J Am Oil Chem Soc (2011) 88:1503–1510
DOI 10.1007/s11746-011-1811-2

ORIGINAL PAPER

Influence of Polydimethylsiloxane on the Formation of 4-Hydroxynonenal in Soybean Oil at Frying Temperature

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Received: 14 September 2010 / Revised: 7 February 2011 / Accepted: 15 February 2011 / Published online: 5 April 2011

Abstract Soybean oils treated with 25 or 100 ppb polydimethylsiloxane (PDMS) and a control with no PDMS were heated at 180 °C for 48 h. The decomposition of linoleate and tocopherols was monitored, as well as the changes in concentration of 4-hydroxynonenal (HNE). HNE was rapidly formed at the beginning of the heating period in the control and in the oil containing 25 ppb PDMS. HNE reached a maximum concentration of 0.033 μmol/g oil and then began to slowly decline. The maximum HNE concentration was attained at 18 h in the control oil compared with 28 h in the oil with 25-ppb PDMS. In the oil with 100-ppb PDMS the HNE increased very slowly during the first 32 h after which the HNE increased faster, reaching 0.033 μmol/g oil at 46 h and showed no decline during the 48 h heating period. Thus, PDMS had a beneficial effect in preventing the formation of the toxic HNE.

Keywords 4-Hydroxynonenal · Polydimethylsiloxane · Soybean oil · Frying · Tocopherol

Introduction

During frying, oils are exposed to oxygen and high temperatures. These stressful conditions are especially critical for frying oils such as soybean oil that are rich in polyunsaturated esters. Polyunsaturated fatty acid oxidation products include aldehydes, ketones, alcohols and hydrocarbons. Linoleic acid, a fatty acid making up about 50% of ordinary soybean oil, can be degraded during frying to 4-hydroxy-2-(*E*)-nonenal (HNE) [1]. The physiological role of HNE has been studied extensively [2]. It can react spontaneously with glutathione (GSH) [2], which is abundant in the cells of the gastrointestinal tract where it serves as a defense against oxidative stress. This HNE-mediated reduction of GSH concentration may impair the body's defenses against oxidative compounds [3]. DNA and protein synthesis also have been reported to be affected by HNE at concentrations between 1 and 50 μM [4].

Polydimethylsiloxane (PDMS) is a silicon-based polymer used by the fried-food industry as an antifoaming agent during frying. Previous studies have demonstrated a protective effect of PDMS in frying oils when used in amounts greater than that necessary to form a monolayer of PDMS in the air–oil interface [5, 6]. The effect of PDMS on the formation of HNE in oils rich in linoleic acid has not been evaluated. The objective of this paper was to study the influence of PDMS on the formation and degradation of HNE, and to measure the duration of PDMS's protective effect at frying temperature.

Experimental Procedures

Materials

The soybean oil was refined, bleached, and deodorized and treated with citric acid (Golden Chef, Archer Daniels Midland Company, Decatur, IL, USA). The PDMS was food-grade Dow Corning 200 with a viscosity of 350 cSt (Dow Corning Co., Midland, MI, USA).

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Treatments

A stock solution containing 100 ppm of PDMS in hexane was prepared, and appropriate amounts were added to 100 × 50 mm crystallizing dishes (Pyrex, Corning Inc., Corning, NY, USA), and the solvent was evaporated. Two replicates of all treatments were prepared. Two hundred grams of soybean oil was added to each container giving an initial surface to volume ratio of 0.36 cm^{-1}. The treatments were heated simultaneously to 180 °C and held for 48 h. Oil aliquots of 2.5 mL were removed every 2 h for further analysis and immediately frozen by immersion in liquid nitrogen, and stored in glass vials at –80 °C. The oil removed was not replaced.

Fatty Acid Composition

Oil aliquots were converted to fatty acid methyl esters (FAME) according to Hammond [7]. The FAME were analyzed by gas chromatography using a Hewlett-Packard 5890 Series II chromatograph with a flame ionization detector and split/splitless injector. The column was 15 m with a 0.25 mm × 0.2 μm film of SP-2330 (Supelco, Bellefonte, PA, USA). The chromatographic conditions were the same as those for Gerde et al. [6]: 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 flow (He) was 19.4 mL/min. Hydrogen flow was 13.9 mL/min, and air flow 426 mL/min. The split ratio was 24:1. The disappearance of methyl linoleate (18:2) was monitored by using the amount of methyl palmitate present in the oil as an internal standard and the linoleate to palmitate ratios (18:2/16:0) were calculated and transformed to μmol 18:2/g FAME. The natural logarithm of the concentrations was computed and plotted versus time. Linear or bilinear equations, if points of change in slope were present, were fitted to pseudo first-order kinetics for the degradation of 18:2, and the rate constants were calculated before and after the change of slopes (k_1 and k_2) [6].

Tocopherol Concentration

Oil aliquots were accurately weighed and diluted with hexane to obtain 0.1 g/mL solutions. The concentrations of the various tocopherols were determined by injecting 20 μL of the solution in a Beckman Coulter System Gold HPLC (Beckman Coulter Inc., Fullerton, CA, USA) equipped with a 25 cm × 4.6 mm 5 μ 60 Å LiChrosorb Silica column (ES Industries Chromega Columns, West Berlin, NJ, USA) and a photo diode array detector set at 292 nm. The elution solvent was isopropanol:hexane (5:95 v/v) at a flow rate of 0.7 mL/min. The tocopherol concentrations were expressed in ppm using external standards for quantification. It was assumed that the disappearance of the tocopherols followed first order kinetics, and the natural logarithms of the tocopherol concentrations were plotted versus time. Linear equations, or bilinear equations if there were changes in slope, were fitted, and the rate constants were calculated before and after the changes in slope (k_1 and k_2) [6].

HNE Concentration

The HNE concentration in the oil was measured as described by LaFond [8]. After adding a known amount of 4-hydroxy-9,9,9-d_3-non-2*E*-enal (HNE-d_3) (Cayman Chemical Co., Ann Arbor, MI, USA), the oil aliquots were extracted twice for 20 min with 10 mL water to remove the HNE, and the combined water extracts were treated with 1 mL of 1% *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA, Sigma-Aldrich Corp., Saint Louis, MO, USA) solution in methanol to derivatize the aldehyde group. The PFBHA solution also contained 0.1% tert-butyl hydroxytoluene (BHT) to minimize oxidation. The reaction mixture was sonicated at room temperature for 1 h and extracted twice with 10 mL pentane. After evaporating the pentane under a gentle stream of nitrogen, the extracts were treated with 200 μL of *N,O*-Bis (trimethylsilyl) trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS, Sigma-Aldrich Corp., Saint Louis, MO, USA) (9:1 v/v) and heated at 90 °C in sealed tubes to derivatize the alcohol group. Then the reaction mixtures were diluted to 1 mL with methylene chloride, and the samples were analyzed by gas chromatography-electron impact mass spectrometry (GC–MS). The GC–MS was an Agilent 6890 (Agilent Technologies Inc., Santa Clara, CA, USA) connected to a Micromass GCT Time of Flight (TOF) mass spectrometer (Waters Corp., Milford, MA, USA).

The GC separation was done using a 30 m × 0.25 mm × 0.25 μm film DB-5MS capillary column (Agilent Technologies Inc., Santa Clara, CA, USA) with a 1-m guard column (uncoated, Agilent Technologies Inc., Santa Clara, CA, USA). The chromatographic parameters were: injector temperature, 260 °C and oven temperature program, 100 °C for 1 min, 100–240 °C at 8 °C/min, and 240–300 °C at 25 °C/min with a final holding time of 3.1 min. The carrier gas (helium) flow was 1.0 mL/min. The mass spectrometer conditions were: 2 scans/s, ionization mode, positive electron impact, function type, TOF MS, and mass range 45–600. The *m/z* (mass to charge ratio) 352, 226, and 242 fragments were used to identify the HNE peaks and the *m/z* 352, 229, and 245 were used to identify the HNE-d_3 peaks. Because the *m/z* 352 fragment is common to HNE and HNE-d_3, only the areas of the integrated peaks corresponding to the *m/z* 226 and 242

fragments and the *m/z* 229 and 245 fragments were used for HNE and HNE-d_3 quantification, respectively. The concentration of HNE and HNE-d_3 standard solutions were monitored spectrophotometrically by evaporating the solvent of an aliquot of the standard solution, re-dissolving it in water, and reading it in the spectrophotometer at $\lambda = 223$ nm. The concentration was calculated by using the molar extinction coefficient of HNE in water at $\lambda = 223$ nm $\varepsilon = 13{,}750$ to verify the concentrations reported by the supplier [9, 10].

Kinetics Model Parameters

The equation parameters were estimated by using GraphPad Prism software version 4.03 for Windows (GraphPad Software, San Diego, CA, USA) and all the regression curves fitted had an $R^2 > 0.9$.

Statistical Analysis

The estimated kinetic coefficients were analyzed by using analysis of variance (ANOVA) with the SAS 9.1 software mixed-models procedure (SAS Institute Inc., Cary, NC, USA). Comparisons were evaluated by contrasts using Tukey's modification at a level of significance of $\alpha = 0.05$ unless otherwise indicated [11].

Results and Discussion

Degradation of 18:2 and Tocopherols

For both the 25- and 100-ppb PDMS treatments, there was an increase in slope (rate of degradation) in the plots of ln [18:2] versus time during the heating of the oil (Fig. 1) in agreement with previously reported data [6]. The times of change in the rate of degradation (T) were calculated, and the rates before and after this time were compared (Table 1). The rates after T were different from the rates before T at this significance level ($p < 0.065$). For the control oil, no change in rate was observed. The rate after T for the 25-ppb PDMS treatment was not significantly different from that of the control oil. But for the 100 ppb PDMS treatment, the rate of 18:2 degradation after T remained lower than that of the control oil. T was later for the 100 ppb PDMS treatment than for the 25 ppb PDMS treatment at just over significance level of $\alpha = 0.05$ ($p = 0.055$). This change in slopes of 18:2 degradation may be controlled by the disappearance of tocopherols at PDMS concentrations greater than the monolayer concentration [6].

For γ-tocopherol disappearance, there was a change in rate only in the 100-ppb PDMS treatment (Fig. 2), and no change in rate was detected for the 25-ppb PDMS

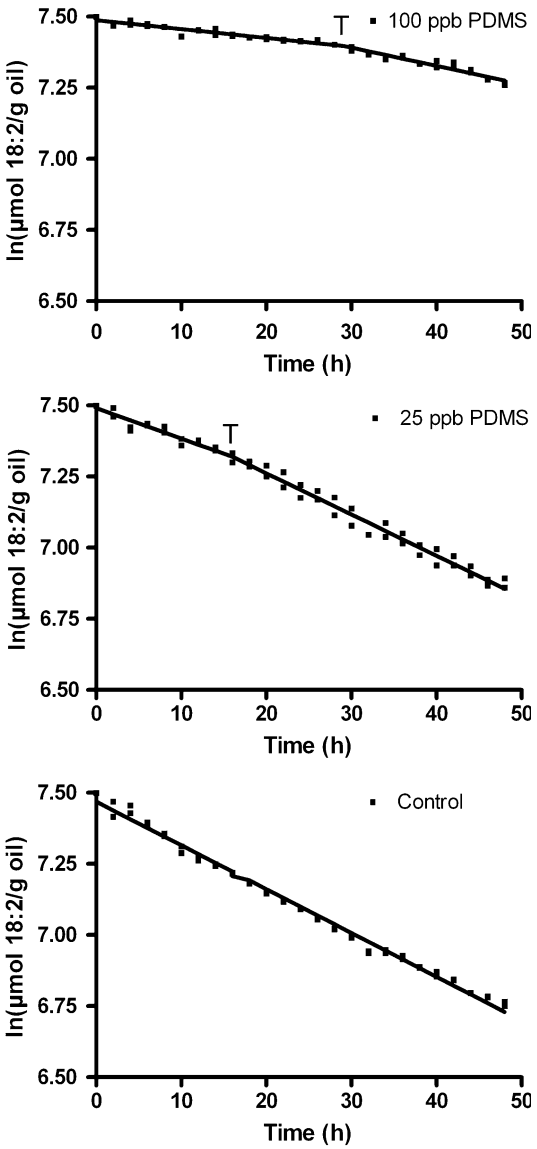

Fig. 1 Decrease of the natural logarithm of the [linoleate] in two replications of control soybean oil containing no polydimethylsiloxane (PDMS) and in soybean oil treated with 25- or 100-ppb PDMS during heating at 180 °C and the curves generated from the mean of the parameters of the respective fitted curves

treatment. The rate after *T* in the 100-ppb PDMS treatment was greater than the rates of γ-tocopherol in the control or 25-ppb PDMS-treated oils (Table 2).

The degradation of δ-tocopherol showed rate changes for both the 25- and 100-ppb PDMS-treated oils (Table 2) in agreement with previously reported results [6]. The T occurred later in the 100-ppb PDMS treatment than in the 25-ppb PDMS treatment. For the 25 ppb PDMS treatment, the rate after *T* was not different from the rate of the degradation of δ-tocopherol in the control oil (Fig. 2). For the 100 ppb PDMS treatment, the rate after *T* was greater

Table 1 The time of change in rates (T) and rates of linoleate destruction (1st order kinetics) in a control soybean oil with no PDMS added and in soybean oil with 25 or 100 ppb PDMS heated at 180 °C

PDMS treatment (ppb)	Mean T (h)	Mean rate ($k_{18:2}$)	
		Before change (k_1)	After change (k_2)
0 (control)	–	0.0154^{x}	0.0154^{x}
25	17^{y}	$0.0108^{a,y}$	$0.0146^{b,x}$
100	29^{x}	$0.0031^{a,z}$	$0.0064^{b,y}$

[a,b] Different superscripts in the same row of columns 3 and 4 indicate significant differences at $p \leq 0.065$

[x–z] Different superscripts in the same column indicate significant differences at $p \leq 0.055$

than in both the control and the 25-ppb PDMS-treated oils. Table 2 shows that γ-tocopherol degraded faster than δ-tocopherol, in agreement with previous reports [6, 12]. Interfering compounds co-eluted with α-tocopherol, so its rate of disappearance could not be determined.

4-Hydroxynonenal Formation

For the control oil, the HNE concentration rapidly increased during the first 14 h of heating, then slowed, reaching a maximum concentration of 0.034 μmol/g oil at ~18 h heating (Fig. 3). For the 25-ppb PDMS oil, the increase in HNE concentration was less steep, and the maximum, 0.033 μmol/g oil, occurred at 28 h (Fig. 3). For both treatments, there was a slow decrease in the HNE concentration with time after reaching the maximum. For the 100-ppb PDMS treatment, the increase in HNE concentration was much slower than in the other treatments during the first 32 h heating. After 32 h the HNE concentration increased faster, and after 46 h of heating, reached levels comparable to the maxima found for the other treatments (0.033 μmol/g oil) (Fig. 4). There was no perceptible decline in HNE concentration during the 48 h the oil was heated.

HNE is formed as a product of linoleate degradation, but it may further degrade by additional reactions. Assuming pseudo first-order kinetics for these degradations:

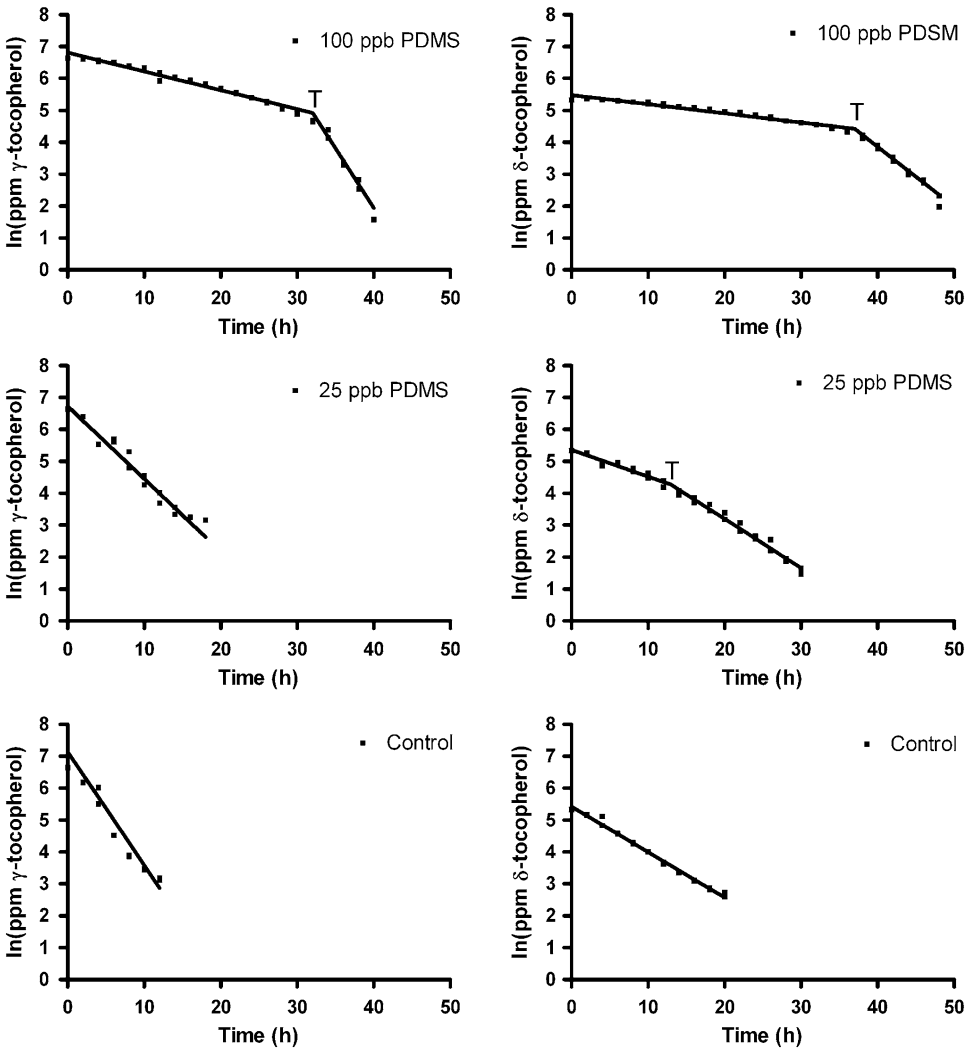

Fig. 2 Decrease of the natural logarithm of the [γ-tocopherol] and [δ-tocopherol] in two replications of control soybean oil containing no polydimethylsiloxane (PDMS) and in soybean oil treated with 25- or 100-ppb PDMS during heating at 180 °C and the curves generated from the mean of the parameters of the respective fitted curves

Table 2 The time of changes in rates (T) and rates of destruction of γ- and δ-tocopherol in a control soybean oil with no PDMS added and in soybean oil with 25 or 100 ppb PDMS heated at 180 °C

	Treatment (ppb PDMS)	Mean T (h)	Mean rate before change (k_1)	Mean rate after change (k_2)
γ-Tocopherol	0 Control	–	0.2306^{x}	0.2306^{y}
	25	–	0.2279^{x}	0.2279^{y}
	100	32	$0.0590^{a,y}$	$0.3724^{b,x}$
δ-Tocopherol	0 Control	–	0.1424^{x}	0.1424^{y}
	25	13^{y}	$0.0835^{a,y}$	$0.1536^{b,y}$
	100	37^{x}	$0.0287^{a,z}$	$0.1963^{b,x}$

[a,b] Different superscripts in the same row of columns 3 and 4 indicate significant differences at $p \leq 0.05$

[x–z] Different superscripts in the same column indicate significant differences at $p \leq 0.05$ within each tocopherol type

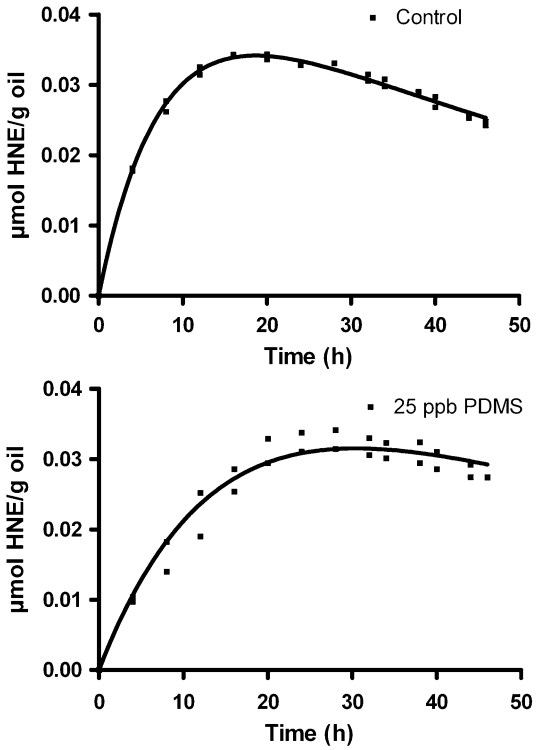

Fig. 3 Change in HNE concentration (µmol/g) in two replications of control soybean oil with no PDMS added and soybean oil with 25-ppb PDMS heated at 180 °C and the curve generated from the mean of the parameters from the respective fitted curves

$$18{:}2 \xrightarrow{k_{18:2}} \text{HNE} + \text{other products}$$

where $k_{18:2}$ could be k_1 or k_2, depending on the stage of degradation of 18:2 [6].

$$18{:}2 \xrightarrow{k_f} \text{HNE} \xrightarrow{k_d} \text{degradation products}$$

$$\frac{d[18{:}2]}{dt} = -k_{18:2}[18{:}2] \quad (1)$$

$$\frac{d[\text{HNE}]}{dt} = -k_f[18{:}2] - k_d[\text{HNE}] \quad (2)$$

$$[18{:}2] = [18{:}2]_0 e^{-k_{18:2}t} \quad (3)$$

$$[\text{HNE}] = [\text{HNE}]_0 e^{-k_d t} + \frac{k_f[18{:}2]_0}{k_d - k_{18:2}}(e^{-k_{18:2}t} - e^{-k_d t}) \quad (4)$$

For the control oil and the 25 ppb (the monolayer concentration) treatments $[\text{HNE}]_0$ was 0, as measured in the unheated oil, with the model for those treatments described by Eq. 5.

$$[\text{HNE}] = \frac{k_f[18{:}2]_0}{k_d - k_{18:2}}(e^{-k_{18:2}t} - e^{k_d t}) \quad (5)$$

Although there was a slight change in slope during heating of the 25-ppb PDMS treatment, to simplify the model, degradation of 18:2 was assumed to follow a pseudo first-order kinetics with a constant slope $k_{18:2} = 0.0134$. Based on this assumption, the kinetic parameters of the degradation of 18:2 and the formation and degradation of HNE in the control oil and the 25 ppb PDMS oil are presented in Table 3 and the data points, with the curves generated from the mean of the parameters of the respective fitted curves, in Figs. 3 and 4.

In the treatment with 100-ppb PDMS, the model is more complicated so the data was fitted by dividing the plot into several intervals (Fig. 4). At the beginning of the heating period (before 4 h zone I), there was an abrupt increase in the HNE concentration. After this period, there was a linear increase in the concentration of HNE for approximately 32 h (zone II). At this point there was a transition zone (zone III), where the velocity of the reaction increased until the concentration of HNE followed kinetics similar to that of the control oil (38–48 h, zone IV). In zone I, the rapid increase in HNE concentration probably resulted from the decomposition of peroxides formed during the temperature rise in the oil, coupled with the protective effect at higher temperatures of ample amounts of PDMS that reduced the destruction of HNE to very low levels. The initial period lasted 4 h in this study because that was the first aliquot analyzed after the system reached 180 °C.

During the second stage (zone II) the concentration of HNE increased at a very low rate (Fig. 4). Because of the very low concentration of HNE and the comparatively high

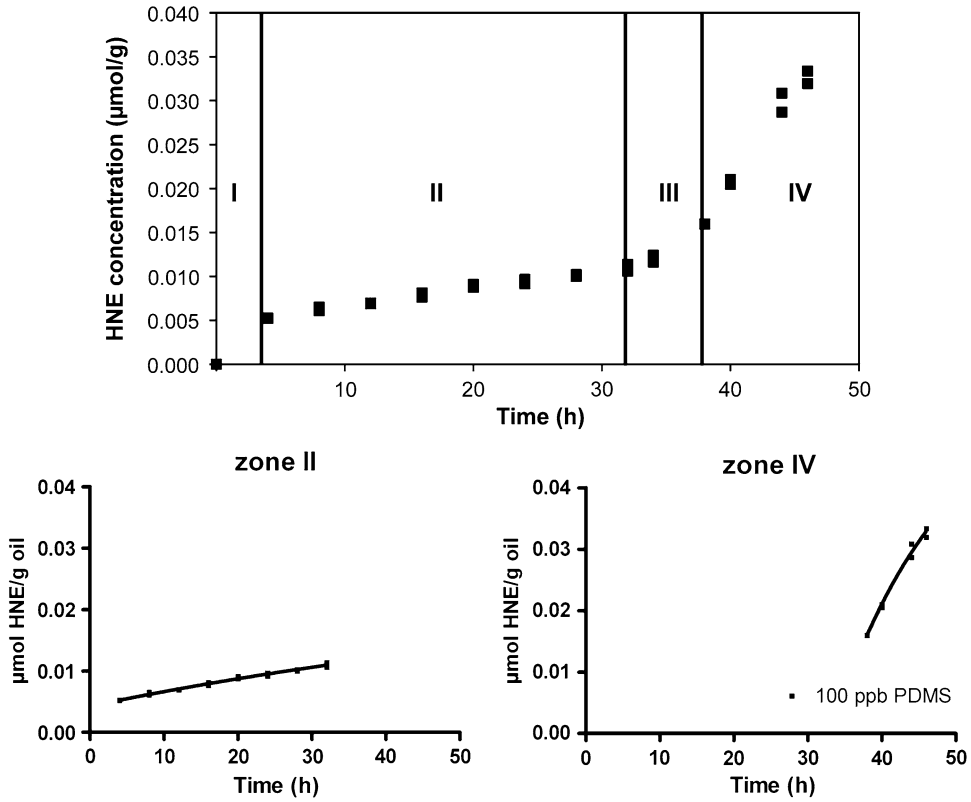

Fig. 4 Change in HNE concentration (µmol/g) in two replications of soybean oil treated with 100-ppb PDMS heated at 180 °C. The chart was divided into four zones, designating the different stages of HNE concentration evolution to simplify curve fitting. Details of *zones II* and *IV* data points with their corresponding fitted curves are presented

Table 3 Mean kinetic parameters for the formation of HNE in soybean oil with 0, 25 or 100 ppb PDMS held at 180 °C

	100 ppb PDMS		25 ppb PDMS	Control
	Zone II $t = t - 4$ h	Zone IV $t = t - 38$ h		
$[18:2]_0^a$	1,771 µmol/g	1,531 µmol/g	1,807 µmol/g	1,807 µmol/g
$k_{18:2}^a$	0.0031	0.0064	0.0134[b]	0.0154
Rate of HNE formation (k_f)	1.598E-7[e]	2.310E-6[cd]	1.720E-6[d]	3.262E-6[c]
Rate of HNE degradation (k_d)	0.0082[e]	0.0529[d]	0.0656[d]	0.1295[c]
$k_f/k_{18:2}$	5.19E-5[e]	3.524E-4[c]	1.300E-4[de]	2.121E-4[cd]

[a] $[18:2]_0$ and $k_{18:2}$ were obtained from the curves representing degradation of 18:2 versus time and fixed during the fitting of the other parameters

[b] 18:2 degradation in 25 ppb PDMS was considered to be linear to simplify the calculations

[c–e] Different superscripts in the same row indicate significant differences at $p \leq 0.05$

concentration of 18:2, the probability of oxygen or a free radical attacking HNE instead of 18:2 was very low. Thus, it was assumed that, during this period, the degradation of HNE should be very small compared to the rate of formation of HNE. To compare the rest of the parameters with the models obtained for the control and the 25-ppb PDMS treated oils, the time (t) and the initial concentration of HNE ($[HNE]_0$) were adjusted to consider 4 h the initial point of zone II. Thus, $t = t - 4$ h and $[HNE]_0$ was the [HNE] measured in the initial point of zone II (4 h after the start of heating). Likewise, the degradation of 18:2 that occurred in zone I was taken into account; therefore, the initial concentration of 18:2 ($[18:2]_0$) was the concentration of 18:2 after heating the oil for 4 h.

Zone III was likely a transition zone between zones II and IV, in which the system adjusted to a lower PDMS level similar to that of the unprotected soybean oil. Also during this period, the changes in the rate of degradation of tocopherols and 18:2 occurred. For zone IV (Fig. 4) it was again necessary to consider the changes that occurred in the system before the starting time and to adjust the parameters appropriately: $t = t - 38$, $[HNE]_0$ and $[18:2]_0$ were the concentrations of HNE and 18:2 at $t = 38$ h, respectively. In zone II of the 100-ppb PDMS treatment both k_f and k_d were smaller than they were in zone IV, and both k_f and k_d were smaller than those in the control oil and the 25-ppb PDMS treatment. In zone IV k_f for the 100-ppb PDMS treatment was not different from the k_f in the control or the

25-ppb PDMS treatments. But k_d of the 100-ppb PDMS treatment was less than that of the control oil, but similar to that of the 25-ppb PDMS treatment (Table 3).

The kinetic constant for the formation reaction of HNE k_f, is a function of $k_{18:2}$. Therefore, the ratio of $k_f/k_{18:2}$ is a measure of the proportion of HNE formed compared to other 18:2 degradation products. This ratio was greater in zone IV and in the control oil than in zone II, probably because of the effect of PDMS on the rate of oxygen uptake by the oil [13]. After the PDMS degraded to a level where it could no longer maintain a low oxygen concentration in the oil (zone IV), the formation of oxygenated degradation products, such as HNE, would have been favored, thus explaining the similarity of $k_f/k_{18:2}$ for the control oil and the 100-ppb PDMS treatment during zone IV.

The production of HNE in heat-abused oils has been previously studied [1, 14]. In one study, soybean oil was heated at 185 °C in a round bottom flask while air was bubbled through the oil. The HNE increased rapidly in the beginning followed by a decrease after reaching a maximum concentration. The maximum HNE concentration (0.27 μmol/g oil) occurred after 6 h heating [14]. In another study, pure methyl linoleate was heated at 185 °C and the maximum HNE concentration occurred at 3 h heating (0.54 μmol/g FAME) followed by a decrease [1]. These values are considerably higher than those found in the current study, but show similar trends. Bubbling air through the oil would produce much better oxygenation, leading to higher levels of HNE in the early stages when there would be abundant amounts of linoleate. Another study reported the presence of 0.021 μmol HNE/g oil after heating soybean oil in an open beaker for 8 h with constant air bubbling [15]. This value is much closer to the values obtained in the current study.

The change in the kinetic constants of the disappearance of both tocopherols and 18:2 and in the formation and degradation of HNE for the three treatments suggests that the protective effect of PDMS is lost after heating for several hours. PDMS has been reported to depolymerize and degrade by a free radical mechanism when heated to high temperatures (290 °C in the presence of air) [16], and this may occur slowly at 180 °C.

Conclusions

The protective effect against oxidation by PDMS was confirmed in soybean oil. To be effective, the concentration of PDMS seemingly must be greater than the calculated monolayer concentration, which, under our conditions, was about 25 ppb of the oil. In soybean oil with 100 ppb PDMS, the slopes of γ- and δ-tocopherol and 18:2 degradation decreased compared to the control, and changes in rates occurred during the heating period. The PDMS concentration also influenced the formation and degradation of HNE. To facilitate the analysis of the formation of HNE in soybean oil with 100-ppb PDMS, the data was divided into four intervals (zones I, II, III, and IV). The times at which the changes in rates for 18:2 and tocopherol degradation occurred were close to or within the transition zone III. The change in slopes of 18:2 degradation may be controlled by the disappearance of tocopherols at PDMS concentrations greater than the monolayer concentration. However, the increase in the rate of formation of HNE in zone IV of the 100-ppb PDMS treatment may have occurred because of PDMS degradation. Thus, an increase in the uptake of oxygen may be the reason for the greater $k_f/k_{18:2}$ ratio in zone IV of the 100-ppb PDMS treatment than in either the 25-ppb PDMS treatment or in the control oil.

Acknowledgment The authors would like to thank Sean I. LaFond, John P. Jerrell, Keith R. Cadwallader, and William E. Artz (University of Illinois at Urbana-Champaign) for providing the method for the HNE analysis. Our research was funded by the United States Department of Agriculture (USDA) through a Special Grant to the Nutrition and Wellness Research Center (NWRC) at Iowa State University (Project No. 2008-3411519372).

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