectively. As a whole, the changes for both were similar: relative oxygen content abruptly decreased at 120℃ and became very low at 180℃. After cessation of heating, the oil was allowed to cool resulting in an abrupt absorbance of oxygen around 100℃. The oxygen

Table 2 Relative oxygen content and specific gravity in canola oil and PDMS.

Canola oil		PDMS	
Relative oxygen content (%)	Specific gravity	Relative oxygen content (%)	Specific gravity
6.7	0.91855 ± 0.00001	5.0	0.96970 ± 0.00001
19.6	0.91854 ± 0.00001	71.9	0.96961 ± 0.00001
46.6	0.91852 ± 0.00001	96.0	0.96957 ± 0.00001
68.3	0.91852 ± 0.00001	104.3	0.96940 ± 0.00001
96.4	0.91840 ± 0.00001		

Values are expressed as mean ± SD. PDMS: polydimethylsiloxane.

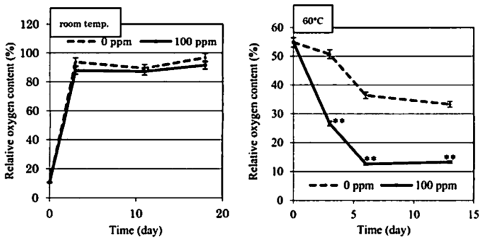

Fig. 2A Relative oxygen content of canola oil covered with polydimethylsiloxane. Oxygen content was determined by DO/O_2/Temp Meter. Values are expressed as mean ± SD. $^{**}p < 0.01$ significantly different from the corresponding value of 0 ppm by Student's *t* test.

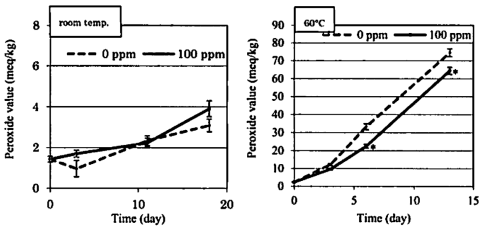

Fig. 2B Peroxide value of canola oil covered with polydimethylsiloxane. Values are expressed as mean ± SD. $^{*}p < 0.05$ significantly different from the corresponding value of 0 ppm by Student's *t* test.

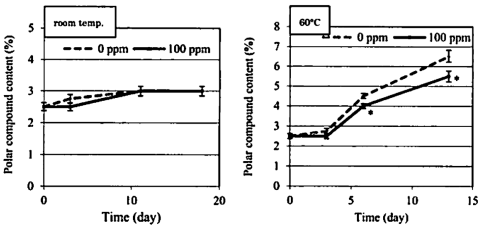

Fig. 2C Polar compound content of canola oil covered with polydimethylsiloxane. Values are expressed as mean ± SD. $^{*}p < 0.05$ significantly different from the corresponding value of 0 ppm by Student's *t* test.

content reached about 80%. There were significant differences in the oxygen contents between canola oil and PDMS-containing canola oil at 120℃, 150℃ (during heating) and 60℃ (during cooling).

The oxygen content of PDMS-containing canola oil was

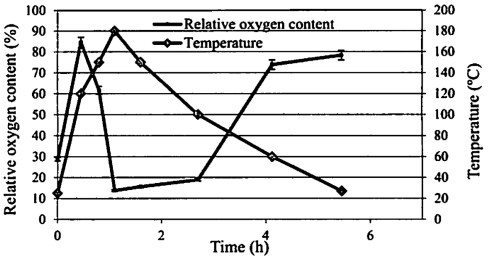

Fig. 3A Relative oxygen content of canola oil. Oxygen content was determined by DO/O_2/Temp Meter. Values are expressed as mean ± SD.

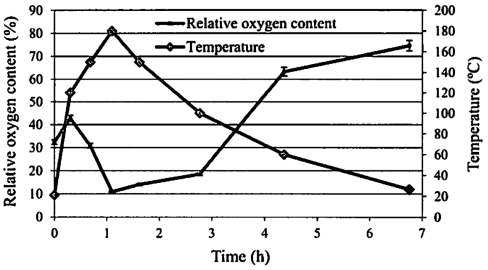

Fig. 3B Relative oxygen content of canola oil containing 10-ppm polydimethylsiloxane. Oxygen content was determined by DO/O_2/Temp Meter. Values are expressed as mean ± SD.

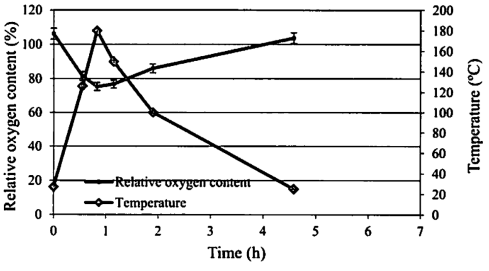

Fig. 3C Relative oxygen content of polydimethylsiloxane. Oxygen content was determined by DO/O_2/Temp Meter. Values are expressed as mean ± SD.

relatively low up to 150℃, which agrees well with the result of Gerde[12]. Once heated, the oxygen content at room temperature did not return to the initial low value but increased to 75%. In the second heating, a high oxygen content was maintained, which then decreased at 120℃[10] (data not shown). Exposure of PDMS-containing oil to high temperature might alter the dispersion of PDMS in oil,

resulting in an oxygen content increase. On the other hand, the oxygen content of PDMS was higher than that of canola oil saturated with oxygen, 100%, at room temperature and between 75-85% over 100℃ (Fig. 3C); the content at 180℃ was 8 times higher than that of canola oil. However, PDMS added to canola oil in the ppm range does not change the oxygen content of canola oil.

3.6 Intermittent heating of oil containing PDMS

The pattern of oxygen content change agreed very well with the results of our previous paper[10] using blended oil of rapeseed and soybean oils. PDMS-containing canola oil showed a low PV due to unstable peroxides at high temperature[10] and very low oxygen content at 180℃. After standing for 2-3 days at room temperature, PV was low but the oxygen content increased significantly (Fig. 4A, 4B). In the case of canola oil, PV and the oxygen content were low at 180℃ as well, but PV increased when the oxygen content stayed relatively low. This implies that the oxygen consumption by oxidation was faster than oxygen penetration from air to oil.

Figure 4C shows the total amounts of oxygen dissolving in oil and the oxygen consumed for peroxide formation. Oxygen contained in the secondary products generated from peroxides is excluded. The total oxygen amounts of PDMS-containing canola oil were roughly half as much as those of canola oil and the PVs were low, but the oxygen content in the interval exceeded 2 v/v% (saturated oxygen content in canola oil is 2.43 v/v% at 0℃)[11] as shown in Fig. 4B. This means that oxidation of canola oil was inhibited by PDMS in canola oil that contained plenty of oxygen (Fig. 4A) and that the total oxygen amounts of PDMS-containing canola oil were low as a result.

The increase of AnVs, which indicates thermal oxidation, was also suppressed by PDMS (Fig. 5). It was confirmed that PDMS exhibited an antioxidative effect in intermittent heating.

4 DISCUSSION

When canola oil and PDMS were allowed to stand at room temperature, the rate of oxygen absorption by PDMS was far higher than that of canola oil. After 60 h, the relative oxygen content of PDMS and canola oil reached 95.6% and 82.5%, respectively (Fig. 1B). Both contents increased easily by shaking for a few seconds (data not shown).

PDMS concentration analysis of long standing PDMS-containing canola oil showed a tendency that the PDMS concentration decreased as the depth of oil increased, and that of the bottom part was obviously low (Table 1). Although the PDMS concentration was adjusted to 10 ppm in the preparation, the three parts analyzed contained less than 10 ppm PDMS. If a sample had been collected just

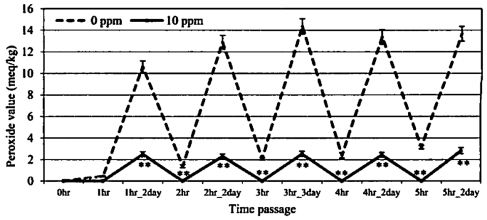

Fig. 4A Peroxide value of polydimethylsiloxane-containing canola oil heated intermittently. Values are expressed as mean ± SD. $^{**}p < 0.01$ significantly different from the corresponding value of 0 ppm by Student's *t* test.

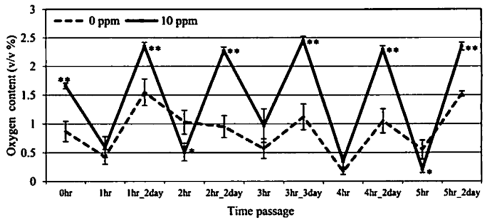

Fig. 4B Oxygen content of polydimethylsiloxane-containing canola oil heated intermittently. Oxygen content was determined by gas chromatography. Values are expressed as mean ± SD. $^{*}p < 0.05$, $^{**}p < 0.01$ significantly different from the corresponding value of 0 ppm by Student's *t* test.

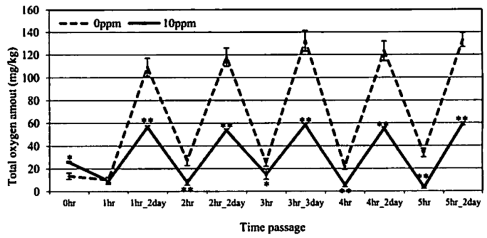

Fig. 4C Total oxygen amount of polydimethylsiloxane-containing canola oil heated intermittently. Values are expressed as mean ± SD. $^{*}p < 0.05$, $^{**}p < 0.01$ significantly different from the corresponding value of 0 ppm by Student's *t* test.

from the surface of the oil, values greater than 10 ppm might have been obtained on condition that PDMS formed a monolayer on an oil surface[9]. Used laminated steel canister, glass, plastics, etc. can be the reason for the low value due to their extremely high affinities for PDMS[11].

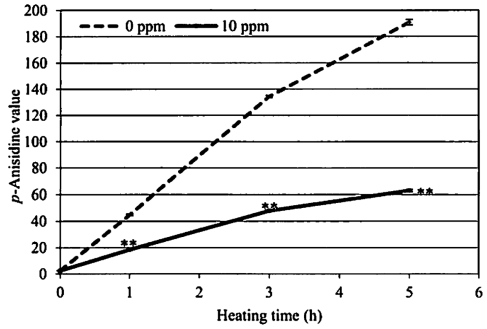

Fig. 5 Increase of *p*-anisidine value by intermittent heating of canola oil containing polydimethylsiloxane. Values are expressed as mean ± SD. $^{**}p < 0.01$ significantly different from the corresponding value of 0 ppm (canola oil) by Student's *t* test.

It is intriguing that the upper part of the oil contained more PDMS than the bottom part did in spite of the high specific gravity of PDMS (Table 2). This may confirm the existence of a PDMS monolayer[9] on the surface of the oil that was prepared by addition of a PDMS-hexane solution. On the other hand, PDMS exists in every part of the oil, although PDMS is not dispersed in oil uniformly. It is possible that PDMS forms very stable colloid-like particles in oil. PDMS KF-96ADF used in the present study has an average molecular weight of 6000 and a polymerization degree of 85[13]. The number of atoms in one PDMS molecule amounts to 850, which is very close to the category of colloids, 1000, as proposed by Staudinger[14]. When PDMS-containing canola oil was irradiated by light in the dark, the light passage characteristic of a colloid could be observed (data not shown).

As mentioned in section 2.2, the oxygen content in oil is a balance of oxygen absorbed from air and that consumed for oxidation[10]. From the results described in section 3.4, it was suggested that PDMS localized on the surface of oil inhibited oxygen penetration into oil at 60℃ (Fig. 2A). At room temperature, the oxygen consumption due to oxidation was low, and oxygen penetration into oil was faster than the consumption. Thus, it is interpreted that the covering effect of PDMS was not shown at room temperature clearly. However, a phenomenon similar to that at 60℃ described above was also observed at the beginning of heating PDMS-containing canola oil as reported in section 3.5 (Fig. 3A). The complete PDMS layer on the surface and dense PDMS dispersion on the top of the oil inhibited the oxygen penetration.

In the heating and cooling experiment (Fig. 3A, 3B), recovery of oxygen content during cooling was a little slower in PDMS-containing canola oil than in canola oil, but the oxygen contents at room temperature did not differ at all. Kusaka *et al.*[15] did not find a clear influence of PDMS on oxygen contents of safflower and soybean oils when heated from room temperature to 200℃.

Figure 4A and Fig. 5 clearly show that PDMS has an antioxidative effect at 180℃ and room temperature. Before 1980, it was believed that PDMS did not inhibit autoxidation. Kusaka *et al.*[16] observed a slight antioxidative effect of PDMS at room temperature and 55℃ in soybean and linseed oils at the concentration of 0.1-100 ppm PDMS. In the present intermittent heating, the oil was stirred gently so as not to take oxygen into oil while heating. The concentration of PDMS in the oil seems relatively high at the top of the oil but PDMS existed throughout the oil. During standing at room temperature, the oxygen content of PDMS-containing oil increased to the level close to its saturation value (Fig. 4B)[11]. Dispersed PDMS did not inhibit oxygen penetration into oil resulting in high oxygen content in oil, but the oxidation was suppressed. This conclusion does not agree with the explanation that PDMS covering oil[17] inhibits oxygen penetration[9] to suppress oxidation.

Freeman *et al.*[9] and Kusaka *et al.*[18] reported that PDMS inhibited convection currents in oil heated without stirring. The surface temperature of PDMS-containing oil was 10℃ or more lower[19] than that of oil without PDMS due to reduced convection currents[9]. As oxidation of oil occurs primarily in the top part of oil, thermal deterioration of oil without stirring occurs less drastically in PDMS-containing oil than in intact oil due to its low surface temperature and convection currents[20]. However, this is not the case in the present study because our thermal treatment was performed under stirring or in a chamber maintained at 60℃.

Because PDMS reveals the antioxidative effect in the amount less than some thousandths of the optimal concentration for tocopherol to provide the effect, it seems that the antioxidation mechanism of PDMS is not the same as the chemical reaction between tocopherol and peroxide radical. Most of PDMS is not dissolved but dispersed in canola oil, that is, PDMS particles exist outside canola oil; -Si- is located in the interface between PDMS and canola oil, and methyl branches in the oil, ether bonds inside PDMS[11]. On the other hand, the result that the PDMS concentration in the standing canola oil decreased as the depth of oil increased resembles the oxygen concentration in standing oil[11]. This suggests the possibility of relation between PDMS and oxygen. And oxygen solubility in PDMS is greater under the atmospheric pressure than in canola oil as shown in Fig. 1B and Fig. 3C. Number of methyl branches of PDMS added 10 ppm in canola oil is close to that of oxygen molecules dissolving in the oil. If there were the interaction[21] between PDMS and oxygen molecules in oil, the antioxidative effect of PDMS would be due to hy-

drogen atoms in the methyl branches. In addition, we previously reported that oxidation of oil was drastically inhibited by reducing the atmospheric pressure from 100 to 97 kPa[22]. It is possibly assumed that PDMS added to oil would inhibit oxidation of oil by the interaction between PDMS and dissolved oxygen, resulting in reduction of free oxygen molecules in the oil. But further study is needed to prove the speculation described above.

Conclusion

When PDMS-containing canola oil was allowed to stand, PDMS did not disperse in the oil uniformly but there was a tendency that the PDMS concentration decreased as the depth of oil increased: the concentration of the bottom part was obviously low. With time passage the oxygen content of oil with/without PDMS addition increased, but oxidation of PDMS-containing canola oil was inhibited during heating and standing with intermittent heating. It was suggested that PDMS exhibited an antioxidative effect regardless of whether it covered the oil or was dispersed in it.

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