Abstract: Strong and stable antioxidation effects of polydimethylsiloxane (PDMS) are widely accepted and utilized in commercial frying oil; however, the mechanism is not fully established. On the other hand, canola oil contains about 700 ppm (mg/kg-oil) of the natural antioxidant, tocopherol. Canola oil containing 0, 1 and 10 ppm added PDMS was heated at 180°C for 1 h under stirring, then left for 2-3 days at room temperature; this treatment was repeated 5 times. Compared to pure canola oil, PDMS-containing canola oil exhibited remarkably lower peroxide, p-anisidine and acid values, a lower decrease in tocopherol content but a higher oxygen content during the heating experiments, implicating low oxygen consumption for the oxidation. While PDMS has not been known to exhibit antioxidative effects at ambient temperatures, the present results show that PDMS prevents autoxidation as well as thermal oxidation. In addition, PDMS, not tocopherols, provided the major antioxidative effect during intermittent heating, and the decrease of tocopherols was significantly inhibited by PDMS. Phase contrast microscopy confirmed that PDMS contained in canola oil was suspended as particles. Also, the oxygen content in standing PDMS-containing canola oil decreased as the depth of oil increased, corresponding to the PDMS distribution, which also decreased as the depth of oil increased. Moreover, PDMS had a higher affinity for oxygen than canola oil in a mixture of canola oil/PDMS, 1:1 v/v. Thus, it is suggested that PDMS restricted the behavior of oxygen dissolved in canola oil by attracting oxygen in and around the PDMS particles, which is wholly different from the radical scavenging antioxidation of tocopherol.

Key words: polydimethylsiloxane, tocopherol, antioxidation mechanism, suspension

1 Introduction

When polydimethylsiloxane (PDMS) is added to oil, it shows extraordinarily strong and stable antioxidative effects under thermal treatment\(^\text{1}\). It has been reported that PDMS inhibits oxygen dissolution into oil by forming a monolayer on the surface of the oil, thereby reducing thermal oxidation\(^\text{2}\). Cooking oil produced in Japan for domestic use does not contain PDMS, so natural antioxidative substances are deactivated during thermal treatment\(^\text{3}\). Przybylski et al.\(^\text{4}\) revealed that total tocopherols in soybean oil decreased drastically after deep frying a second time, while the content of polar compounds, p-anisidine and polymers increased. Gerde et al.\(^\text{5}\) heated soybean oil containing ≥ 0.025 ppm PDMS and found that oxidation of the oil was inhibited by tocopherols present in the oil during the initial heating; after destruction of tocopherols by heating, oxidation was inhibited by PDMS. Our previous paper\(^\text{6}\) proposed that PDMS added to oil would inhibit the oxidation of oil by interacting with dissolved oxygen, thereby reducing free oxygen molecules in the oil. In addition, we previously reported that oxidation of oil was drastically inhibited by reducing the atmospheric pressure from 100 to 97 kPa\(^\text{7}\).

In the present paper, canola oil containing PDMS was heated intermittently according to a typical deep frying practice, and the relation between natural tocopherols and PDMS in the antioxidative effect was investigated to grasp the antioxidation mechanism of PDMS by determining the residual tocopherol, chemical properties and oxygen content of the oil. In addition, thermal changes of oxygen content in PDMS and canola oil, and oxygen distribution in mixtures of PDMS and canola oil were measured to collect basic information for the antioxidative mechanism of PDMS.
2 Experimental

2.1 Materials

PDMS KF96ADF (molecular mass 2.5 × 10^4 g/mol, polymerization degree 3.5 × 10^5, specific gravity 0.965 at 25°C, vapor pressure 133 Pa at 220°C) was purchased from Shin-etsu Chemical Industry (Tokyo, Japan). Canola oil was a product of J-Oil Mills Inc. (Tokyo, Japan), and was composed of 0.1% myristic acid, 4.4% palmitic acid, 0.2% palmitoleic acid, 2.5% stearic acid, 60.9% oleic acid, 20.2% linoleic acid, 7.9% α-linolenic acid, 3.8% others. A solution of PDMS in hexane was added to canola oil, followed by desolvation under reduced pressure and bubbling with nitrogen gas. The PDMS-containing canola oils, thus prepared, were kept in 4-L laminated steel canisters until use. All solvents and reagents were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan).

2.2 Intermittent heating

Very fresh canola oil (1000 g) and canola oil (1000 g) containing 1 or 10 ppm added PDMS were respectively poured into 2-L four-necked separable round-bottomed flasks 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 oil was heated from room temperature to 180°C in 30 min; the surface to volume ratio was 0.15 cm⁻¹. When the oil temperature reached 180°C, stirring was maintained for 1 h, then a sufficient sample was removed by pipetting through the open neck of the flask to fill a 50-mL brown vial completely. The vial was closed with a cap lined with heat-stable sealant, ensuring that no air was trapped in the vial.

The remaining oil was kept in the flask at room temperature for 2–3 d open to the air, then the oil was heated with stirring to 180°C and maintained for 1 h again, as described above. This process was repeated four more times. The overall heating time was 5 h.

2.3 Instrumental analyses

The oxygen content of oil was determined by the following two methods. The absolute amount of oxygen (v/v %) was determined using a gas chromatographic method (for 2.2) using a Chromatograph GC-8AHT (Shimadzu, Kyoto, Japan) equipped with a SUS column (2.0 mm × 3.0 mm i.d.) filled with molecular sieve 5A (60/80 mesh). The separation conditions were: helium as the carrier gas, 39 mL/min; column temperature, 70°C; TCD temperature, 100°C, sample injection volume, 5 μL. The second method (for 2.6 and 2.7) employed a DO/O₂/Temp Meter (UC-12-SOL; Central Science, Tokyo, Japan) equipped with a polarographic electrode. The oxygen content reading (relative oxygen content) of canola oil saturated with oxygen by bubbling air at 25°C was set as 100%.

Tocopherols (α, β, γ and δ-tocopherols) were analyzed using a Prominence HPLC system (Shimadzu) equipped with an InertSil® NH2 column (25 cm × 2.1 mm i.d.; GL Sciences Inc., Tokyo, Japan) under the following conditions: column temperature, 60°C; mobile phase, n-hexane-isopropyl alcohol 98:2 v/v; flow rate, 0.5 mL/min; injection volume, 2 μL. Analytes were detected (Ex: 295 nm, Em: 325 nm) with a fluorescence detector (Prominence RF-10AXL, Shimadzu).

2.4 Chemical properties

Peroxide value (PV), p-anisidine value (AnV), and acid value (AV) were determined according to the standard methods of the Japan Oil Chemists’ Society for analysis of fats, oils, and related materials.

2.5 Phase contrast microscopic observation of PDMS particles suspended in canola oil

Canola oil containing 10 and 1000 ppm PDMS was prepared as in 2.1 and subjected to phase contrast microscopy using a System Biological Microscope CX41 (Olympus, Tokyo, Japan).

2.6 Thermal changes in oxygen content of canola oil with and without PDMS

According to the procedure described in 2.2, 1 kg fresh canola oil was heated from room temperature to 180°C. After the oil temperature reached 180°C, heating under stirring ceased 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°C, and 25°C by pipetting through the open neck of the flask, completely filling a 50-mL brown vial. As soon as the sample temperature decreased to 25°C, the relative oxygen content was measured using the DO/O₂/Temp Meter. The same experiment was carried out with pure PDMS.

2.7 Oxygen affinity difference between canola oils and PDMS

Canola oil containing 10 ppm PDMS (initial relative oxygen content was adjusted at 40% and 72% by bubbling air into the oil) was poured into a 300-mL cylindrical separatory funnel gently and completely (no air at the top), and set vertically after wrapping in aluminum foil to shield from the light. The two samples employed were generated to ensure that initial oxygen content did not affect the result. After one week at room temperature, the oil was dripped from the funnel to obtain samples from the lower, central and upper parts of the oil into three 50-mL brown vials at a drip rate of 6.5 mL/min; no air was allowed to penetrate into the oil samples and any mixing in the funnel was avoided. The relative oxygen content was measured immediately using the DO/O₂/Temp Meter.

Canola oil (50 mL) and PDMS (50 mL) were vigorously mixed together in a 200-mL beaker to saturate the two
phases with oxygen, then poured into a 30-mL cylindrical separatory funnel completely, which was positioned vertically after wrapping in aluminum foil to shield from the light. After one week at room temperature, the canola oil (upper layer) and PDMS (lower layer) samples were separately dripped gently as above from the funnel to two 50-mL brown vials. The relative oxygen content was measured immediately by the DO/O₂/Temp Meter.

2.8 The experimental design
In order to examine Freeman’s proposal that PDMS inhibits oxygen dissolution into oil by forming a monolayer on the surface of the oil, thereby reducing thermal oxidation, following experiments were carried out in the present study. Oil containing tocopherols and PDMS was heated intermittently, and PV, AnV, AV, residual tocopherols, and oxygen content of the oil were determined to find the relation between tocopherols and PDMS in the antioxidative effect. Because tocopherols eliminate peroxide radicals formed from lipid radicals and oxygen, oxygen dissolved in oil is consumed in the antioxidative process. On the other hand, PDMS has nothing to do with the oxygen consumption. In addition, it was confirmed by phase contrast microscopic observation if PDMS was dispersed in oil, and also confirmed if the PDMS-rich region in oil contained increased levels of oxygen. Oxygen affinity of PDMS and oil was determined.

2.9 Statistical analyses
All values obtained for oxygen content, PV, AnV, AV, tocopherols are revealed 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 Results and Discussion
3.1 PV
PVs were low just after heating at 180°C and high after standing at room temperature regardless of the presence or absence of PDMS (Fig. 1; time is described as only heating time or heating time plus standing days, for example, 1 h or 1 h_2 d, respectively.), but were remarkably higher in pure canola oil than in PDMS-canola oil after standing. Peroxide was actively formed in pure canola oil⁶, while it was inhibited in PDMS-canola oil. Canola oil containing 1 ppm PDMS had a tendency toward higher PVs than oil containing 10 ppm. PV of pure canola oil just after each heating increased gradually, however that of PDMS-canola oil did not increase, showing that the antioxidative effects of PDMS were active during heating (Fig. 1).

3.2 Oxygen content
Figure 2 shows the content of dissolved oxygen converted into the weight of dissolved oxygen in 1 kg canola oil. Also in Fig. 2, time is described as only heating time or heating time plus standing days, for example, 1 h or 1 h_2 d, respectively. Intermittent heating of canola oil resulted in very low oxygen content just after heating, but the content increased markedly during standing at room temperature regardless of the presence or absence of PDMS⁶. This agrees very well with our previous results⁶, in which during cooling, the oxygen content started to increase abruptly at around 100°C and reached 80% saturation at room temperature⁶.

Canola oil containing 10 ppm PDMS had a tendency toward higher oxygen content than oil containing 1 ppm. PDMS decreased oxygen consumption due to oxidation of unsaturated fatty acids. In other words, canola oil was oxi-
dized actively in the absence of PDMS, and the amount of oxygen consumed for peroxide formation exceeded the amount absorbed from the air (Fig. 2).

3.3 p-AnV and AV

p-AnV reflects the content of the secondary oxidation product. Figure 3 shows the AnVs just after heating at 180°C; clearly, the AnVs for pure canola oil were higher than in PDMS-canola oil; however, there was no difference in values between 1 ppm and 10 ppm PDMS.

AVs of pure canola oil were higher than those of PDMS-canola oil (Fig. 4). The present thermal treatment involved simple heating and did not replicate deep frying conditions; therefore, all the values were small.

3.4 Tocopherol content

The total amount of natural tocopherols (α, β, γ, and δ-tocopherols) contained in canola oil were 672 μg/g. Intermittent heating slightly decreased total tocopherols in PDMS-canola oil (Fig. 5), whereas very large decreases were observed with pure canola oil, with 92% of the tocopherols destroyed following the fifth heating.

Tocopherols are antioxidants that should function independently in eliminating radicals regardless of the presence or absence of PDMS in canola oil, assuming that PDMS does not interfere with tocopherol activity. However, residual total tocopherols were obviously high in PDMS-canola oil.

Oxygen levels in pure canola oil were low as shown in Fig. 2. In the oxidation of oil, fatty acid radicals initially generated are attacked by oxygen to form peroxide radicals, then tocopherols react with the radicals, resulting in stable products. This process involves oxygen consumption; tocopherols decrease with the radical elimination and thermal decomposition. On the other hand, PDMS should not react with the radicals described above nor consume oxygen. Thus, PDMS inhibited the oxidation of canola oil in a manner different from the radical elimination of tocopherols and prevented the consumption of tocopherols. The amount of PDMS (1 or 10 ppm) added to canola oil did not affect the decrease in tocopherols (Fig. 5), likely because 0.03 ppm PDMS is sufficient to provide antioxidative effects. The amount of PDMS added to the canola oil in the present study was selected to be similar to levels utilized in commercial oils.

Gerde et al. heated PDMS-containing soybean oil at 180°C for 50 h and found that PDMS had a protective effect; a PDMS concentration of ≥ 0.025 ppm inhibited the degradation of linoleic acid and tocopherols. In addition,
they reported that tocopherols initially controlled oxidation, but that once their concentration dropped to a low value, the rate of linoleic acid oxidation was controlled by the PDMS present. However, soybean oil containing 0.1 ppm PDMS retained a high concentration of tocopherols for more than 27 h at 180°C, thereafter decreasing. It is unclear how tocopherols control oxidation during the initial heating, since PDMS itself has a strong, stable antioxidative effect in oil. We believe that the effect of tocopherols become apparent after the destruction/evaporation of PDMS by heating.

3.5 Phase microscopic observation of PDMS particles suspended in canola oil

When PDMS was mechanically mixed with canola oil, large and irregular spherical particles were observed in the oil (data not shown). On the other hand, the PDMS-hexane solution produced small, regular particles (≤ 7 μm in diameter) in the oil (Fig. 6A, B). PDMS shows poor solubility in canola oil and was found to be dispersed in the oil. This is likely the reason why PDMS-canola oil appears slightly turbid when exposed to light. In addition, a discontinuous layer could not be observed on oil surface when PDMS-canola oil was vigorously stirred in an effort to disrupt the presumed PDMS layer. These results make it difficult to solely attribute the antioxidative effect of PDMS to monolayer formation on the surface of the oil (as described above). It is also dubious that the numerous bubbles generated during frying do not disturb the monolayer in practical deep-frying.

3.6 Thermal changes in oxygen content of canola oil and PDMS

The relative oxygen content of canola oil increased with heating; however, it decreased abruptly at 120°C and reached 15% at 180°C. When allowed to stand at room temperature, it gradually increased until 100°C and abruptly thereafter, reaching about 80% at room temperature (Fig. 7).

The relative oxygen content of PDMS decreased with heating and reached 76% at 180°C. When allowed to stand at room temperature, it gradually increased, reaching 102%. Thus, the oxygen content of PDMS was always higher than that of canola oil, due to the initial relative oxygen content of canola oil being low, since the oil was employed directly from a newly opened bottle.

3.7 Oxygen distribution

The oxygen content of canola oil containing 10 ppm
Table 1 Distribution of oxygen dissolved in standing canola oil containing 10 ppm polydimethylsiloxane.

| Oxygen distribution in canola oil (%) | Initial relative oxygen content 40% | Initial relative oxygen content 72% |
|--------------------------------------|------------------------------------|------------------------------------|
| Upper region                         | 42.2 ± 0.2                      | 74.0 ± 0.4                        |
| Center                               | 40.0 ± 0.2                      | 73.1 ± 0.4                        |
| Lower region                         | 37.4 ± 0.1                      | 70.9 ± 0.4                        |

Values are expressed as mean ± SD. Values with different superscript letters are significantly different (p < 0.05) by Dunnett’s multiple comparison post hoc test.

PDMS, sequestered from air and light and left for 1 week at room temperature, was remarkably higher in the upper part than the lower part (Table 1). As the experimental conditions involved a closed system, the oxygen content of the upper region did not increase as a result of oxygen penetration from the air. During sampling and oxygen content determinations, oxygen penetration into oil does not proceed quickly, as shown in our previous paper. In addition, oxygen molecules dissolved in oil continuously collide with oil molecules and others; thus, oxygen is not likely to gather in the upper region of the oil.

We previously reported that the PDMS distribution in 10 ppm PDMS-canola oil left at room temperature for 1 week was as follows: 6.5 ± 0.7 ppm at the surface, 5.4 ± 0.6 ppm in the center, 4.7 ± 0 ppm at the bottom. That is, the PDMS content decreased as the depth of oil increased. The same held true for oxygen content. The region of high PDMS content also showed high oxygen content, and vice versa. Strong interaction between PDMS and oxygen can be expected. Because PDMS is added at only 10 ppm in canola oil and because there is only a small difference in oxygen dissolution between PDMS and canola oil at ambient temperatures (Fig. 7), it is difficult to attribute the oxygen amount corresponding to the content difference between upper and lower regions to oxygen dissolved only in PDMS particles.

The oxygen contents in the oxygen-saturated mixture of PDMS and canola oil, sequestered from air and light and left at room temperature for 1 week were 102.7 ± 0.5% for the canola oil phase (upper layer) and 106.8 ± 0.5% for the PDMS phase (lower layer): relative saturated oxygen contents are 100% and 109% for canola oil and PDMS-canola oil, respectively. In the oil phase, trace PDMS is suspended and trace oil was suspended in the PDMS phase. This resulted in a slight elevation of oxygen content in the oil phase and a slight decline of oxygen content in the PDMS phase. But, the content was obviously higher in the PDMS phase than in the oil phase, indicating that oxygen affinity of PDMS in a mixture is higher than that of canola oil, as well as in pure and single PDMS and canola oil.

Thus, it is suggested that the affinity of PDMS for oxygen is higher than that of canola oil, and that there is an interaction between PDMS particles and oxygen molecules. The interaction appears to restrict oxygen behavior, resulting in antioxidation of unsaturated fatty acid moieties.

**Conclusion**

When canola oil containing tocopherols and added PDMS was heated intermittently, both thermal oxidation and autoxidation of the oil were remarkably inhibited. Because tocopherols decreased minimally in the thermal treatment, it is suggested that the antioxidation effect was attributed mostly to PDMS, and that suspended PDMS restricted the behavior of oxygen molecules, resulting in reduced oxidation of unsaturated fatty acid moieties.

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