Open access • Journal Article • DOI:10.1080/02652030600699064

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Published on: 01 Aug 2006 - Food Additives and Contaminants Part A-chemistry Analysis Control Exposure & Risk Assessment (Taylor & Francis)

Topics: Low-density polyethylene, Controlled release and Cyclodextrin

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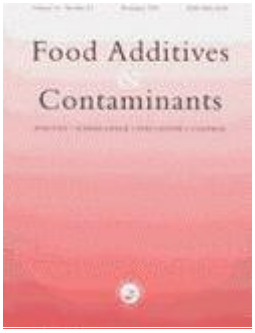

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Journal:	*Food Additives and Contaminants*
Manuscript ID:	TFAC-2005-409.R1
Manuscript Type:	Original Research Paper
Methods/Techniques:	Chromatography - HPLC
Additives/Contaminants:	Packaging - food simulants, Antioxidants, Packaging - migration modelling, Packaging active packaging
Food Types:	Cereals, Oils and fats

Release of alpha-tocopherol from antioxidative low density polyethylene film into fatty food simulant: Influence of complexation with beta-cyclodextrin

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Abstract

The release of alpha-tocopherol from two formulations (with and without complexation with beta-cyclodextrin) of low density polyethylene (LDPE) film was examined. Specific migration studies were performed at 7.0 ± 0.5°C using plastic bags filled with 95% ethanol as fatty food simulant. The amount of complexed and free (non-complexed) alpha-tocopherol migrating into the food simulant was followed by a high performance liquid chromatography (HPLC). It was concluded that complexation with beta-cyclodextrin had a significant effect on the release rate of the antioxidant. Using a mathematical model for the description of the migration, a decrease in diffusion coefficient (D) of one order of magnitude was calculated in the case of complexed alpha-tocopherol compared to the free form. Total migration of alpha-tocopherol from both films was observed, meaning that the partition coefficient of tocopherol was not influenced by the incorporation with cyclodextrin. Thus, complexation might be the key to a long lasting antioxidative effect of such kind of active packaging.

Keywords: active packaging, alpha-tocopherol, antioxidants, beta-cyclodextrin, controlled release, diffusion coefficient;

Introduction

To prevent or retard any deterioration in quality of packaged foods, active packaging including the concept of the controlled release of active components to foodstuffs has shown the greatest potential to improve storage stability (Miltz et al. 1995, Vermeiren et al. 1999, Appendini & Hotchkiss 2002, LaCoste et al. 2005). The motivation for developing controlled release packaging is to transfer the active agent from the polymeric carrier to the surface of the food in order to maintain a predetermined concentration and thus to prolong the shelf-life without adding excess additives directly to food products. This transfer of the active agent is a result of the diffusion in the polymer matrix and the partition process between the polymer and the food surface. The diffusion is described by the diffusion coefficient (D), while the partition is characterised by the partition coefficient (K) (Garde et al. 2001, Helmroth et al. 2002, Hernandez-Muñoz et al. 2002).

Controlled release of drug delivery has been used for some time (Colombo et al. 1996, Kuijpers et al. 1998, Bezemer et al. 2000), and procedures for achieving release under various conditions are well-established. However, considerable research on testing the concept of controlled release of active compounds from food packaging did not appear until the last decade (Floros et al. 2000). The promulgation of EC regulation 1935/2004 on materials and articles intended to come into contact with food may facilitate the development of controlled release packaging concepts (EC 2004). This regulation states that, unlike traditional packaging materials and articles, active packaging concepts are not inert by their design. They are designed to deliberately incorporate ‘active’

components intended to be released into the food or to absorb substances from the food, therefore they may change the composition or the organoleptic properties of the food. These changes, however, always should comply with the Community provisions applicable to food, such as the provisions of Directive 89/107/EEC on food additives. In particular, substances such as food additives deliberately incorporated into certain active food contact materials and articles for release into packaged foods or the environment surrounding such foods, should be authorised under the relevant Community provisions. Besides the main requirements of use established in EC regulation 1935/2004, further regulations should be addressed in specific measures, to include positive lists of authorised substances and/or materials and articles, which should be adopted as soon as possible.

Antioxidant packaging is a promising type of controlled release concepts, in which antioxidants are incorporated into or coated onto food packaging materials to reduce oxidation in the packed food (Vermeiren et al. 1999, LaCoste et al. 2005). For example, incorporation of synthetic antioxidant compounds, such as butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) in high-density polyethylene has been shown to protect cereals from oxidation (Miltz et al. 1987, Wessling et al. 2000a). In recent years, however, there has been a growing interest in the use of natural antioxidants such as tocopherols in food packaging applications, because of an emerging concern regarding long-term safety and negative consumer perception of synthetic antioxidants (Yu et al. 2002, Maisuthisakul et al. 2006). For example, BHA and BHT have been suspected of being responsible for liver damage and carcinogenesis (Onyeneho and Hettiarachchy 1992, Yu et al. 2002). Tocopherols are non-toxic

compounds with a positive public perception, broad regulatory approvals, and environmentally friendly appeal to the consumers (Wessling et al. 2000b, LaCoste et al. 2005). Besides being an effective antioxidant for reducing oxidation in foods, tocopherols are also excellent stabilizers for polymer processing (Al-Malaika et al. 1994, Billingham and Garcia-Trabajo 1995, Al-Malaika et al. 1999, 2001a, 2001b). Therefore, tocopherols can serve dual functions when added to packaging: as a stabilizer for polymer processing and as an antioxidant in controlled release to reduce oxidation (LaCoste et al. 2005).

The release of alpha-tocopherol from packaging material depends on several factors. Wessling et al. (1999) revealed that the retention of alpha-tocopherol is influenced by the type of the polymer as well as the fat, alcohol and organic acid content of the food product (Wessling et al 2000c). Heirlings et al. (2004), however, found that the polarity of the polymer matrix had only a slight effect on the migration rate of alpha-tocopherol. In this latter study the antioxidant was also adsorbed onto silica materials in order to give a protection during extrusion and to ensure a controlled release. By this way antioxidant release could be elongated for about three-four days at 7 °C. For some food applications, however, an even slower antioxidant release would be desired.

Recently there has been an increasing interest in the use of cyclodextrins as a tool for controlled release of active compounds due to their outstanding ability to form molecular complexes with hydrophobic guest molecules. Cyclodextrins (CD) are obtained by degradation of starch. They are cyclic oligosaccharides consisting of six (alpha-CD), seven (beta-CD) or eight (gamma-CD) glucopyranose units, which are

bound together by alpha (1-4)-linkages forming a torus-shaped ring structure. Due to their polar hydrophilic outer shell and relatively hydrophobic cavity, they are able to build up host-guest complexes by inclusion of suitable hydrophobic molecules (e.g. alpha-tocopherol). The formation of these complexes leads to significant changes of the solubility and reactivity of the guest molecules, but without any chemical modification (Szejtli 1996).

In this study the influence of complexation by beta-cyclodextrin on the migration of alpha-tocopherol from LDPE was investigated. The migration of alpha-tocopherol both complexed in beta-cyclodextrin and non-complexed from Low Density Polyethylene (LDPE) polymer into a fatty food simulant was followed at 7.0 ± 0.5 °C. A migration model suggested by Hamdani et al. (1997) and Piringer (2000) was fitted to the migration profiles and diffusion coefficients were calculated. Besides protecting the antioxidant against high temperature during extrusion, beta-cyclodextrin is also expected to slow down the release of alpha-tocopherol from LDPE thus ensuring a longer lasting antioxidative effect.

Materials and methods

Complexation process in beta-cyclodextrin

Pharma-grade beta–CD (Wacker Chemie, Germany, Lot No. 70T179, 227 g, 0.17 mol) was suspended in 700 mL distilled water by stirring at ambient temperature. Technical grade alpha-tocopherol [Irganox® E201=3,4-Dihydro-2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridecyl)-2H-1-benzopyran-6-ol] (Ciba Specialty Chemicals, Basel, Switzerland) (43.06 g, 0.1 mol) dissolved in 50 mL 96% ethanol (analytical reagent grade, Merck, Darmstadt, Germany) was added to the aqueous suspension by continuous stirring. The stirring was continued for 0.5 h at 60 C and for 8 h at ambient temperature, then the suspension was left to stay in the refrigerator for approximately 16 hours. The next day it was filtered and the filtrate was dried for 2 days at room temperature in vacuum exsiccator beside phosphorus pentoxide till constant weight. The complex obtained (214 g) contained 15.5% alpha-tocopherol as measured by the following method. 25.0 mg complex was dissolved in 25.0 ml water-ethanol (1:1) mixture and the absorbance was measured at 292 nm by a HP 8452 UV-VIS diode array spectrophotometer (Hewlett-Packard Co., Palo Alto, CA, USA).

Heat stability measurements

The heat stability of free and complexed alpha-tocopherol was characterized by thermo-gravimetric analysis (TGA) as suggested by Ferdinando et al. (2001). A MOM Derivatograph PC (MOM, Hungary) was used to obtain differential thermo-gravimetric (DTG) curves. Experiments were carried out on 15-20 mg of sample in aluminum-oxide

open pan at a heating rate of 5 °C min^{-1}, under pure nitrogen at a flow rate of 40 mL min^{-1}. Samples were heated up to 250 °C.

Preparation of packaging materials

The experiments were carried out using Low Density Polyethylene (LDPE, Lot No. FB 243-51) polymer provided by Tiszai Vegyi Kombinát (Tiszaújváros, Hungary). Two types of film were prepared: film A contained free alpha-tocopherol while film B comprised this antioxidant complexed into beta-cyclodextrin. The antioxidant alpha-tocopherol, free and complexed was mixed with the LDPE granulates at a nominal concentration of 2000 mg kg^{-1} by a simple scroll extruder, and the granulates were transformed into films on a blown film line (Kuhne K36, Kuhne GmbH, Germany). Besides alpha-tocopherol (Irganox® E201) the films contained no further antioxidants. The thicknesses of film A and film B, measured by a micrometer (Mitutoyo, Mitutoyo Corporation, Japan), were approximately 60 µm and 50 µm, respectively.

Determination of the initial alpha-tocopherol concentrations

The exact initial alpha-tocopherol content of the polymer was determined prior to the migration experiment using the procedure described by Heirlings et at. (2004) with some slight modifications. Briefly, 1.0 g film was weighed and cut into small pieces (approximately 10 mm x 10 mm) then dissolved in 70 mL toluene (analytical reagent grade, Reanal, Budapest, Hungary). During the dissolving process the solution was heated up to 65 °C and stirred by a magnetic stirrer (MLW RH3, VEB MLW, Freital, Germany). After 15 minutes, 50 mL cold methanol (analytical reagent grade, Reanal,

Budapest, Hungary) was added in order to precipitate the polymer. Afterwards the solution was filtered through a paper filter (Macherey-Nagel GmbH, 614 $^{1/4}$ ∅ 150mm, Düren, Germany). The solvents were evaporated to dryness in a rotary evaporator (Heidolph VV2000, Heidolph Elektro GmbH & CO KG, Kelheim, Germany) at 50°C. The residue was resolved in 5 mL methanol of HPLC grade (Reanal, Budapest, Hungary). After filtering through a Nyfalo® Z269514 syringe filter (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), the samples were analysed by a high performance liquid chromatography (HPLC) system described under.

High performance liquid chromatographic analysis

A Shimadzu HPLC system was used (Shimadzu Corporation, Kyoto, Japan), which consisted of a Shimadzu LC-10AD solvent delivery pump and a Shimadzu SPD-10A UV-VIS detector. Samples were injected manually through a Model 7725i injection valve with a 20 µL sample loop (Rheodyne, Cotati, CA, USA). A Discovery C18 (250 x 4.6 mm, 5µm) column equipped with a Supelguard® guard column (20 x 4.0 mm, 5µm) (Supelco, Bellefonte, PA, USA) was used. Elution with a flow rate of 1.0 mL min^{-1} was monitored by UV detection at 292 nm. 100% HPLC methanol was used as mobile phase. The injection volume was 20 µl and total analysis time was set at 13 minutes. Data acquisition and processing were accomplished with a workstation using Class-VP 4.3 software (Shimadzu). Alpha-tocopherol was identified by matching of its retention time with the corresponding peak in the standard solution. Quantification was carried out by the integration of the peak areas and external calibration.

The linearity of the determination method was measured by injecting alpha-tocopherol solutions of different concentrations (100, 250, 500, 750 and 1000 mg L^{-1}). Then the peak areas were calculated and were expressed as a function of the concentration. The response was linear within the examined range with a correlation coefficient of 0.9996.

Repeatability and recovery of the HPLC analysis were evaluated by analysing five replicates of 50, 250, 750 and 1000 mg L^{-1} of alpha-tocopherol standard solutions. The obtained relative standard deviations (RSD) were between 0.7-1.2% and the recovery found to be 95.8-106.0%.

Specific migration studies

Migration profiles of alpha-tocopherol from the two kinds of film were investigated using bags filled with food simulant. The experimental set was based on the migration study of Heirlings et al. (2004). As food simulant 95% ethanol (analytical reagent grade, Reanal, Budapest, Hungary) was used instead of the normally proposed olive oil in order to avoid the difficulties associated with the sample preparation of oil and the quantification problems arising from the originally high alpha-tocopherol content of olive oil.

The migration bags with a size of 0.1 m x 0.1 m were filled entirely with 100 mL 95% ethanol (< 1 mL air/bag). The weight of the empty bags was approximately 1.2 g and 1.0 g for film A and film B, respectively. After filling the bags, they were heat-sealed (Model N200, Cromat®, Zagreb, Croatia) and stored at 7.0 ± 0.5 °C in a refrigerator with forced ventilation for 65 and 145 days in case of film A and film B, respectively.

In order to provide the proper contact area and time for both sides of the bag, they were turned daily.

To determine the amount of alpha-tocopherol migrated in the food simulant, the whole amount of food simulant (95% ethanol) was evaporated to dryness in a rotary evaporator at 50 °C and the residue was resolved in 1.0-5.0 mL methanol of HPLC grade, then the samples were filtered and injected into the chromatographic system. The concentration of alpha-tocopherol was determined by the HPLC method described above. In each time of measurements three bags of film A and B were analysed. Samples were analysed once or twice a day at the beginning of the migration experiment and less frequently as the migration process was nearing the equilibrium. In total 72 and 90 bags of film A and film B were analysed, respectively. All prepared samples were injected at least duplicate. Mean values and standard deviations were calculated by Microsoft® Excel 2000 (Microsoft Corporation, USA).

Migration modelling

A migration process was fully described by the kinetics of migrant diffusion in each phase (expressed by the diffusion coefficient, D) and the chemical equilibrium (expressed by the partition coefficient, K). The partition coefficient of a migrating compound between the polymer and the food was defined as follows:

$$K_{P/F} = \frac{c_{P,\infty}}{c_{F,\infty}} \quad (1)$$

where $c_{P,\infty}$ (mg kg^{-1}) and $c_{F,\infty}$ (mg kg^{-1}) are the equilibrium concentrations of the component in the polymer and the food, respectively.

The apparent diffusion coefficient (D) of alpha-tocopherol was determined from the migration versus time data, which was fitted to Fick's second law for an infinite slab in contact with an infinite volume of solvent (Crank 1975):

$$\frac{M_{F,t}}{M_{F,\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left[-\frac{(2n+1)^2 \pi^2}{4 d_P^{\,2}} Dt \right] \quad (2)$$

where $M_{F,t}$ (mg) is the amount of the migrant in the food at particular time t; $M_{F,\infty}$ (mg) is the amount of the migrant in the food at equilibrium; d_P (cm) is the thickness of the polymer; D ($cm^2\ s^{-1}$) is the diffusion coefficient of the migrant in the polymer and t (s) is the contact time.

The diffusion coefficient (D) was determined by minimising the sum of squares in errors (SSE) between the estimated and measured values.

Results and discussion

Influence of the complexation process on heat stability

During extrusion, granulates and polymer additives are exposed to relatively high temperatures, often reaching 200 ± 30 °C depending on the type of polymers. Therefore, polymer additives should be stable up to this temperature range.

Cyclodextrins are often used to increase heat stability of several compounds. In our experiment the effect of complexation on the heat stability of alpha-tocopherol was also assessed. In Figure 1 the differential thermo-gravimetric (DTG) curve of alpha-tocopherol/beta-cyclodextrin complex is compared to the DTG curves of the free

components (alpha-tocopherol and beta-cyclodextrin). It can be seen that the DTG curve of alpha-tocopherol was flat between 50 and 190°C, which means that it is stable until 190°C. It started decomposition at 191°C. The DTG curve of beta-cyclodextrin showed a single peak between 38 and 127°C (with 90°C peak temperature). This stage is related to the dehydration with 12.7% of water weight loss. Up to 250°C no evidence of decomposition were experienced. This corresponds to the information found in the literature, which stated that decomposition of cyclodextrins occurs only at around 300 °C (Hedges et al. 1995).

The solid line in Figure 1 represents the DTG curve of alpha-tocopherol/beta-cyclodextrin complex. Only one stage appeared on the curve between 35 and 138°C. This peak corresponds to the water loss process. The DTG peak minimum temperature was 87°C with 7.8% of water weight loss. After this peak no further weight loss was detected until 197°C, when the decomposition of the complex started.

"[insert Figure 1 about here]"

Heat stability measurements indicated that both the free alpha-tocopherol and the alpha-tocopherol/beta-cyclodextrin complex are stable up to 190°C. The complexation process did not increase the heat stability of alpha-tocopherol significantly, however, alpha-tocopherol is anyway quite heat stable.

Initial alpha-tocopherol concentrations in the films

The exact alpha-tocopherol content of the films was determined by HPLC-UV at the beginning of the migration experiment. Ten replicate analyses were performed for both

film A (free alpha-tocopherol) and film B (complexed alpha-tocopherol). The recovery of the analyses, determined by subjecting solutions containing 2000 mg L^{-1} alpha-tocopherol in methanol to the dissolving, filtering and evaporation procedure, was 80.6 ± 4%. Alpha-tocopherol concentrations in film A and B found to be 1621±107 mg kg^{-1} and 1500± 322 mg kg^{-1}, respectively. It is assumed that a significant part of the originally added alpha-tocopherol (2000 mg kg^{-1}) was lost during manufacturing of the film, which was experienced also by other authors. For example Wessling et al. (2000b) found that approximately 66% of the originally added alpha-tocopherol was lost during LDPE film processing. Heirlings et al. (2004), however, found lower loss of alpha-tocopherol in LDPE films after processing but this was explained by the presence of other types of antioxidant in the polymer besides alpha-tocopherol. When analysing the initial alpha-tocopherol concentration in film B, rather high relative standard deviation (21.5%) was found. This was probably due to the inhomogeneous distribution of the complexes in the film, which was even visible. Because of the relatively polar nature of the outer shell of cyclodextrin molecules, it is fairly difficult to distribute them in the apolar LDPE matrix. Further problems occurred due to the development of CD agglomerates, resulting in unfavourable optical characteristic of the film: visible white spots in the LDPE matrix.

Specific migration experiments

The migration of an additive from the packaging material into the food simulant can be followed by determination of its concentration either in the polymer or in the food simulant. This former method, however, suffers from a substantial disadvantage: namely, that the extraction of the analyte from the polymer matrix is often quite difficult

and time-consuming. Therefore in the present study the migration process was followed by determining the amount of alpha-tocopherol migrated into the food simulant at 7.0 ±0.5 °C as a function of time. Progress of migration was expressed as the ratio of the migrated amount of alpha-tocopherol in a particular time and at equilibrium ($M_{F,t}$ / $M_{F,\infty}$).

The migration profiles of film A and B are compared in Figure 2. As it can be seen in the figure, a significant difference in the rate of migration was found between film A and film B. As alpha-tocopherol is fat soluble fast migration from LDPE into ethanol was expected. In case of film A containing alpha-tocopherol in free (non-complexed) form this assumption was verified. As can be seen in Figure 2, in about 400 hours approximately 85% of the total amount of alpha-tocopherol had migrated from film A to the fatty food simulant. In the first two weeks, migration showed an exponential increase and reached an equilibrium in the following weeks, similarly to previous experiments reported by Heirlings et al. (2004). Considering real food packaging applications, this practically means, that the high initial rate of release of antioxidant could inhibit the initiation step of oxidation taking place at the early stage of the storage. It can result in a high antioxidant concentration at the food surface and hence in increased diffusion rate from the surface into the bulk food due to the high concentration.

Film B contained alpha-tocopherol complexed into beta-cyclodextrin with the aim to protect the antioxidant during film production on one hand, and to ensure slower, but sufficient release to the food simulant on the other hand. Migration profile of alpha-

tocopherol released from film B into the food simulant is showed also in Figure 2. It can be concluded, that 85% of the total amount of alpha-tocopherol at equilibrium had migrated in 2324 hours from the polymer to the food simulant, while total migration was reached in about 3500 hours. This means that the migration rate of alpha-tocopherol from film B is significantly lower than that of film A.

"[insert Figure 2 about here]"

The initial amount of alpha-tocopherol in the bags can be calculated as follows. In the case of film A the initial concentration of AT was 1621±107 mg kg^{-1}, thus the migration bags weighing 1.2 g contained approximately 1.94 mg alpha-tocopherol. As the initial concentration in film B found to be 1500± 322 mg kg^{-1} and the bags weighed 1.0 g, therefore the initial amount of alpha-tocopherol was 1.50 mg.

At equilibrium approximately 1.95 mg and 1.48 mg alpha-tocopherol had migrated into the food simulant from film A and film B, respectively. These amounts correspond to the total original alpha-tocopherol content of the bags, thus a total migration was observed for both films. It means that 95% ethanol proved to be a potent extractant and the partition between the polymers and the food simulant was neglectable. This finding is in accordance with the results of Wessling et al. (1998) and Heirlings et al. (2004) for free alpha-tocopherol. It can be also concluded that the partition coefficient of alpha-tocopherol between the polymer and food simulant was not influenced by the complexation.

Reliable migration predictions require the description of the physical migration process by a correct mathematical equation, i.e. good agreement between predicted values and experimental data. The migration profiles of the two different films were fitted towards equation (2) to estimate the diffusion coefficient (D). It can be concluded that the model fitted the experimental values very well for both types of film. The sum of squares in errors (SSE) between the estimated and measured values was found to be as low as 0.05. The calculated values for D were 1.53E-11 $cm^2\ s^{-1}$ and 1.68E-12 $cm^2\ s^{-1}$ for film A and B, respectively. There is no doubt that this difference is a consequence of the complexation of alpha-tocopherol in beta-cyclodextrin. It should be emphasised, however, that the calculated diffusion coefficient of alpha-tocopherol in film B is only an apparent value. In general the migration of a compound from a polymer into a food or simulant is of a very complex nature depending on several parameters, thus some simplifications are often made. Modelling this mass transfer process usually considers only a single phenomenon, generally the diffusion of the compound, which is then described by a single and constant diffusion coefficient. It is well known, however, that the presence of large amounts of other substances interferes with the diffusion process. Most of the models applied however do not take into account specific molecular interactions (e.g. association-dissociation processes in molecular complexes). In the present study it was expected that the molecular encapsulation in beta-cyclodextrin would also significantly influence the migration of alpha-tocopherol. The release kinetics of a complexed substance depends not merely on diffusion, but also on the ratio between its complexed and uncomplexed fractions, which is governed by the complex association/dissociation equilibrium characterized by the complex stability constant

($K_{1:1}$). This thermodynamic equilibrium for beta-cyclodextrin (CD) and alpha-tocopherol (AT) can be described by the following equations.

$$CD + AT \leftrightarrow CD\ AT \quad (3)$$

$$K_{1:1} = \frac{[CD\ AT]}{[CD\ ][AT]} \quad (4)$$

where $K_{1:1}$ represents the stability constant of the beta-cyclodextrin/alpha-tocopherol complex, while [CD], [AT] and [CD AT] correspond to the solubility of beta-cyclodextrin, alpha-tocopherol and their complex, respectively. As beta-cyclodextrin is insoluble in 95% ethanol it can be supposed that it remains in the polymer matrix.

Regarding alpha-tocopherol a partition can be expected between its complexed and uncomplexed form. However, as complexation is a dynamic and usually reversible process, this partition could only be interpreted for a particular moment: both association and dissociation of the complexes take place at the same time. It is presumable that only molecules being uncomplexed can participate in the migration process. The amount of the uncomplexed alpha-tocopherol at a particular moment depends on the equilibrium described above. Most of the studies of cyclodextrin complex stability have been carried out in aqueous solutions and only a few workers have investigated complex formation in organic solvents (Connors 1997). In general, the decrease of the complex stability is assumed in function of increasing apolar nature of the solvent. This can be explained by the fact, that apolar organic solvents decrease the hydrophobic driving force: namely, apolar guests prefer solvents to semi-apolar

cyclodextrin cavity. Moreover, molecules of the organic solvents can function as competitive guest molecules, thus displacing the primary guests.

Conclusions

Complexation by beta-cyclodextrin was found to be an effective tool for controlling the release of alpha-tocopherol from antioxidative active packaging. Complexation had a significant influence on the migration profile and release rate. Migration of complexed antioxidant was rather slow compared to that of free alpha-tocopherol. Depletion of the antioxidant was completed in about 1000 hours compared to about 3500 hours in case of free and complexed alpha-tocopherol, respectively. The slower release rate was proved also by the significant difference between the diffusion coefficients determined by using a mathematical model to describe the release rate numerically. The migration model fitted the experimental values very well. Rather small sum of squares in errors between the estimated and measured values was found. The diffusion coefficient for the complexed alpha-tocopherol was one order of magnitude lower than for the uncomplexed additive. Therefore, it can be stated that a controlled release of alpha-tocopherol from LDPE packaging films was achieved by inclusion complexation with beta-cyclodextrin.

Acknowledgements

This work was supported by the Economic Competitiveness Operational Program of Hungary (GVOP 3.1.1). The plastic packaging films were extruded and supplied by Plastline Ltd, Pilisszántó, Hungary. All contributions are gratefully acknowledged.

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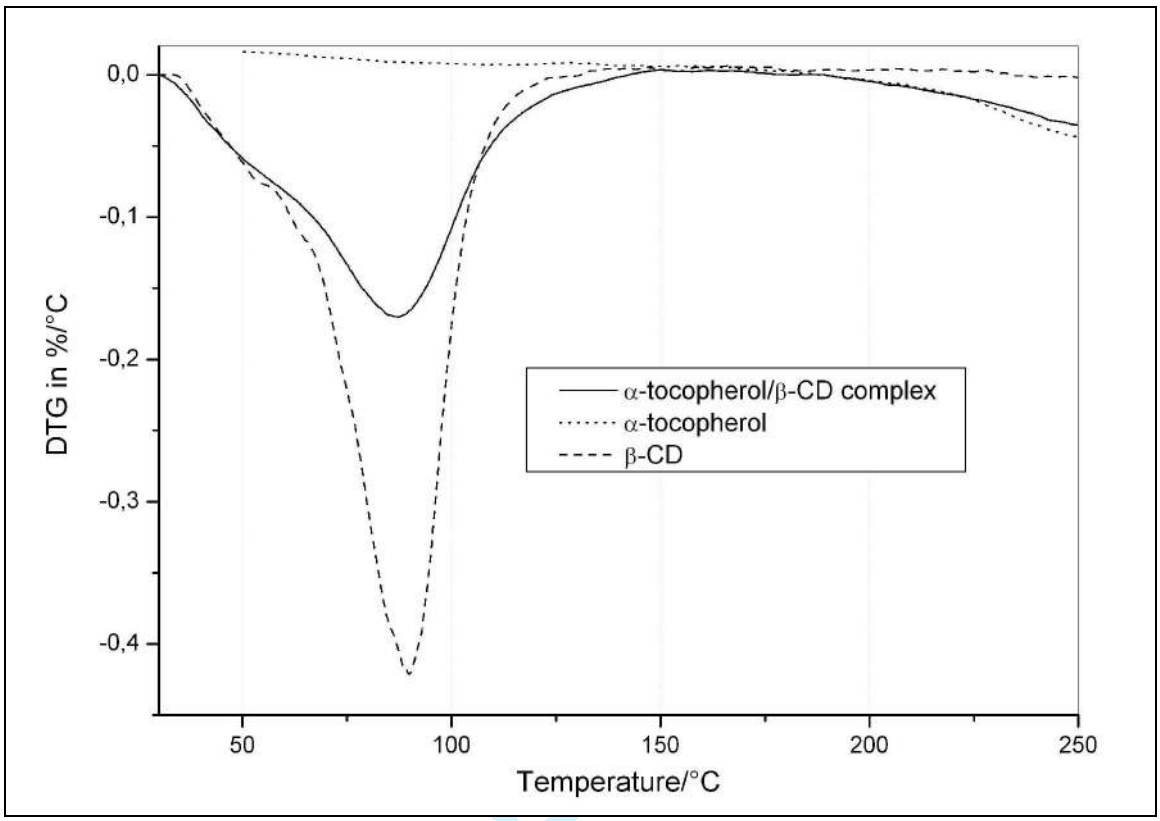

Figure 1

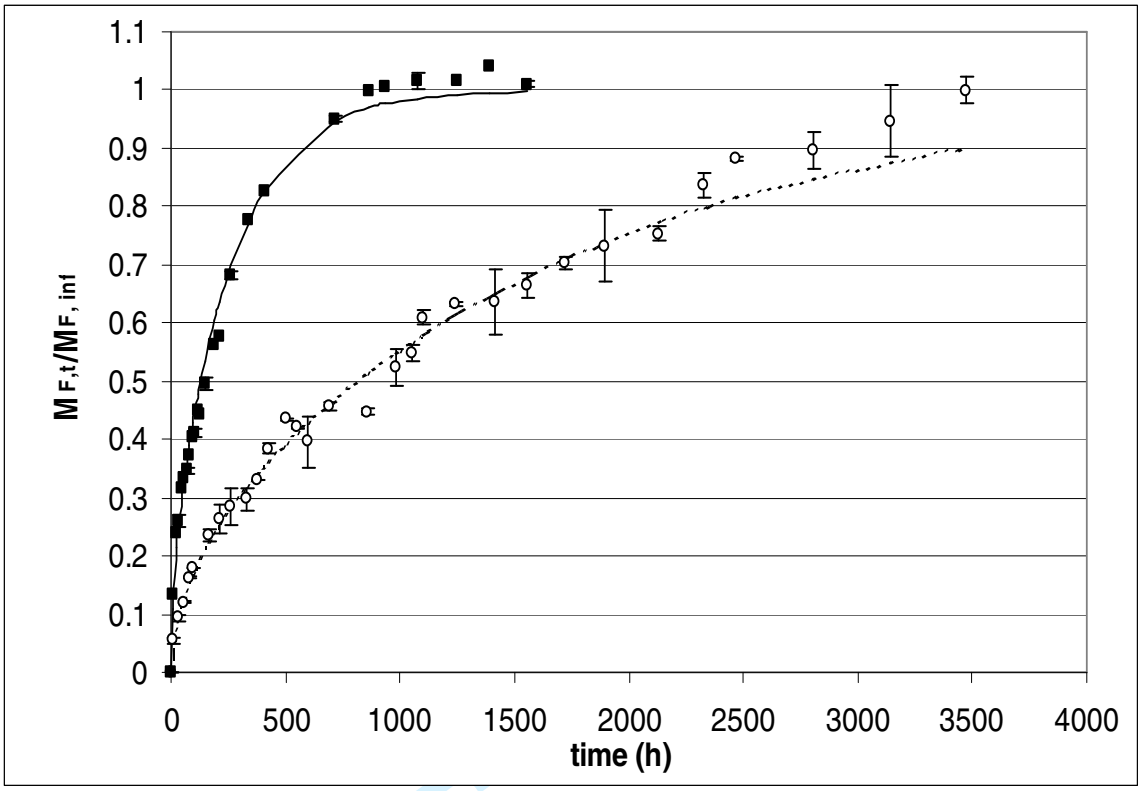

Figure 2

Figure 1 Differential Thermo-gravimetric curve (DTG) of free alpha-tocopherol (dotted line), beta-cyclodextrin (dashed line) and alpha-tocopherol/beta-cyclodextrin (solid line) complex

Figure 2 Migration of alpha-tocopherol from Film A (■) and Film B (○) into food fatty food simulant at 7.0 ± 0.5°C. Data expressed as the mean of three measurements and error bars shows the standard deviations. Solid line (Film A) and dashed line (Film B) represent the estimated migration of alpha-tocopherol based on a migration model

(**Film A**: LDPE 2000 mg kg^{-1} free alpha-tocopherol; **Film B**: LDPE 2000 mg kg^{-1} alpha-tocopherol complexed in beta-cyclodextrin)