Antioxidants in Margarine Emulsions

V. FILIP, I. HRÁDKOVÁ and J. ŠMIDRKAL*

*Department of Dairy and Fat Technology, Institute of Chemical Technology in Prague, 166 28 Prague, Czech Republic, *E-mail: vladimir.filip@vscht.cz*

Abstract: The lipid oxidation in margarine takes place in continuous liquid oil phase. The extension of fat interfaces in the system – emulsion of water in oil and the dispersion of fat crystals in liquid oil influences on the peroxidation, decomposition of hydroperoxides to aldehydes and the oxidative stability in the comparison with oxidation in the fat blend. Different antioxidants were used in margarine dispersions: *L*(+)ascorbic acid, ascorbyl palmitate and DL-α-tocopherol. Increasing polarity and decreasing molecular size of antioxidants have the positive influence on lipid oxidation: DL-α-tocopherol is the least effective antioxidant of all antioxidants, ascorbic acid is the most effective antioxidant and ascorbyl palmitate possesses similar, however, lesser effect. The combination of all three antioxidants restricts the production of hydroperoxides, the decomposition of hydroperoxides to aldehydes and the increase of oxidative stability was also achieved. Content of antioxidants 0.02% as ascorbic acid or ascorbyl palmitate mostly restrict the extent of lipid oxidation in the margarine dispersion with existent content of naturally present tocopherols in fat blend.

Keywords: antioxidant; ascorbic acid; ascorbyl palmitate; emulsion; margarine; tocopherol

INTRODUCTION

Lipid oxidation in the simplest system takes place in a liquid phase, oxygen diffuses to oil through macroscopic interface air/oil. The situation is more complicated in the case of food dispersions: the lipid oxidation in o/w emulsions takes place in droplets and on their surface. Oxygen diffuses in this case from air through the continuous water phase to the surface of lipid particles. The oxidation in o/w emulsions is relatively well studied; it is very often case in foods. In the margarine emulsion (w/o type) oxygen diffuses from air directly to the continuous oil phase where the oxidation takes place. Oxygen diffusion can be decreased by an interface form: the interface o/w and oil/solid crystal forms, presenting monoacylglycerole emulsifier creates a membrane on both interface and decreases considerably the oxygen diffusion, thus, the oxidation rate (Pokorná *et al.* 2004). A type of used emulsifier determines the decrease of lipid oxidation rate in droplets (Silvestre *et al.* 2000). Emulsifier can also influence antioxidant distribution in the o/w emulsion (Yuji *et al.* 2007).

Antioxidants possess different polarity and solubility in water and in oil; lipophilic antioxidants possess surface activity and together with emulsifier form interface. Interfacial phenomena are keys to a better understanding of antioxidant action in heterogenous foods (Frankel 1996). Tocopherols are surface active substances; therefore they are more effective than Trolox (hydrophilic analog) as inhibitors of hydroperoxide formation and their decomposition (Huang *et al.* 1996). Ascorbic acid acts as an antioxidant in aqueous system, a pro-oxidant, a metal chelator, a reducing agent of heavy metals or as an oxygen scavenger. The mixture of tocopherols and ascorbic acid exhibits a strong synergistic effect because ascorbic acid reduces tocopherols radicals. This can take place also in w/o olive oil emulsion (Mosca *et al.* 2008a) and efficiency of this synergism depends on specific surface area of aqueous dispersed phase. Ascorbyl palmitate increases the effect of ascorbic acid as antioxidant and also as emulsifier (Mosca *et al.* 2008b). Application of antioxidants depends on initial oxygen content in lipid system and on the type of oxygen supply limitation in lipid system.

MATERIAL AND METHODS

Composition of model margarine (% w/w): Fat blend 70%; solid fat content profile (%): $SFC_{10°C}$ 26.8, $SFC_{20°C}$ 15.1, $SFC_{30°C}$ 5.8, $SFC_{35°C}$ 4.5, $SFC_{40°C}$ 2.5. Fatty acid composition: SFA 23.4%, C18:1 25.1%, C18:2 50.2%, C18:3 0.4%, *trans*-FA 1.6%; content of tocopherols 0.045%. Emulsifier D (mixture of monoacylglycerols) – 0.02%. Sodium chloride 0.10%, lactic acid 0.02% (adjustment of water phase pH on 4.0 ± 0.25), water up to 100% (CaO 100 mg/l). Used antioxidants: L(+) ascorbic acid (99.7%; Merck) – AA, ascorbyl palmitate (> 99.0%; Fluka) – AP, DL-α-tocopherol (> 99.0%; Fluka) – TO. Used antioxidant content – 0.01, 0.02 and 0.025% w/w.

Margarine preparation: Laboratory mixer – Stephan, amount of one bath – 2.5 kg. The emulsification and the crystallisation – under argon atmosphere: agitation 1500 rpm, cooling from 45°C to 20–21°C during 25 minutes. The filling – 250 g of sample to the pot with plastic lid, no air in the package (air could diffuse through the lock between the lid and the pot).

Storage temperature and time – 15°C, 15 weeks. Analytical methods: the peroxide value (PV) of margarine emulsion (ISO3960/1994), the *p*-anisidine value (AV) of isolated fat phase (ISO6885/1994). The oxidation stability (induction period at 100°C – IP) – ML-Oxidograph. The average samples were taken from emulsion. Results are expressed as definite integral of the measured dependence $X = X(\tau)$, where X is PV, AV or IP. Primary data are not presented, exception to the oxidation stability. Series of margarine emulsions: A = control emulsion; B = 0.01% of ascorbic acid; C = 0.025% of AA; D = 0.01% of AP; E = 0.025% of AP; F = 0.01% of TO; G = 0.025% of TO; H = 0.02% of AA + 0.02% of AP; I = 0.02% of AA + 0.02% of TO; J = 0.02% of AP + 0.02% of TO; K = 0.01% of AA + 0.01% of AP + 0.01% of TO; L = fat blend.

RESULTS AND DISCUSSION

The extension of fat interfaces in emulsion w/o and the dispersion of fat crystals in liquid oil (the sample A) influences on the rate and on the extent of oxidation, in the comparison with oxidation in the fat blend (the sample L) from the point of view of the formation of hydroperoxides, their decomposition to aldehydes and the oxidative stability. The fat blend is the simple dispersion of fat crystals in liquid oil. The main component, that oxidises, is linoleic acid. The definite integrals were counted from measured dependences of the peroxide value, the *p*-anisidine value and the oxidative stability, because of the induction period could not be determined (Figures 1, 2 and 4).

It is obvious, that increasing polarity and decreasing molecular size of antioxidants have the positive influence on lipid oxidation in the dispersive system of the margarine. DL-α-tocopherol (the samples F and G) is the least effective antioxidant of all antioxidants. The content 0.025% of tocopherol has already prooxidative effect. If natural content of tocopherols in fat blend is added up, the total content of tocopherols (0.057%) exceeds the limit, when tocopherol has antioxidant effect (Frankel 1996). Ascorbic acid is the most effective antioxidant, if it is used only one antioxidant (the samples B and C) (Mosca *et al.* 2008b), the minimal concentration of hydroperoxides and consequently

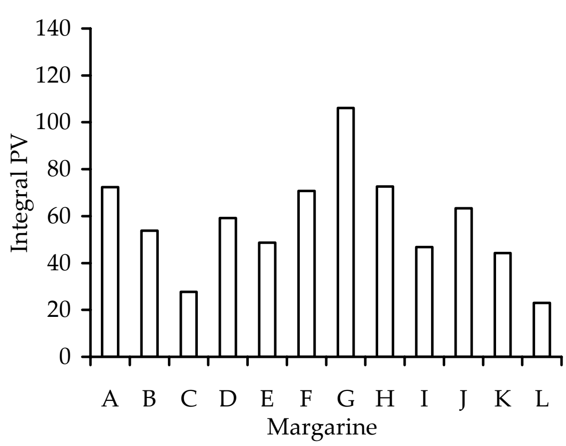

Figure 1. Integral of peroxide value of overall margarine emulsion

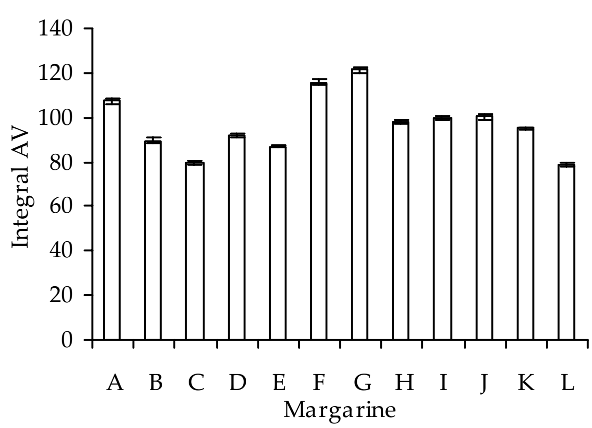

Figure 2. Integral of *p*-anisidine value of fat phase of margarine emulsion

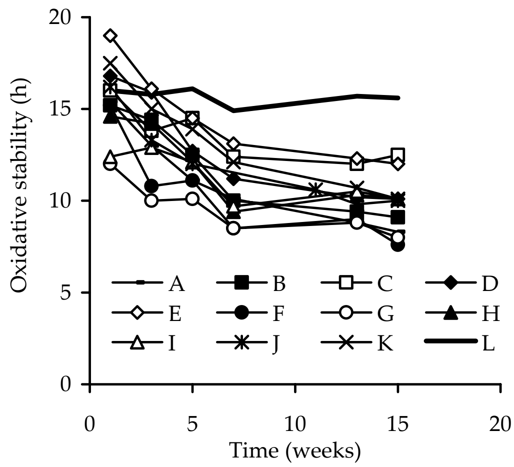

Figure 3. Oxidative stability of fat phase of margarine emulsion

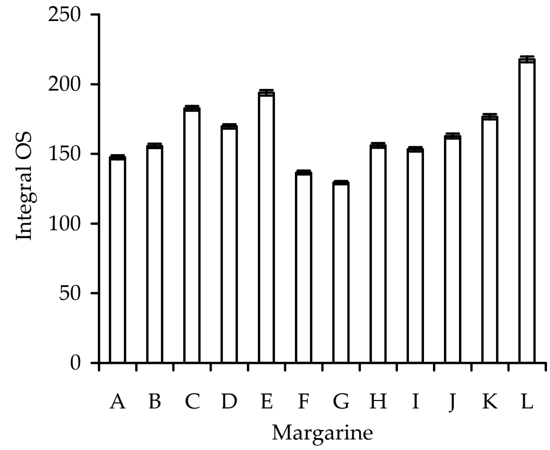

Figure 4. Integral of oxidative stability of fat phase of margarine emulsion

of aldehydes forms at the concentration 0.02%. Ascorbyl palmitate possesses similar, however, lesser effect (the samples D and E). It is interesting, that lower degree of oxidation and higher oxidative stability are not achieved by the combination of ascorbic acid and ascorbyl palmitate (the sample H) as well as ascorbyl palmitate and tocopherol (the sample J), in the comparison with only ascorbic acid and ascorbyl palmitate. The combination of ascorbic acid with tocopherol (the sample I) affects positively the formation of hydroperoxides, that decompose to aldehydes in higher rate (Figures 1 and 2), so the oxidative stability does not increase. The combination of all three antioxidants restricts the production of hydroperoxides, the decomposition of hydroperoxides to aldehydes and the increase of oxidative stability was also achieved (Figures 3 and 4). The increase of oxidative stability of the margarine (Figures 3 and 4) with 0.02% of ascorbic acid (the sample C) and 0.02% of ascorbyl palmitate (the sample E) corresponds to minimal extent of peroxidation and minimal decomposition of hydroperoxides to aldehydes.

CONCLUSION

Antioxidants as ascorbic acid or ascorbyl palmitate mostly restrict the extent of lipid oxidation in the margarine dispersion with existent content of naturally present tocopherols in fat blend.

Acknowledgements: This work was supported by funding from the Ministry of Education, Youth and Sports of the Czech Republic (Project No. MSM 6046137305).

References

Frankel E.N. (1996): Antioxidants in lipid foods and thein impact on food duality. Food Chemistry, **57**: 51–55.

Huang S.H., Hopia A., Schwarz K., Frankel E.N., German J.B. (1996): Antioxidant activity of α-tocopherol and Trolox in different lipid substrates: Bulk oils vs. oil-in-water emulsions. Journal of Agricultural and Food Chemistry, **44**: 444–452.

Mosca M., Ceglie A., Ambrosone L. (2008a): Antioxidant dispersions in emulsified olive oils. Food Research International, **41**: 201–207.

Mosca M., Ceglie A., Ambrosone L. (2008b): Biocompatible water-in-oil emulsion as a model to study ascorbic acid effect on lipid oxidation. Journal of Physical Chemistry B, **112**: 4635–4641.

Pokorná I., Filip V., Šmidrkal J. (2004): Lipid oxidation in margarine emulsions. Czech Journal of Food Sciencce, **22**: 140–143.

Silvestre M.P.C., Chaiyasit W., Brannan R.C., McClements D.J., Decker E.A. (2000): Ability of surfactant headgroup size to alter lipid and antioxidant oxidation in oil-in-water emulsions. Journal of Agricultural and Food Chemistry, **48**: 2057–2061.

Yuji H., Weiss J., Villeneuve P., Giraldo L.J.L., Figureo-Espinoza M.C., Decker E. (2007): Ability of surface-active antioxidants to inhibit lipid oxidation in oil-in-water emulsion. Journal of Agricultural and Food Chemistry, **55**: 11052–11056.