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Influence of Polydimethylsiloxane on the Degradation of Soybean Oil at Frying Temperature

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Abstract Soybean oils treated with 5, 10, 25, 50, and 100 ppb polydimethylsiloxane (PDMS) and a control soybean oil (no PDMS) were heated at 180 °C for 48 h. The decomposition of linoleate (18:2) and tocopherols was monitored. The degradation of 18:2 and both γ- and δ-tocopherols followed pseudo first-order kinetics. For 25 ppb PDMS (the concentration necessary to form a PDMS monolayer on the air-oil interface) and greater concentrations, 18:2 degradation decreased at a rate comparable to the control. However, for the samples with 25 ppb or more PDMS, there was a subsequent increase in the rate of 18:2 degradation during the 48 h of heating period. The same trend seen for 18:2 degradation also was observed for the rates of degradation of both γ- and δ-tocopherols; but, for the tocopherols the treatment with 10 ppb PDMS also decreased the rate of degradation. For those PDMS treatments in which a subsequent increase in degradation rates were observed, the rates of degradation after the change were similar to the rate of degradation in the control oil. In general, the time that the changes in rates occurred increased with the PDMS concentrations. The occurrence of these changes was attributed to decreases in the concentrations of tocopherols or PDMS such that the protective effects were lost.

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Introduction

Oils subjected to frying temperatures undergo a variety of degradation reactions, most of which are oxidative. Oils rich in polyunsaturated fatty acids are particularly affected by these oxidative reactions. Polydimethylsiloxane (PDMS), a silicon-based polymer, is widely used by the food industry as an anti-foaming agent in frying. The use of PDMS at very low concentrations has a protective effect on oil oxidation [1], and extensive research has been done regarding this protection [1, 2]. However, low-viscosity PDMS (less than 5 centistokes, cSt) did not have a protective effect, whereas PDMS with viscosities between 20 and 100 cSt were protective [1, 2]. The protective effect also has been associated with the ability of PDMS to affect the oil-air interface of a frying oil. The minimal effective PDMS concentration is estimated to be 0.05–0.06 μg/cm^2 in the air–oil surface [3].

Two mechanisms have been proposed to explain PDMS's protective action. The first proposes that PDMS on the surface of the oil affects oxygen transfer to the oil by inhibiting convective currents. The second mechanism suggests that the accumulation of PDMS in the air-oil interface acts as a barrier to oxygen diffusion [3].

The impact of PDMS on the rate of degradation of linoleate (18:2) in soybean oil at 180 °C has been reported [4]. The initial rate of 18:2 degradation in oil treated with PDMS was lower than that of a pure soybean oil (control). After 12 h at 180 °C degrees the rate of 18:2 degradation in the PDMS-treated oil became the same as that for the control.

Tocopherols are antioxidants naturally present in vegetable oils, and their presence is important to the storage life of fried products [5]. Soybean oil is particularly rich in γ- and δ-tocopherols, and γ-tocopherol has a stronger antipolymerization effect during frying than α-tocopherol [5, 6]. Thus, tocopherol degradation is an important factor in frying applications.

The objectives of this study were to determine the impact of PDMS concentration on the degradation rate of 18:2 and of tocopherols in soybean oil held at frying temperature (180 °C), and to gain insight into the protective mechanism of PDMS.

Experimental Procedures

Oil Heating and Sampling

Refined, bleached, and deodorized soybean oil with citric acid added (Golden Chef) was obtained from Archer Daniels Midland Company (Decatur, IL). The oil treatments (200 g) were heated in 100 × 50 mm crystallizing dishes (Pyrex, Corning Inc., Corning, NY) for 48 h at 180 °C. The initial surface-to-volume ratio was 0.36 cm^{-1}. The PDMS was food-grade Dow Corning 200, 350 cSt (Dow Corning Co., Midland, MI).

Treatments

Previous research showed a minimum effective concentration of PDMS of 0.05–0.06 μg/cm^2 [3]. Considering a PDMS monomer to have a surface area of 20–25 $Å^2$ [7], and assuming that at frying temperature practically all PDMS is at the oil-air interface, the concentration necessary to have a theoretical PDMS monolayer in the system was calculated according to (Eq. 1) as ~25 ppb by weight in the oil. Oil treatments included two PDMS concentrations greater than the monolayer concentration (100 and 50 ppb), two less than (10 and 5 ppb) the monolayer concentration (25 ppb PDMS), and a control (no PDMS).

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

Where $\mathrm{mw}_{\mathrm{monomer}}$ is 74.1 g/mol, the area of the container was 7,850 mm^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 converted to ppb by multiplying by 10^{23}.

Treatments containing selected concentrations of PDMS were prepared using a stock solution containing 100 ppm of PDMS in hexane. Appropriate amounts of PDMS were added to the crystallizing dishes and the solvent was evaporated before adding the oil. All the treatments were heated simultaneously. Two replicates of each treatment were made and the replicates were treated as blocks in the statistical analysis. Oil aliquots (2 ml) were removed every 2 h and stored in glass vials at −22 °C until analyzed. The oil removed was not replenished.

Fatty Acid Composition

Oil aliquots were converted to fatty acid methyl esters (FAME) [8]. The FAME were injected into a Hewlett-Packard 5890 Series II chromatograph with a flame ionization detector and split/splitless injector. A 15 m × 0.25 mm × 0.2 μm film SP-2330 silica capillary column (Supelco, Bellefonte, PA) was used. The chromatographic parameters were: injector temperature, 230 °C, detector temperature, 230 °C, oven temperature program, 150–180 °C at 5 °C/min with no holding time. The carrier gas (He) was set at 5.4 mL/min, the auxiliary gas (He) at 19.4 mL/min, H_2 at 13.9 mL/min, and air at 426 mL/min. The split ratio was 24:1. The FAME composition was expressed as uncorrected relative area percentages of the detector output. Oil degradation throughout the heating time was evaluated by assessing the disappearance of methyl linoleate (18:2) with methyl palmitate (16:0) as a naturally present internal standard [4]. The linoleate-to-palmitate ratios (18:2/16:0) were calculated and the natural logarithms of the 18:2/16:0 ratios were plotted versus time (Eq. 2). The slopes of the linear regressions were estimated and used as a measure of the rate of the 18:2 disappearance.

$$\mathrm{Ln}(18{:}2/16{:}0) = \mathrm{Ln}(18{:}2_0/16{:}0_0) - k_1 t \quad (2)$$

where $18{:}2_0/16{:}0_0$ is the linoleate to palmitate relative concentration in the fresh oil (time 0), k_1 is the rate constant, and t is the time in hours.

If there was a point of change in the rate of degradation, the kinetic model was split into two pseudo first-order kinetics (before and after the change; Eqs. 3, 4):

$$\mathrm{Ln}(18{:}2/16{:}0) = \mathrm{Ln}(18{:}2_0/16{:}0_0) - k_1 t \quad t \le T \quad (3)$$

$$\mathrm{Ln}(18{:}2/16{:}0) = \mathrm{Ln}(18{:}2_0/16{:}0_0) - k_1 T - k_2(t-T) \quad t > T \quad (4)$$

where k_2 is the rate of reaction after the change in the rate of degradation, and T is the time at which the change in the rate of degradation occurred.

Tocopherol Content

Accurately weighed oil amounts were diluted with hexane to obtain 0.1 g/mL solutions, which were analyzed by HPLC using a Beckman Coulter System Gold (Beckman Coulter Inc., Fullerton, CA) equipped with a 25 cm × 4.6 mm 5 μ 60Å LiChrosorb Silica column (ES Industries Chromega Columns, West Berlin, NJ) with UV detection at

292 nm. The column was eluted with isopropanol:hexane (5:95 v/v), and the flow was set at 0.7 ml/min. The concentrations of the various tocopherols were expressed in ppm and external standards were used for quantification. In a manner similar to the calculations used for 18:2 degradation, the natural logarithm of γ- and δ-tocopherol concentrations were plotted versus time and the slopes of the linear regressions calculated and used as an estimate of the rate of disappearance of the tocopherol types (Eq. 5).

$$\mathrm{Ln(tocopherol)} = \mathrm{Ln(tocopherol_0)} - k_1 t \quad (5)$$

where $\mathrm{tocopherol_0}$ is the ln of the γ or δ-tocopherol concentration in the fresh oil (time 0), k_1 is the rate constant, and t is the time in hours.

If there was a change in the rate of degradation, the kinetic model was again split into two pseudo first-order plots, to determine slopes before and after the change in the rate of degradation (Eqs. 6, 7).

$$\mathrm{Ln(tocopherol)} = \mathrm{Ln(tocopherol_0)} - k_1 t \quad t \leq T \quad (6)$$

$$\mathrm{Ln(tocopherol)} = \mathrm{Ln(tocopherol_0)} - k_1 T + k_2 (t - T) \quad t > T \quad (7)$$

where k_2 is the rate constant after the change in rate of degradation and T is the time at which the change occurred.

Kinetics Model Parameters Estimation

The parameters were estimated using GraphPad Prism software version 4.03 for Windows (GraphPad Software, San Diego, CA) and all the regression curves fitted had an $R^2 \geq 0.9$ unless otherwise indicated.

Statistical Analysis

The data used to determine the slopes was based on two replicates of each treatment and the replicates were treated as blocks in the statistical analysis. The slopes were analyzed by using analysis of variance (ANOVA) with the PROC GLM of SAS 9.1 software (SAS Institute Inc., Cary, NC). Comparisons were assessed by contrasts using Tukey's adjustment for multiple comparisons. The level of significance was set at $\alpha = 0.05$ unless otherwise indicated.

Results and Discussion

Linoleate Disappearance

The degradation during frying of 18:2, the major fatty acid in conventional soybean oil, was previously documented and a first-order kinetics was fitted as the most appropriate [4]. During continuous heating of soybean oil in the presence of PDMS, the rate of the reaction accelerated at a certain time (the point at which the slope of the plot changed), and thereafter the 18:2 degraded at the same rate as 18:2 in pure soybean oil [4].

In the current study, the rate of degradation changed at a specific time, after which, the rate of 18:2 disappearance accelerated for PDMS concentrations equal to or greater than the calculated PDMS monolayer concentration (25 ppb). Figure 1 illustrates the disappearance of 18:2 and shows plots for each PDMS concentration. For 100 ppb of PDMS, the rate after T was lower than that of the slope of the control oil. The rates after T for the calculated monolayer concentration (25 ppb PDMS) and for 50 ppb PDMS were not different from the rate of the control oil. For concentrations of PDMS below the monolayer concentration no change in rate was found. For a PDMS concentration of 5 or 10 ppb, the rate of 18:2 degradation was not different from that of the control (pure soybean oil) (Table 1). In a previous paper [4] rates after the point of change were similar to those of their control oils even though the PDMS concentrations were much greater (5 and 10 ppm), but the approximate surface to volume ratio also was greater (0.92 $\mathrm{cm^{-1}}$ compared to 0.36 $\mathrm{cm^{-1}}$ in the present experiments). In a typical commercial deep-fat fryer (Star Twin Pot deep-fat fryers, model 530TA, Star Manufacturing International Inc. St. Louis, MO) the surface-to-volume ratio is much less, $\sim$0.1 $\mathrm{cm^{-1}}$.

Tocopherol Degradation

The γ- and δ-tocopherols were monitored during oil heating. Interfering compounds eluted at the same retention time as α-tocopherol; thus, it could not be accurately measured. Because the α-tocopherol is present in small concentrations in soybean oil [9] and is known to be less potent than γ- and δ-tocopherol [10], the omission is likely not important to the findings in the current study. The γ- and δ-tocopherol concentrations were determined until their concentrations became so low that co-eluting oxidation compounds interfered with their quantification.

Changes in the rates of γ-tocopherol degradation were found for PDMS concentrations of 10 ppb and greater (Fig. 2). In the samples treated with 50 and 100 ppb of PDMS, the rate after time T was not as great as that of the control. For 25 ppb, the calculated PDMS monolayer concentration, and 10 ppb, the degradation rate of γ-tocopherol after T was not different from that of the control. For 5 ppb of PDMS no change in rate was found. The rate changes tended to occur later as the PDMS concentration increased.

The δ-tocopherol degradation occurred at a slower rate than did γ-tocopherol degradation as shown in Tables 2 and 3. This pattern agrees with Barrera-Arellanos et al. [11] and confirms the greater resistance of δ-tocopherol than γ-tocopherol in high-temperature oxidations.

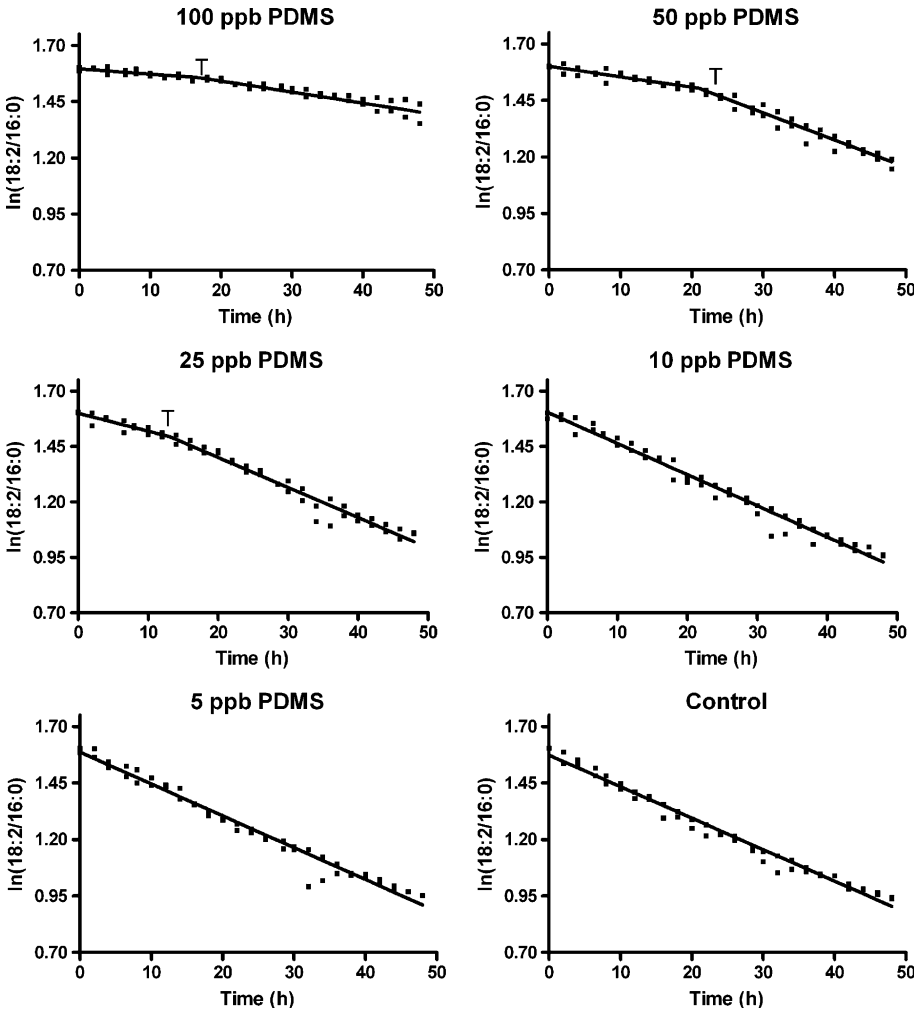

Fig. 1 Semi logarithmic plots of the 18:2/16:0 ratio versus time of soybean oil without added PDMS (control) and of soybean oil treated with 5, 10, 25, 50, and 100 ppb PDMS and the curves generated from the mean of the parameters of the respective fitted curves

Table 1 The time of change in rates (T) and rates of ln(18:2/16:0) versus time in soybean oil with various amounts of PDMS heated to 180 °C

Treatment (ppb PDMS)	Mean T (h)	Mean rate before change (k_1)	Mean rate after change (k_2)
0 Control	–	0.0139^{w}	0.0139^{w}
5	–	0.0141^{w}	0.0141^{w}
10	–	0.0141^{w}	0.0141^{w}
25	13^{w}	$0.0080^{a,\ x}$	$0.0135^{b,\ w}$
50	21^{w}	$0.0046^{a,\ y}$	$0.0121^{b,\ w}$
100	17^{w}	$0.0023^{a,\ z}$	$0.0049^{b,\ x}$

$^{a,\ b}$ Different superscripts in the same row indicate significant differences at $p < 0.05$

$^{w-z}$ Different superscripts in the same column indicate significant differences at $p < 0.05$

Similar to γ-tocopherol, degradation of δ-tocopherol at PDMS concentrations >10 ppm followed pseudo first-order kinetics until a time where the reaction accelerated (Fig. 3). The rate of δ-tocopherol disappearance after T was not different from that of the control oil. In treatments with 5 ppb PDMS no change of rate was observed, and the rate of the reaction was not different from that of the control oil. In the oil treated with 25 ppb PDMS, T was similar to that of γ-tocopherol; however, at PDMS concentrations greater than the monolayer concentration, the T at which the degradation of δ-tocopherol accelerated, was later than for γ-tocopherol.

At the monolayer concentration of PDMS (25 ppb), the 18:2 and γ- and δ-tocopherol degradation plots all

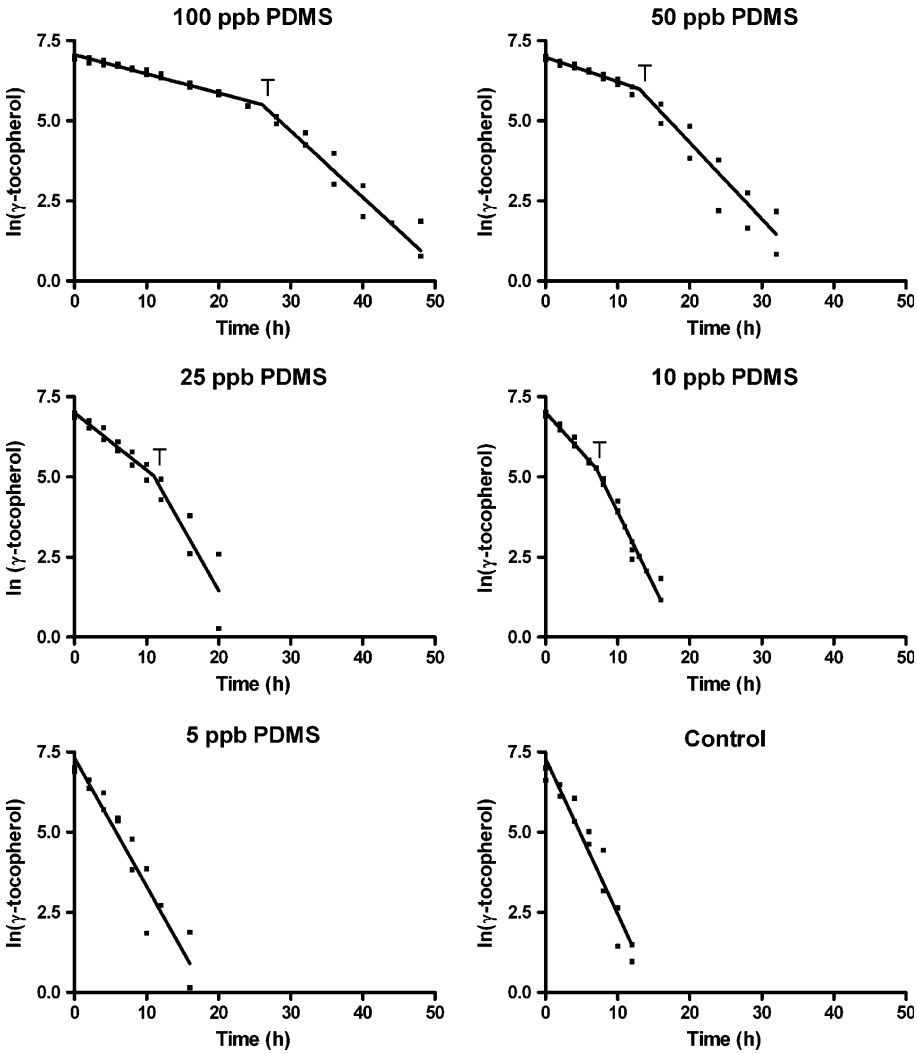

Fig. 2 Semi logarithmic plots of the [γ-tocopherol] versus time of soybean oil without added PDMS (control) and of soybean oil treated with 5, 10, 25, 50, and 100 ppb PDMS and the curves generated from the mean of the parameters of the respective fitted curves

Table 2 The time of change in rates (T) and rates of ln(γ-tocopherol) versus time in soybean oil with various amounts of PDMS at 180 °C

Treatment (ppb PDMS)	Mean T (h)	Mean rate before change (k_1)	Mean rate after change (k_2)
0 Control	–	0.4852^{x}	0.4852^{x}
5	–	0.4003^{x}	0.4003^{xy}
10	7^{x}	$0.2486^{a,\ y}$	$0.4578^{b,\ x}$
25	11^{x}	$0.1788^{a,\ yz}$	$0.3968^{b,\ xy}$
50	13^{x}	$0.0756^{a,\ z}$	$0.2380^{b,\ yz}$
100	26^{x}	$0.0597^{a,\ z}$	$0.2068^{b,\ z}$

[a, b] Different superscripts in the same row indicate significant differences at $p < 0.05$

[x–z] Different superscripts in the same column indicate significant differences at $p < 0.05$

had similar values for T, and the rates of oxidation of all three substrates increased at time T to match the rate of the control soybean oil. These changes in the rates of oxidation suggested that, at this time, the PDMS had become ineffective, probably because of degradation [12].

The rates of degradation of 18:2 and tocopherols before any change in rate (k_1) generally were affected by the initial concentrations of PDMS. For the 18:2 degradation, no difference in rate was detected between 5 and 10 ppb, but at higher concentration of PDMS, the rate of disappearance of 18:2 decreased nonlinearly with increasing

Table 3 The time of change in rates (T) and rates of ln(δ-tocopherol) versus time in soybean oil with various amount of PDMS at 180 °C

Treatment (ppb PDMS)	Mean T (h)	Mean rate before change (k_1)	Mean rate after change (k_2)
0 Control	–	0.1390^{x}	0.1390^{x}
5	–	0.1710^{x}	0.1710^{x}
10	5^{x}	$0.0604^{a,\ xyz}$	$0.1211^{b,\ x}$
25	10^{x}	$0.0467^{a,\ yz}$	$0.1143^{b,\ x}$
50	19^{x}	$0.0287^{a,\ yz}$	$0.1480^{b,\ x}$
100	35^{y}	$0.0217^{a,\ z}$	$0.1444^{b,\ x}$

[a, b] Different superscripts in the same row indicate significant differences at $p < 0.05$

[x–z] Different superscripts in the same column indicate significant differences at $p < 0.05$

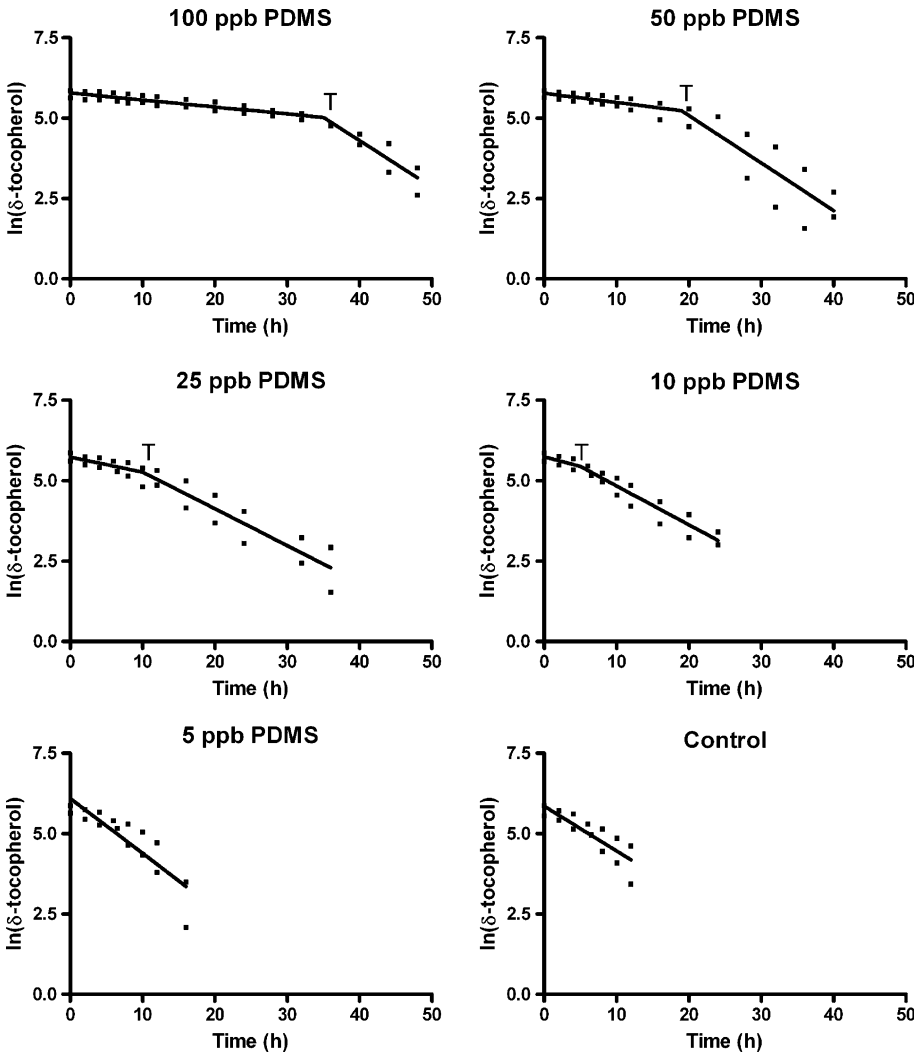

Fig. 3 Semi logarithmic plots of the [δ-tocopherol] versus time of soybean oil without added PDMS (control) and of soybean oil treated with 5, 10, 25, 50, and 100 ppb PDMS (rep 2 of the 5 ppb PDMS treatment had $R^2 = 0.7$) and the curves generated from the mean of the parameters of the respective fitted curves

PDMS. For both γ- and δ-tocopherols, the rates of degradation decreased nonlinearly with increasing PDMS concentrations, over the entire range of concentrations studied. For both tocopherol types, the influence of the concentration of PDMS on the rates of degradation was similar (Fig. 4). The addition of 100 ppb PDMS in the oil decreased the rate of degradation of both tocopherols and 18:2 by about ~83–87%, compared to the untreated oil. At 5 and 10 ppb PDMS, tocopherol degradation was more affected by PDMS than was 18:2 degradation, possibly because tocopherols have greater reactivity than 18:2 (Fig. 4).

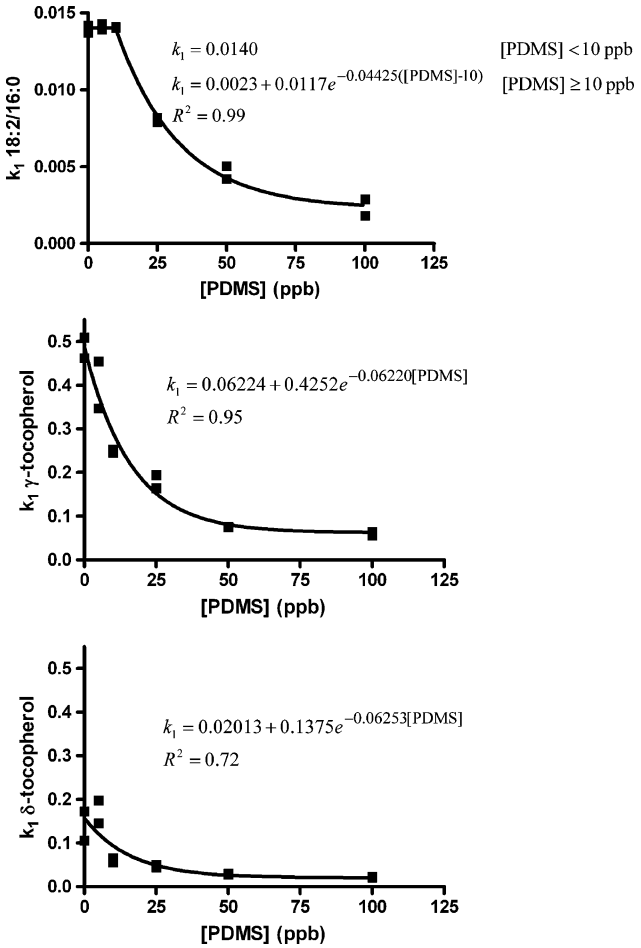

Fig. 4 Relationship between initial degradation rates (k_1) for 18:2 and γ- and δ-tocopherols versus [PDMS] and their respective coefficients of determination

Although color and viscosity were not measured in a systematic fashion, in all cases, the oils clearly became progressively darker and the viscosity became greater with heating time. This trend was greater at lower PDMS concentrations.

Conclusions

PDMS had a protective effect on the rate of disappearance of 18:2 and tocopherols if the concentration was equal or greater than the monolayer concentration. This suggests that PDMS acted as a barrier to oxygen transfer. The results also suggest that the tocopherols 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, as well as the tocopherols, can lose its protective effect with time, presumably because of degradation. The loss of γ-tocopherol was faster than that of δ-tocopherol, suggesting that it spared the oxidation of the δ- until γ-tocopherol reached a low concentration. The kinetics of disappearance of 18:2 may be a good measure of the capacity and effectiveness of antioxidants and other oxidation inhibitors in frying oils.

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