DEVELOPMENT OF TARGET RELEASE RATE CONCEPT FOR CONTROLLED RELEASE PACKAGING

by

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ABSTRACT OF THE DISSERTATION

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FOR CONTROLLED RELEASE PACKAGING

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Controlled release packaging is a technology for producing a new generation of packaging materials which can release active compounds such as antioxidants or antimicrobials in a controlled manner to enhance food safety and quality. The objective of this research is to develop a new concept called "target release rate", which is the rate of releasing active compounds to achieve desirable results. The target release rate is a critical but a missing link for advancing this technology.

The first task was to define the target release rate in a meaningful way. A syringe pump was used to release tocopherol (a natural antioxidant) into linoleic acid (a food simulant) at various rates and temperatures. Methodologies were then developed to define the target release rates based on the degradation of tocopherol (measured by high pressure liquid chromatography) and induction periods of lipid oxidation of linoleic acid

(measured by UV spectrophotometer and gas chromatography). Results showed that the target release rate of tocopherol was temperature dependent, around 40, 80 and 150 ppm per day at 30, 40 and 50°C, respectively.

The second task was to study the release rates of tocopherol from polymeric packaging films. Polyethylene/polypropylene polymer blended films containing tocopherol were produced by using the cast film and blown film processes. Tocopherol release rates, degradation of tocopherol, and lipid oxidation of linoleic acid were measured as the functions of time and temperature. Increasing the polypropylene ratio in the film retarded the release of tocopherol from the film but increased the induction period of lipid oxidation. The results confirmed the observation from the syringe pump experiment that degradation of tocopherol and induction period was dependent of the release rate of tocopherol. They also suggested that the release behavior of tocopherol might be manipulated by varying the polymer composition and processing conditions, with the aim of matching the desirable target release rate.

Research was done to test real food, and to characterize physical properties of polymer films. Sesamol released from films increased shelf life of cereal up to 50% longer than the control. Release of tocopherol from film reduced browning of cheese spread.

ACKNOWLEDGEMENTS

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1 INTRODUCTION

With the urbanization of the modern society, food products require extended shelf life to survive a longer transportation time and storage. The life styles have changed so that the busy consumers can no longer shop daily and need to be able to keep foods longer at home. The military must provide a nutritious diet to maintain its forces, so requires a minimum of three-year shelf life for its MRE (meal ready to eat) combat rations. In global food trading, transportation time is long and storage conditions are often severe, particularly in tropical or desert areas. All these needs provide a challenge for both food manufactures and food scientists: how can we provide wholesome, safe food for the consumers with long shelf life?

Lipid (oil and fat), one of the major components of food, is highly susceptible to oxidation even under the normal ambient conditions. Lipid oxidation is a thermodynamically favored reaction because the activation energy for lipid oxidation is only 10-15 Kcal /mole, almost as low as enzymatic catalyzed reaction [1]. Also commonly known as oxidative rancidity, lipid oxidation is one of the main chemical reactions degrading food quality and determining the shelf life of food in long-term storage, and in particular generates unpleasant odors and taste in food [2]. The good news is, like microbiologic deterioration, there is also an induction period for lipid oxidation. The induction period is also called lag phase by some researchers [3]. The induction period is a steady state period before active lipid oxidation takes off, during which, induction period, there is little degradation of lipid and food quality remains good. Therefore, the induction period should be maintained as long as possible to achieve a long term shelf life. After the

induction period, active lipid oxidation occurs and oxidation products such as peroxides and aldehydes are generated. For example, if the volatile compound, hexanal, generated from lipid oxidation, exceeds the sensible threshold, consumers can smell the rancid odor and will then reject the food [2].

Antioxidants, such as tocopherol, quench lipid free radicals and stop the chain reactions of lipid oxidation. Thus, incorporation of antioxidants is necessary for providing even short shelf life in high lipid foods such as mayonnaise and salad dressing, and it is critical for extending shelf life beyond a few months. It should be pointed out that antioxidants are also necessary for low fat food such as cereal food.

The conventional way of adding an antioxidant is to mix it into the food product as part of the base formulation (hereafter referred as instant addition). However, antioxidants are used up as they inhibit lipid oxidation, and the levels sufficient for long term stabilization cannot be added all at once due to legal limitations and high cost.

These disadvantages can be avoided by slowly releasing antioxidants into foods to replenish antioxidants which are consumed by chemical reaction. Previous research in our laboratory demonstrated the principle that slow release of active compounds into food over time can increase storage stability [4]. Nisin (an antimicrobial peptide) was delivered by instant addition, slow release, and a combination of the two, and the induction period for the cell growth of *Lysteria monocytogenes* was measured. Combined instant addition and slow release inhibited the cell growth throughout the experimental period, while the instant addition inhibited growth for the shortest time. This has led to the assumption that controlled release, i.e. delivery of antioxidants slowly over time in a controlled manner can

replenish antioxidants that are consumed and maintain levels sufficient to prevent onset of active lipid oxidation.

To prove this assumption, exploratory research was conducted in this dissertation project to investigate possible ways of delivering antioxidants using timed delivery modes (slow release over time). The effectiveness of three timed delivery modes (syringe, syringe pump, and packaging film) was tested compared for their effectiveness. The syringe mode uses a syringe to manually inject antioxidants into food or food simulant over time. The syringe pump mode uses syringe pump to inject antioxidants into food or food simulant at a pre-determined rate. In the controlled release packaging mode, antioxidants are delivered from packaging material into food in a controlled manner. Results showed that all three timed delivery modes provided better antioxidant effectiveness than instant addition with appropriate delivery rates.

Controlled release packaging (CRP) is a practical ways to achieve slow release or timed delivery of antioxidants, and this may provide an innovative approach to extend shelf life of food. Here 'controlled' means that we can deliberately manipulate different variables such as polymer compositions to provide specific release rates of the active compounds. Previous research in our group has developed a systematic approach to investigating factors that affect the release rates of tocopherol from packaging films into food simulants. Food research has also been conducted to determine the shelf life of food products such as cereal, peanut, peanut butter and cheese spread in packaging with and without antioxidants. However, there is a missing link between our packaging research and food research. That is, what release rate of tocopherol should be built into a packaging film for a given food product? For example, it was required to extend the shelf life of peanut

butter to 3 years at 25°C. If, by studying the food oxidation kinetics, it is found that a release rate of 20 μg of tocopherol per day is needed in order to prevent active lipid oxidation, a packaging film can be produced using the technology such as polymer blending to release the tocopherol at 20 μg per day. The release rate of 20 μg per day from the packaging into the food in order to achieve the desired shelf life is the target release rate which we are trying to determine. Therefore, target release rate is an important factor to fill the research gap between food research and packaging research. And it is critical for the success of controlled release packaging technology.

Figure 1 demonstrates a conceptual framework for the development of controlled release packaging project and the related sections of this dissertation [5, 6]. Most of the chapters focus on target release rates and related variables. Chapters 1, 2, 5 and 6 are general chapters for introduction, literature review, objective and materials and methods. Some variables in the conceptual framework are not discussed in this dissertation. However, they either have been addressed in our previous research or will be discussed in our future work.

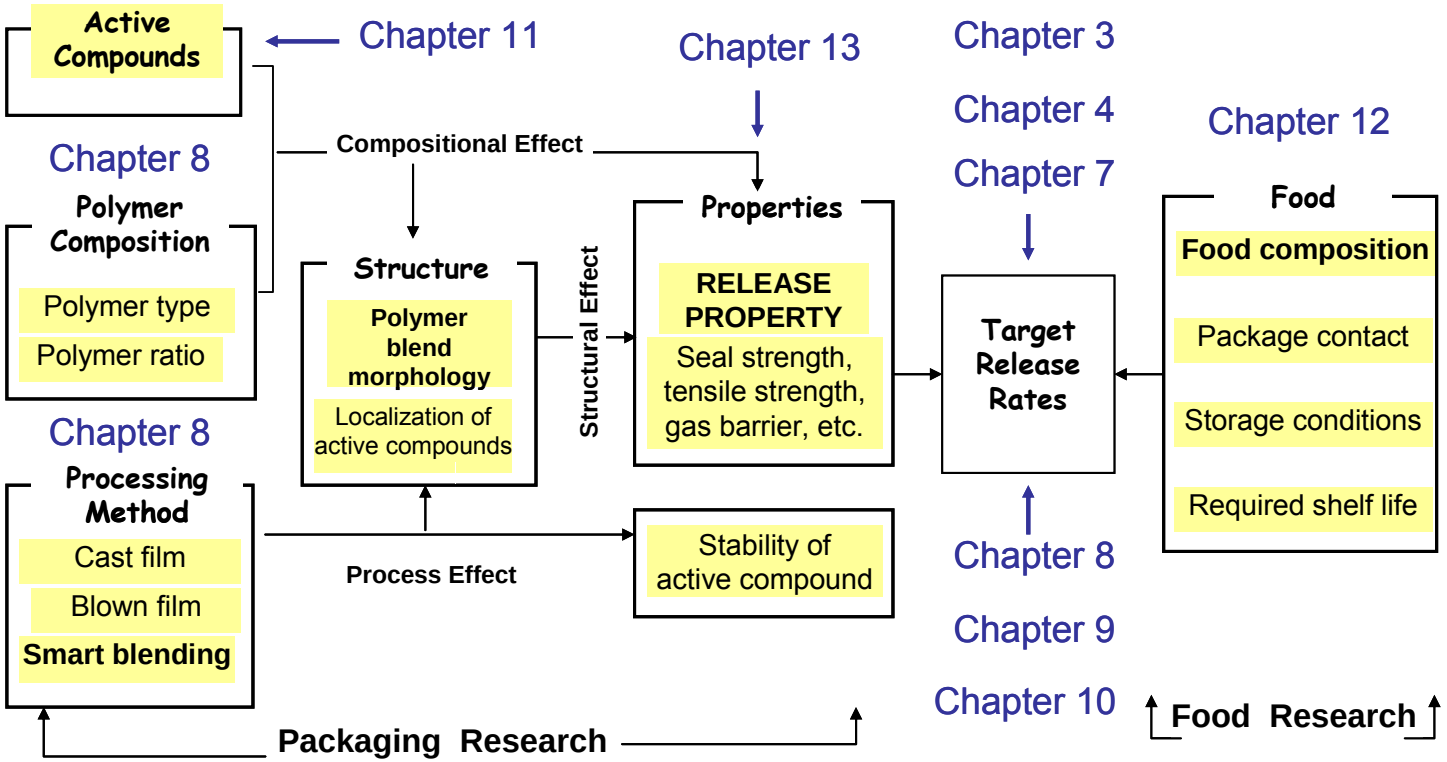


Figure 1 An illustration of structure of this dissertation

Chapter 1, 2, 5 and 6 are general chapters for introduction, literature review, objective and materials and methods.

2 LITERATURE REVIEW

2.1 Basic chemistry of lipid oxidation

Lipids are one of the major components of food. Lipids in food include triacylglycerol (TGs, commonly known as oil and fat) and phospholipids. Oil and fat, especially vegetable oils (unsaturated lipids), are particularly susceptible to lipid oxidation, which deteriorates food quality by degrading nutrients, flavor, texture and color [7].Consumers taste off-flavor from lipids at ppb levels and they reject foods with <1% lipid oxidation. In addition, lipid oxidation products interact with and co-oxidize other food components. For example, free radicals generated by lipid oxidation can be transferred onto protein molecules and cause oxidation of protein in food [8]. Some researchers also reported lipid oxidation products were toxic or carcinogenic [9-11]. In addition, lipid oxidation products such as 4-hydroxy-2-alkenals or 4,5-epoxy-2-alkenals were found to be toxic and might contribute carcinogenesis, mutagenesis, alzheimer disease, and aging [12, 13]. It has been proposed that oxidized fatty acids in food can be absorbed by the intestine and incorporated into lipoproteins, thereby, imposing an oxidative stress and exacerbating atherogenesis [14].

Generally speaking, lipid oxidation is a free radical chain reaction [15]. Lipid oxidation involves many possible chemical reaction pathways under different conditions such as temperature and light [16, 17]. The major pathway is auto-oxidation during food storage. Figure 2 shows a schematic pathway (the classic pathway) for auto-oxidation which includes four steps: initiation, propagation, branching and termination [2, 16, 18]. However, Figure 2 is an over-simplified version of lipid oxidation pathways. In reality,

lipid oxidation is a much more complicated reaction which involves several possible pathways under different conditions (Schaich, 2005). More details will be discussed in the next section.

Initiation

$RH + O_2 \longrightarrow R^{\bullet} + RO_2^{\bullet} + OH^{\bullet} + H_2O$

Propagation

$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$ (1)

$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$ (2)

Branching

$ROOH \longrightarrow RO^{\bullet} + OH^{\bullet}$ (3)

$2ROOH \longrightarrow ROO^{\bullet} + RO^{\bullet} + H_2O$ (4)

Termination

$2R^{\bullet} \longrightarrow R.R$ (5)

$R. + RO_2^{\bullet} \longrightarrow ROOH$ (6)

$RO_2^{\bullet} + RO_2^{\bullet} \longrightarrow ROOH + O_2$ (7)

Where $R^{\bullet}$= fatty acid radical, ROOH= fatty acid hydroperoxide, $RO_2^{\bullet}$= peroxy radical, $RO^{\bullet}$= alkoxyl radical, RH=fatty acid, O_2=oxygen.

Figure 2 A schematic flow chart of lipid autoxidation
Adopted from Hamilton and Laguerre [16, 19].

2.2 Lipid oxidation and food shelf life

2.2.1 Determine shelf life using quality factors

For long term storage, lipid oxidation is one of the major chemical deterioration modes determining the shelf life of lipid containing food. While for short term storage, microbial spoilage is one of the most important deterioration modes determining the shelf life of food products. Quality factors such as sensory values (color, flavor, taste, and texture), lipid oxidation products, and total microbial counts have been used in food research to determine the shelf life of food product during food storage.

For example, conjugated dienes (major initial lipid peroxidation product) and peroxide value (measurement of lipid oxidation product peroxide) is widely used to determine the quality of food oil and the shelf life of oil or lipid containing food. Besides, other changes of sensory attributes such as discolor, off-odor, etc caused by lipid oxidation also can be used as quality factors. Figure 3 illustrates the idea of using lipid oxidation products to determine shelf life. During lipid oxidation, volatile compounds, such as hexanal, will accumulate over time. If the concentrations of volatile compounds exceed the upper limit (sensory threshold), consumers will smell the rancid odor and discard the food product.

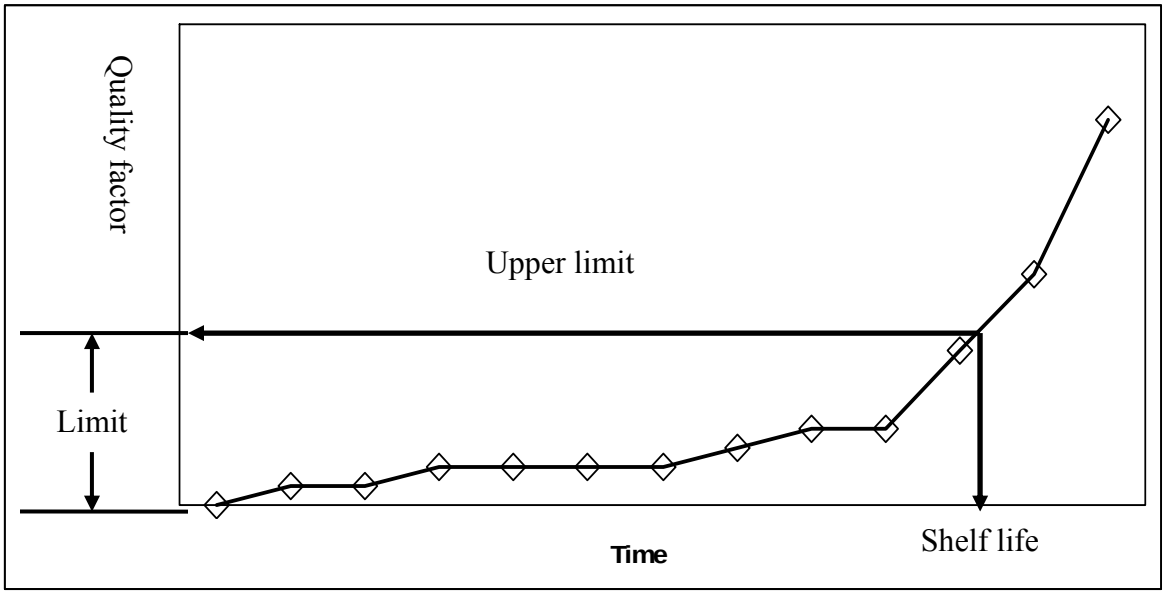


Figure 3 A hypothetic illustration for determination of shelf life by quality factors
Independent variable: time. Dependent variable: quality factor such as flavor, color, texture, and etc. The shelf life ends when limit exceeds the maximum allowable.

2.2.2 A systematic approach to measure lipid oxidation

The lipid oxidation undergoes many possible chemical reaction pathways under different conditions; therefore, lipid oxidation is a dynamic process with constantly changing oxidation products. Thus, determination of the extent of lipid oxidation in food system requires multiple assays to provide a fingerprint of all the products present. This is particularly important because peroxides accumulate and then decompose to a variety of products; a low peroxide value could thus occur with little or no oxidation or with extensive oxidation and significant secondary degradation (personal communication with Dr. Karen Schaich). To facilitate our understanding of lipid oxidation, Dr. Schaich and Dr. Yam have developed a systematic road map for determining the lipid oxidation and shelf

life as shown in Figure 4 [20]. Moreover, an example of possible pathways and oxidation products for linoleic acid which undergoes auto-oxidation is given in Figure 5.

However, this framework (Figure 4) may not be able to demonstrate exactly what is happening during the induction period. This induction period may be of a great importance because it is a good indicator for shelf life. The author was asked by the committee members to investigate the possible chemical changes during the induction period. The author found that one of the important chemical reactions is tocopherol degradation (or consumption of tocopherol) during induction period (Please see detailed result and discussion in chapter 9 and 10). The finding of tocopherol degradation during the induction period is of a great importance because it provides one approach to determine target release rate.

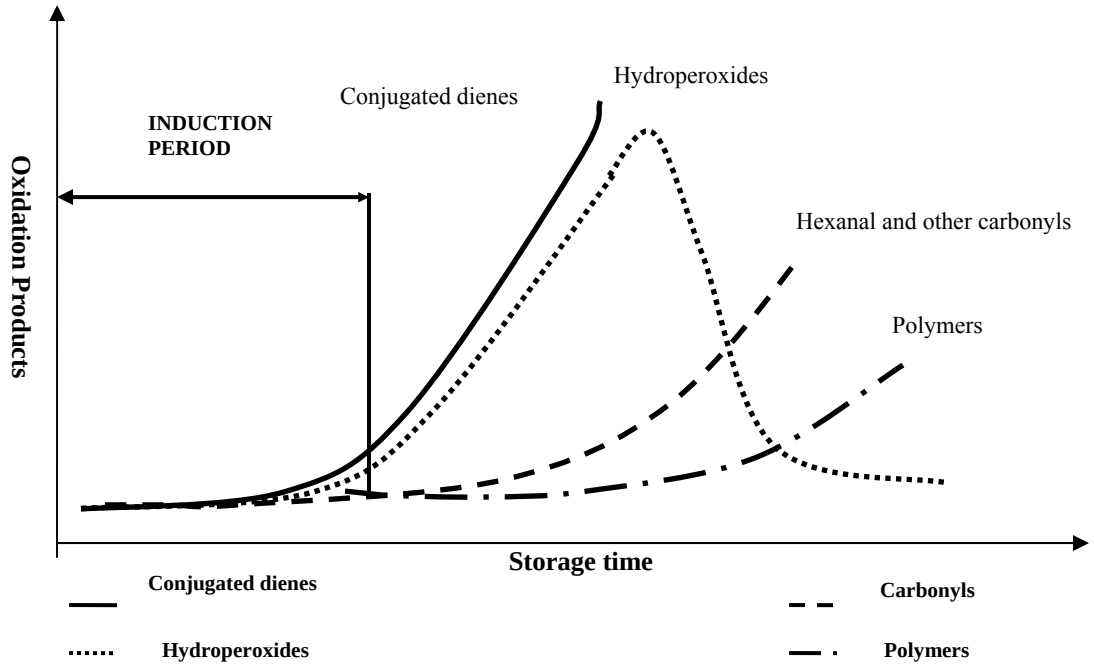


Figure 4 A conceptual framework for determining degree of lipid oxidation
Adapted from Schaich [20]

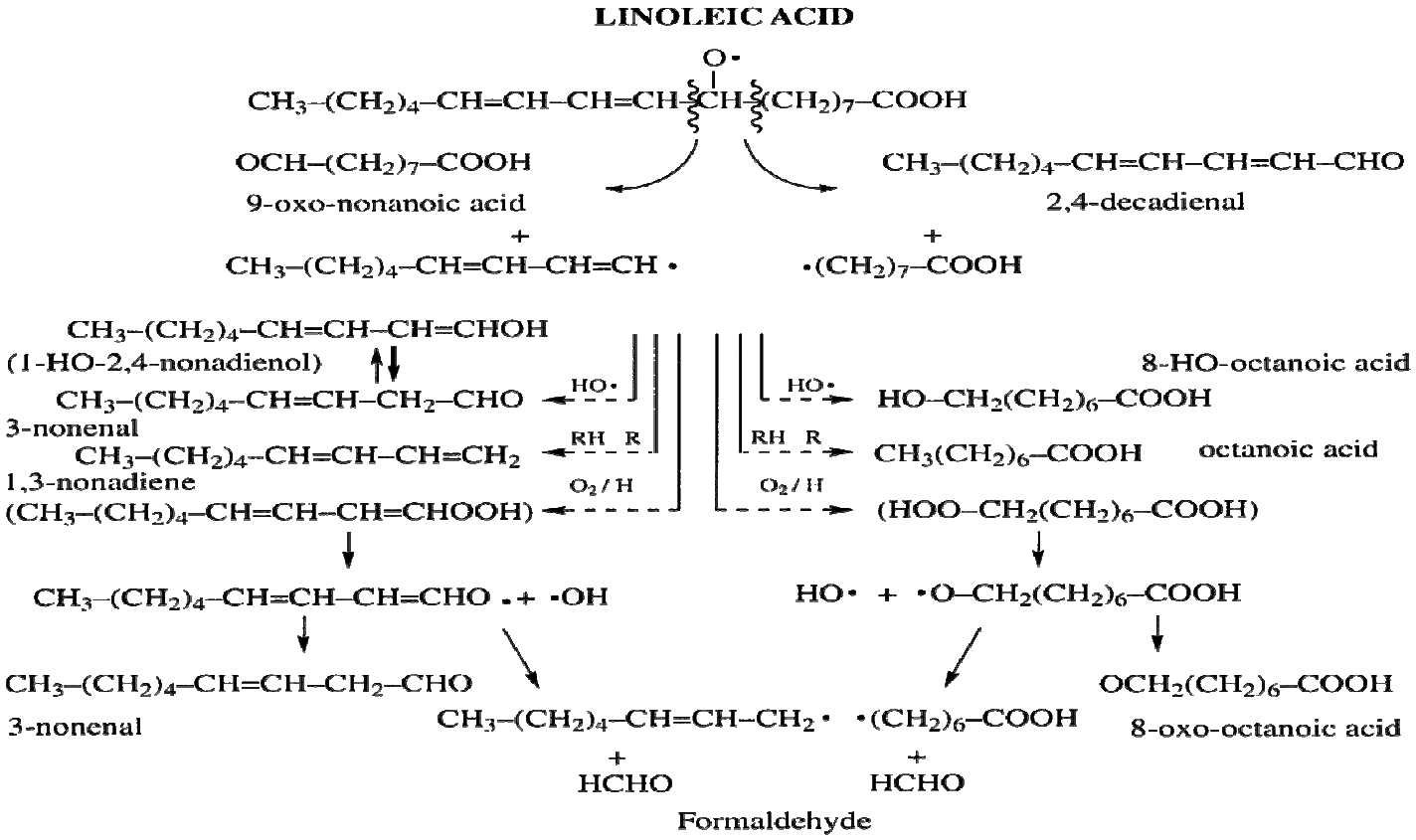


Figure 5 A framework for linoleic acid oxidation pathways

Adapted from Schaich [21]

2.2.3 Induction period of lipid oxidation

In the early stage of oxidation progress, there is a steady state period commonly known as induction period and is used as an indicator for shelf life [22]. Sometimes, this induction period is also called lag phase by some researchers [3]. The induction period was defined as the initial slow phase of a chemical reaction which later accelerates (www.chem.qmul.ac.uk/iupac/gtpoc/I.html). The induction period is correlated with shelf life. The rule of thumb is that a longer induction period indicates a longer shelf life. Since drastic chemical changes occur after induction period, effort should be taken to maintain the food system within the induction period. Figure 6 showed an example of how we determine induction period of lipid oxidation. Linoleic acid was stored in dark at 40°C. Lipid oxidation products were measured over time. Linear regression was done on data points after lipid oxidation taking off. The calculated x intercept was the induction period. Lipid oxidation products, including conjugated dienes, peroxide values, volatile compounds, viscosity, refractive index, oxygen consumption, etc. can be measured to determine the induction period.

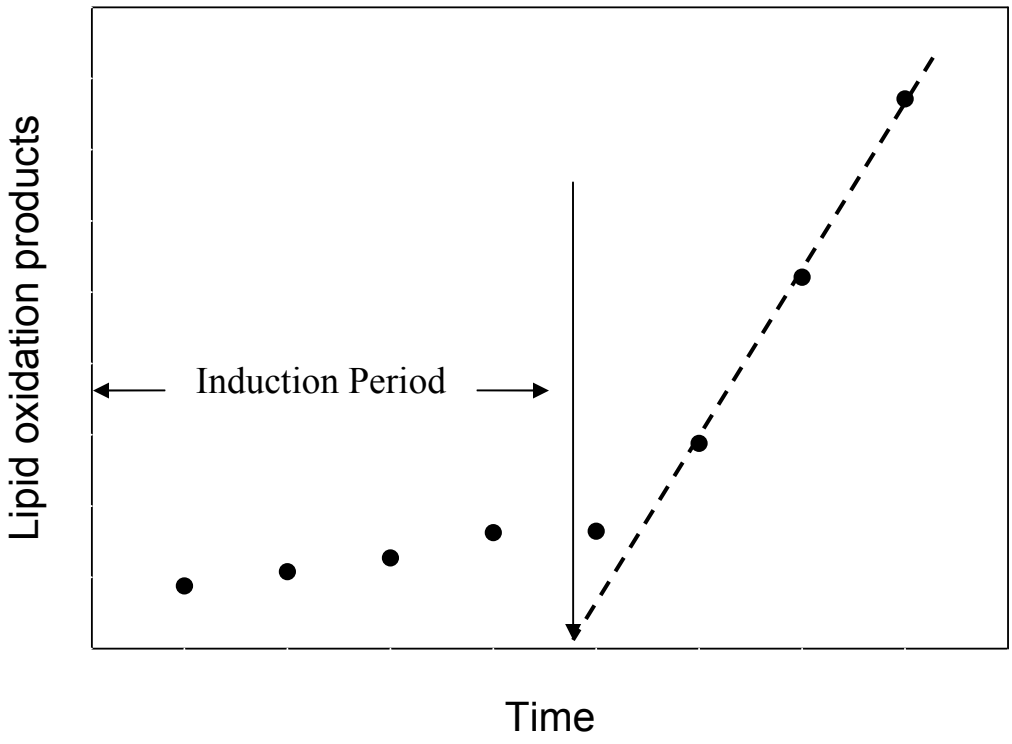


Figure 6 Using the induction period of lipid oxidation to predict shelf life

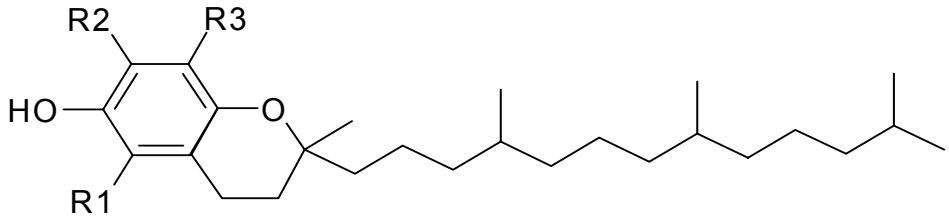
2.3 Tocopherol as an example of antioxidants

In order to achieve a longer food shelf life, and minimize the hazardous effects of oxidized lipids on the food quality and human health, it is necessary to retard lipid oxidation in food. One of the most effective ways is to use antioxidants. In food manufacturing, synthetic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tert-butylhydroquinone (TBHQ) and propyl gallate (PG) are widely used in order to retard lipid oxidation and extend the shelf life of food. However, research has found that some synthetic antioxidants, such as BHT and BHA, may have carcinogenic effects on human body [23, 24]. Consumers become more health awareness and reluctant to select food with synthetic additives such as BHT and BHA. Accordingly, food companies try hard to use new technologies and natural compounds to replace the synthetic additives to achieve healthy image of their food products.

Tocopherol is a natural antioxidant found in many foods. Cereals, oil-seeds, nuts, and vegetables (peas, beans, and carrots) are rich sources of tocopherol. Tocopherol has α, β, γ, and δ-homologues whose relative antioxidant activities vary with the environmental conditions [25]. Recently, there is a growing interest in using tocopherol as an additive to stabilize packaging polymers during extrusion [26]. Tocopherol is usually found in natural sources as a mixture of four homologues as shown in Figure 7. The tocopherol product used in this research is extracted from soybean, which contains 10% α-, 5% β-, 65% γ-, and 20% δ-tocopherol homologues (Table 1).

Table 1 Composition in the natural tocopherol product used in this study

Homologues	Percentage
α-tocopherol	10%
β-tocopherol	5%
γ-tocopherol	65%
δ-tocopherol	20%



Form	R1	R2	R3
Alpha	CH_3	CH_3	CH_3
Beta	CH_3	H	CH3
Gamma	H	CH_3	CH_3
Delta	H	H	CH_3

Figure 7 Chemical structures of tocopherol homologues

Figure 8 demonstrates the major chemical reactions of lipid oxidation under the inhibition of tocopherol (vitamin E). In the presence of initiators such as metals and light, oils and fats form free radicals and react with oxygen in chain reactions that generate hydroperoxides. Hydroperoxides break down into low molecular weight volatile compounds such as hexanal, which are responsible for rancid odors. Antioxidants, such as tocopherol, quench the lipid free radicals and stop the chain reactions of lipid oxidation. For example, tocopherol scavenges the peroxyl radicals formed during propagation and branching stages of lipid oxidation. Tocopherol forms tocopherol radicals which are much less reactive and more stable compared with lipid radicals and therefore do not continue the radical chain reaction. Tocopherol radials can further dimerize into more stable tocopherol dimmers. Therefore, antioxidants are consumed in order to prevent lipid from oxidation and need to be replenished over time. Once all the antioxidants have been consumed during reaction, the lipid oxidation will take off and end the shelf life of the food. Therefore, continuously replenishing the antioxidant during the storage will maintain an effective concentration of antioxidant and extend the shelf life much longer by inhibiting lipid oxidation[27, 28].

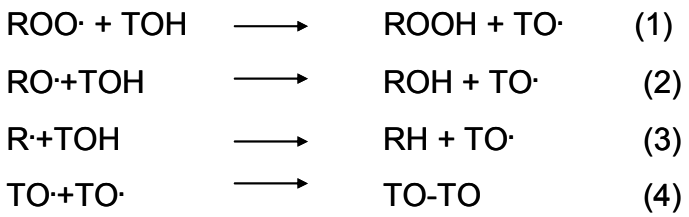


Figure 8 The antioxidant activity of tocopherol as a radical scavenger
Adapted from Frankel and Kamal-Eldin [27, 29]

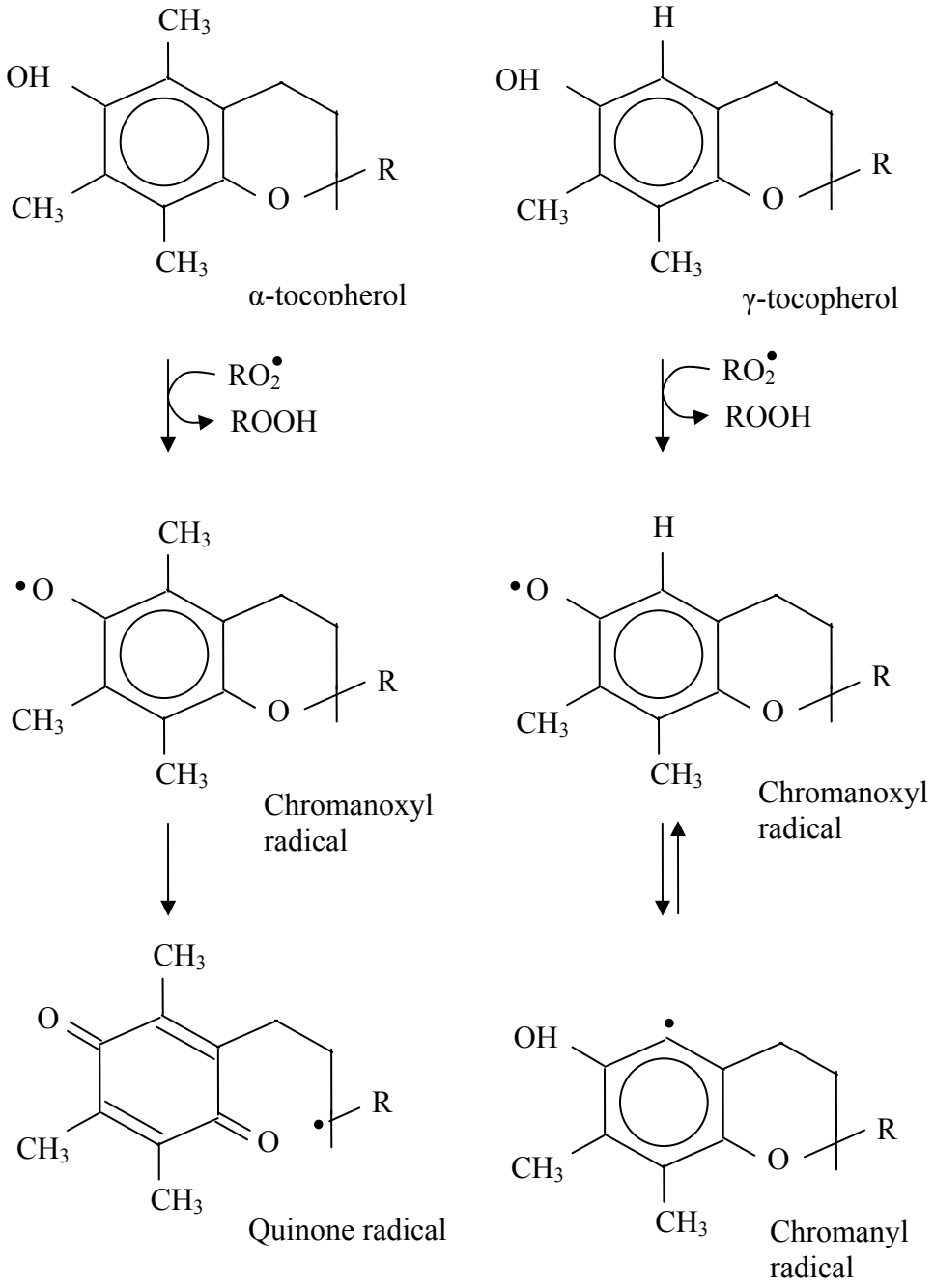


Figure 9 Reactions of α and γ-tocopherol with peroxyl radicals

Adapted from Belitz [30]

In food systems, antioxidant activity of tocopherol decreases in the order of δ > γ > β > α. As shown in Figure 9, tocopherol scavenges the peroxyl radicals formed during propagation and branching stages of lipid oxidation. The rate of reaction with peroxyl radicals decreases from α to δ, which is the reverse of the activities in food (Table 1). The higher antioxidant efficiency of δ-tocopherol is due to the higher stability of δ-tocopherol. Alpha-tocopherol may scavenge peroxyl radicals; however, it generates an alkyl radical, which is a relatively slow reacting chromanoxyl radical and can cause autoxidation of lipid. δ--tocopherol also can generate the chromanoxyl radical; however, due to no opening of the chroman ring of δ-tocopherol, the prooxidative effect is smaller than α-tocopherol (Figure 9).

For CRP application, it's very important to know that tocopherol is non-volatile antioxidant. Tocopherol has good solubility in lipid (oil and fat) and organic solvent. Therefore, in controlled release packaging application, tocopherol is a good antioxidant when there is good food and packaging contact. However, solid types of food products usually do not have good contact with packaging material. For solid food products, volatile antioxidants such as sesamol should be used.

2.4 Sesamol as an example of volatile antioxidants

Nowadays, food companies are trying to replace synthetic additives with natural additives in order to have a greener labeling and meet consumers' demand for more natural products. Sesamol, a natural antioxidant from sesame seed has generated interest because it is volatile antioxidant and therefore can replace synthetic antioxidants such as BHT (Table 2). Sesamol, one of the most important components of sesame oil, is found to be a super antioxidant to make sesame oil extremely stable against oxidation [31]. It has been demonstrated that sesame cake extract (contain sesamol) is more effective in protecting vegetable oil from oxidation than BHT [32]. Nam and Ahn applied 100 ppm sesamol and tocopherol into ground beef before irradiation and this treatment effectively reduced lipid oxidation and off flavors. They also found that as storage time increased, the antioxidant effectiveness of sesamol and tocopherol combination was better than that of ascorbic acid [33, 34]. Yoshida et al. investigated the antioxidant effectiveness of tocopherol and sesamol at various concentrations in oils during microwave heating. Their results demonstrated that gamma-tocopherol and sesamol combination showed the best effectiveness to inhibit lipid oxidation of food oil [35].

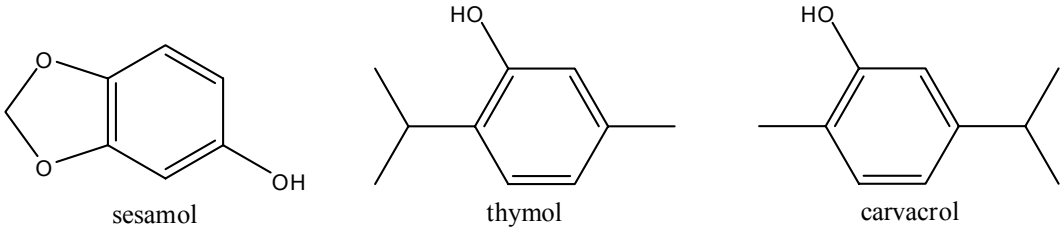
Since sesamol is a volatile antioxidant, it is assumed that it can be incorporated into polymer films, and then evaporate into the headspace of a package and condense on the food surface to inhibit lipid oxidation then extend shelf life of food. The sustained release of antioxidant from polymer film onto food surface may be extremely useful for solid type of food products such as breakfast cereal which does not have a good contact with packaging films. The combination of volatile (sesamol) and non-volatile antioxidant

(tocopherol) may be more effective than single antioxidant for different types of food products.

Table 2 Properties of alpha-tocopherol, BHT and sesamol

	Alpha tocopherol	BHT	Sesamol
MW	430.72	220.34	138.12
Melting point °C	2.5-3.5	71	63-65
Boiling point °C	200°C	265	N/A
Volatility	Low	High	High

There are other natural volatile antioxidants which can be used for CRP. Examples are rosemary extract, thyme extract, and oreganol extract [28, 36]. Figure 10 showed the structures of some natural antioxidants, such as 1-thymol; 2-carvacol and sesamol. Moreover, rosemary extract, thyme extract, and oreganol extract have anti-microbial activities. Therefore, it is possible to develop controlled release packaging films which have both antioxidant and anti-microbial properties.



sesamol thymol carvacrol

Figure 10 Chemical structures of sesamol, thymol and carvacrol

2.5 Delivery modes of antioxidants

2.5.1 Instant addition of antioxidants

The conventional way of adding antioxidants is to mix them into the food product as part of the base formulation. This method is defined as instant addition mode. During long time storage, antioxidants (instantly added) are used up as they inhibit lipid oxidation, and the levels sufficient for long term stabilization cannot be added all at once. Therefore, instant addition of antioxidant is effective for short storage period. The instant addition mode is limited to extend the shelf life for long term storage (more than 1 year). This has led to experimentation with slow release (timed delivery) of antioxidants. The assumption is that by using timed delivery, it is possible to replenish antioxidants that are consumed and maintain levels sufficient to prevent onset of active lipid oxidation. Controlled release of antioxidant is a type of slow release of antioxidants.

2.5.2 Timed delivery (slow release) of antioxidants

There are several ways to achieve timed delivery (slow release) of antioxidants. For example, antioxidants can be delivered with syringe, syringe pump, controlled release packaging and microcapsules in a controllable manner. Syringe mode means using syringe to inject antioxidants (tocopherol) into food or food simulant manually (by hand). Syringe pump mode means using syringe pump to inject antioxidants (tocopherol) into food or food simulant at a pre-determined rate. Syringe pump is used to simulate the release of tocopherol from packaging film. In real food application, one of the practical ways to achieve timed delivery (slow release) of antioxidants is using a new generation of

packaging material called controlled release packaging (CRP). CRP is defined as a delivery mode of antioxidants from packaging material into food in a controlled manner. By ‘controlled’, we mean to control the variables such as polymer type to deliberately control the release rate of active compounds [5]. It was found that the antioxidant effectiveness of CRP was modulated by the release rate (delivery rate) of active compounds [37]. The optimum rate which provides the longest induction period is defined as target release rate and will be determined by this research. Since the concept of target release rate is new and no reference has been found based on our best knowledge, we would like to discuss the concept in detail in Chapter 3.

2.6 Controlled release packaging

Traditionally, packaging is used to provide functionalities such as containment, communication, convenience and protection [38]. Recently, a new function of packaging has emerged, which is known as active packaging.

2.6.1 Active packaging

Active packaging is defined as a packaging system that actively changes the condition of the package to extend shelf life or to improve safety or sensory properties of the food during storage [39]. An example of active packaging is using oxygen scavenger to reduce oxygen concentrations inside the package and thus minimize lipid oxidation of the food [40].Controlled release packaging (CRP) is one type of active packaging because it can release active compounds in a controllable manner to enhance food quality and safety.

2.6.2 Concept of controlled release packaging

Controlled release packaging (CRP) is a new concept to achieve slow release (timed delivery) of active compounds. CRP is defined as: using packaging as a delivery system to release active compounds (antioxidants and antimicrobials) from packaging material (polymer matrix) into food in a controlled manner. The uniqueness of CRP is to use packaging as a delivery system for active compounds [5]. Figure 11 is a conceptual illustration of CRP.

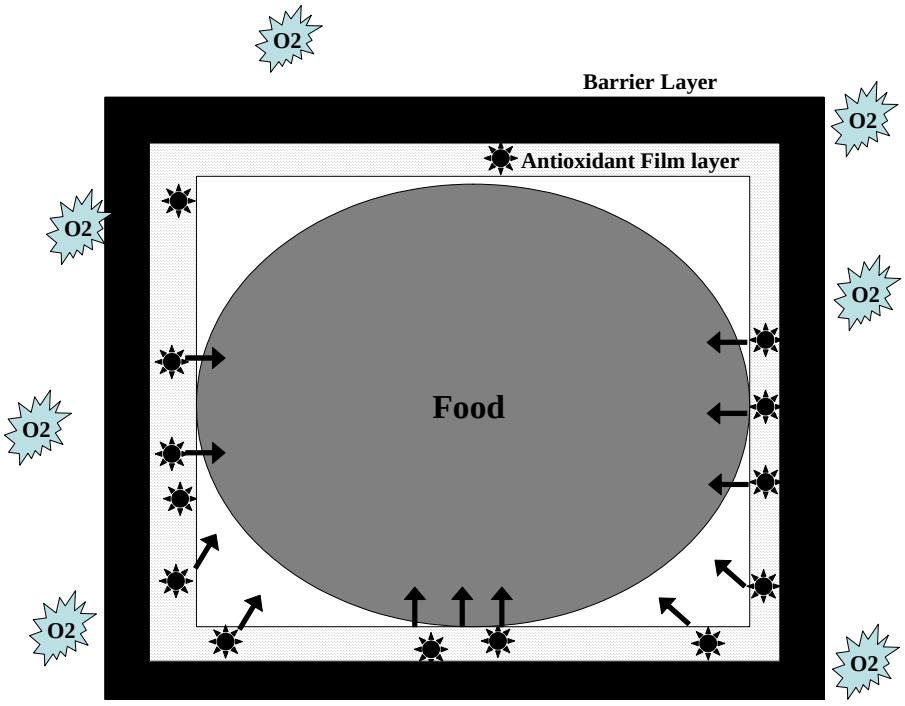


Figure 11 A conceptual illustration of CRP
Adapted from Obinata [6].

The advantages of CRP include: (1), CRP can continuously replenishing food with additives over time instead of dumping all the additives at the beginning. (2), CRP can release the additives onto the food surface instead of the whole food, therefore less

additives are needed. (3), CRP is the promising solution for special foods. Examples are: combat ration which needs three year shelf life, and food extremely perishable, such as a high lipid food.

Several antioxidants have been suggested for antioxidant packaging application, including butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), ascorbic acid and tocopherol [41]. In 1987, high density polyethylene (HDPE) films incorporated with butyl hydroxytoluene (BHT) were reported to successfully extend the shelf life of a cereal product by releasing the entrapped BHT into the package headspace [42]. Since then, various types of BHT-containing antioxidant films have been developed and are now commercially available, especially for cereal products [43-46].

However, there are some concerns regarding the use of synthetic antioxidants such as BHT and BHA in food packaging materials [47]. As a result, people are more interested in using natural antioxidants such as tocopherol (vitamin E), rosemary extract, and etc [30]. For example, release of alpha-tocopherol from LDPE film was found to be able to enhance the color of fresh beef [48].

Wessling et al. (2000) showed that a low density polyethylene (LDPE) film containing 3400 ppm α-tocopherol inhibited the oxidation of an emulsion of 0.31% (v/v) linoleic acid at 6°C under the conditions of darkness and open-air exposure, whereas no significant retardation was observed at 20°C and 40°C [49]. Lee et al. reported that a laminated pouch consisting of a HDPE layer and a heat seal layer impregnated with 73 ppm α-tocopherol failed to retard the oxidation of a packed model solid food containing 0.36% (w/w) linoleic acid at 45°C and 50% RH [50]. It is suggested from the reports that

the success of α-tocopherol containing film in retarding lipid oxidation may depend on how adequately the tocopherol release is controlled under a given storage condition.

The tocopherol release could be controlled by altering the matrix structure of the packaging film, because the release of migrant is often limited by its molecular diffusion within the polymer matrix. Wessling et al (1999) reported that under given conditions, α-tocopherol in a polypropylene (PP) film was not released into tested liquid media, but released when incorporated within an LDPE film [51]. Our preliminary experiments also showed that the release of natural tocopherol from PP into 95% aqueous ethanol was much slower than that from HDPE, which was in turn slower than that from LDPE [6]. In addition, it was shown by scanning electron microscopy that the blend films of LDPE and PP, which are not compatible to each other, had different matrix morphology depending on LDPE/PP blending ratio [6]. It was assumed from these observations that tocopherol-impregnated LDPE/PP blend films of different blending ratios might have different tocopherol release behaviors, and accordingly the antioxidant capacity of the blend film could be modulated by changing the blending ratio. Our assumption was that by slowing the antioxidants release rate from packaging film into food, longer shelf life can be achieved by inhibiting lipid oxidation compared with instant addition of tocopherol. Table 3 summarized recent research on tocopherol containing packaging films conducted by Dr. Kit Yam and Dr. Karen Schaich's group as compared with other research groups.

Table 3 A brief summary of literature review on development of CRP

Comparison	Other Research Groups	Yam and Schaich's Group at Rutgers University
Research Approach	Mostly empirical	Systematic
Polymer used	Single polymer	Polymer blend of various polymers
Ability to control the release rate	Did not evaluate the release rate	Controlled by manipulating polymer composition and morphology
Effectiveness to inhibit lipid oxidation	Not effective compared with control films (no tocopherol)	Provided longer induction period of lipid oxidation compared with control films
Conclusion	Release rates too fast	Effectiveness determined by release rates

Summarized from references [5, 6, 42, 43, 49-55]

2.6.3 Production of CRP films by extrusion

Extrusion of plastic (synthetic) films is a process commonly used in the food packaging industry. Commercial grade synthetic polymer resin pellets are heated inside the barrel of an extruder and melted into a viscose polymer flow. The polymer melt is then pushed out of a die (narrow slot) and cooled into thin layer (with uniformed thickness) of films. Therefore, the film production by extrusion is by and large a physical processing (melting and cooling). The rational for using extrusion method to produce tocopherol containing films are four folds. First, it will be easy to scale up in the future commercial production of tocopherol containing film since the extrusion is the major commercial film production method. Second, using commercial extrusion method can produce polymer films with more uniform film properties. Third, high shear generated by screw of extruder will enhance the mixing of polymer melt and tocopherol and enhance the uniform distribution of tocopherol inside the polymer matrix. Fourth, commercial grade synthetic polymers (i.e. LDPE, PP) have very consistent and repeatable properties from batch to batch.

In this research, packaging films containing tocopherol were prepared at different blending ratios (w/w) of LDPE/PP (100/0, 25/75, 50/50, 75/25, and 0/100), using a single screw extruder (Davis-Standard, LLC., Pawcatuck, CT, USA) as shown in Figure 12 and Figure 13. For each polymer composition, tocopherol was mixed with synthetic polymer resin at a concentration of 3000 ppm, and the mixture was extruded at a temperature of 221°C and a screw speed of 70 rpm. The control films (containing no tocopherol) were also prepared for each polymer composition under same conditions.

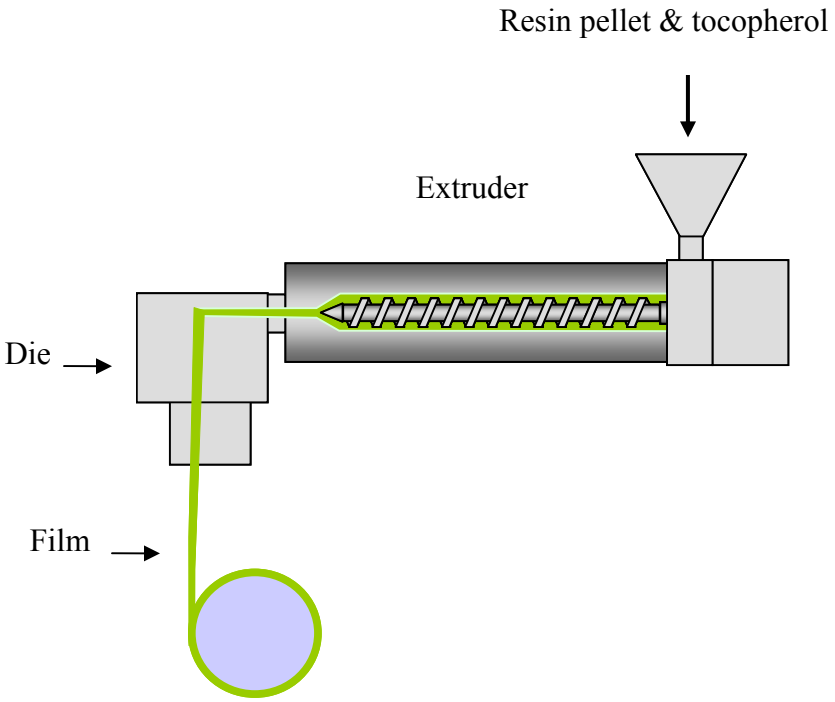


Figure 12 A schematic diagram showing film production by extrusion
Courtesy of Dr. Kit Yam

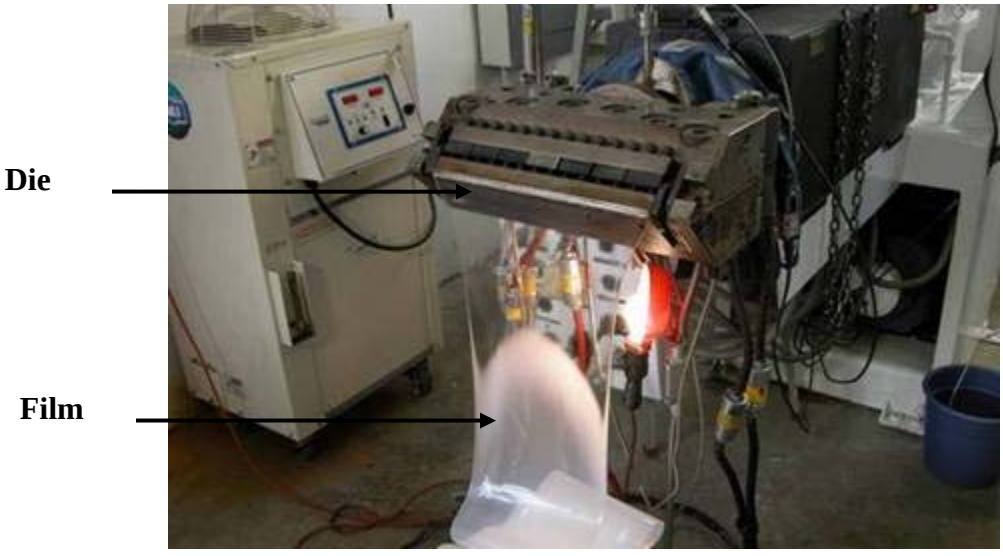


Figure 13 A picture showing polymer film coming out of die of extruder
Courtesy of Dr. Kit Yam

2.6.4 Mechanism of active compound release

Releasing of active compounds from packaging polymers into foods involves three steps: (1) diffusion within the polymer matrix; (2) mass transfer across the interface; (3) diffusion into the food (Figure 14) [56]. Within the polymers, the concentration gradient provides the driving force for diffusion of active compounds [57]. Molecular transport may be expressed by Fick's first law of diffusion [58].

$$F = -D\, dC/ dx$$

In the above equation, F is the rate of transfer per unit area (moles/s), D is the diffusion coefficient, C is the concentration of diffusing substances (moles/ cm^3), and x is the distance diffused (cm).

The rate of transfer of active compounds from polymers into foods is affected by polarity and solubility [59]. Diffusion into the bulk food matrix is driven primarily by the concentration gradient. The rate of diffusion may be affected by the state of food (liquid and solid). The rate of diffusion is faster in liquid foods than solid food.

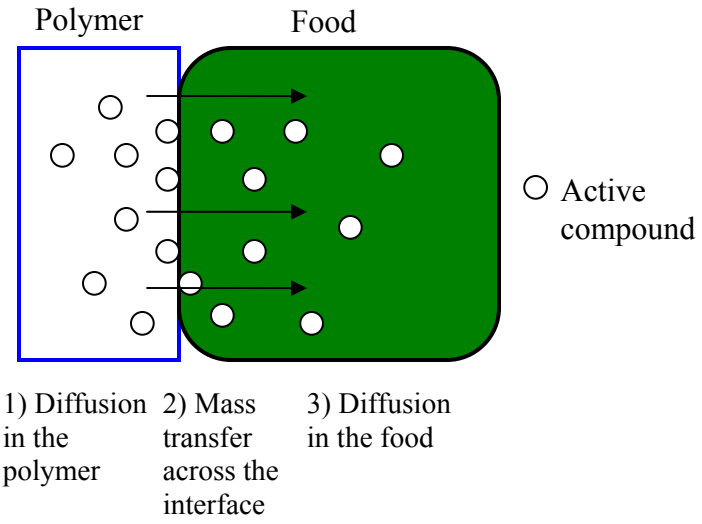


Figure 14 A hypothetic illustration of active compounds diffusion
Adapted from Noe Obinata, 2006.

2.6.5 Factors affecting the release of antioxidant from polymer matrix

The release of active compounds is influenced by the chemical nature of the active compounds (molecular weight, volatility, and polarity), polymer characteristics (density, crystallinity, and glass transition temperature), environmental conditions (temperature and moisture), and contact between polymer (film) and food.

The active compounds pass through the open spaces in the polymers, so the molecular weights of the active compounds will affect their diffusivity in the polymers. Wessling et al. (1998) compared the release of BHT (MW: 220) and α-tocopherol (MW: 431) from LDPE films into liquid fatty food simulants. BHT decreased much faster than tocopherol in the films because BHT is smaller; while α-tocopherol is less mobile in the polymers due to its higher molecular weight [54].

Polymer characteristics include density, crystallinity, glass transition temperature (Tg), etc. These characteristics are determined by chemical structure, molecular weight, branching of the polymers, as well as polymer processing history. Usually, linear chain polymers like HDPE, which has few branches, can pack together closely so that sufficient intermolecular force can develop to hold the chains in a crystal lattice. This crystalline region hinders the invasion of the diffusing compounds. Active compounds therefore have lower diffusivity in the higher crystallinity polymers. Marcato et al. reported that crystallinity of polymers greatly affected the release rates of antioxidants into a fatty food simulant. The release rates of antioxidants were in the order of amorphous ethylene-propylene copolymer (crystallinity 30%) > PP (crystallinity 52%) > HDPE (crystallinity 70%) [60]. Tg is an important factor affecting release rate. Below Tg, polymer molecules are stiff (glassy state) and mobility of polymer chains is restricted. On the other hand, polymer molecules are flexible (rubbery state) above Tg. Therefore, higher temperatures increase polymer mobility and diffusivity of compounds [61, 62].

Environmental conditions, which affect release of active compounds, include temperature, agitation (shaking), food contact, and etc. For example, the release rate of active compounds will increase at higher temperatures.

3 CONCEPT OF TARGET RELEASE RATE

3.1 Conceptual framework for CRP

After five-year exploratory research on developing controlled release packaging (CRP), Yam and Schaich at Rutgers University have developed a conceptual framework for designing CRP. This framework represents a systematic research approach for CRP development which includes four components: composition, processing, structure/morphology, and properties (Figure 15) [5, 6]. This conceptual framework provides a clear research map to guide the research on CRP to achieve better controlled release of active compounds and applications of CRP in food. Part of the conceptual framework has been published by Lacoste et al. of our research group [5].

In the conceptual framework for CRP, there are four important variables: process, structure, property, and food variables. The first three variables are under the scope of packaging research. Food variables belong to food research. There is an important factor called target release rate (between number 6 and 7), which serves as an important connection between packaging research and food research.

Process variables are related to the factors involved in the production of CRP and can be controlled through experimental conditions. Active compounds, polymer compositions, and processing methods are considered to be process variables. The processing methods include conventional methods (cast film extrusion and blown film extrusion) and an innovative polymer blending method (smart blending based on the science of chaotic advection). Processing methods may also include the polymer

processing conditions such as processing temperature, screw type, and screw rotation speed of extruder.

Structure variables refer to polymer morphologies and distribution of active compounds in the polymer matrix. It should be pointed out that structure variables are dependent on the process variables. Morphologies are defined in our lab as the micro scale structures of the packaging polymers developed by polymer blending, including the thickness of polymer layers, the size of polymer droplets, and the dimensions of interfaces between the two polymers. Distribution of the active compounds refers to the dispersion of the active compounds in the packaging polymers.

Property variables refer to the release properties of the active compounds from films into the food or food simulant. Controlling the release properties through the manipulation of the process variables and understanding of structure variables have been investigated by Obinata and Lacoste of our group [6, 53]. Packaging properties (heat seal strength, tensile strength, and gas barrier properties) and stability of the active compounds have been taken care of by our group and Pliant Company under the scope of the overall research project.

Food variables are the factors that affect the target release rate which is needed for the active compounds. Food variables include: food composition, contact between food and packaging, storage conditions (temperature, RH and light) for food products, and the required shelf life. Food variables are important factors in determining the target release rate.

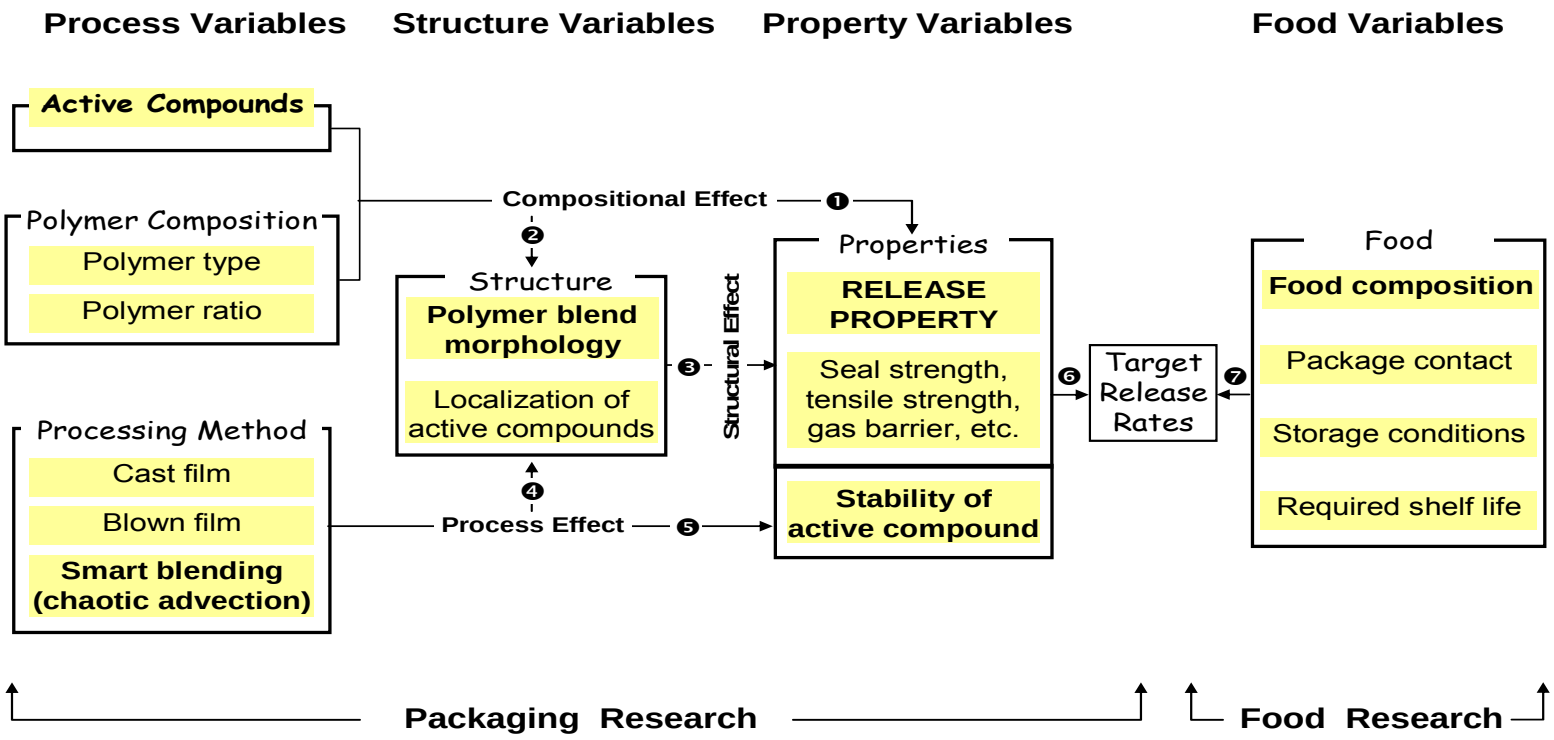
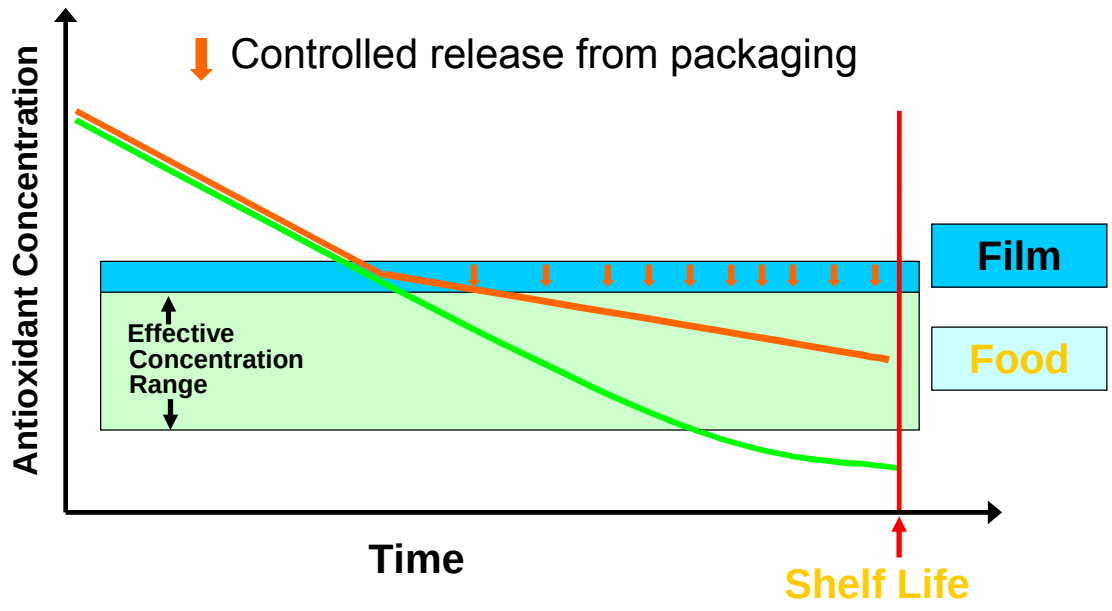


Figure 15 The conceptual framework for developing CRP

Adapted from Yam et al. [5]

3.2 Definition of target release rate

In controlled release antioxidant packaging, the target release rate has been defined by our group as the rate at which antioxidant must be released from the packaging into the food in order to maintain an adequate concentration of antioxidant by replenishing that which is consumed, and therefore inhibiting active lipid oxidation until the end of the desired shelf-life. Simply speaking, we are targeting the release rate of antioxidants from packaging for different food under different storage conditions.



Green line means instant addition. Orange line means controlled release.

Figure 16 A hypothetic illustration of concept of target release rate

Here is an example to explain the concept of target release rate as shown in Figure 16. It is required to protect packaged peanuts from lipid oxidation in a long term storage.

Tocopherol is added during food processing (instant addition). A most common scenario is that at the beginning of the storage, there is more tocopherol than actually needed. Over time, tocopherol will be consumed. Therefore, there may not be sufficient the tocopherol in the peanut after a curtained period of time. When the concentration of tocopherol drops below a critical level, oxidation will take off and shelf life will shorten. However, if tocopherol can be released into the peanuts continuously from the packaging so that the concentration of the tocopherol is maintained within an effective range, protection can be provided over greatly extended periods. And there should be a desirable release rate (or a range of release rates) which can provide a maximum protection over an extended period of storage. The above desirable release rate is the target release rate which we are discussing.

Research results of Dr. Kit Yam and Dr. Karen Schaich's lab demonstrate that we are able to develop the polymer films with a wide range of tocopherol release rates [6, 37]. The author has also conducted food research to determine the shelf life of food products such as cereal, peanut, peanut butter and cheese spread. However, there is a missing link between our packaging research and food research. That is, what should be the release rate of tocopherol being built into a packaging film for a certain food product? For example, we want to extend the shelf life of a peanut butter to 3 years at 25°C. By studying the food lipid oxidation kinetics, it is found that a release rate of 20 μg of tocopherol per day is needed in order to prevent the active lipid oxidation (this is an arbitrary number just as an example). Then, packaging film, which can release the tocopherol at 20 μg per day, can be produced by using the technology such as polymer blending. Here, the release rate of 20 μg per day from the packaging into the food in

order to achieve the desired shelf life is the target release rate we are trying to determine. Therefore, target release rate is an important factor to fill the research gap between food research and packaging research. And it is critical for the success of the controlled release packaging technology.

3.3 Importance of target release rate

This dissertation is going to define the concept of target release rate and develop systematic approaches to determine target release rate, which will build a connection between packaging research and food research (Figure 17). This connection is critical for the success of the development of CRP technology. Based on our knowledge up to date, the concept of target release rate is new and has not been investigated in the food science area and therefore may contribute to the development of science of controlled release for food industry. Target release rate is also important for other applications such as drug delivery.

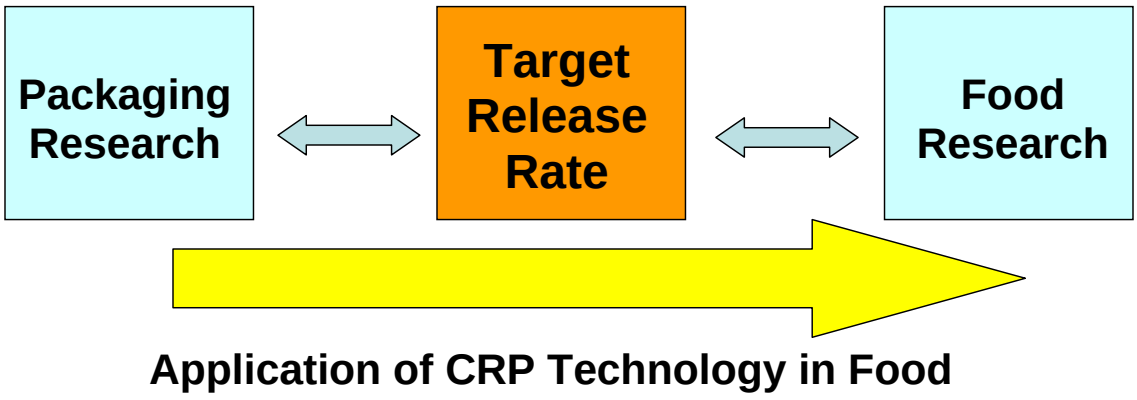


Figure 17 Target release rate is the connection between packaging and food research

3.4 Factors affecting target release rate

In real food system, target release rate may be affected by many factors which can be categorized as food factor, packaging factor and environmental factor. The food factor includes food composition, initial antioxidant load, types of antioxidants, metal chelators, food structure and type (solid, semi-solid, and liquid), etc. The packaging factor includes type of the packaging materials, permeability, morphology, release property, and etc. The environmental factor includes temperature, oxygen, light, etc. All these factors mentioned above may contribute to the determination of target release rate as shown in Figure 18.

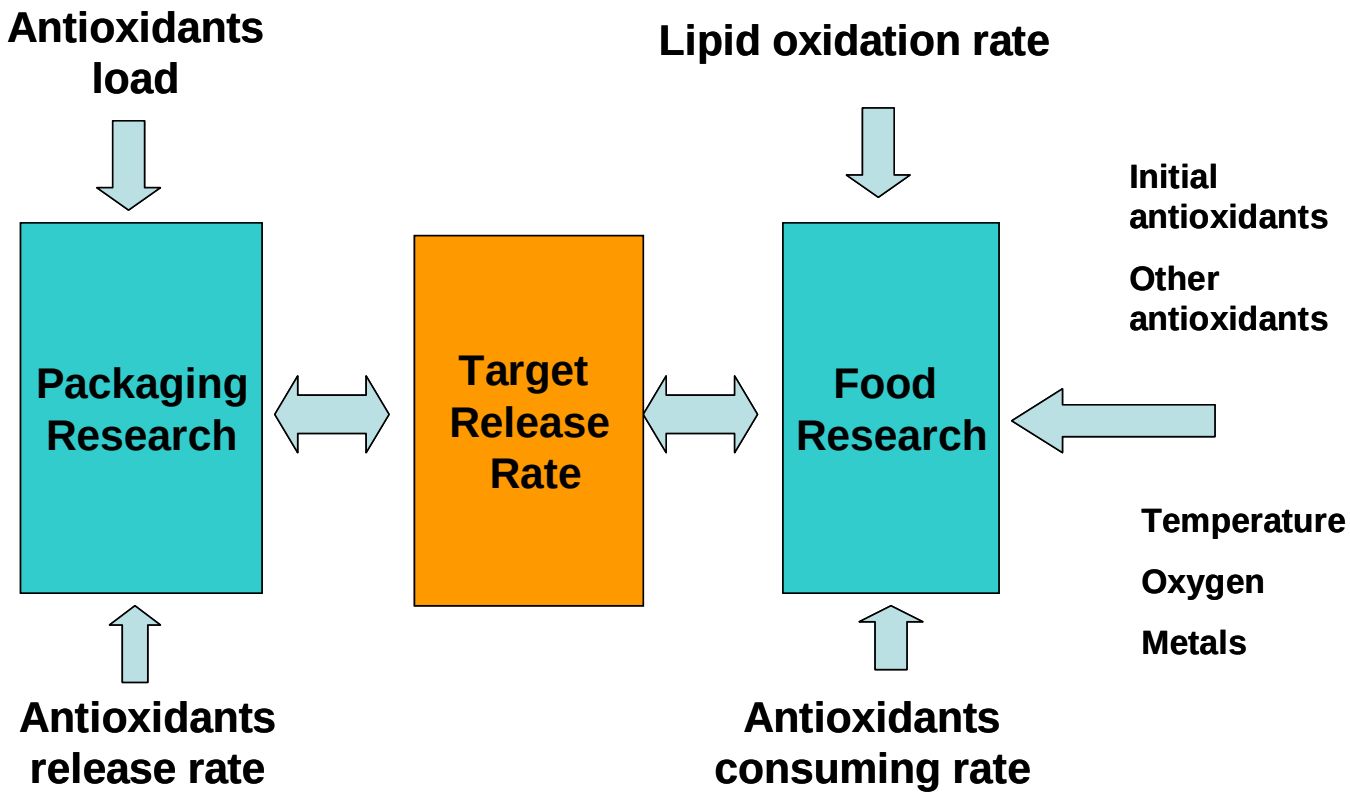


Figure 18 Factors determine target release rate

3.5 Approaches to determine target release rate

3.5.1 Using food model system

Based on the simplicity, easy of analysis and relevance, we selected linoleic acid (one of the major components of unsaturated food oil) as a model food system. Tocopherol will be delivered at pre-determined rate into linoleic acid. Lipid oxidation and tocopherol consumption will be measured to determine target release rate (Figure 19).

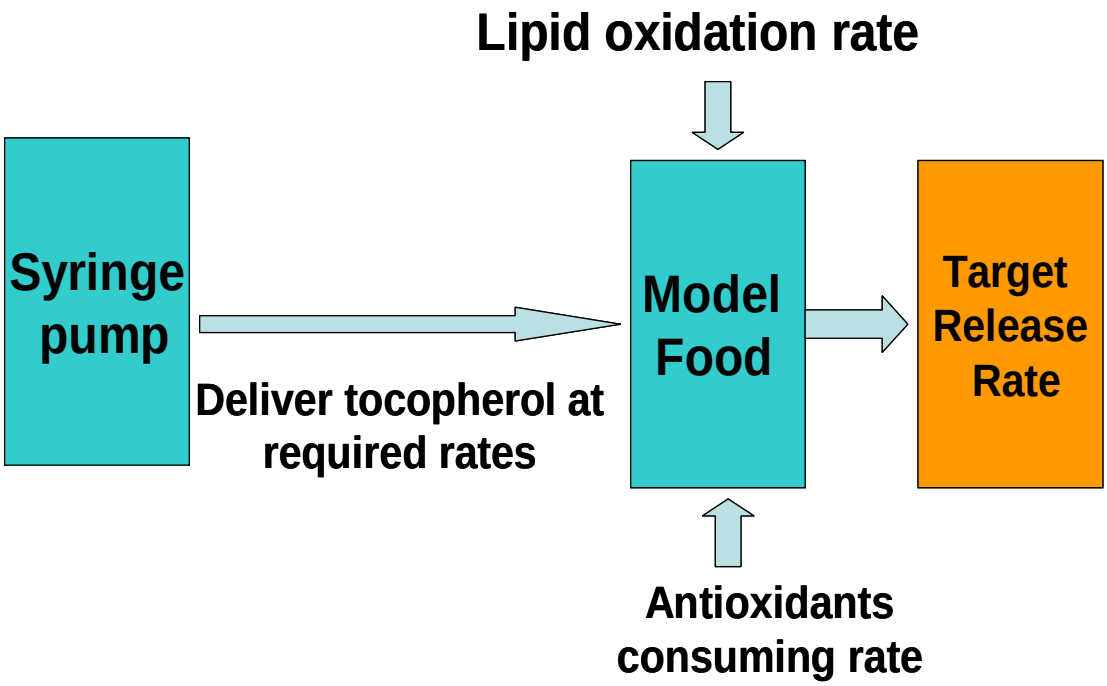


Figure 19 Determine target release rate using food model system

3.5.2 Determine target release rate using syringe pump

We propose two approaches to determine the target release rate. The first approach is a direct approach using a syringe pump. Tocopherol will be delivered into a food (linoleic acid) at different rates. The rate which can provide the longest induction period will be considered as the optimum release rate (hence the **target release rate**). Figure 20 and Figure 21 is the illustration of the syringe pump experimental set up. Detailed information about this approach will be discussed in Chapter 10.

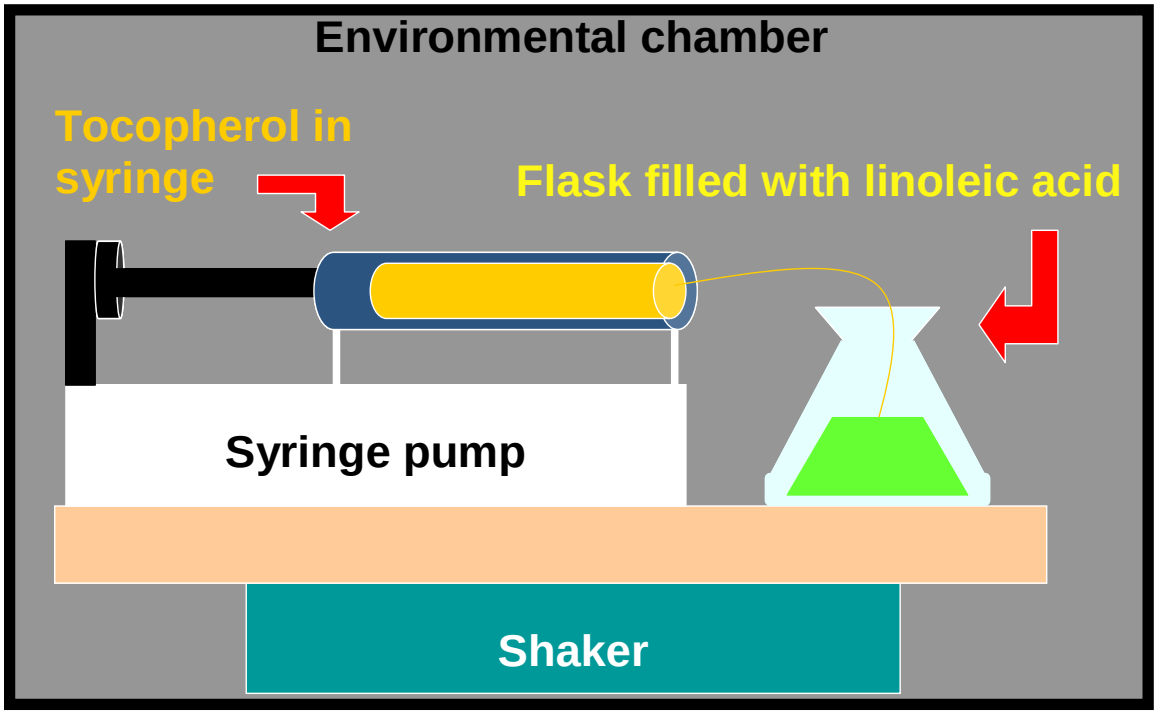


Figure 20 Delivery of tocopherol into linoleic acid using a syringe pump

Figure 21 A syringe pump was used to release tocopherol

3.5.3 Determine target release rate by matching tocopherol degradation

The second approach to determine target release rate is an indirect approach by matching the degradation rate (consumption rate) of tocopherol. The idea is: if we can determine how much and how fast tocopherol is consumed in a certain food system, we can release the tocopherol at similar rate to replenish the degraded tocopherol. In this case, we assume that target release rate is equal to the tocopherol degradation rate. In order to determine the degradation rate, different concentrations of tocopherol are put into linoleic acid (instant addition). The changes of tocopherol concentrations in linoleic acid are measured over time. The degradation kinetics of tocopherol can be obtained as shown in Figure 22. Using the law of addition, we can extrapolate the degradation kinetics from instant addition mode to slow release mode. We have also conducted experiments at different temperatures so that we can predict the target release rate at different

temperatures based on Arrhenius equation. Detailed information about this approach will be discussed in Chapter 10.

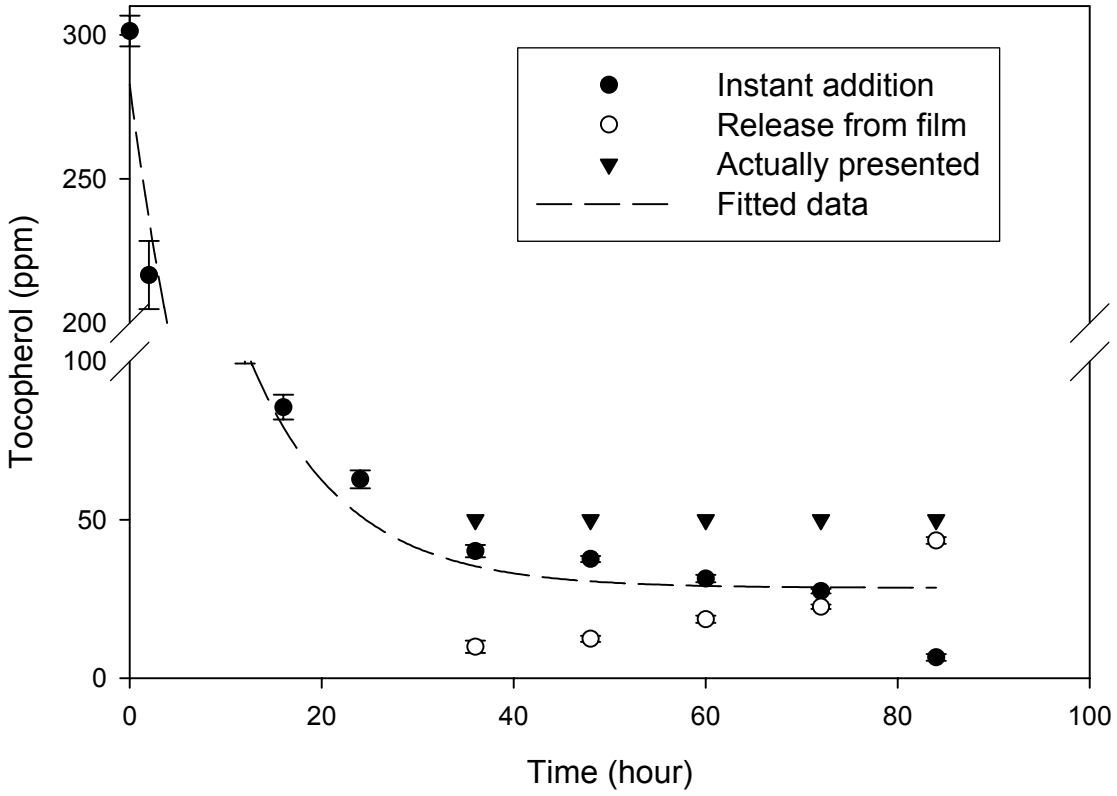


Figure 22 A hypothetic illustration of degradation and replenishment of tocopherol in model food system

3.5.4 Integrating the data using mathematic modeling

Once we acquire the kinetic data of lipid oxidation, tocopherol release and tocopherol degradation, we need to build a mathematic model to determine the target release rates under different conditions. As shown in Figure 23, we will have an input function model. Once we factor in the independent variables, such as temperature and oxygen concentration, we will be able to predict the dependant variable, the target release rate. Finally, the determined target release rate can be built into the packaging films.

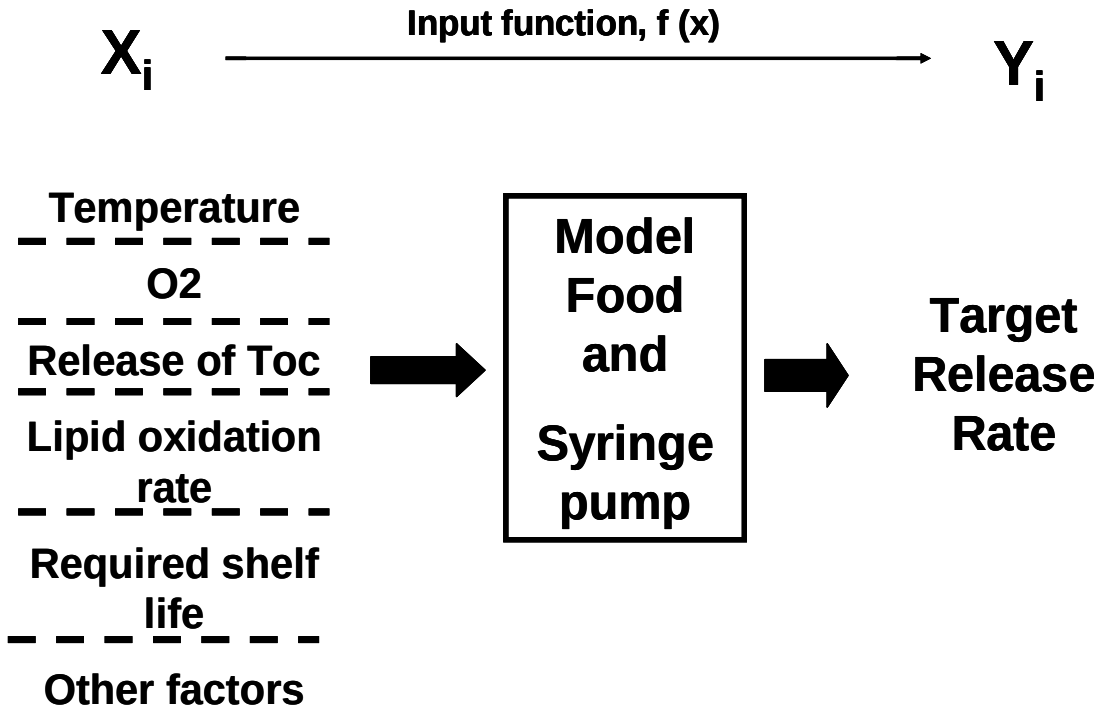


Figure 23 A hypothetic mathematic model for determining target release rate

3.6 Verify model food system results with real food items

Data from a model food system may prove the concept and provide justification for controlled release and CRP technology. However, the above concept, which is developed by using a model food system, needs to be verified with a real food products such as MRE cheese spread, peanut, peanut butter and chicken.

4 OBJECTIVES

4.1 Assumptions

The assumption for controlled release antioxidant packaging is that slow release of antioxidant may provide more beneficial effects to inhibit lipid oxidation than instant addition. If this assumption is true, it will lead to the second assumption that it is necessary to define a new concept of target release rate. The target release rate is a critical yet missing link between packaging research and food research in the conceptual framework (Figure 15).

4.2 Objectives

Our long term research goal is to develop the controlled release packaging to enhance food quality and safety. As a part of the whole controlled release packaging project, this dissertation focuses on investigating the relationship between packaging research and food research (pathway 6 and 7 in the conceptual framework in Figure 15) by defining and determining the target release rate. The innovative concept of target release rate is critical for determining at what rates active compounds should be released to enhance the safety and wholesomeness of the food products.

The overall objective of this dissertation research is: (1), to prove the assumption that slow release of antioxidant may provide more beneficial effects to inhibit lipid oxidation than instant addition. (2), to develop a systematic approach to define and determine target release rate of antioxidant for controlled release packaging—this is an optimum rate at which an antioxidant must be released from a food package to replenish antioxidant in food

that is consumed in reaction, thereby maintaining an adequate antioxidant concentration and inhibiting active lipid oxidation until the end of product shelf life.

4.3 Specific Tasks

- Define the concept of different delivery modes and rates; prove the assumption that slow release over time (timed delivery) has better effect on inhibiting lipid oxidation than instant addition.
- Develop a precise syringe pump method to deliver tocopherol into a food to generate kinetic data on lipid oxidation and tocopherol degradation (consumption).
- Define and determine the target release rate using data generated from syringe pump.
- Develop the packaging films (containing tocopherol, sesamol and etc.) made from different polymers and polymer blends.
- Characterize the film physical properties and correlate with release rates of antioxidants.
- Investigate the possible mechanism why timed delivery (slow release) of antioxidant resulting in a better effect in inhibiting lipid oxidation.
- Test the real food products (peanut butter, cheese spread) to evaluate the controlled release packaging films.
- Test other active compounds such as sesamol to investigate the effect of properties (such as volatility) of the active compounds.

- Provide approaches and justification for future research work to develop CRP and the target release rate.

5 EXPERIMENTAL DESIGN

5.1 Materials

A natural tocopherol product extracted from soy bean containing α, β, γ, and δ-tocopherol was donated by Cargill Inc. Barefoot polymer resins (resin without added antioxidant) low density polyethylene (LDPE), polypropylenes (PP), high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and ethylene-vinyl acetate (EVA) were provided by Pliant Co. (Chippewa Falls, WI, USA). Some of the characteristic information of resins used was summarized in Table 4. Sesamol (98%), linoleic acid (99%) and all organic solvents (HPLC grade) were purchased from Fisher Scientific Inc. (Suwanee, GA, USA). Butyl hydroxytoluene (BHT, 99%), hexanal (99%) and 2-methyl-pentanal (98%) were purchase from Sigma-Aldrich Co. (Milwaukee, WI USA). Commercial-type oatmeal cereal product, cheese spread, peanut butter and peanut were obtained from Plaint Co. (Chippewa Falls, WI, USA). The cereal product was formulated to contain no incorporated antioxidants.

Table 4 Data on synthetic polymer resins used in this research

Polymer	Density (g/cm^3)	MW (Dalton)	Crystallinity (%)	Tg (K)
LDPE	0.91-0.94	$3\text{-}40*10^4$	33-53	140-170
LLDPE	0.915-0.925	N/A	33-53	N/A
HDPE	>0.941	$1*10^3\text{-}8*10^6$	35-90	140-153
PP	0.95	$10\text{-}60*10^4$	50-70	275-284
EVA	0.93-0.95	$11\text{-}13*10^4$	N/A	231-235

Adapted from Polymer data handbook [63] and Obinata [6].

5.2 Experimental design to determine target release rate

The experimental design for determine target release rate was described in Figure 24. Natural antioxidant, tocopherol, was used as a model of active compounds. Tocopherol was delivered into the simulated food (linoleic acid) using different delivery modes and different delivery rates (release rates). Lipid oxidation of linoleic acid occurred under different environmental conditions such as different temperatures. The lipid oxidation was inhibited by tocopherol as a function of tocopherol delivery modes and rates. The effectiveness of different tocopherol delivery modes and rates was evaluated by measuring the induction period of lipid oxidation (Figure 25). The longer the induction period was, the better the effectiveness of tocopherol delivery modes and rates were. The delivery rate that provided the longest induction period was defined as the target release rate (optimum delivery rate of antioxidant). An alternate approach was to match the tocopherol degradation (consumption) rate.

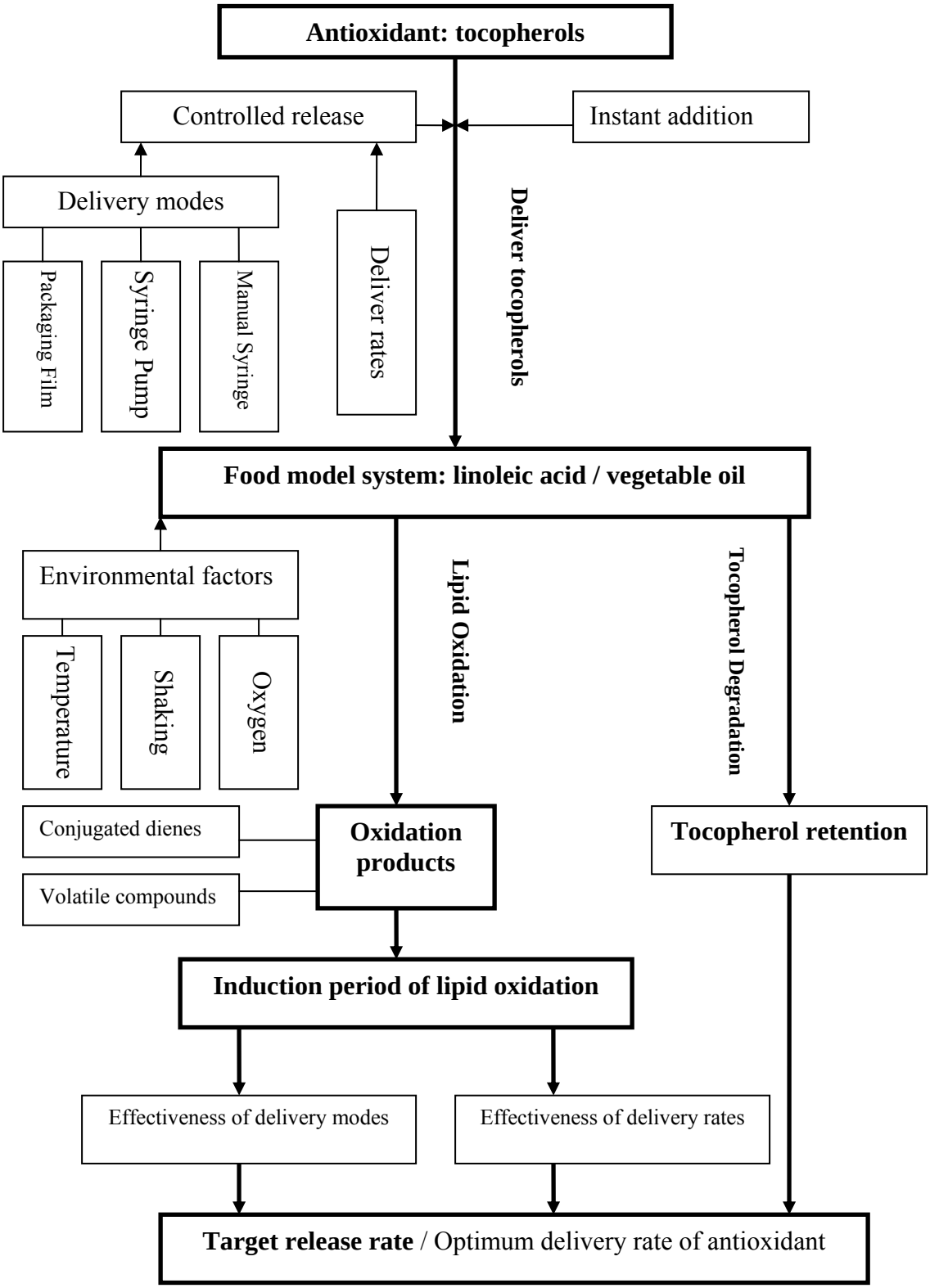
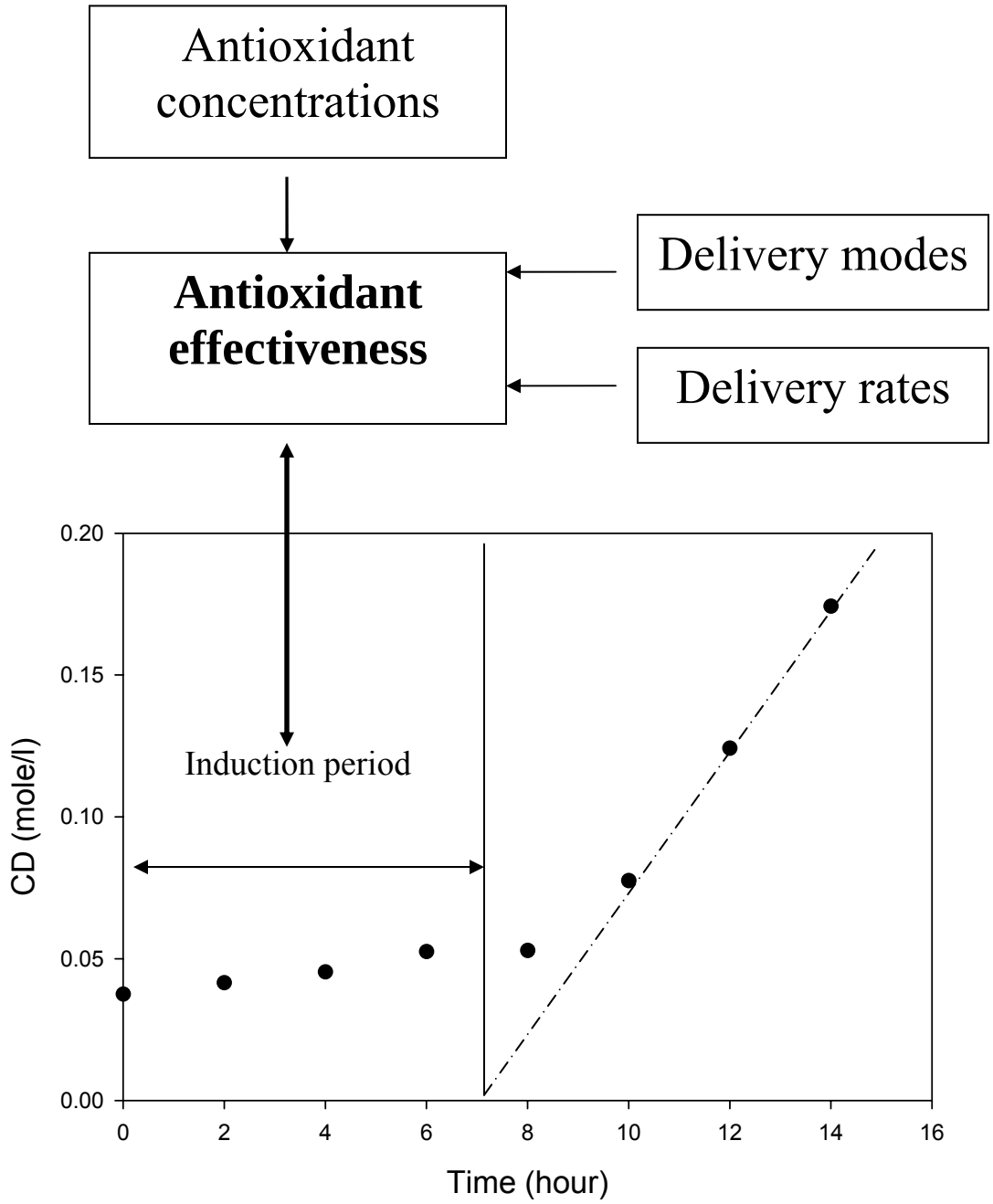


Figure 24 Experimental design for determine target release rate



CD stands for conjugated dienes.

Figure 25 Evaluate the effectiveness of antioxidant

5.3. Food model system

In this study, linoleic acid was used as a simulated food to evaluate the antioxidant effectiveness of tocopherol as functions of different delivery modes and rates. Linoleic acid was chosen because it is the major component of vegetable oil. The experiment setup was developed based on the methods used by Wessling et al. [49] and Farhoosh et al. [64]. Linoleic acid (10.0g) was put into a 250 ml Erlenmeyer flask. The flask was exposed to air in dark under constant rotary shaking (100 rpm) controlled by a digitally controlled shaker (C25KC, New Brunswick Scientific, USA). The reaction temperatures were controlled by an environmental chamber (Lab-line, IL, USA). Since linoleic acid layer was very thin under constant agitation, it was assumed that lipid oxidation occurred in a kinetics regime. At a high oxygen concentration (saturated), the diffusion rate of oxygen into linoleic acid did not influence the oxidation rate. The linoleic acid samples were withdrawn periodically and checked by UV spectrophotometer (234nm), gas chromatography and viscometry to monitor the lipid oxidation progress. The induction period of lipid oxidation was determined to evaluate the effectiveness of anti-oxidation with varying delivery modes and delivery rates. Tocopherol concentration in linoleic acid over time was also measured by HPLC.

5.4. Real food products

Real food products including oatmeal cereal, cheese spread, peanut, and peanut butter were tested during our study to evaluate the effectiveness of controlled release packaging films.

For the cereal test, a cereal product was made of oatmeal without adding antioxidants. Film A (control film without antioxidant), Film B (containing 646.1±18.3 ppm sesamol) and film C (containing 1605.5±29.2 ppm BHT) were fabricated into flexible uniform sized pouches (30 cm*22 cm). Each pouch contained 200g of cereal products which were made from oatmeal. The pouches were then heat sealed with an impulse sealer (12AS, Sencorp System, Inc., Hyannis, MA, USA). All the pouches were stored in a chamber at 23°C in dark. After 1 year, hexanal concentration in cereal samples was measured by GC. Internal sensory evaluation was also carried out to compare the odor of cereal samples with different packaging.

For the cheese spread test, three different films were produced at the Pliant Pilot Plant using commercial scale extrusion line. The first film was the control film without any antioxidants added. The second film was a 100% PP film containing 3000 ppm of tocopherol. The third film was a polymer blend of PE and PP with 3000 ppm of tocopherol. The above films were laminated into aluminum foil and then fabricated into pouches. The cheese spread was packed at Portion Pac (Georgia), the current and the only supplier of this product to the military. The pouches were stored at three temperatures (60, 40 and 23°C) and samples were drawn periodically for each temperature (60°C: every week, 40°C: every 2 weeks, and 23°C: every 4 weeks) to determine the progress of the lipid oxidation.

For the peanut test, three different films were produced at the Pliant Pilot Plant using commercial scale extrusion line. The first film was the control film without any antioxidants added. The second film was a 100% PP film containing 3000 ppm of tocopherol. The third film was a polymer blend of PE and PP with 3000 ppm of tocopherol. The above films were laminated into aluminum foil and then fabricated into pouches. Two

types of peanuts (dry peanut and oil roasted peanut) were filled into the pouches and heat sealed. The pouches were stored at three different temperatures (60, 40 and 23°C). Samples were taken periodically for chemical analysis to determine the progress of the lipid oxidation and the shelf life of the peanuts.

5.5. Deliver tocopherol by different modes and rates

5.5.1. Instant addition

The tocopherol stock solution (1%) was made by dissolving tocopherol (1.000g) into 100 ml methanol. The tocopherol stock solution was then flushed with nitrogen gas and stored at -18°C before use. For instant addition, the tocopherol stock solution was added into a 250 ml Erlenmeyer flask containing linoleic acid all at once at time zero. No more tocopherol solution was added after that. The flask was exposed to the air in the darkness under constant rotary shaking (100 rpm) in an environmental chamber using two temperatures (40°C and 23°C). The linoleic acid samples were withdrawn periodically and checked with UV spectrophotometer (234nm) and viscometer to monitor the lipid oxidation progress.

5.5.2. Timed-release (slow release)

The timed-release (slow release) modes include using manual syringe, syringe pump and tocopherol containing films. See definition of the terms in Chapter 3.

In slow release, the tocopherol stock solution (1%) was added into a 250 ml Erlenmeyer flask containing linoleic acid continuously or at different time intervals. The flask was exposed to air in dark place under constant rotary shaking (100 rpm) in an

environmental chamber using two temperatures as 40°C and 23°C. The linoleic acid samples were withdrawn periodically and checked by UV spectrophotometer (234nm) and viscometer to monitor the lipid oxidation progress.

5.5.2.1. MANUAL SYRINGE DELIVERY OF TOCOPHEROL

Several doses of the tocopherol stock solutions (1%) were manually added into food (linoleic acid) by using syringe at different time intervals for several times.

5.5.2.2. SYRINGE PUMP DELIVERY OF TOCOPHEROL

The tocopherol stock solutions were withdrawn into a 3 ml syringe. The syringe was then mounted on a digitally controlled syringe pump (New Era Pump Systems, NY, USA). The tocopherol solution was continuously injected into the linoleic acid by using the syringe pump. The delivery rates (release rates) were controlled by the syringe pump.

5.5.2.3. DELIVERY BY TOCOPHEROL CONTAINING FILMS

The polymer film (1.0g, contains 3000 ppm tocopherol) was cut into 1cm × 1cm square pieces and immersed into 10.0 grams of linoleic acid in a 250 ml Erlenmeyer flask. The control samples were prepared by adding 3000 ppm tocopherol into 10.0 grams of linoleic acid as well as one gram of films containing no tocopherol.

5.6. Production of tocopherol containing films

Tocopherol containing films were produced from a single screw extruder (Davis-Standard, Pawcatuck, CT., USA) using various synthetic polymers and polymer blends. Barefoot polymer resins without any antioxidants were used to simplify the analysis. Tocopherol was pre-mixed with the polymer resin before extrusion. The die

temperature was set at 430F. With a screw speed of 70 rpm, films with a thickness of 75 μm were obtained. The control films for each polymer composition were produced with the same conditions without adding tocopherol. All films were produced at Pliant Corporation (Chippewa Falls, WI, USA). Formulations of tocopherol containing films were summarized in Table 5.

Table 5 Formulation of tocopherol containing films

No.	Film Name	Film Composition	Added Tocopherol
1	A	100% LDPE	3000 ppm
2	B	75% LDPE 25% PP	3000 ppm
3	C	50% LDPE 50% PP	3000 ppm
4	D	25% LDPE 75% PP	3000 ppm
5	E	100% PP	3000 ppm

Films were produced at Pliant Co., WI, USA.

5.7. Analytical methods

5.7.1. Analytical methods for evaluating lipid oxidation

The analytical methods for evaluating the lipid oxidation were summarized in Figure 26.

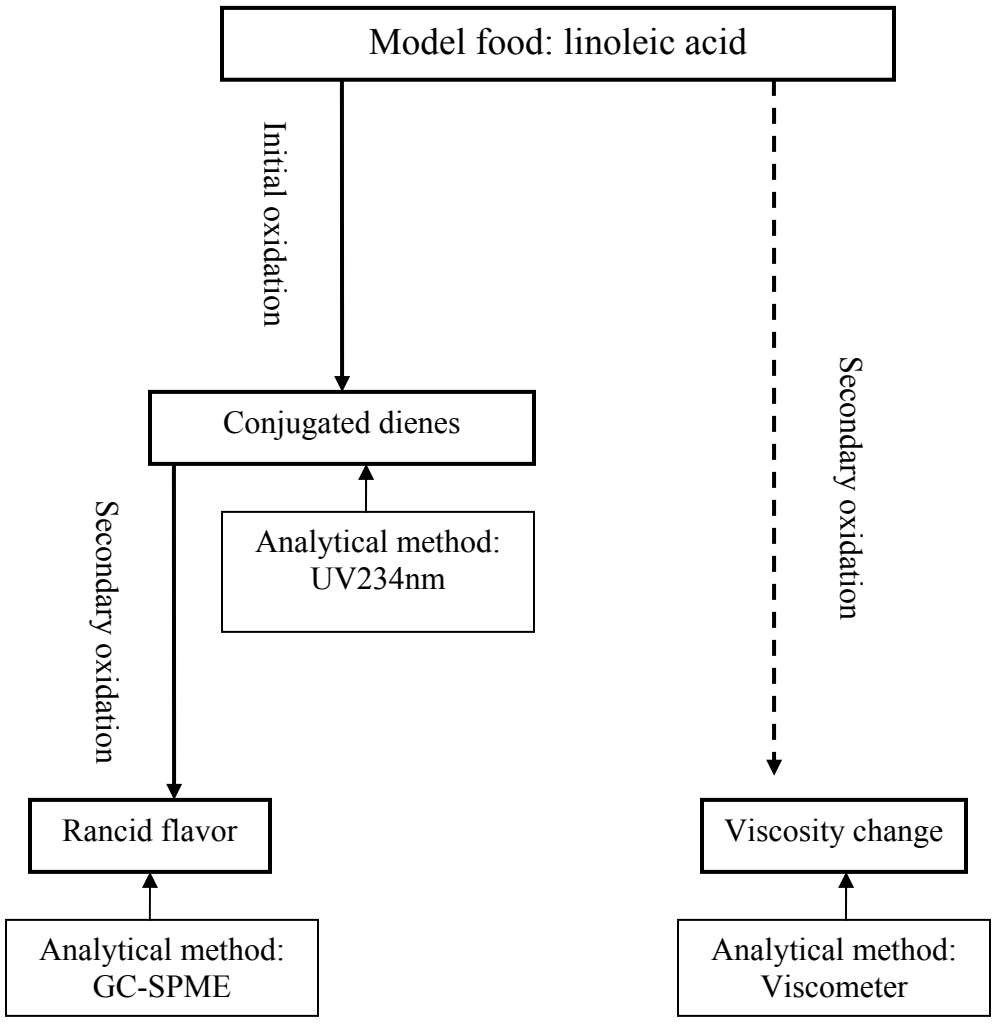


Figure 26 Analytical methods for evaluation of lipid oxidation

5.7.1.1. MEASUREMENT OF CONJUGATED DIENES

The method based on Shaker et al. [65] and Ng et al. [66] was employed to measure the conjugated dienes in linoleic acid. The linoleic acid sample (0.010g) was dissolved in 5ml cyclohexane and the absorbance of the solution was measured at 234nm using UV-visible spectrophotometer (UV1700, Shimadzu, Japan). Concentration of conjugated dienes (mol/l linoleic acid) was calculated based on molar absorptivity of 26,000 l/mol.cm.

5.7.1.2. MEASUREMENT OF HEXANAL (RANCID ORDO)

A SPME (solid phase micro-extraction) GC method developed by Nigel et al. and Okabe et al. was modified and adapted to determine the concentration of hexanal in the food samples [67, 68]. Food sample (1.0 g) was put into a 20 ml headspace vial and immersed in a water bath (70°C). SPME fiber (carboxen/PDMS, Supelco, USA) was injected into the vial for 5 minutes and then injected into the GC (Agilent 6890N, Agilent Inc., USA) with a FID detector and a HP5 capillary column (60m, ID 0.32mm, J & W Scientific Inc., USA). Initial oven temperature was 80°C (holding 1 minute). The oven temperature was raised with a rate of 8°C / minute to temperature 180°C (holding 1minute). After that, the oven temperature was raised to 250°C (holding 5 minute) to equilibrium the column before next injection. Nitrogen was used as the carrier gas with a flow rate of 1 ml/minute. Hexanal (99%) and 2-methyl-pentanal (98%) were used as internal standards to identify and calculate the concentration of hexanal. The concentration of hexanal in the cereal was expressed as micromole of hexanal in per kilogram of cereal (μmole/Kg).

5.7.1.3. MEASUREMENT OF VISCOSITY OF LINOLEIC ACID

The viscosity of linoleic acid was measured using a viscometer (Brookfield, MA, USA) at 23~25°C (room temperature). The 2# spindle was used with a rotational speed of 100 rpm [22].

5.7.1.4. MEASUREMENT OF TOCOPHEROL CONCENTRATION IN LINOLEIC ACID

A HPLC method was developed to analyze the tocopherol concentration in linoleic acid. The linoleic acid interfered with the separation and detection of tocopherol because the linoleic acid also has a very strong UV absorption at 295nm. To achieve a better separation of tocopherol from linoleic acid, 1% NH_4OH was added into HPLC mobile phase (97% MeOH, 2% H_2O) in order to neutralize the linoleic acid. The linoleic acid reacted with NH_4OH and became very polar (forming salt) and then washed away with water. The tocopherol did not react with NH_4OH and bonded to the column. The four tocopherol homologues (α-, β-, γ-, and δ-tocopherol) were detected at 295 nm and quantified using their standards (99%, Calbiochem Inc., Darmstadt, Germany). The concentration of tocopherol was obtained by adding the concentrations of the four homologues.

5.7.2. Analytical methods for tocopherol containing films

The analytical methods for evaluating tocopherol containing films were summarized in Figure 27.

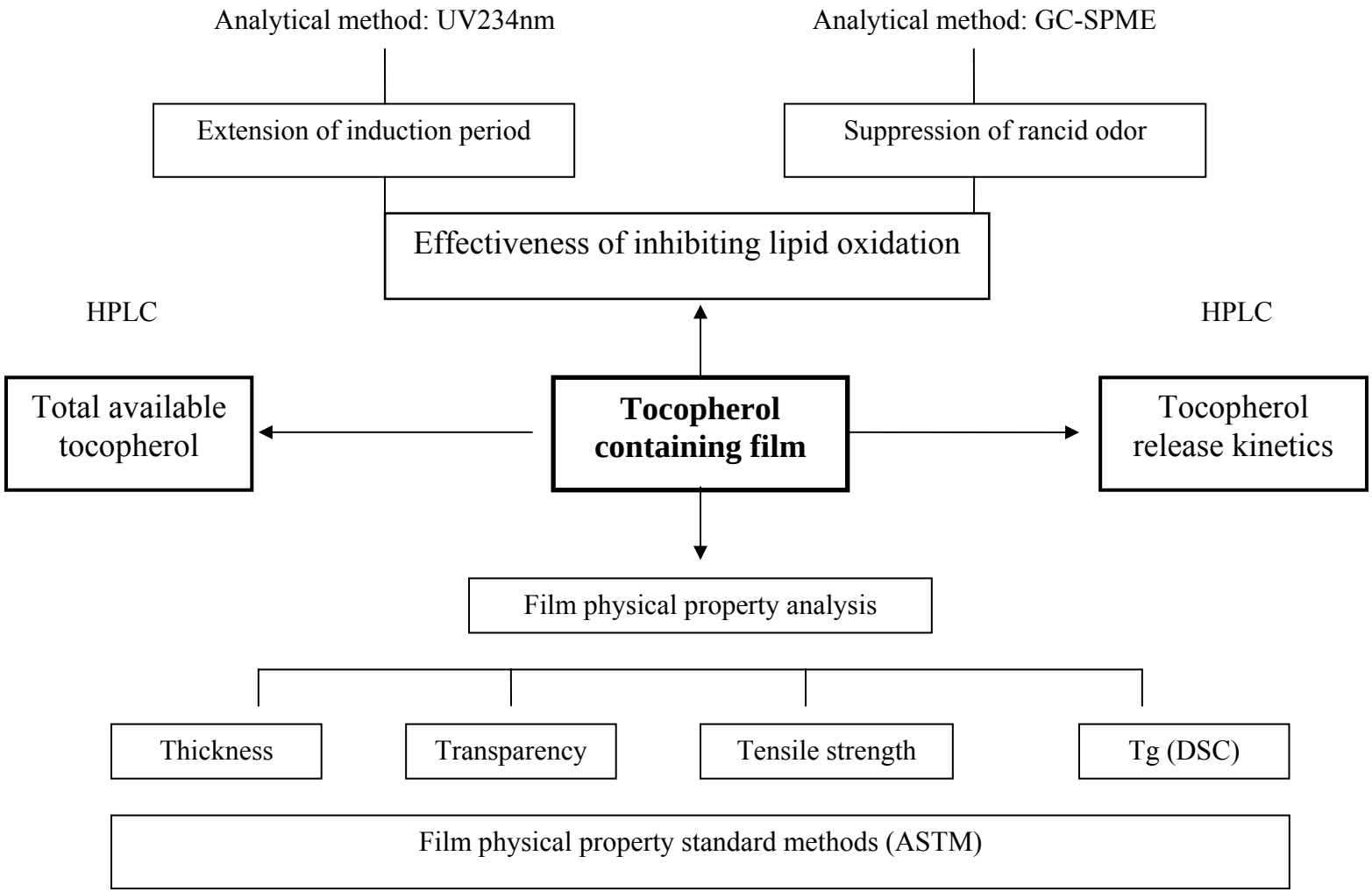


Figure 27 Methods to evaluate the release and anti-oxidation properties of tocopherol containing polymer films

5.7.2.1. TOTAL EXTRACTION OF TOCOPHEROL FROM FILMS

Solvent extraction studies were conducted to examine the total availability of tocopherol which has been incorporated into the films. Extractable tocopherol was defined as

$$\text{Extractable tocopherol (\%)} = \frac{\text{Extracted tocopherol}}{\text{Tocopherol originally added to film}} \text{ x } 100$$

The film (1.0g) was cut into 1cm × 1cm square pieces and immersed in 40 ml of methylene chloride in a 125 ml Erlenmeyer flask. The flask was shaken at 100 rpm and stored at 37°C using an incubator (C25KC, New Brunswick Scientific, USA). The liquid samples were withdrawn periodically and diluted with methanol and injected into HPLC. The four tocopherol homologues (α-, β-, γ-, and δ-tocopherol) were detected at 295 nm and quantified using their standards (99%, Calbiochem Inc., Darmstadt, Germany). The concentration of tocopherol was obtained by adding the concentrations of the four homologues.

5.7.2.2. DETERMINE THE TOCOPHEROL RELEASE KINETICS FROM FILM INTO SOLVENT

Flask release studies were conducted to examine the tocopherol release kinetics of obtained films. Ethanol (95%) was selected as a food stimulant according to FDA 2002 guidelines for release studies from food-contact packaging materials [69]. The film (1.0g) was cut into 1cm × 1cm square pieces and immersed in 40 ml of ethanol (95%) in a 125 ml Erlenmeyer flask. The flask was shaken (100 rpm) at 40°C and 23°C (room temperature) using an incubator (C25KC, New Brunswick Scientific, USA). The liquid samples were

withdrawn periodically and were injected into HPLC. Samples might be diluted with methanol if necessary. Released tocopherol at a given time was defined as:

$$\text{Released tocopherol (\%)} = \frac{\text{Tocopherol concentration in simulant}}{\text{Total extractable tocopherols in the film}} \times 100$$

5.7.2.3. MEASUREMENT OF TOCOPHEROL CONCENTRATION IN SOLVENT BY HPLC

The concentration of tocopherol in the sample was measured using a HPLC system (LC-10AD VP, Shimadzu Co., Kyoto, Japan) equipped with a diode array detector (SPD-M10A, Shimadzu Co., Kyoto, Japan) and a C30 column (Nomura chemical Inc., Aichi, Japan). A mixture of methanol and water (97:3, v/v) was used as mobile phase with an isocratic flow rate of 0.85 ml/min. The four tocopherol homologues (α-, β-, γ-, and δ-tocopherol) were detected at 295 nm and quantified using their standards (99%, Calbiochem Inc., Darmstadt, Germany). The concentration of tocopherol was obtained by adding the concentrations of the four homologues.

5.7.3. Determination of physical properties of films

5.7.3.1. TENSILE STRENGTH

A TA-XT2i instrument (Stable Microsystems, Godalming, Surrey, UK) was used to determine tensile strength (TS) up to 300% elongation, Elastic (or Young's) Modulus (EM) and the area under each curve (as a measurement of the toughness up to 300% elongation) of plastic films, as described by ASTM D683M standard method. Testing film specimens were rectangular strips (50 mm long and 20 mm wide). A cross-head speed of 0.85 mm/s was used for the tests. All film strips were equilibrated for one week

to 52 ±2% RH in a climatic chamber before the experiments. All parameters were obtained by the stress-strain plots and directly calculated by the software (Texture Expert Exceed, version 2.6.1, Godalming, Surrey, UK). Five independent samples were used for each type of film in order to establish the mean value for each parameter.

5.7.3.2. TRANSPARENCY

Transparency of thee film was determined according to ASTM method (D 1746-88). In particular, transparency of each type of film was measured in terms of specula transmittance, i.e. the transmittance value obtained when the transmitted radiant flux includes only that transmitted in the same direction as that of the incident flux in the range 540–560 nm.

5.7.3.3. THICKNESS

Thickness of the film was measured at 10 random points, to the nearest 0.001 mm at 10 different random positions by using a digital micrometer (Digitrix, Fowler & NSK Co., Tokyo, Japan).

5.7.3.4. THERMAL PROPERTIES

The thermal properties of the film, including the glass transition temperature, the melting temperature and the crystallization temperature, were investigated by using DSC and DMTA. DSC analysis was carried out using two instruments. The first one was a TA instrument Q2000 (Analyzer Inc., USA). The second one was a Mettler DSC823 (Mettler, USA). The scanning rate was 10°C/minute under nitrogen purge. The DMTA analysis was performed using TA instruments Q800 with film tension clamps. The samples (film strips) were subjected to 0.1% strain at 10Hz. The heating rate was 2°C/minute.

5.7.4. Characterization of sesamol containing film

5.7.4.1. MEASUREMENT OF SESAMOL AND BHT USING GC

The concentration of sesamol and BHT in solvent was quantified using a gas chromatography (Agilent 6890N, Agilent, NJ., USA) with a FID detector and HP5 capillary column (60m, ID 0.32mm, J & W Scientific, US). The sesamol or BHT sample (1 µl) was injected into GC by split injection (split ratio 10:1). The initial oven temperature is 40°C (holding 1minute). The oven temperature was raised with a rate of 8°C/minute to temperature 180°C (hold 1minute). After that, the oven temperature was raised to 250°C (holding 5 minute) to equilibrium the column before next injection. Nitrogen was used as the carrier gas with a flow rate of 1ml/minute. The concentrations of sesamol and BHT were calculated by comparing against a standard curve prepared from pure sesamol (98%) and BHT (99%).

5.7.4.2. MEASUREMENT OF HEXANAL IN CEREAL USING GC

SPME (solid phase micro-extraction) GC method developed by Nigel et al. and Okabe et al. [67, 68] was modified and adapted to determine the concentration of hexanal in the cereal product during storage. The cereal samples (1.0 g) were put into a 20ml headspace vial and immersed into a water bath (70°C). A SPME fiber (carboxen/PDMS, Supelco, USA) was injected into the vial for 5 minute and then injected into the GC (Agilent 6890N, Agilent Inc., USA). The GC was equipped with a FID detector and a HP5 capillary column (60m, ID 0.32mm, J & W Scientific Inc., USA). The initial oven temperature is 80°C (holding 1 minute). The oven temperature was raised with a rate of 8°C /min to 180°C (holding 1 minute). After that, the oven temperature was raised to

250°C (hold 5 minute) to equilibrium the column before the next injection. Nitrogen was used as carrier gas with a flow rate of 1 ml/minute. Standard hexanal (99%) and 2-methyl-pentanal (98%) were used as internal standards to identify and calculate the concentration of hexanal. The concentration of hexanal in the cereal was expressed as micromole of hexanal in per kilogram of cereal (μmole/Kg).

5.7.4.3. EVALUATION OF RELEASE PROPERTY OF SESAMOL FILM

Samples of the film (containing 1218.3±11.3 ppm sesamol) were cut into square (20cm*20cm). The film squares were hung in the chamber of an incubator (C25KC, New Brunswick Scientific Inc., New Brunswick, NJ, USA) at 10 and 30°C in dark. Sample of film (1.0g) was cut out from the film squares. The sesamol retained inside the film was measured by using solvent extraction over time. Concentration of released sesamol was calculated by subtracting the retained sesamol form the initial concentration of sesamol in the film.

5.7.4.4. TEST EFFECTIVENESS OF SESAMOL FILM USING LINOLEIC ACID AS FOOD SIMULANT

In order to prove the concept that release of sesamol from polymeric film can inhibit lipid oxidation, the experiment set up showed in Figure 28 (adapted from Jongjareonrak and Nerin) was used to test the effectiveness of sesamol containing film [70, 71]. Sesamol film (1.0g, containing 1218.3±11.3 ppm sesamol) and control film (no antioxidant) were hung in the closed jars (1 liter volume). The jar was filled with 10.0g of linoleic acid and stored at 23 and 40°C. The linoleic acid in the flask was periodically sampled and the concentration of conjugated dienes in the samples was measured using a UV

spectrophotometer (UV-1700, Shimazu Co., Kyoto, Japan) at 234 nm with an absorption coefficient of 26000 l/mol·cm [65, 66]. The induction period for the oxidation of linoleic acid was determined by monitoring the concentration of conjugated dienes over time [22, 72, 73]. The length of induction period was used as an index to evaluate the antioxidant capacity of sesamol containing film.

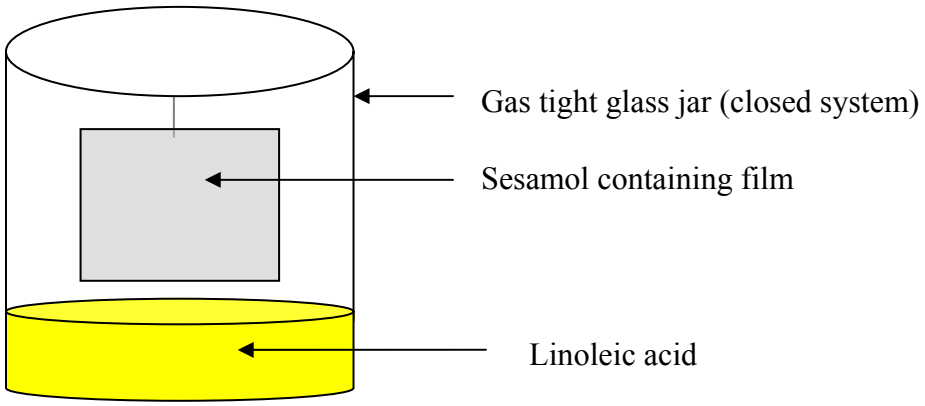


Figure 28 Release of sesamol into linoleic acid

A schematic diagram showing the experimental set up for studying sesamol release from film into linoleic acid in a jar (closed system). The jar was stored in a dark place at 23 and 40°C.

5.7.4.5. TEST EFFECTIVENESS OF SESAMOL AND BHT FILMS ON BREAKFAST CEREAL

Film A (contain no antioxidant), Film B (containing 646.1±18.3 ppm sesamol) and film C (containing 1605.5±29.2 ppm BHT) were fabricated into flexible uniform sized pouches (30 cm*22 cm). Each pouch contained 200g of cereal product made from oatmeal. The pouches were then heat sealed with an impulse sealer (12AS, Sencorp System, Inc., Hyannis, MA, USA). All the pouches were stored in a chamber at 23°C in a dark place. After 1 year, hexanal concentrations in the cereal samples were measured by GC. Internal

sensory evaluation was also carried out to compare the odor of the cereal samples which were packed with different packaging.

5.8. Data analysis

All experiments were done at least in duplicates. Average values were used in all tables and figures. One-way analysis of variance (ANOVA) with the Tukey's comparisons of means was conducted at a confidence level of 95%. Sigmaplot (version 8.0, Systat Software, Inc., San Jose, CA, USA, 2002) and Metlab (version 13, Metlab, Inc.) were used for data analysis.

6 RESULTS OF ANALYTICAL METHODS DEVELOPMENT

6.1 Evaluation of lipid oxidation

In this study, linoleic acid (linoleic acid is a major component of vegetable oil) is used as a simulated food to study the antioxidant effectiveness of different delivery modes and delivery rates of tocopherol. In lipid auto-oxidation, poly-unsaturated fatty acid (linoleic acid) is transformed into conjugated dienes which had strong UV absorption at 234nm. By measuring the concentration of conjugated dienes, we can monitor the progress of lipid oxidation. However, in the early stage of oxidation progress, the UV absorption at 234nm maintained almost flat (with little change) until the active oxidation started (fast increase of UV absorption). This steady state period is commonly known as the induction period and is used as an indicator of shelf life (Figure 29). Linear regression is done using the data points after lipid oxidation taking off. The calculated x interception is the induction period of lipid oxidation. In this research, the induction period of lipid oxidation is used as the major parameter to evaluate the effectiveness of different delivery modes and delivery rates of tocopherol. Generally, the longer induction period indicates the better antioxidant effectiveness.

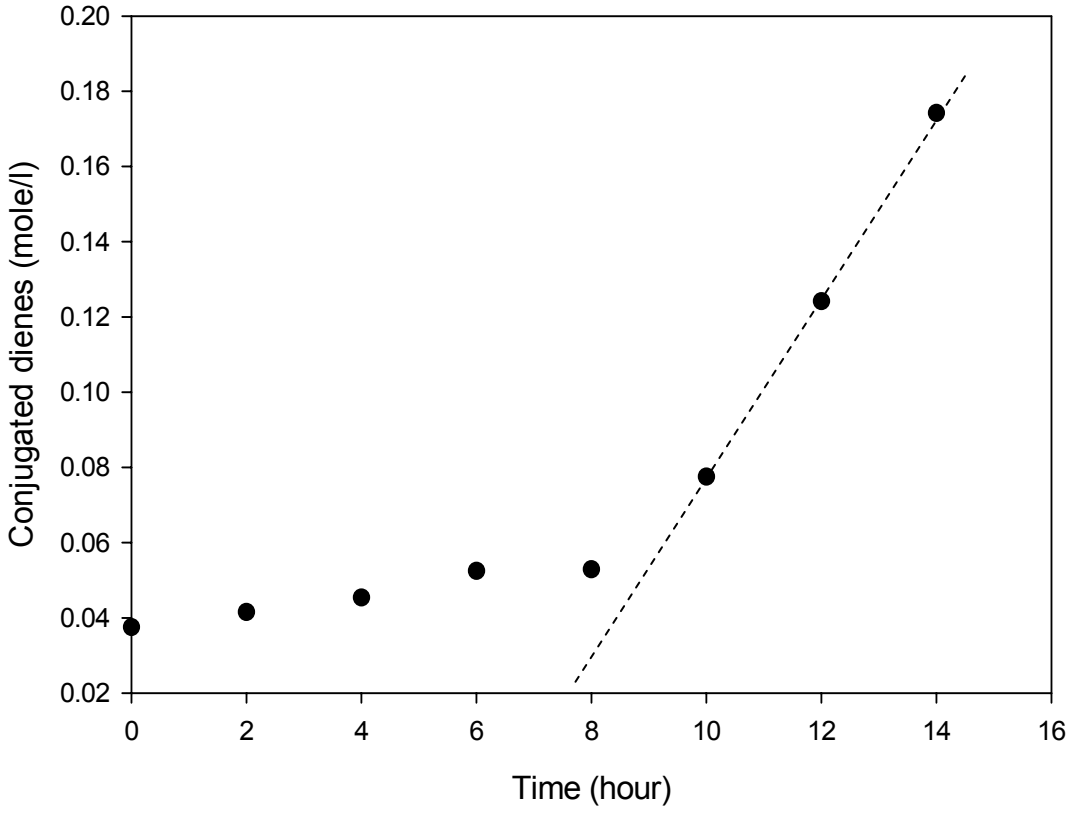


Figure 29 Determination of induction period

Linoleic acid was oxidized at 40°C in dark with 100 rpm shaking. Generation of conjugated dienes was due to oxidation of linoleic acid without antioxidant. Sample was stored at 40°C in dark place with 100 rpm shaking.

After the induction period, the lipids such as linoleic acid underwent active lipid oxidation. For example, hydroperoxides are generated and break down into smaller volatile compounds such as hexanal which are responsible for the rancid odor. The volatile compounds are used as another indicator to evaluate lipid oxidation in this study. The rancid odor is detected using a solid phase micro-extraction (SPME) and gas chromatography (Figure 30). The hexanal is the major volatile compound inside oxidized linoleic acid and oxidized food product. By using the SPME-GC methods (see Chapter five for the details of the method), hexanal is clearly separated from other volatile compounds inside linoleic acid. The isomer of hexanal, 2-methyle-pentenal (98%) is spiked into the linoleic acid samples as an internal standard to quantify the concentration of hexanal. (it is assumed that hexanal and 2-methyle-pentenal have the same response in GC detector since their chemical structures and properties are almost same.) As shown on the Figure 30, the two isomers are clearly separated (base line separation). This result further validates the above SPME-GC method.

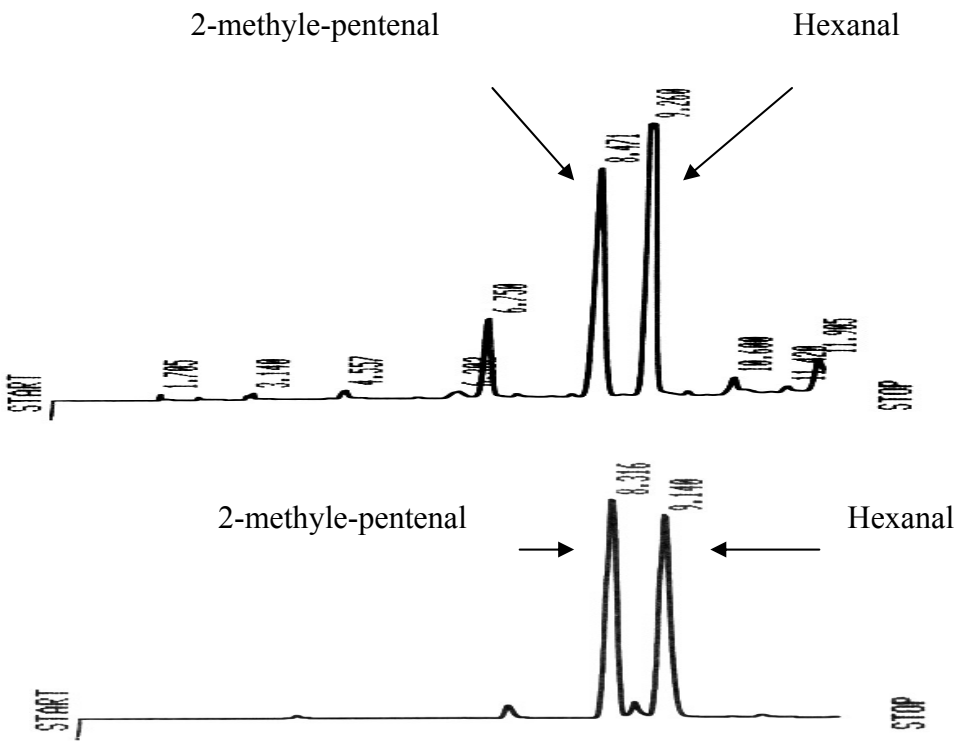


Figure 30 Detection of hexanal by GC-SPME

The up chromatogram was an oxidized linoleic acid sample. The lower chromatogram was for pure standards.

There are other indicators for lipid oxidation. Oxidation products of linoleic acid also undergo polymerization which will increase viscosity (Table 6). The viscosity is measured by using a viscometer (Brookfield, MA, USA). Moreover, in the late stage of the active oxidation, the linoleic acid loses its color and changes from slightly yellow to pale white. The color change is also used to evaluate the lipid oxidation.

Table 6 Change of lipid viscosity during lipid oxidation

	Within induction period	After induction period
UV 234nm	2.53±0.06	13.62±1.58
Viscosity (cp)	55.55±0.07	71.80±1.41

Viscosity was measured at 25°C.

6.2 Analyzing tocopherol inside linoleic acid

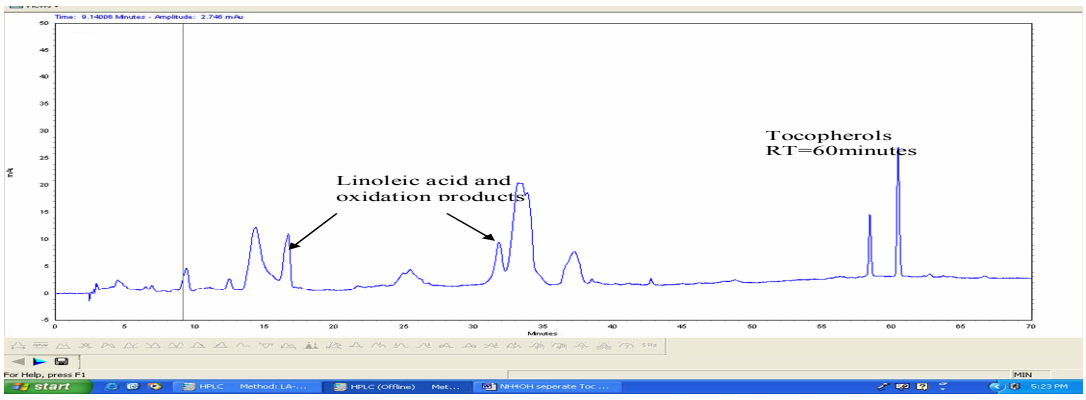
Chromatograph A in Figure 31 showed a HPLC method without adding NH_4OH in the mobile phase to separate tocopherol from linoleic acid. There were peaks of linoleic acid and its oxidation products presented without good peak shape. Moreover, the running time of the HPLC was extended to 70 minutes in order to separate the tocopherol from linoleic acid and the oxidation compounds.

By adding NH_4OH into the mobile phase, tocopherol was separated from linoleic acid within only 35 minutes. Most of the linoleic acid peaks came out of the column within 6 minutes. Tocopherol isomers came out late (after 20minute) and were separated from linoleic acid clearly.

Based on the separation and the running time, the following HPLC conditions were determined. The mobile phase was 97% MeOH, 2% H_2O and 1% NH_4OH. Flow rate was 0.85 ml/min. Run-time was 35minuteutes. Tocopherol was detected at 295nm using UV detector.

The result also shows that the tocopherol product is rich in delta-tocopherol (20%) and gamma-tocopherol (65%). The delta and gamma-tocopherol are better antioxidants in vitro than alpha-tocopherol. Although alpha-tocopherol is believed to be the most physically active in vivo, it turns out to be less effective in food system to prevent lipid oxidation [29].

Chromatograph A



Chromatograph B

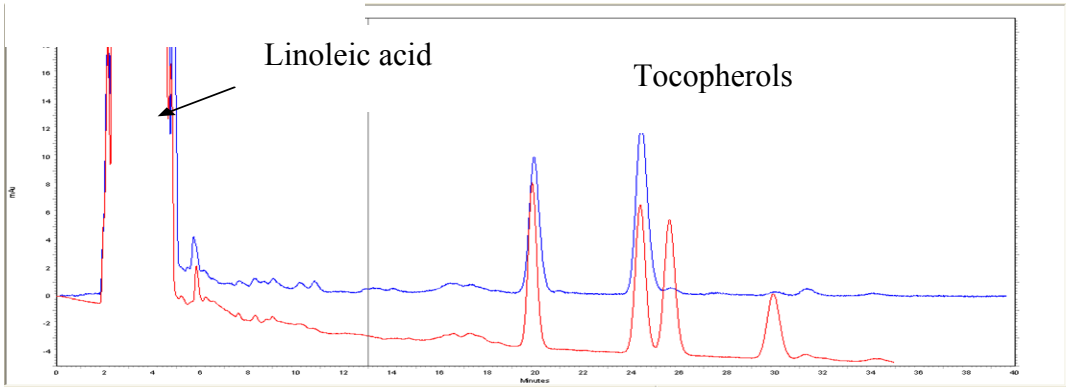


Figure 31 HPLC methods to separate tocopherols inside linoleic acid

Chromatograph A is a method without adding NH_4OH. Chromatograph B is a method with added NH_4OH. Chromatograph B: Red trace is linoleic acid with spiked tocopherol standards. Blue trace is linoleic acid with Cargill mixed tocopherols underwent lipid oxidation.

7 ANTIOXIDANT EFFECTIVENESS OF DIFFERENT DELIVERY MODES AND DELIVERY RATES

7.1 Results of instant addition mode

In instant addition test, different concentrations of tocopherol (0, 100, 300, 600 and 1000 ppm) were added into linoleic acid at time zero. No more tocopherol was added after that. The oxidation kinetics data (40°C) were shown in Figure 32. Without tocopherol (0 ppm), the induction period was about 8 hours. The induction periods for 100 ppm, 300 ppm, 600 ppm, and 1000 ppm tocopherol were about 48 hours, 100 hours, 168 hours, and 180 hours, respectively. The effectiveness of tocopherol was concentration dependent but not in a linear manner. For example, 1000 ppm tocopherol was about 3 times more than 300 ppm in concentration; 1000 ppm tocopherol only extended the induction period of lipid oxidation about 2 times longer than 300 ppm of tocopherol. Similar result was found at 23°C (Figure 33). At 23°C, without tocopherol (0 ppm), the induction period was about 1 day. The induction periods for 100 ppm, 300 ppm, 600 ppm, and 1000 ppm tocopherol were about 8.5 days, 17.5 days, 25 days, and 31 days, respectively. The above results showed that induction period (shelf life) could not be extended long enough just by increasing the concentration of tocopherol. The technologies such as slow release might be necessary for longer term stabilization of the food.

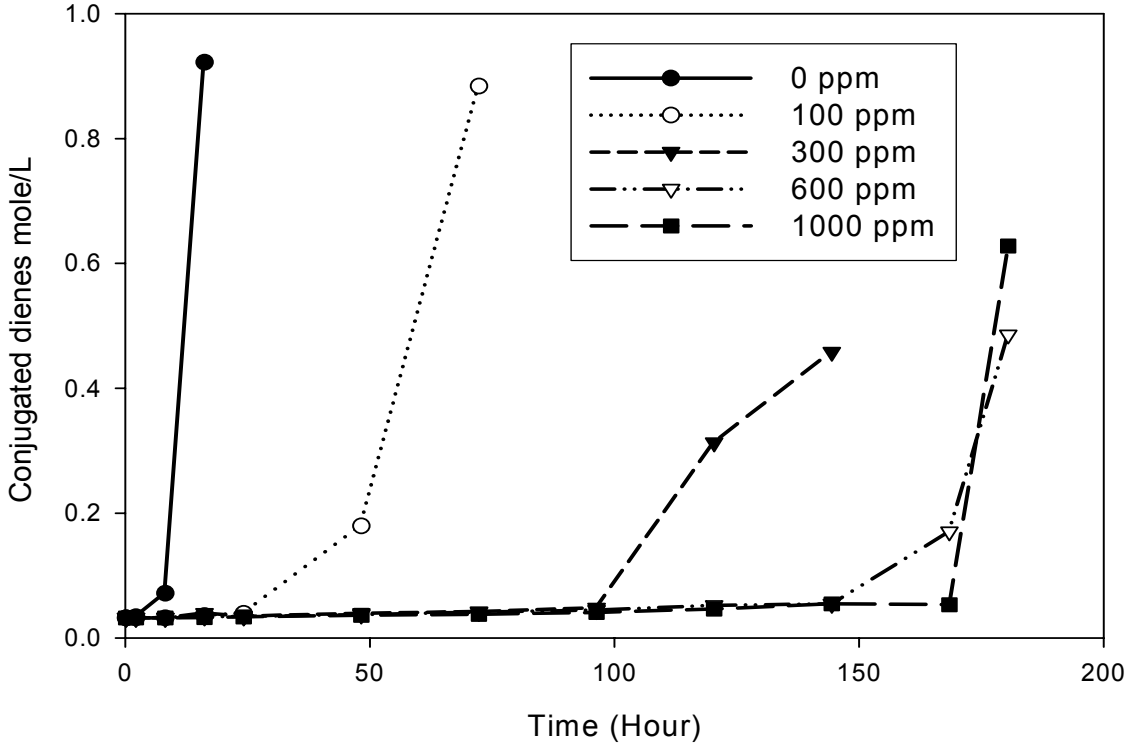


Figure 32 Lipid oxidation kinetics with instant addition of tocopherols at 40˚C

Lipid oxidation kinetics with instant addition of tocopherol at different concentrations. Experiment was conducted at 40˚C in dark place with 100 rpm shaking.

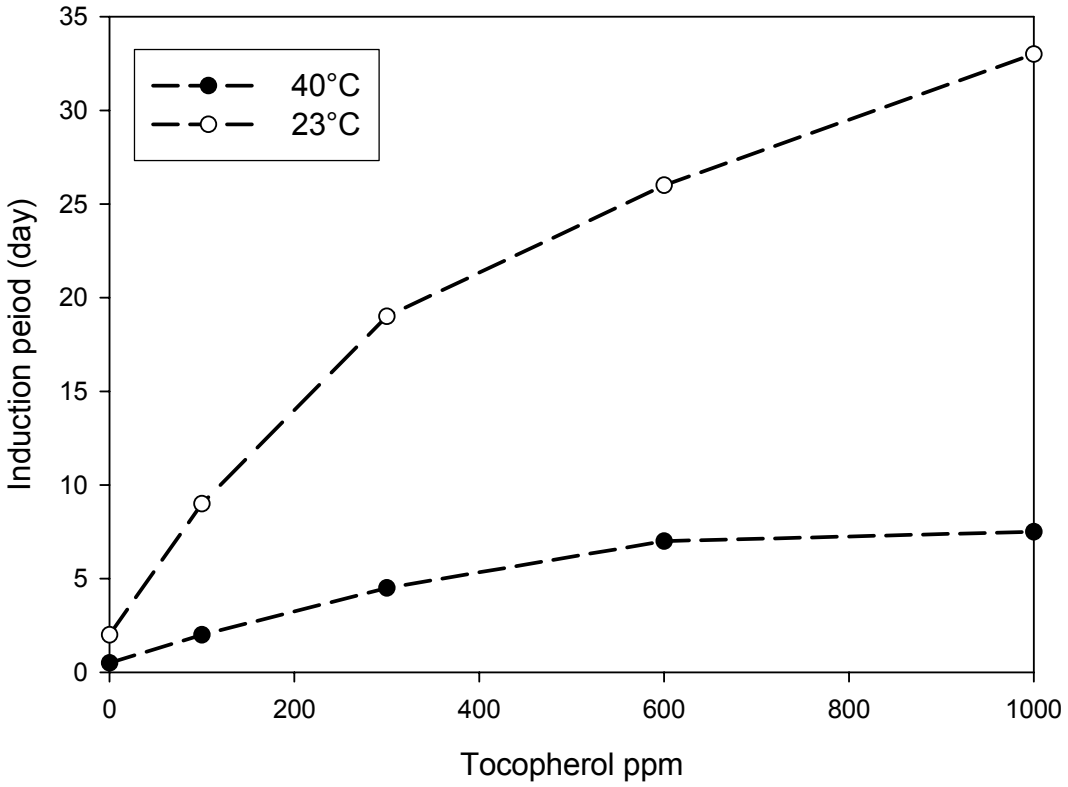


Figure 33 Induction period as a function of tocopherol concentration (instant addition)

Induction period as a function of tocopherol concentration (instant addition) at both 23˚C and 40˚C. Experiment was conducted in dark place with 100 rpm shaking.

7.2 Results of manual syringe delivery mode

In order to prove the concept of controlled release, as the first step of the slow release experiments, tocopherol was manually added into linoleic acid repeatedly at different time intervals (controlled by hand). This was a simulation of slow release from packaging films in a simplified manner. For example, the manual delivering method did not require a sophisticated instrument.

As shown in Figure 34, by continuously delivery of 100 ppm tocopherol into linoleic acid once every 24-hour, the induction period of lipid oxidation was extended more than 400% longer than instant addition of 300 ppm tocopherol. This result proved the concept that continuous replenish of antioxidants (tocopherol) extended the induction period of lipid oxidation and therefore might help to extend the shelf life of food. However, the drawback of this method was that a lot more tocopherol was used (totally 1500 ppm tocopherol over time). Therefore, this method was not economic in the real food application.

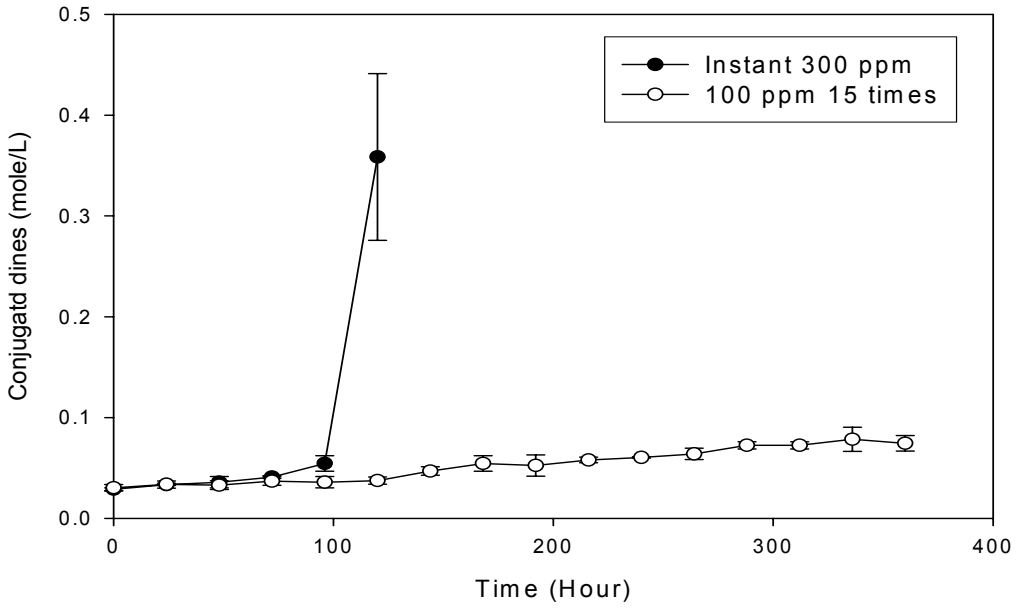


Figure 34 Continuous addition of tocopherol

Continuous addition of 100 ppm tocopherol once every 24-hour extended the induction period much longer than instant addition of 300 ppm tocopherol. Experiment was conducted at 40˚C in dark place with 100 rpm shaking.

Same amount (300 ppm) of tocopherol was added into linoleic acid by two delivery modes (Table 7). The first mode was to add all the tocopherol at time 0 (instant addition). The second mode was to add 50 ppm tocopherol every 24-hour for six times. The second mode provided longer induction period of lipid oxidation than instant addition of 300 ppm tocopherol at 40°C and 23°C (as shown in Figure 35 and Figure 36). By continuous replenishing antioxidants (tocopherol) for several times instead of one time, the induction period of lipid oxidation was extended. This result provided a new concept that by changing the delivery modes (not the amount) of antioxidant, different effectiveness of antioxidant was achieved.

The same method was used to deliver 20 ppm of tocopherol once every 24-hour (total 300 ppm of tocopherol). However, the induction period was not longer than the instant addition of 300 ppm tocopherol (Figure 37). This result suggested that not only the delivery modes, but also the delivery rates contributed to the effectiveness of antioxidant. Considered as the fastest delivery (rate=∞), instant addition did not provide the longest induction period. There should be an optimum rate in between in a certain food system, not too fast (such as instant addition), not too slow (such as 20 ppm / day). This optimum antioxidant delivery rate was defined in this dissertation as the target release rate.

Table 7 Manual delivery of tocopherol using syringe

No.	Frequency of delivery	Total tocopherol added	Temperature
1	Control (Instant addition)	300 ppm	40°C
2	Inject 50 ppm each time for 6 days	300 ppm	40°C
3	Inject 50 ppm every 3 days	300 ppm	23°C
4	Inject 20 ppm each time for 15 days	300 ppm	40°C

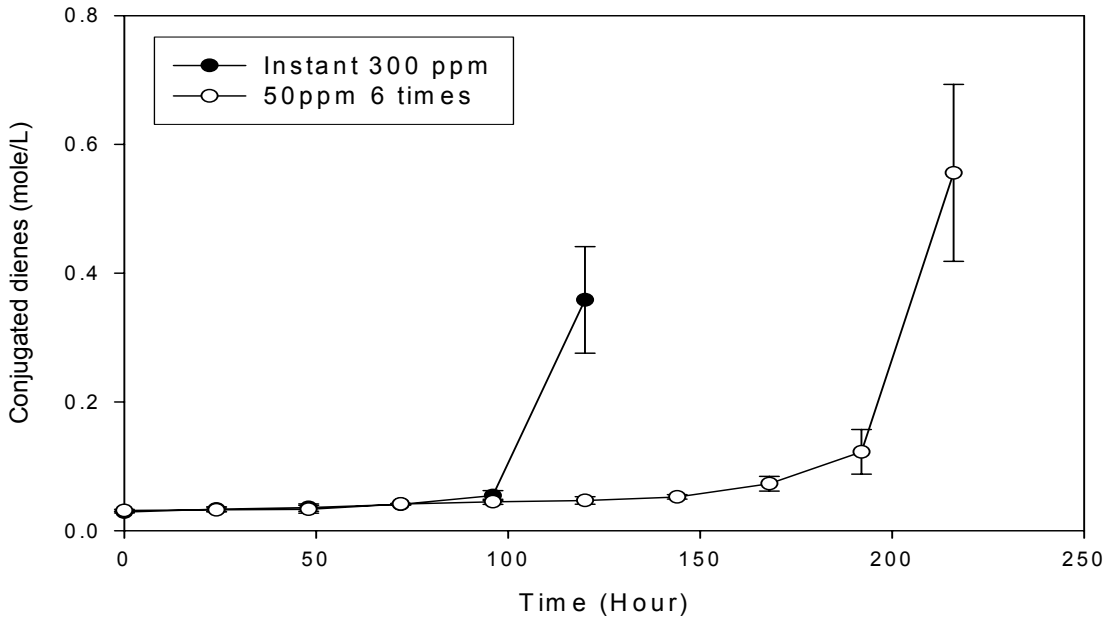


Figure 35 Adding 300 ppm tocopherol by six times (50 ppm each time) at 40˚C

Adding 300 ppm tocopherol by six times (50 ppm every 24-hour) extended the induction period longer than instant addition of 300 ppm tocopherol. Experiment was conducted at 40˚C in dark place with 100 rpm shaking.

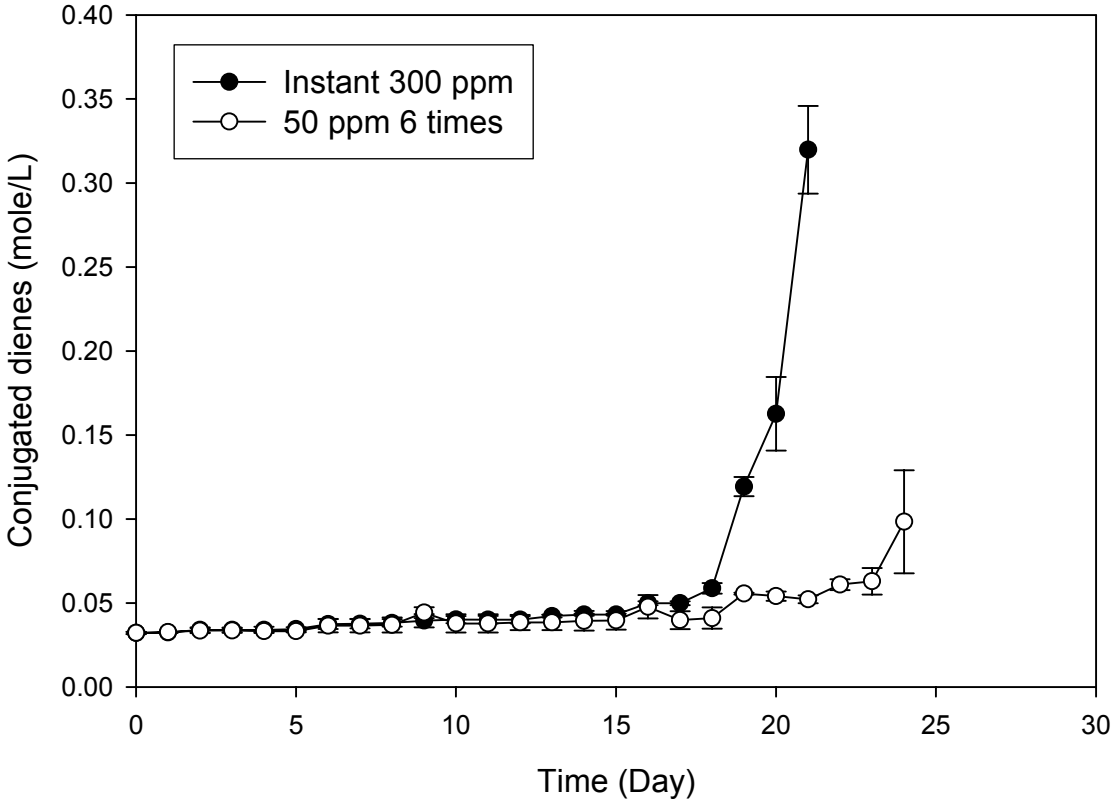


Figure 36 Adding 300 ppm tocopherol by six times (50 ppm each time) at 23˚C

Adding 300 ppm tocopherol by six times (50 ppm every 24-hour) extended the induction period longer than instant addition of 300 ppm tocopherol. Experiment was conducted at 23˚C in dark place with 100 rpm shaking.

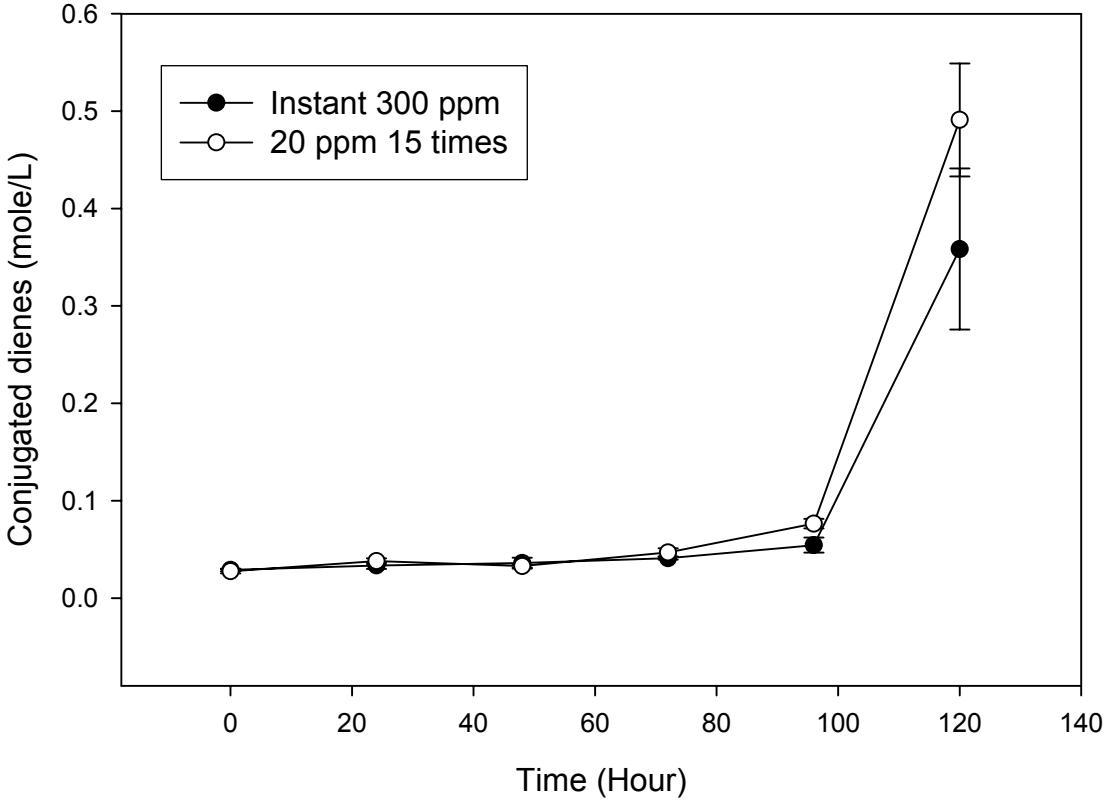


Figure 37 Adding 20 ppm tocopherol repeatedly once every 24 hours at 40˚C

Adding 20 ppm tocopherol repeatedly once every 24 hours did not extend induction period longer than instant addition of 300 ppm tocopherol. Experiment was conducted at 40˚C in dark place with 100 rpm shaking.

7.3 Results of syringe pump delivering mode

Tocopherol was continuously released into linoleic acid by using a digital controlled syringe pump. This was a simulation of slow release from packaging films in a more controllable manner, because the syringe pump controlled the delivery rates very accurately.

Same amount of tocopherol (300 ppm) was delivered into linoleic acid by using syringe pump with four rates at 40°C (see Table 8). Instant addition of 300 ppm tocopherol at time 0 was used as the control. Delivery of 75 ppm and 100 ppm per 24-hour had longer induction period of lipid oxidation than instant addition of 300 ppm tocopherol (Figure 38). Delivery of 30 ppm and 50 ppm per 24-hour did not provide longer induction period of lipid oxidation than the instant addition of 300 ppm tocopherol (Figure 38).

Table 8 Delivery rates of tocopherol using syringe pump

No.	Rate of delivery	Total tocopherol added	Temperature
1	30 ppm/day	300 ppm	40°C
2	50 ppm/day	300 ppm	40°C
3	75 ppm/day	300 ppm	40°C
4	100 ppm/day	300 ppm	40°C
5	Control (instant addition)	300 ppm	40°C

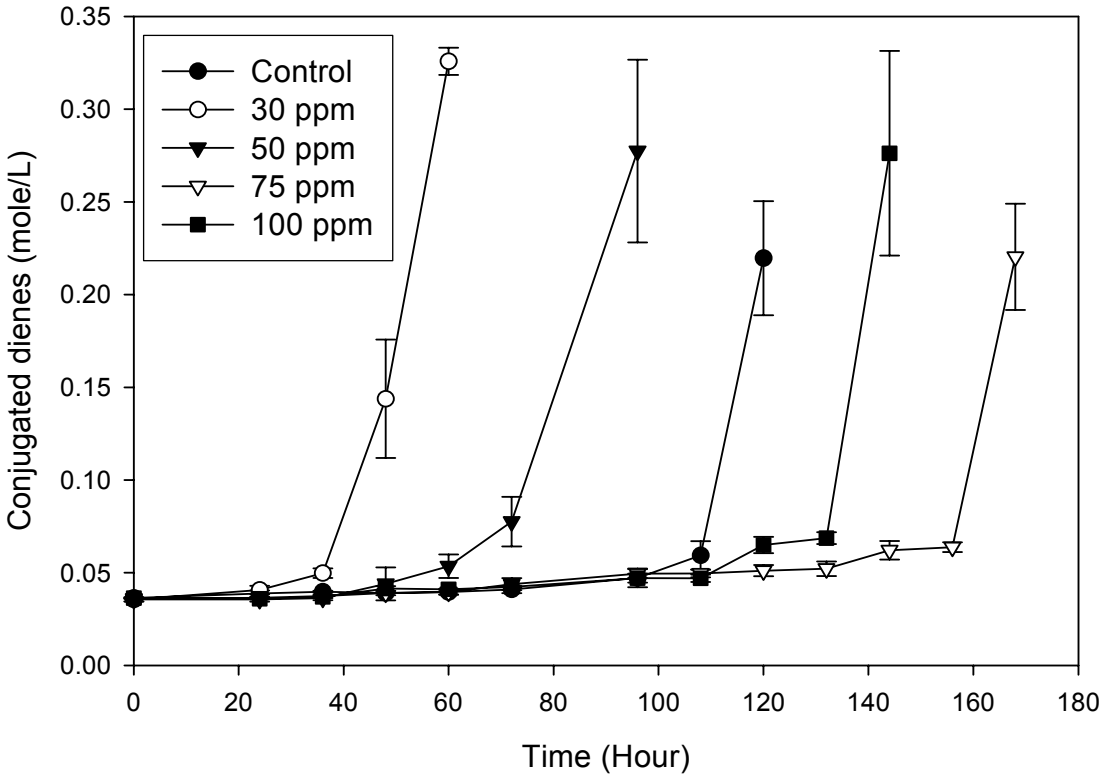


Figure 38 Concentration of conjugated dienes as a function of delivery rates of tocopherol at 40°C

Concentration of conjugated dienes generated from oxidation of linoleic acid as a function of delivery rates of tocopherol at 40°C. Experiment was conducted at 40°C in dark place with 100 rpm shaking.

In summary, by continuous replenishing antioxidants (tocopherol) slowly instead of instant addition, the induction period of lipid oxidation was extended longer than instant addition. This result proved the assumption that slow release of antioxidants provided more benefits to inhibit lipid oxidation (proof of assumption 1). The results from syringe pump experiments also showed that the effectiveness of antioxidants was dependent of delivery (release) rate (proof of assumption 2). Slow release of tocopherol all extended induction

period of lipid oxidation longer than instant addition at 23˚C and 40˚C. The effectiveness of extension varied with delivery modes and rates. HPLC measurement of the tocopherol concentration in linoleic acid during lipid oxidation showed that slow release resulting in a significant higher retention of tocopherol over time, which contributed to longer induction period (see chapter 9). The results indicated an innovative approach to improve antioxidant effectiveness to extend shelf life by manipulating delivery modes rather than concentration. The fundamental understanding of slow release will provide useful information for slow release technology in food and related areas such as controlled release packaging.

The important application of above results was using the controlled release packaging to achieve slow release of antioxidants. After five-year's exploratory research on developing controlled release packaging (CRP), Yam and Schaich at Rutgers University have developed the conceptual framework for designing CRP [5]. This framework proposes a systematic research approach for CRP development which includes four components: composition, processing, structure/morphology, and properties (Figure 15) [38]. This conceptual framework provides a clear research map to guide the research on CRP to achieve better controlled release of active compounds and application of CRP in food. In the conceptual framework for CRP, there are four important variables: process, structure, property, and food variables. The first three variables are under the scope of packaging research. Process variables are related to the factors involved in the production of CRP and can be controlled through experimental conditions. By manipulating the above three variables, we are able to produce packaging films with different release rates. Since different release rates of antioxidants provide different effectiveness to inhibit lipid

oxidation, it is highly desirable to produce packaging films which can release antioxidants at different rates.

In conclusion, the above results proved the assumption that slow release of active compounds can provide better antioxidant effectiveness. Therefore, the encouraging results provide theoretical justification for the controlled release packaging technology.

8 RESULTS OF TOCOPHEROL CONTAINING FILM PRODUCTION

8.1 Film production

The films containing tocopherol were produced in Pliant Company (Chippewa Falls, WI) using a pilot plant scale extruder (single screw). Physical properties of films including tensile strength, glass transition temperature, etc. will be discussed in Chapter 13. Same films were stored in aluminum foil bags flushed with nitrogen and shipped to Rutgers University packaging laboratory for chemical evaluations including release properties and anti-oxidation properties (see Figure 27 in Chapter 5 for details).

Tocopherol containing films were analyzed for total available tocopherol using methylene chloride as a food simulant. Methylene chloride is a very strong solvent and can extract all the tocopherol presented in the films (except the tocopherol chemically bonded to polymers). The result showed that all the films contained at least 2706 ppm tocopherol (more than 90% of 3000 ppm added tocopherol). The result clearly demonstrated that tocopherol had been incorporated into the films (Table 9).

Table 9 Blending ratios and tocopherol concentrations of LDPE/PP blend films

Name	Blending ratio (LDPE/PP, w/w)	Concentration of tocopherol initially added in films (ppm)	Actual concentration of tocopherol in films (ppm)
Film A	100/0	3000	2706 ± 57
Film B	75/25	3000	2937 ± 48
Film C	50/50	3000	2970 ± 66
Film D	25/75	3000	2970 ± 42
Film E	0/100	3000	2859 ± 12

8.2 Tocopherol release kinetics from packaging films

In order to study how much and how fast tocopherol was released from packaging films, solvent (95% ethanol) was used as a food simulant to simulate fatty food. Selection of 95% ethanol for release study was based on two reasons. The first reason was that 95% ethanol was a good food simulant for fatty foods [69]. Another important reason was that tocopherol inside the ethanol (released from packaging films) was very stable with almost no degradation during the period of the release study. The samples were flushed with nitrogen and stored in dark place during release study to minimize possible oxidation of tocopherol. Same films (Film A, B, C, D, E) listed in Table 9 were used in release study. Release study at 40°C and 23°C (room temperature) demonstrated that films with different polymer compositions released tocopherol with different rates. The general trends were the higher the percentage of PP, the slower the release rates of tocopherol from film into food simulant (Figure 39 and Figure 40).

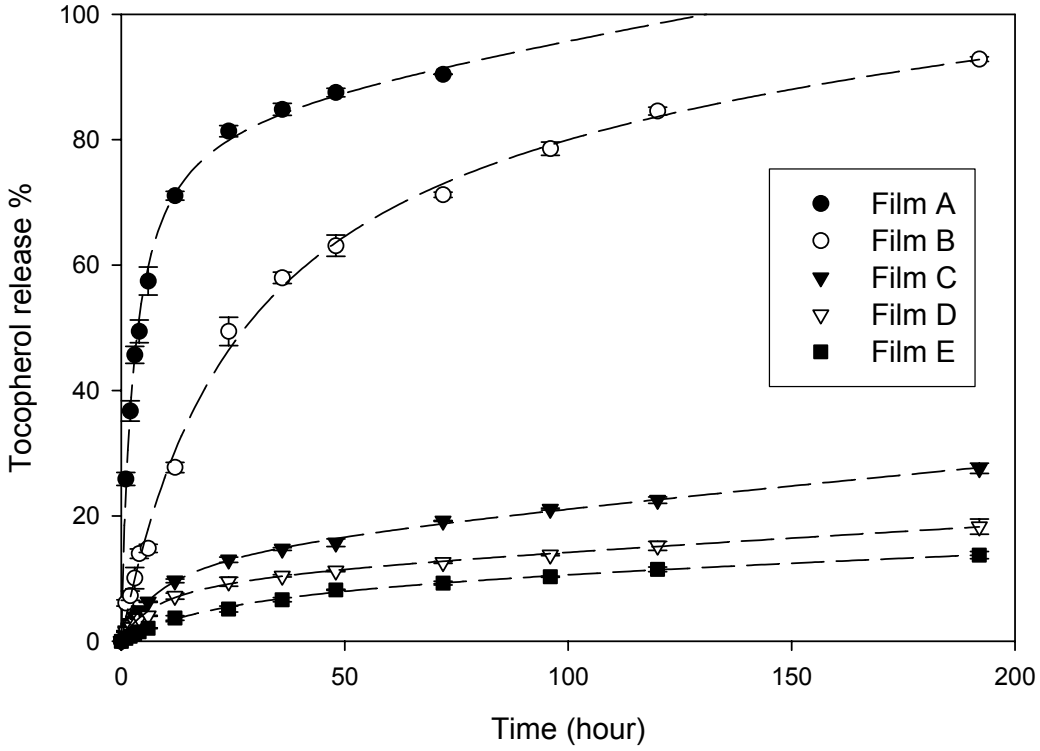


Figure 39 Release kinetics of tocopherol from films into 95% ethanol at 23°C

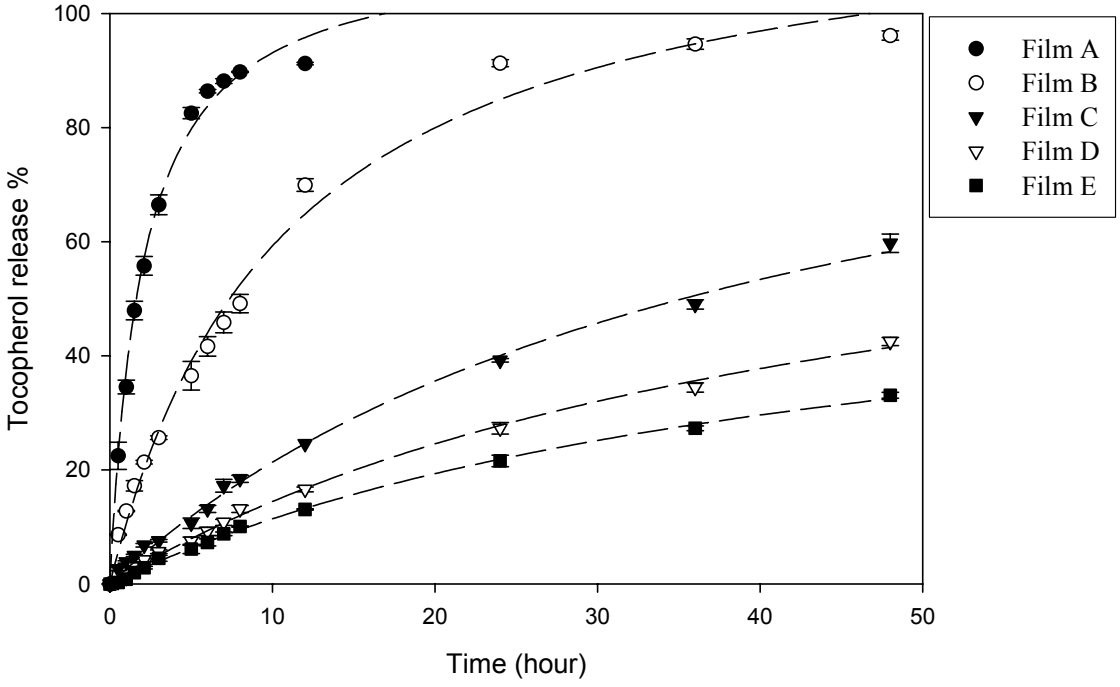


Figure 40 Release kinetics of tocopherol from films into 95% ethanol at 40°C

8.3 Estimation of diffusion coefficients

Diffusion coefficients were estimated from the results of the release studies by using the method adapted from Chung [56] and Obinata [6]. The following conditions were assumed: 1) mass transfer resistance of tocopherol from the film surface into the food simulant was negligible; 2) initial concentration of tocopherol in the food simulant was zero; 3) there was no concentration gradient of tocopherol in the food simulant; 4) partition coefficient and diffusion coefficient were constant at a given temperature; 5) interactions between the food simulant and the film were not considered.

Diffusion is the transport process from one part of a system to another as a result of random molecular motion. The rate of transfer of a diffusing substance can be expressed by Fick's First Law:

$$F = - D \, dC / dx \qquad (1)$$

where F is the rate of transfer per unit area (mole/s), D is the diffusion coefficient, C is the concentration of diffusing substances (mole/ cm^3), and x is distance in direction of diffusion (cm).

If the diffusion occurs only in one direction (x-axis), Fick's Second Law can be used:

$$\partial C / \partial t = D \, \partial^2 C / \partial x^2 \qquad (2)$$

The following equation can be derived from Fick's second law:

$$M_t / M_\infty = (2 / Lp) (Dt / \pi)^{0.5} \qquad (3)$$

where M_t is the amount of tocopherols in the food simulant at time t, M_∞ is the equilibrium amount of tocopherols in the food simulant (95% ethanol), Lp is film thickness, D is diffusion coefficient, t is time, and C is tocopherol concentration in the films at time t and position x. Equation (3) is valid when $M_t / M_\infty \leq 0.6$. The plot of fractional release M_t / M_∞ vs. $t^{0.5}$ should be straight line if the release follows Fickian diffusion. The diffusion coefficient can be estimated from the slope of the plot of M_t / M_∞ vs. $t^{0.5}$.

As shown in Figure 41, plots of the fractional release of Mt/ M∞ vs. $t^{0.5}$ ($second^{0.5}$) were straight lines, indicating that tocopherol release was controlled by Fickian diffusion. Diffusion coefficients calculated from the slopes were listed in Table 10. Film A which

contained 100% LDPE had the highest diffusion coefficient. Film E, which contained 100% PP, had the lowest diffusion coefficient. Diffusion coefficient for LDPE was about 81 times bigger than PP. Similar data on of LLDPE and PP was reported by Obinata of our group [6]. The diffusion coefficients for polymer blends were in the range between LDPE and PP. The overall trend was that as the ratio of PP in the film increased, the diffusion coefficients decreased.

Polypropylene (PP) had higher crystaltinities and more dense morphology compared with polyethylene (PE) [6]. Therefore, PP films had much slower release rates of tocopherol compared with PE films. By blending different ratio of PP and PE together, films with different release rates (diffusion coefficients) had been produced. The results demonstrated that research group at Rutgers University found an effective approach to manipulate the release properties of polymer films for the development of the controlled release packaging [6, 37].

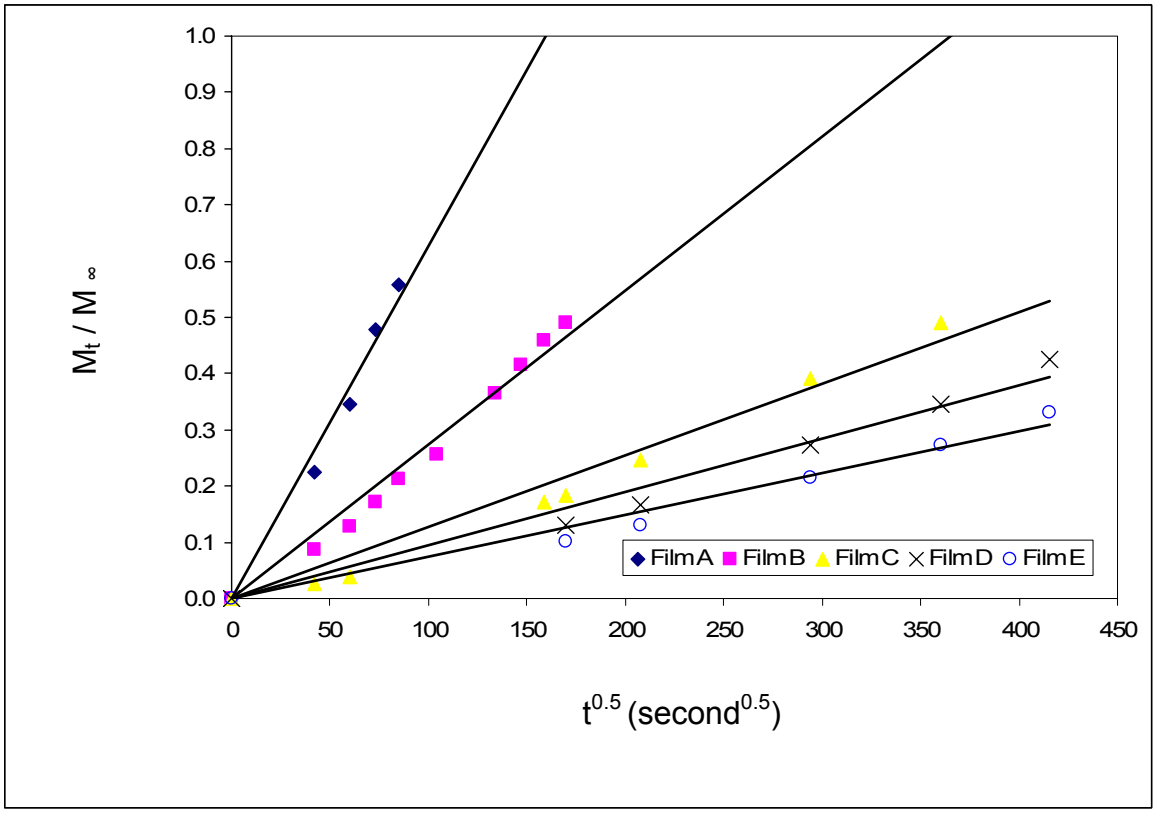


Figure 41 Estimation of diffusion coefficient

Experiment was done at 40°C in dark place with 100 rpm shaking.

Table 10 Estimation of diffusion coefficient

	Film A	Film B	Film C	Film D	Film E
Thickness (μm)	75	75	75	75	75
Equation	y = 0.0063 x	y = 0.0027 x	y = 0.0013 x	y = 0.0009 x	y = 0.0007 x
r^2	0.9811	0.9776	0.9737	0.9762	0.9766
D (cm^2/s)	1.75×10^{-9}	2.32×10^{-10}	7.46×10^{-11}	3.58×10^{-11}	2.16×10^{-11}

D: diffusion coefficient (cm^2/s).

8.4 Delivering of tocopherol by film to inhibit lipid oxidation

Tocopherol was released from packaging films into linoleic acid at different rates which were determined by film compositions. The polymer films of same compositions without (0 ppm) tocopherol were used as the control. This experiment is designed to use linoleic acid as a reactive food simulant to find out the effectiveness of release rates of the antioxidants.

The results (Figure 42 and Figure 43) showed that all the films containing tocopherol provided induction periods longer than control (no tocopherol) at both 23°C and 40°C. The results demonstrated that the films containing tocopherol were effective to inhibit lipid oxidation and therefore might be useful to extend shelf life of food products. The above data were further summarized in Figure 44 to show the relationship between induction period and PP percentage in the films. It was clearly shown that with the increasing percentage of PP in the film, the induction period of lipid oxidation increased. For example, at room temperature, film E (100% PP) extended the induction period up to 31 days, which was the longest.

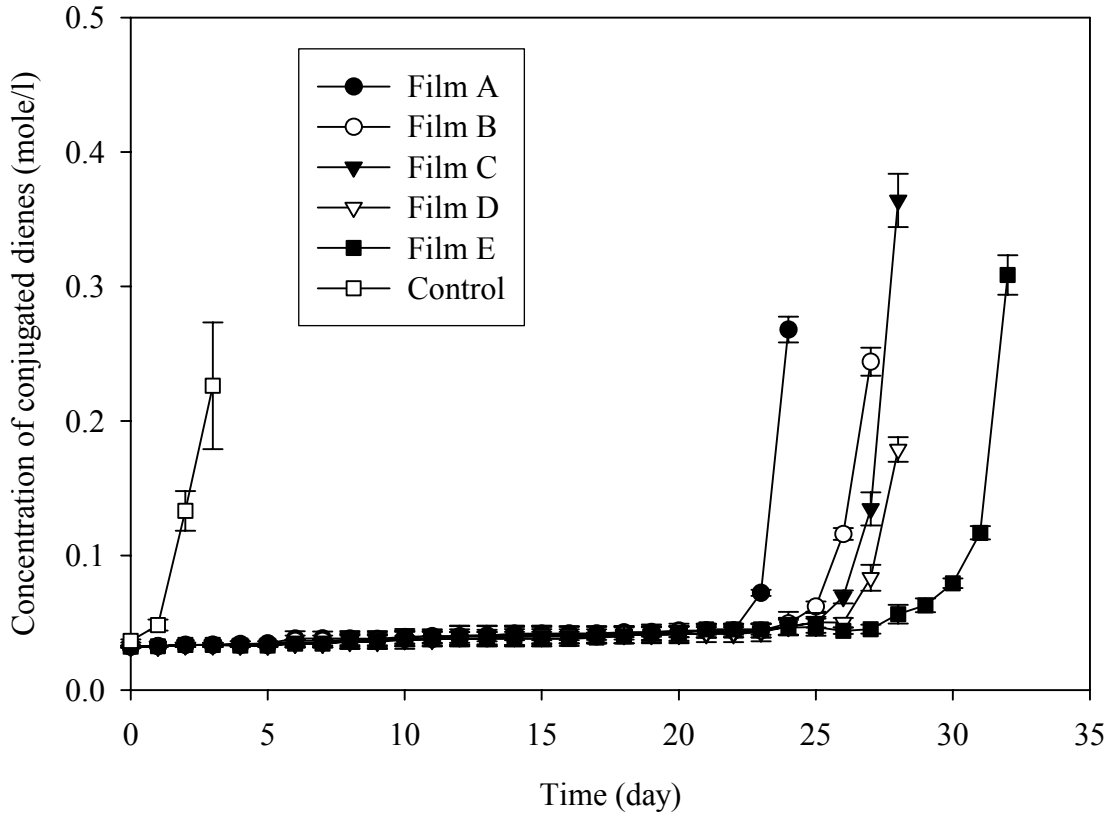


Figure 42 Generation of conjugated dienes in linoleic acid with tocopherol containing films at 23°C

Generation of conjugated dienes in linoleic acid with tocopherol containing films at 23°C. Experiment was conducted in dark place with 100 rpm shaking. Film without tocopherol was used as control.

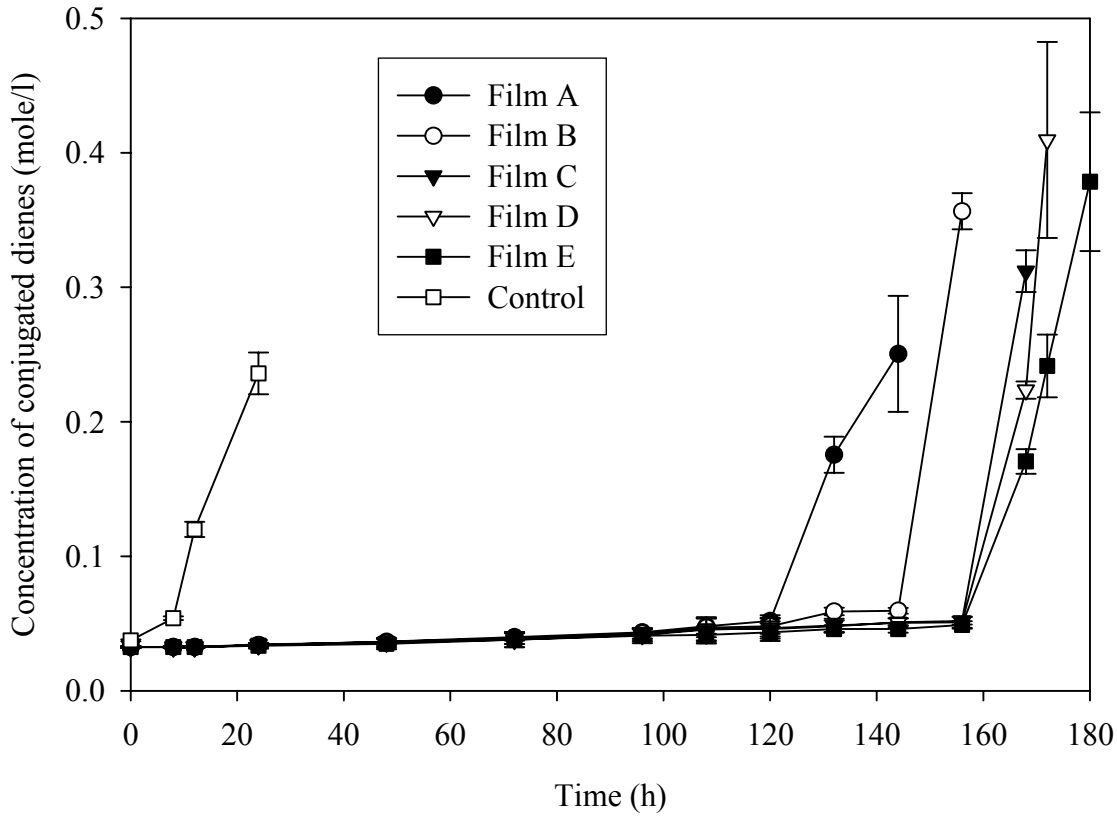


Figure 43 Generation of conjugated dienes in linoleic acid with tocopherol containing films at 40°C

Generation of conjugated dienes in linoleic acid with tocopherol containing films at 40°C. Experiment was conducted at 40˚C in dark place with 100 rpm shaking. Film without tocopherol was used as control.

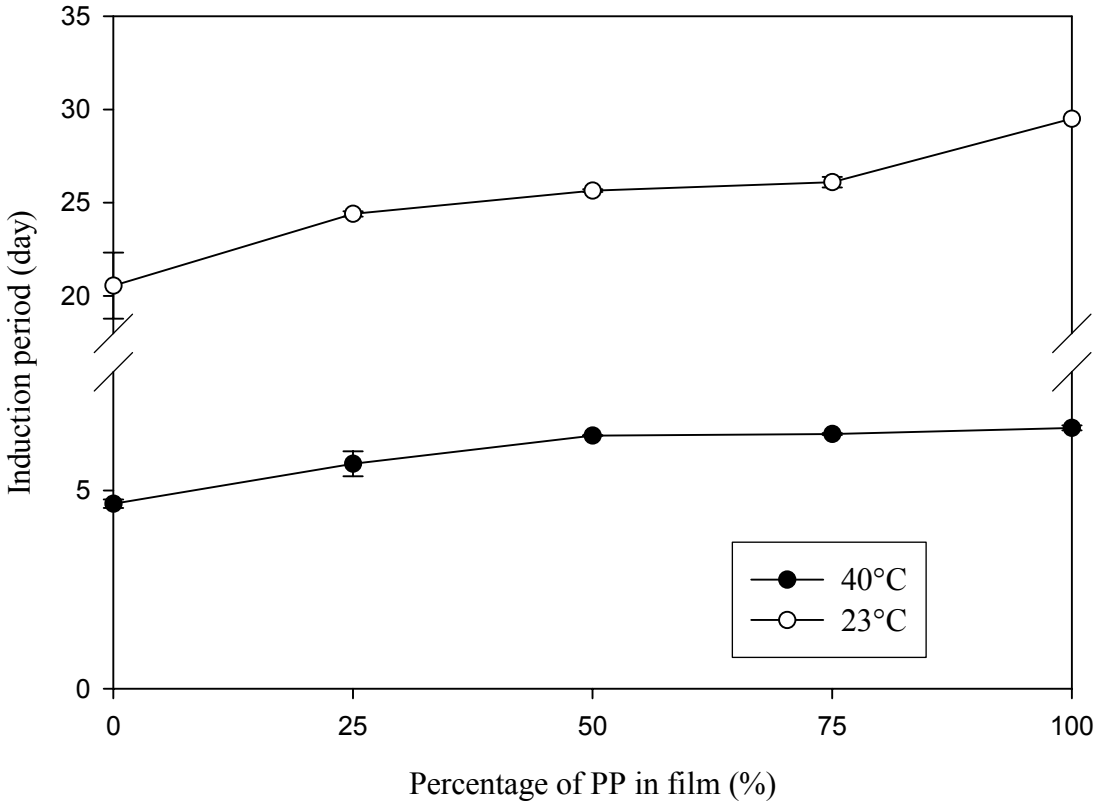


Figure 44 PP% in tocopherol film and induction period

The length of induction period (shelf life) increased with the increasing percentage of polypropylene (PP) in the films at 23ºC and 40ºC storage.

Why films with increasing PP had longer induction period? The effectiveness of the films was clearly dependent on the release rates of the films. The release rates were evaluated using 95% ethanol as food simulant (Figure 39 and Figure 40). The assumption was that tocopherol release trends were similar in linoleic acid as in 95% ethanol. The results showed that the films which had a slower release rate provided a longer induction period. This result proved that slow release of tocopherol from packaging extended the induction period of lipid oxidation and might help to extend the shelf life (proof of

assumption 1). The effectiveness of the films was dependent of release rates of tocopherol (proof of assumption 2). However, our result also showed that another film (100% high crystallites PP, containing 3000 ppm tocopherol) had a shorter induction period than instant addition of 300 ppm tocopherol (Data not shown here). Release study using 95% ethanol showed that 100% high crystallites PP had extremely slow release rate; less than 60% of tocopherol were released into 95% ethanol after three months at room temperature (Data not shown here). The slowest release film did not extend the induction period longer than instant addition. This result suggested that it was not true that the slowest release rate was the optimum release rate or the target release rate. There should be an optimum release rate, not too fast (as demonstrated by 100% PE film) and not too slow (as demonstrated by 100% high crystallites PP film).

In summary (Figure 45), the results from packaging films show that release rate is dependent of the polymer composition; the antioxidant effectiveness is dependent of the release rate of antioxidants from the film matrix. Since there is a clear relationship between release rate of tocopherol and shelf life, this has brought in the need to define the concept of the target release rate; that is: is there an optimum release rate we can target at to achieve the longest or required shelf life? In this dissertation, we define the concept of target release rate as: optimum rate at which an antioxidant must be released from a food package in order to replenish the antioxidant consumed in reaction and to maintain an adequate concentration in the food for inhibiting active lipid oxidation until the end of the shelf life of the food.

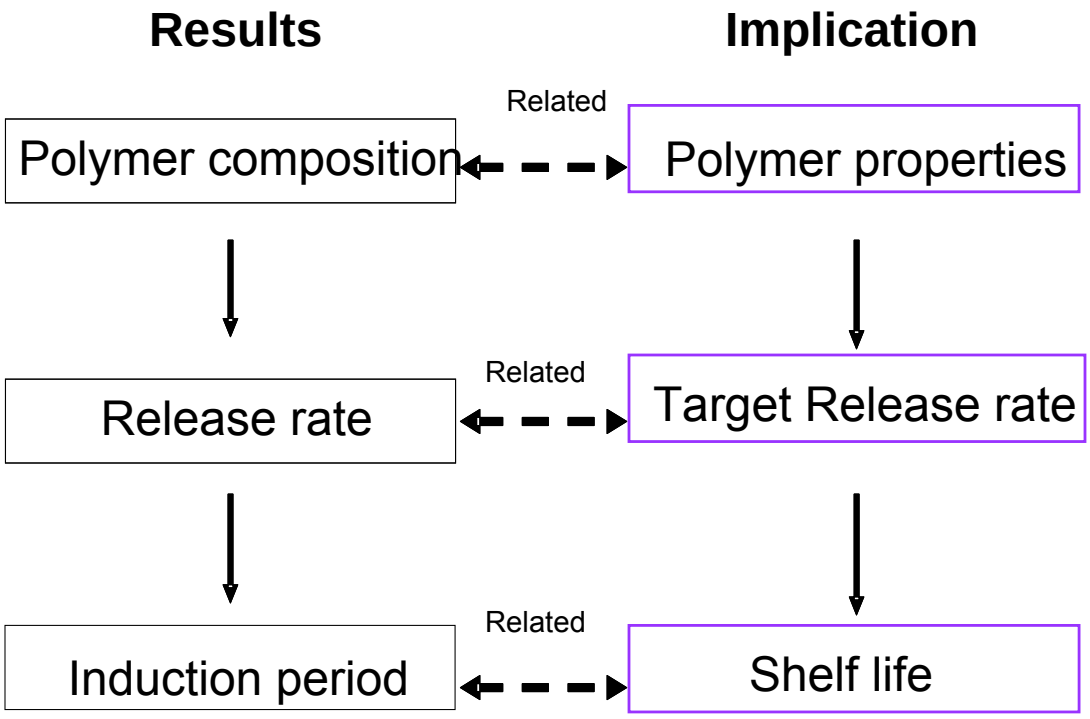


Figure 45 Summary of film delivery mode result

9 RESULTS ON TOCOPHEROL CONSUMPTION

Measuring consumption (degradation) of tocopherol in linoleic acid serves two purposes. First, it may help to explain what happens during induction period of lipid oxidation (tocopherol degrades during induction period of lipid oxidation). It may also help to explain why different delivery modes and rates of tocopherol have different antioxidant effectiveness. Second, it will provide information to determine the target release rate; that is how fast and how much tocopherol is degrading and how fast and how much tocopherol should be replenished accordingly.

We know the initial tocopherol concentration that we add into the linoleic acid. We also can measure the tocopherol concentration inside the linoleic acid over time (tocopherol retention). Therefore the degradation of tocopherol can be calculated by subtraction of tocopherol retention (concentration) inside linoleic acid over time from the initial tocopherol concentration.

$$T_d = T_0 - T_r$$

T_d: tocopherol degraded (consumed) at time t
T_0: initial tocopherol concentration
T_r: tocopherol retained in food (linoleic acid) at time t

9.1 Tocopherol degradation under instant addition

Different concentrations of tocopherol (100, 300, 600 and 1000 ppm) were added into linoleic acid at time zero at 40°C. No more tocopherol was added after that. The tocopherol degradation kinetics data were shown in Figure 46. The instant addition

resulted in drastic degradation of tocopherol at the early stage of lipid oxidation. Similar pattern was also reported by other research groups [74, 75]. A possible reason for the above result is the pro-oxidation effect of the antioxidant. An antioxidant may involve in self-degradation reaction at a higher than the optimum concentration, which results in fast depletion of the antioxidants. This is well known as pro-oxidation effect of antioxidants [76-79].

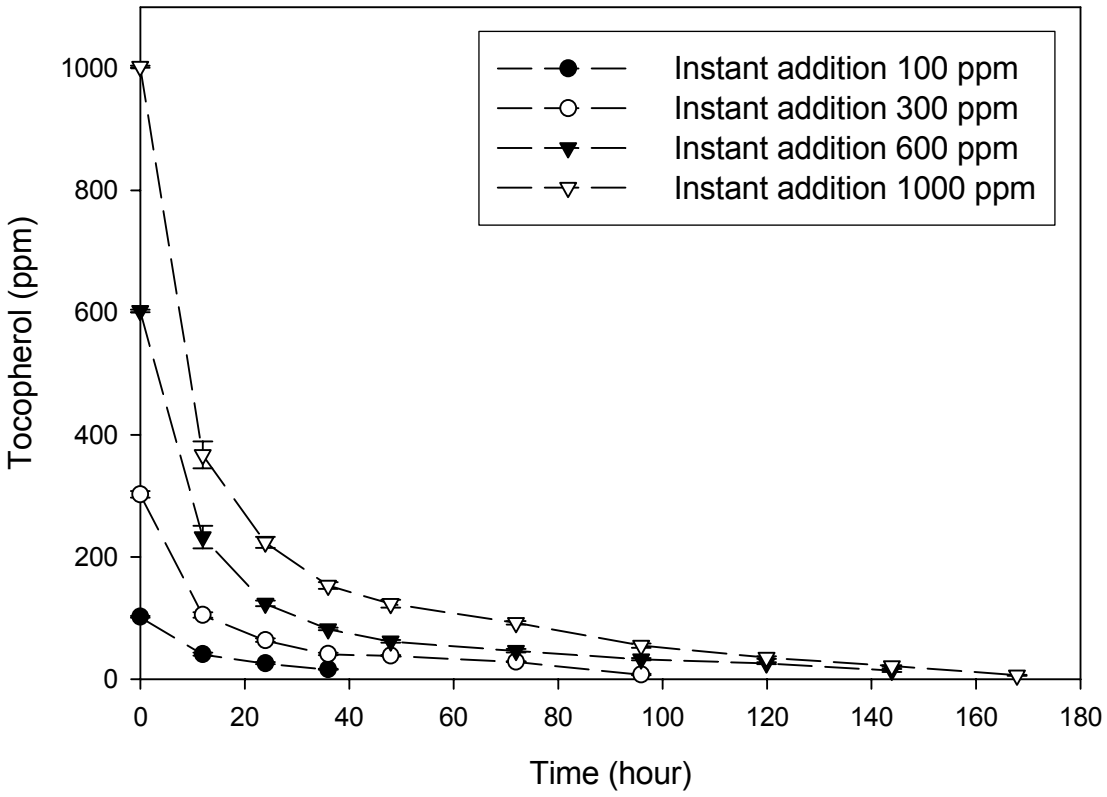


Figure 46 Tocopherol consumption kinetics with instant addition of tocopherol

Tocopherol consumption (degradation) kinetics with different amount of instant addition of tocopherol. Experiment was done at 40°C in dark place with 100 rpm shaking.

In order to confirm the above results and verify that the drastic degradation of tocopherol was caused by the reactivity of linoleic acid (unsaturated fatty acid), tocopherol (300 ppm) was also added into the miglyol oil. The miglyol oil is a kind of synthetic, fully saturated, and non-reactive oil. The miglyol oil with added tocopherol was treated in the same way as linoleic acid and the tocopherol concentration was measured after 90 days at 23°C. The results in Figure 47 showed that there was less than 5% degradation of the total tocopherol. This result clearly demonstrated that the dramatic consumption (degradation)

of tocopherol was due to the reactivity of linoleic acid. The linoleic acid is unsaturated and very reactive while the miglyol oil is fully saturated and non-reactive.

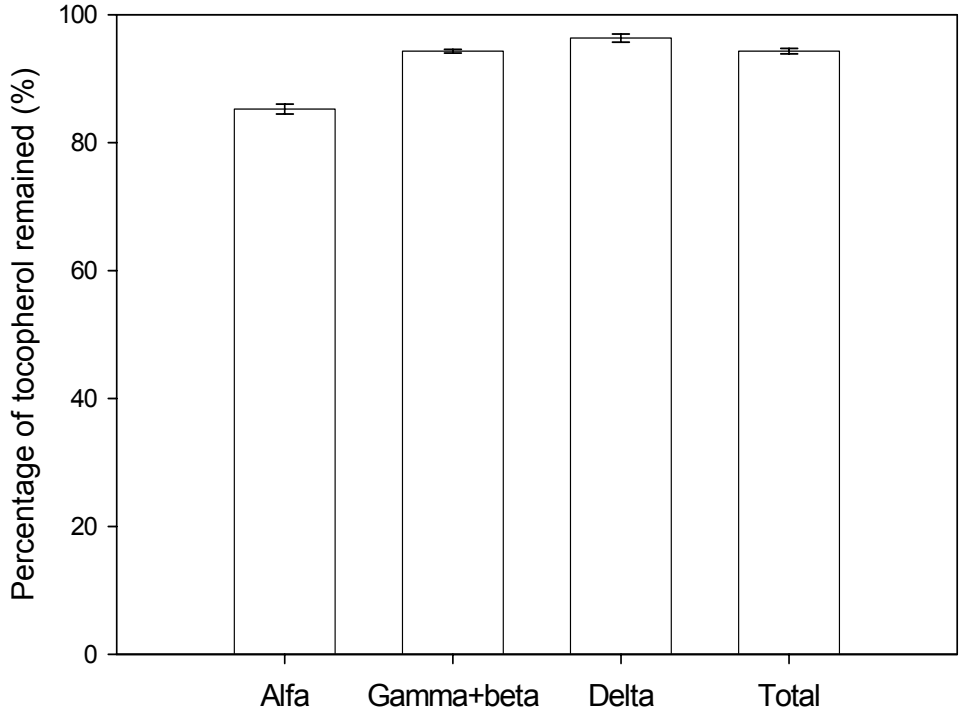


Figure 47 Tocopherol in miglyol oil stored at 23°C

This is to prove that lose of tocopherol is because the reactivity of linoleic acid. Experiment was done at 23°C in dark place with 100 rpm shaking.

9.2 Tocopherol consumption under manual delivery mode

Same amount (300 ppm) tocopherol was added into linoleic acid by two delivery modes. The first mode was to add all the tocopherol at time 0 (instant addition). The second mode was to add 50 ppm tocopherol every 24-hour for six times. The second mode provided longer induction period of lipid oxidation than instant addition of 300 ppm tocopherol at 23°C. Figure 48 showed that manual delivery of tocopherol (slow release) resulted in higher retention of tocopherol inside linoleic acid in the later stage of the lipid oxidation.

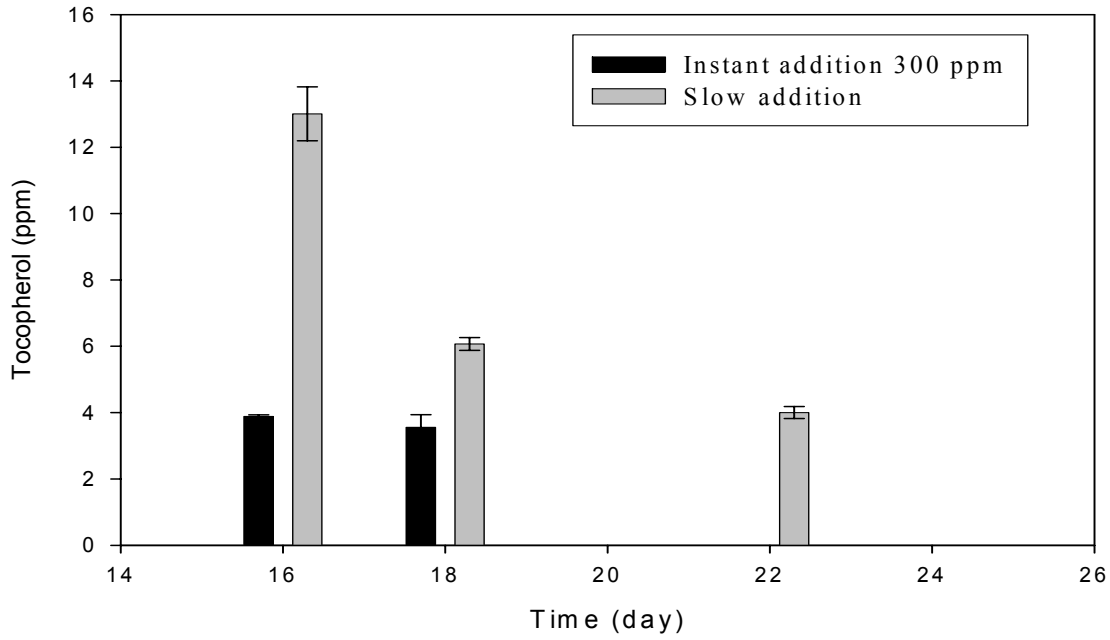


Figure 48 Retention of tocopherol with manual delivery mode

Retention of tocopherol in linoleic acid over time at 23°C. Slow addition: adding 50 ppm per day for six times.

9.3 Tocopherol consumption under syringe pump delivery mode

Same amount of tocopherol (300 ppm) was delivered into linoleic acid by using syringe pump with three rates. The first rate was 100 ppm tocopherol per 24-hour for 3 days. The second rate was 75 ppm tocopherol per 24-hour for 4 days. The third rate was 50 ppm tocopherol per 24-hour for 6 days. Instant addition of 300 ppm tocopherol was the control. The results showed that the rate of 75 ppm per 24-hour resulted in the highest retention of tocopherol (Figure 49). Instant addition of 300 ppm tocopherol resulted in the lowest tocopherol retention. Release rates of 100 ppm and 50 ppm tocopherol were in between.

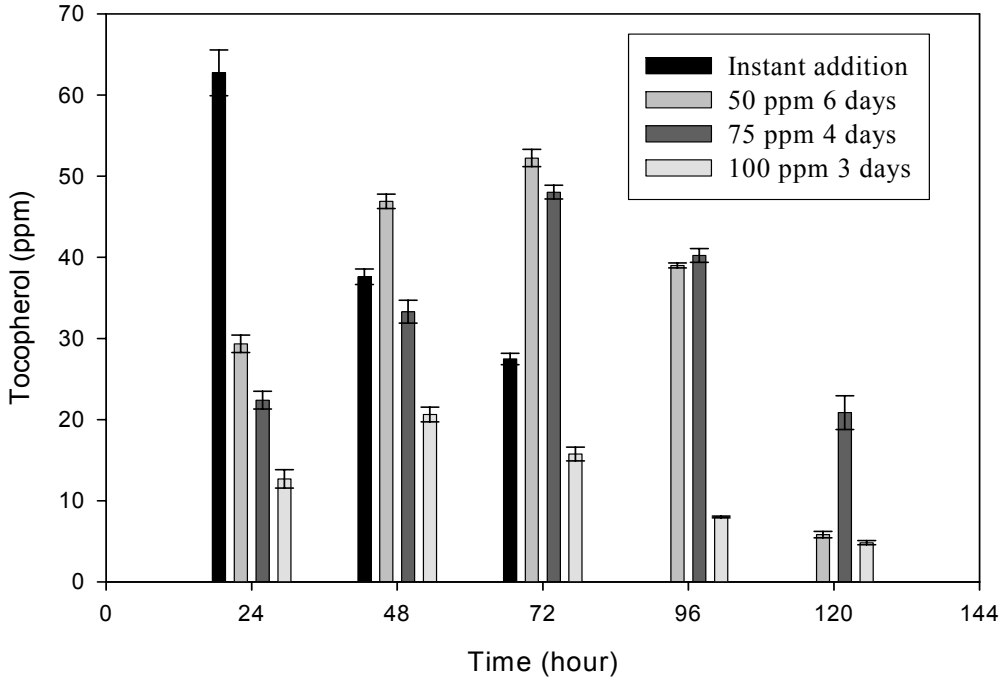


Figure 49 Retention of tocopherol (ppm) in linoleic acid over time at 40°C

Retention of tocopherol (ppm) in linoleic acid over time at 40°C. Experiment was conducted in dark place with 100 rpm shaking.

9.4 Tocopherol consumption under film delivery mode

In order to elucidate why a film of higher PP ratio had a higher antioxidant effectiveness against linoleic acid oxidation, the concentration profiles of tocopherol released from the LDPE/PP blend films into linoleic acid was obtained under the conditions of open-air, dark place, and rotary shaking at 40°C (Figure 50). For the linoleic acid stored with the film of 0, 25, or 50% PP ratio, the concentration of tocopherol sharply increased up to about 70 ppm after 24 hours of storage and then continuously decreased to almost zero during the subsequent storage period. For the linoleic acid stored with the film of 75 or 100% PP ratio, the tocopherol concentration increased relatively slowly until 48 hours of storage, followed by continuous decrease during the rest of storage. The slower initial increase of tocopherol concentration in the linoleic acid stored with a film of higher PP ratio was because the release of tocopherol was more hindered by PP molecules compared to LDPE molecules, as observed in our preliminary study [6]. The succeeding continuous reduction of tocopherol concentration was probably because the tocopherol molecules in linoleic acid were consumed for preventing lipid oxidation and/or chemically degraded in a faster rate than replenished by their release from the films. It was also shown in Figure 50 that in spite of the slower tocopherol release, a higher tocopherol concentration was retained in the linoleic acid stored with a film of higher PP ratio during most of storage period, indicating that the film of higher PP ratio released the entrapped tocopherol in a more sustained manner under given conditions. This is why the film prepared with higher PP ratio showed higher antioxidant effectiveness.

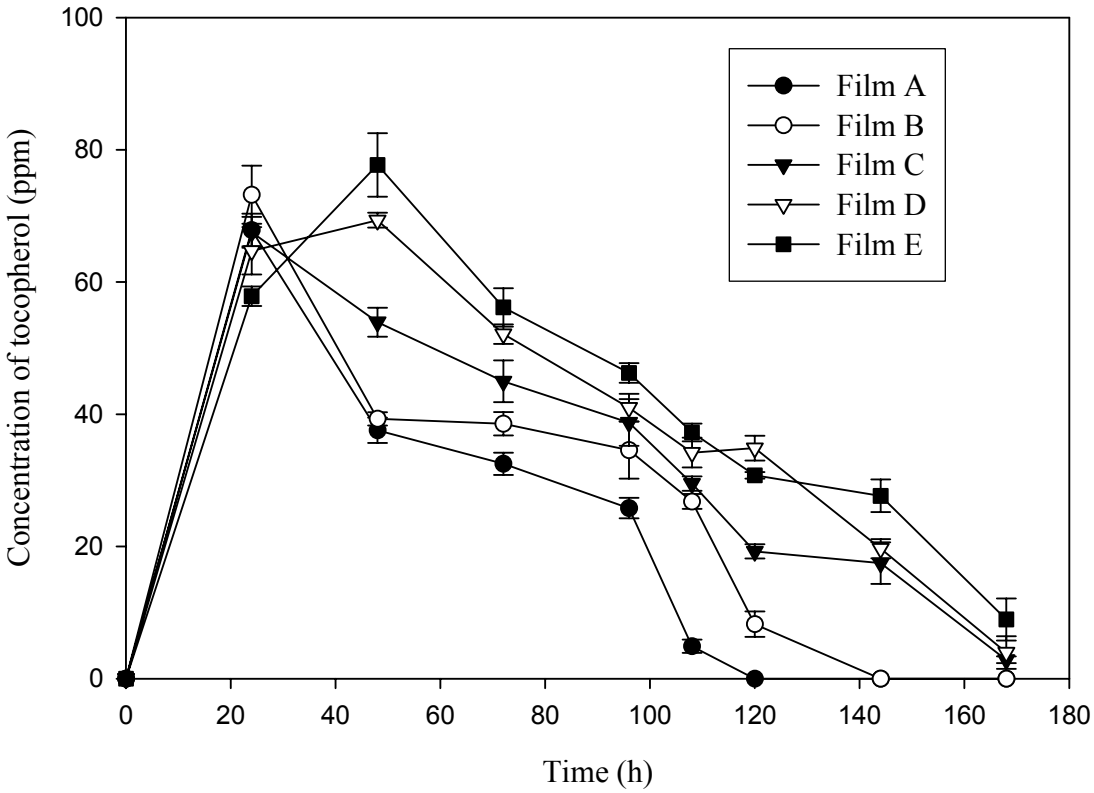


Figure 50 Degradation of tocopherol released from films

Experiment was conducted in dark place with 100 rpm shaking at 40°C.

10 DEFINATION AND DETERMINATION OF TARGET RELEASE RATE

10.1 Definition of target release rate

Traditionally, the antioxidants were added into food formulation all at once (instant addition). The effect was concentration dependent but not in a linear trend (Figure 33). For example, 1000 ppm tocopherol was 3.3 times more than 300 ppm in concentration, 1000 ppm tocopherol only extended the induction period of lipid oxidation two times longer than 300 ppm. Moreover, adding high concentration of tocopherol at time zero resulting in drastic consumption (degradation) of tocopherol at the early stage of the lipid oxidation (Figure 46). The above results suggested that the shelf life of food could not be extended long enough just by increasing the concentration of antioxidant. More than that, legal limitation of antioxidants also precluded the approach of adding high amount of antioxidants for certain foods.

To overcome the above limitations with the instant addition mode, exploratory research work was conducted in this dissertation to investigate the possible way of delivery antioxidants using timed-delivery (slow release) modes. Three timed-delivery modes (manual syringe, syringe pump, packaging film) were established and tested for their effectiveness to inhibit lipid oxidation. The results showed that all three timed-delivery modes provided better antioxidant effectiveness with proper delivery rates. For example, delivering 75 ppm / 24 hours tocopherol continuously for 4 days by using syringe pump provided more than 40% longer induction period of lipid oxidation than instant addition of 300 ppm tocopherol at 40°C. Similar results were found with the manual addition and the tocopherol containing films. Putting together the above results from different delivery

modes verified the concept that a better effectiveness of antioxidants was achieved by just using timed (slow) delivery modes. Moreover, it was also found that in the timed-delivery (slow release) modes, the antioxidant effectiveness was clearly dependent on the delivery rates. As shown in Figure 38, the delivery rate of 50 ppm / 24 hours did not provide longer lipid induction period than instant addition of 300 ppm tocopherol (too slow rate was not good). Delivery rate of 100 ppm/day provided longer induction period than instant addition of 300 ppm tocopherol but shorter than that achieved by delivery rate of 75ppm/day (too fast was not good either). Therefore, there should be an optimum rate in between (release rate not too fast and not too slow). Results from tocopherol containing films also verified that antioxidant effectiveness was dependent on release rates. Therefore, this optimum rate to deliver antioxidant was conceptually proved and was defined as the target release rate in this dissertation.

We have defined the target release rate as: the optimum rate at which an antioxidant must be released from a food package in order to replenish the antioxidant consumed in reaction and to maintain an adequate concentration in the food for inhibiting active lipid oxidation until the end of shelf life of the food.

In this research, two approaches have been used to determine target release rate. The first approach is using syringe pump to simulate the release of the tocopherol from the packaging films. The second one is by matching the tocopherol consumption (degradation) rate.

10.2 Using syringe pump to determine target release rate

In order to prove the concept and find the approach to determine the target release rate, a syringe pump was used in our study to achieve the slow release of tocopherol. We

used syringe pump to release a total 300 ppm of tocopherol at different rates into the linoleic acid. Then the induction period of lipid oxidation was measured at 40°C. The induction period was plotted against release rate in Figure 51. The result showed that the induction period firstly increased with the increasing release rates. The induction period reached the maximum at about 80 ppm. After that, the induction period decreased with the increasing release rates. The data were fitted with peak function (log normal). If we want to extend the shelf life as long as possible, the release rate corresponding to the apex of the curve was the target release rate and therefore could be predicated.

We did the same experiments at 30°C (Figure 52) and 50°C (Figure 53). Similar patterns were found at 30°C and 50°C as compared with 40°C. However, at 30°C, the predicted target release rate was about 40 ppm which was slower than that of 40°C. At 50°C, the predicted target release rate was about 150 ppm which was faster than that of 40°C and 30°C. Therefore, the target release rate changed with temperature. At lower temperature, the lipid oxidation slowed down, less tocopherol was consumed; therefore, the tocopherol should be released at a slower rate. At higher temperature, lipid oxidation occurred faster, more tocopherol was consumed; therefore, tocopherol should be released at a faster rate. However, releasing tocopherol too fast caused the self reaction of tocopherol and compromised the effectiveness of tocopherol in the linoleic acid. The implication from the above result was that it was possible for us to generate a math model to predict the target release rate corresponding to different conditions such as temperature.

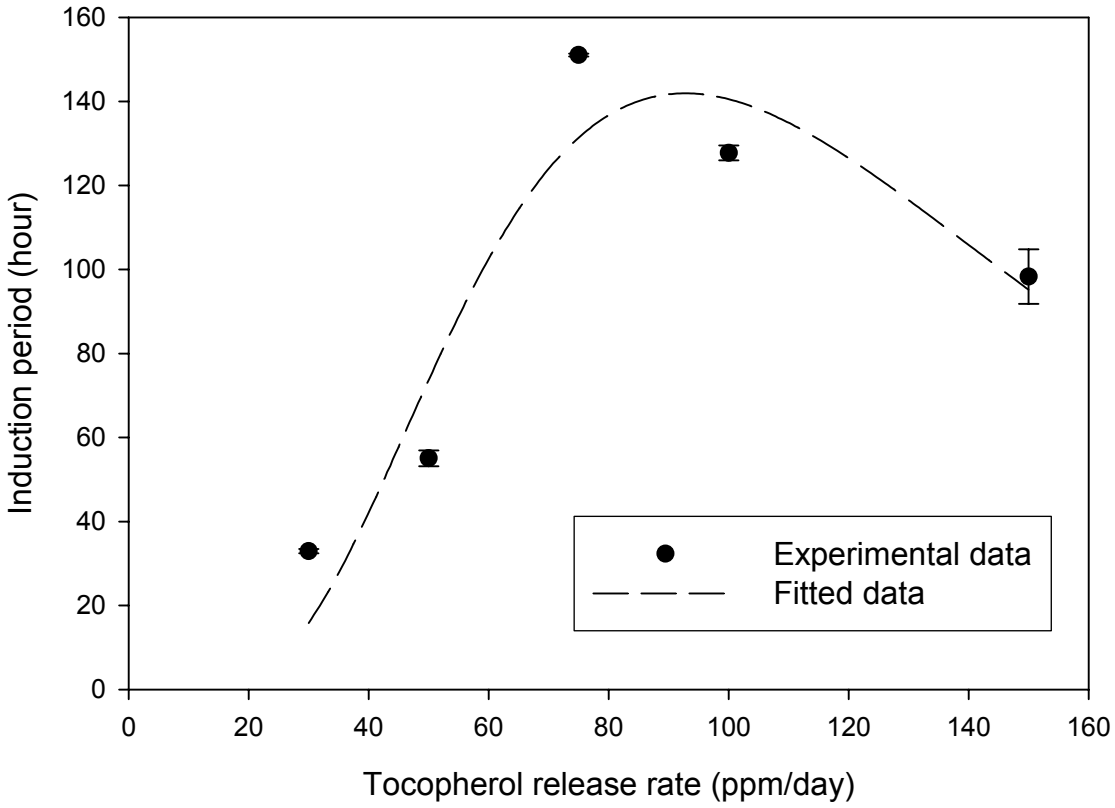


Figure 51 Determine target release rate using syringe pump at 40°C

Data was fitted with peak (log normal) function. Experiments were done in dark place with 100 rpm shaking at 40°C.

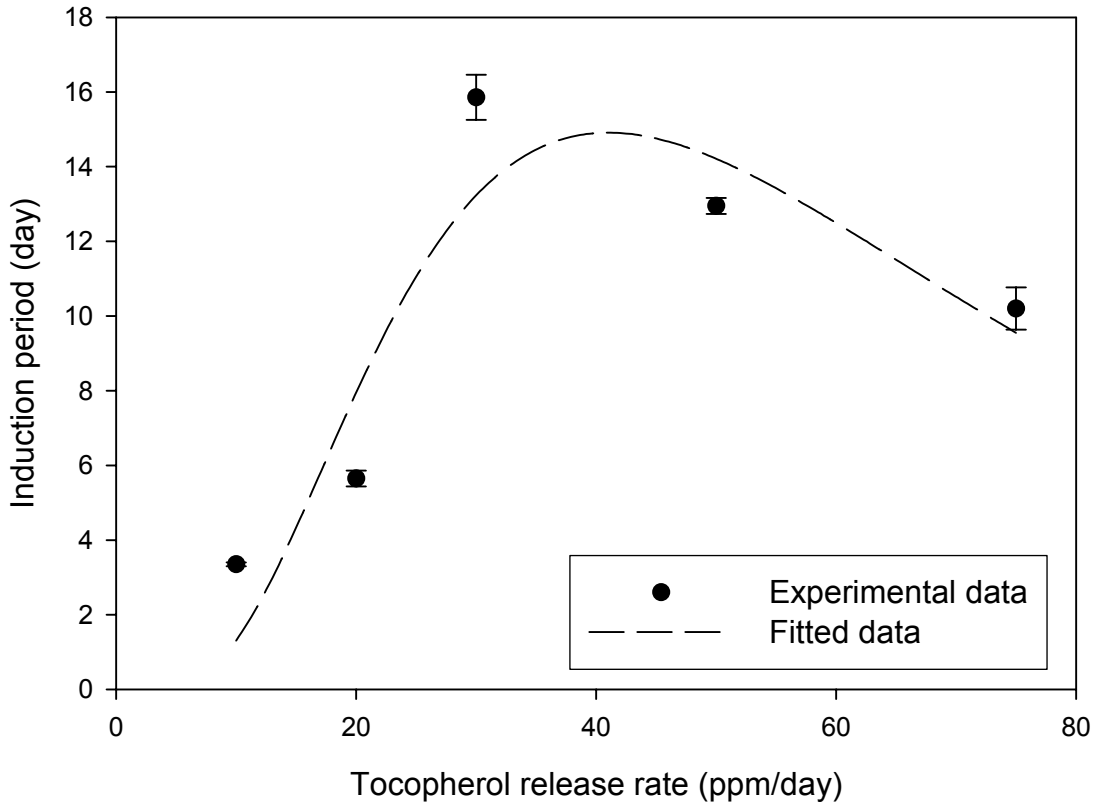


Figure 52 Determine target release rate using syringe pump at 30°C

Data was fitted with peak (log normal) function. Experiments were done in dark place with 100 rpm shaking at 30°C.

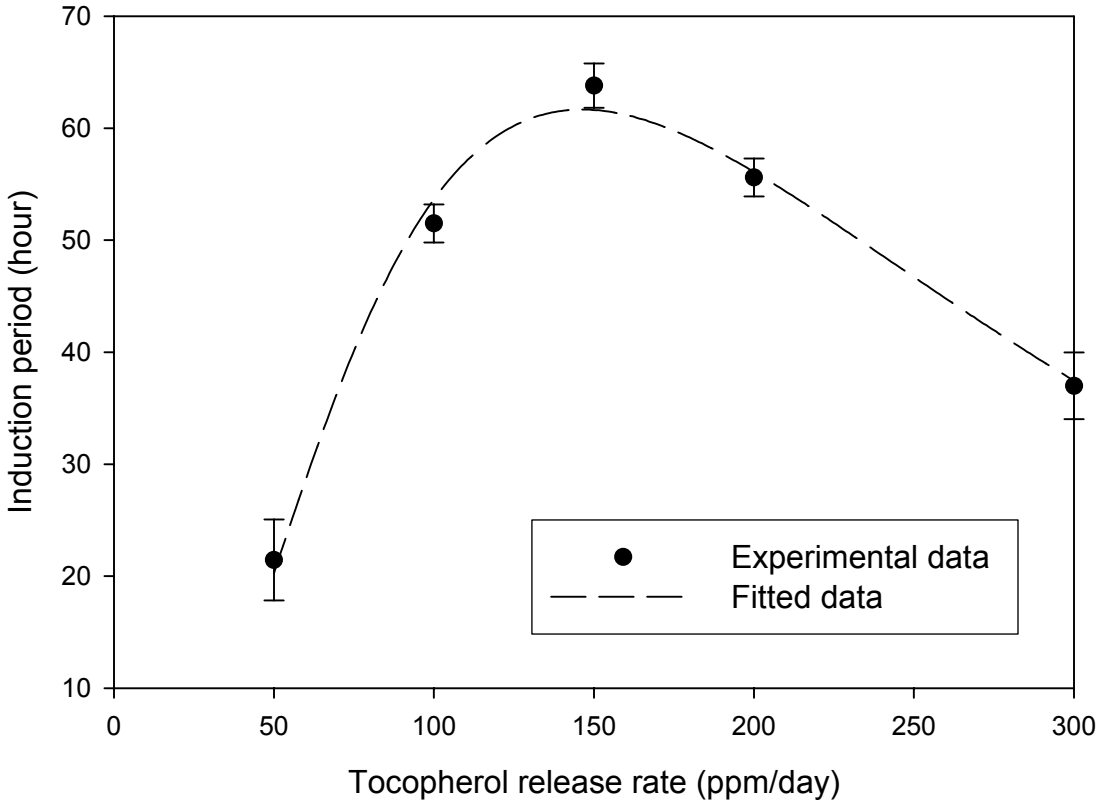


Figure 53 Determine target release rate using syringe pump at 50°C

Data was fitted with peak (log normal) function. Experiments were done in dark place with 100 rpm shaking at 50°C.

10.3 Determine target release rate by matching tocopherol consumption

In order to determine the target release rate, an attempt was taken to investigate the degradation kinetics (consumption rate) of tocopherol. The assumption was that by matching antioxidant degradation kinetics, math models could be built to determine the target release rate of antioxidant. The initial attempt to model the degradation kinetics found that the tocopherol degradation data fitted well with exponential equation. By measuring the tocopherol degradation kinetics, it was also found that timed-delivery

resulted in a higher retention of tocopherol inside linoleic acid over time which partly explained why the slow release had better antioxidant effectiveness.

At time zero, 300 ppm tocopherol was added into the linoleic acid all at once (instant addition). The tocopherol concentrations were measured over time at 40˚C. The tocopherol retention data were curve fitted using both the polynomial (Figure 54) and the exponential equation (Figure 55). It was clearly shown that the exponential equation fitted the tocopherol degradation kinetics better than the polynomial equation.

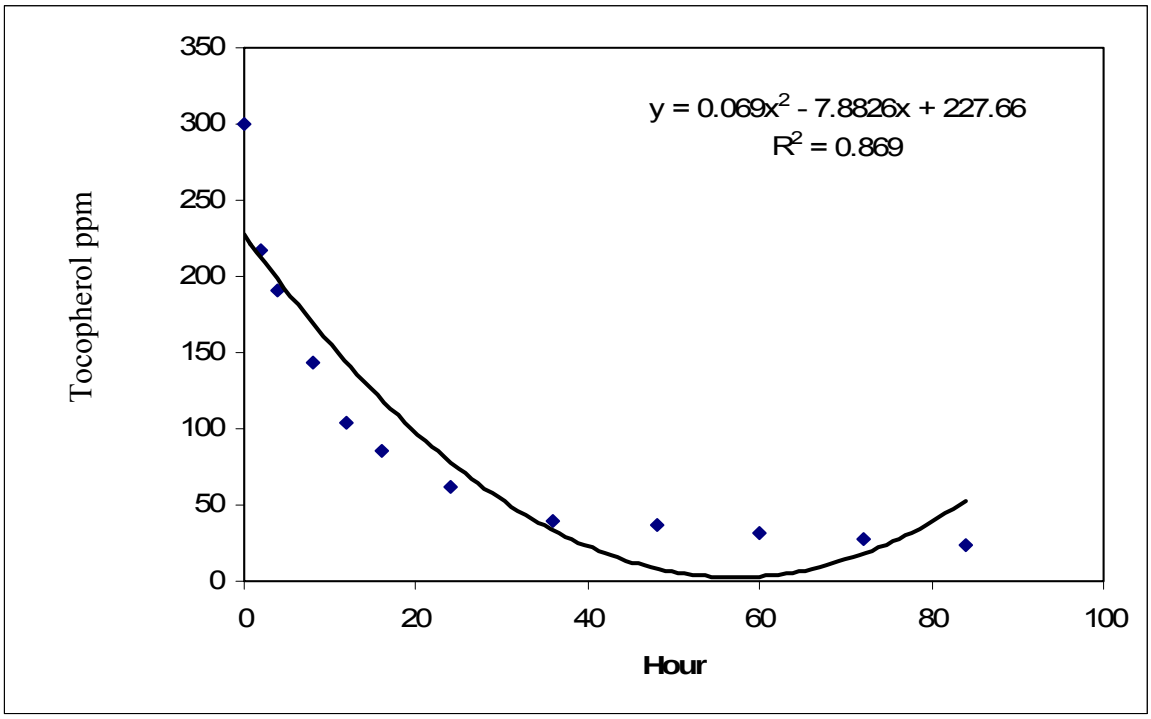


Figure 54 Curve fitting tocopherol degradation data with polynomial equation

Curve fitting tocopherol degradation data with polynomial equation. Experiment was done with 300 ppm instant addition of tocopherols at 40°C.

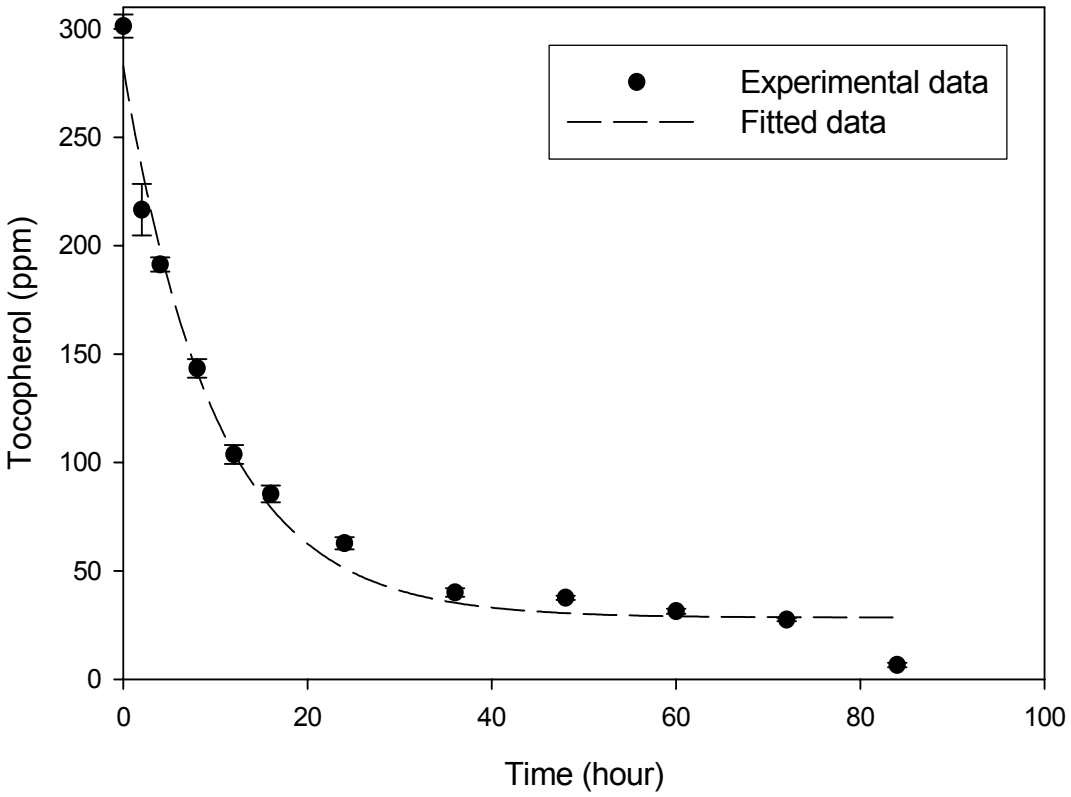


Figure 55 Curve fitting tocopherol degradation data with exponential decay mode

Data was fitted with exponential decay model. Experiment was done with instant addition of 300 ppm tocopherol into linoleic acid at 40°C in dark place with constant shaking.

10.4 Factors affecting target release rate

10.4.1 Effect of temperature on induction period

As we know that temperature is one of the most important factors affecting induction period of lipid oxidation and the shelf life. It will be necessary to build a model to predict the induction period at different temperatures. One of the most useful models is Arrhenius equation. As shown in Figure 56, the nature logarithm of induction period was

plotted against the temperature. A straight line (y=ax+b) was generated by making the linear regression of the data.

Then the linear model was verified by extrapolating the temperature to 50°C (Figure 57). The extrapolated data was very close to the experiment data at 50°C. This example shows that it is possible to predict the induction period and the shelf life with different storage temperatures. It means that we can build model to predict the induction period or the shelf life with different temperatures. It also suggests that it may be possible to take the same approach to predict the effect of other factors such as food compositions, oxygen concentrations, etc. Kaya et al. carried out accelerated shelf life testing on sunflower oil and vegetable oil. Their results showed that they were able to make similar plot (induction period (log scale) against temperature) [72]. They confirmed that they could extrapolate the result of accelerated shelf life testing (high temperature and short term storage) to low temperature long term storage based on above plot (linear regression). The Q_{10} was 2.0 for the sunflower oil and 2.1 for the olive oil. The shelf life of the sunflower oil was estimated to be 10.6 month at 20°C. The shelf life of the sunflower oil was estimated to be 20.8 month at 20°C.

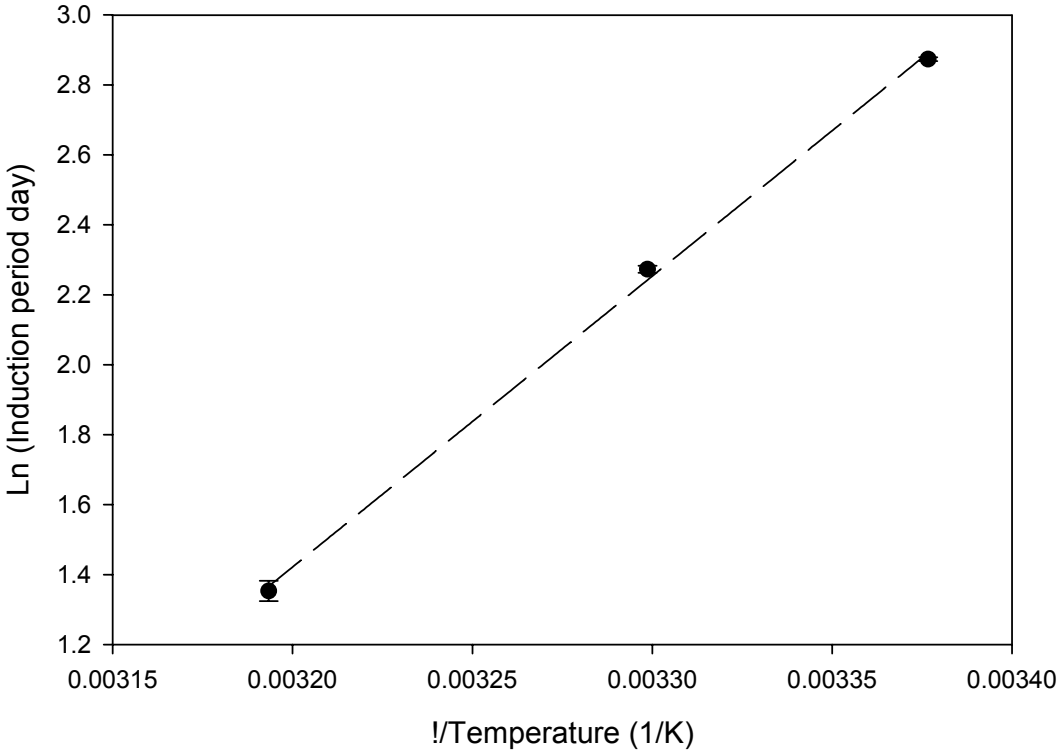


Figure 56 Effect of temperature on induction period

Experiment was done with instant addition of 300 ppm tocopherol into linoleic acid in dark place with constant shaking.

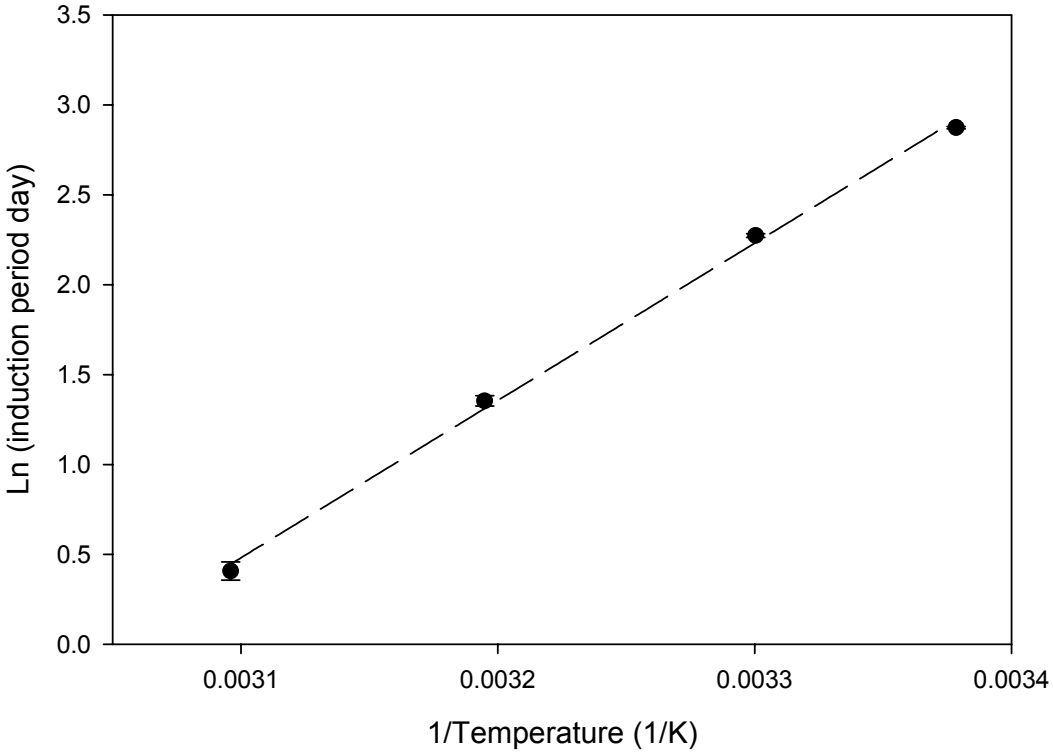


Figure 57 Predict effect of temperature on induction period

Experiment was done with instant addition of 300 ppm tocopherol into linoleic acid in dark place with constant shaking.

10.4.2 Effect of temperature on tocopherol consumption

The results from the degradation of 300 ppm tocopherol at 23°C (Figure 58) showed similar tocopherol degradation (consumption) pattern. The data was fitted with similar model as compared with degradation of 300 ppm tocopherol at 40°C.

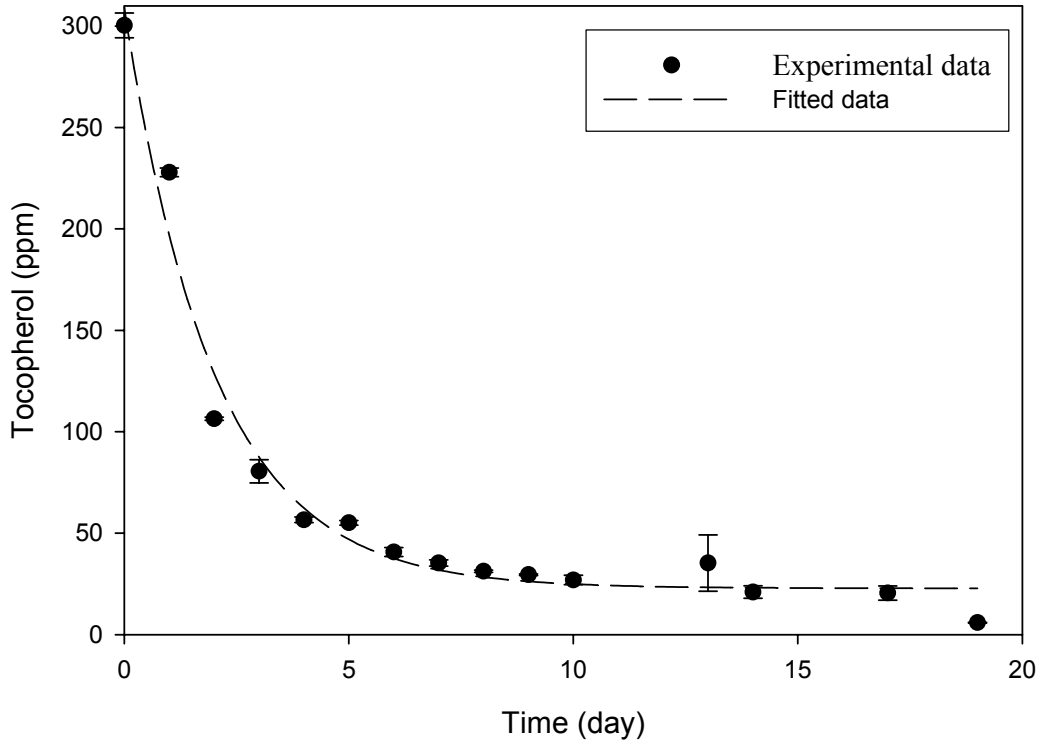


Figure 58 Tocopherol degradation at 23°C

Experiment was done with instant addition of 300 ppm tocopherol into linoleic acid in dark place with constant shaking at 23°C.

10.4.3 Effect of concentration on tocopherol degradation

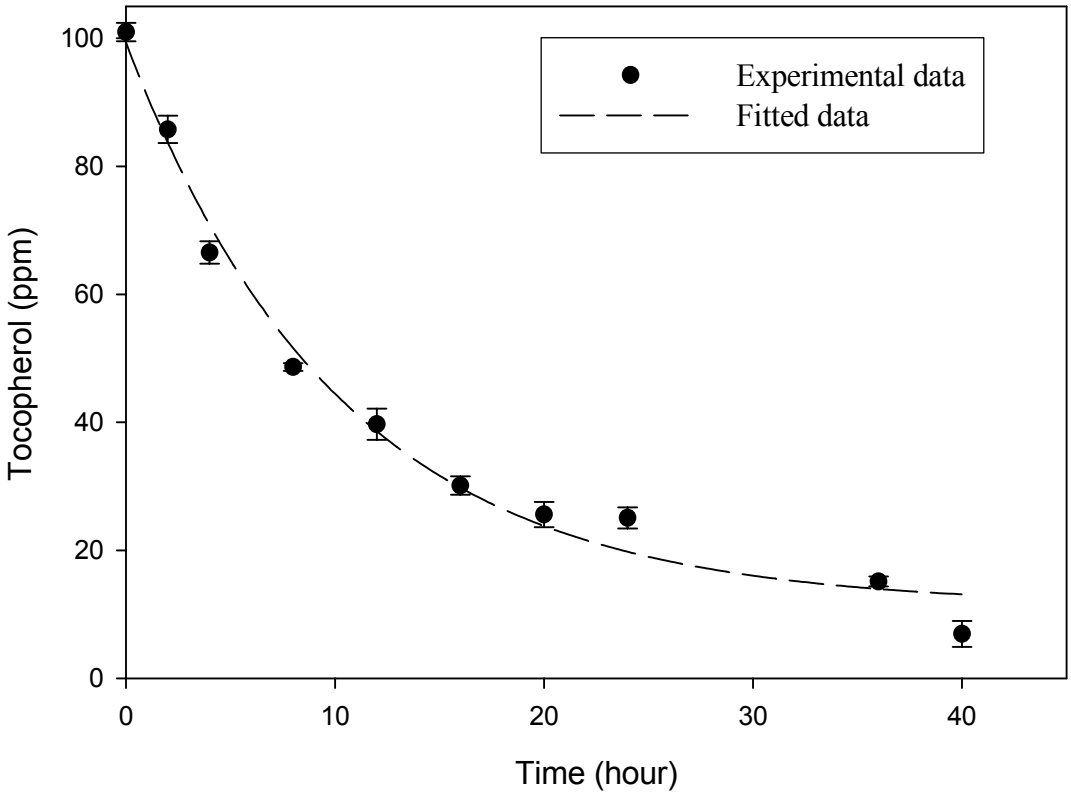


Figure 59 Tocopherol (100 ppm) degradation at 40°C

Experiment was done with instant addition of 300 ppm tocopherol into linoleic acid in dark place with constant shaking at 23°C.

The results from instant addition of 100 ppm tocopherol showed similar tocopherol degradation (consumption) pattern (Figure 59). The data was fitted with similar model as compared with the degradation of 300 ppm tocopherol at 40°C.

In summary, above results proved our assumption that it was possible to determine the target release rate based on tocopherol consumption (degradation) kinetics.

11 VOLATILITY OF ACTIVE COMPOUNDS

In the conceptual framework for controlled release packaging, there is a factor called active compounds. This chapter will discuss the properties of active compounds especially the volatility. Tocopherol is a non-volatile active compound and it may be used for the liquid or the semi-liquid food where a food product has good contact with the packaging films. In the case of the solid type food products, where there is no good contact of the food product and the packaging film, the volatility of the active compounds will be important. It is assumed that volatile active compounds can be first evaporated from the packaging film into head space of the packaging and then condensed on the food surface. Sesamol is selected as an example of volatile antioxidants because it is very potent antioxidant. Another advantage of using sesamol is that sesamol is a natural active compound.

11.1 Extraction of sesamol and BHT in films

The solvent extraction studies were conducted to determine the availability of the sesamol and the BHT in the films. The extraction solvent and conditions were adapted from Obinata [6]. The data in Table 11 showed that film A contained 1218.3±11.3 ppm sesamol, film B contained 646.1±18.3 ppm sesamol. The results confirmed that sesamol was incorporated into polymer matrix.

Table 11 Sesamol and BHT in films

Film #	Antioxidant	Extractable antioxidant	Film structure (layers)
A	Sesamol	1218.3±11.3 ppm	LLDPE/HDPE/HDPE
B	Sesamol	646.1±18.3 ppm	HDPE/HDPE/EVA
C	BHT	1605.5±29.2 ppm	HDPE/HDPE/EVA

Films of same structure and polymer compositions but without antioxidants were produced as control for each of above films.

11.2 Release of sesamol from film into air

A piece of film A (containing 1218.3±11.3 ppm sesamol) was exposed to air to study the release of sesamol from film matrix. This was to simulate the release of sesamol from the packaging film to the package headspace. The release kinetics of sesamol from film into the air was shown in Figure 60 (10°C and 30°C). When the film was exposed to open air, 60% of the sesamol was evaporated out of the film matrix within 6 hours at 10°C. While at 30°C, 60% of the sesamol was evaporated out of the film matrix within 1 hour. The sesamol evaporated from polymer matrix into air very fast due to its volatility. The result suggested that the sesamol in the packaging film could migrate to the packaging headspace easily. The release rate of the sesamol was also temperature dependent. Release rate at 30°C was about 6 times faster than that of 10°C. To further slow down the release of volatile active compounds such as sesamol from polymer matrix, different types of polymers such as EVOH and the multilayer films should be tested.

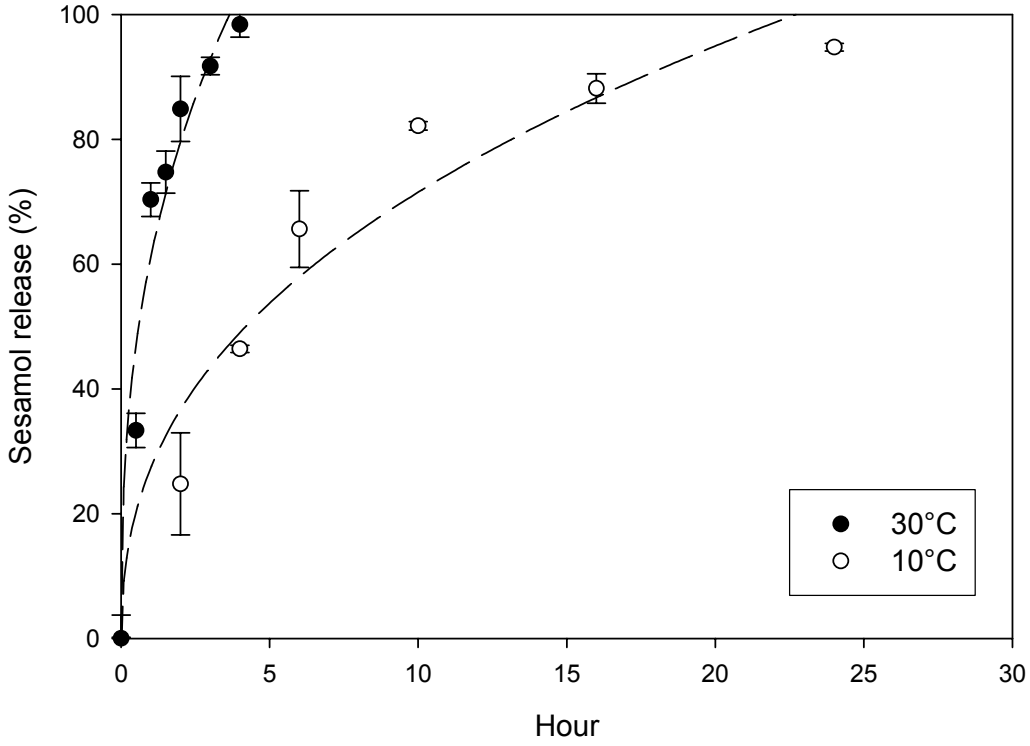


Figure 60 Release of sesamol from film matrix into air phase at 10°C and 30°C

11.3 Effect of sesamol containing film on inhibiting oxidation of linoleic acid

Film A (containing 1218.3±11.3 ppm sesamol) was used in a close jar system containing linoleic acid (Figure 28). The results at 40°C (Figure 61) showed that linoleic acid in the jar with the control film (no antioxidant) had induction period of lipid oxidation of 6.6 hours. The sesamol film had induction period of lipid oxidation of 35.1 hours. Results at 23°C (Figure 62) showed that linoleic acid in the jar with control film (no antioxidant) had induction period of lipid oxidation of 1.3 day. The sesamol film had induction period of lipid oxidation of 10.6 days. Sesamol released from polymer film extended induction period of lipid oxidation 529% and 793% longer than control film (no

antioxidant) at 40 and 23°C, respectively. Since there was no direct contact of film with linoleic acid, sesamol must first evaporate to the headspace and then condensed into linoleic acid and inhibit the oxidation of linoleic acid. Lee et al. also reported that a laminated pouch consisting of a HDPE layer and a heat seal layer impregnated with BHT retard lipid oxidation of linoleic acid while the film containing 73 ppm α-tocopherol failed to retard the oxidation of a packed model solid food containing 0.36% (w/w) linoleic acid at 45°C and 50% RH [50]. Therefore, for food products with little direct contact with packaging film, the packaging film containing the volatile antioxidants such as sesamol and BHT should be used. The volatility of the active compound will therefore, affect the target release rate.

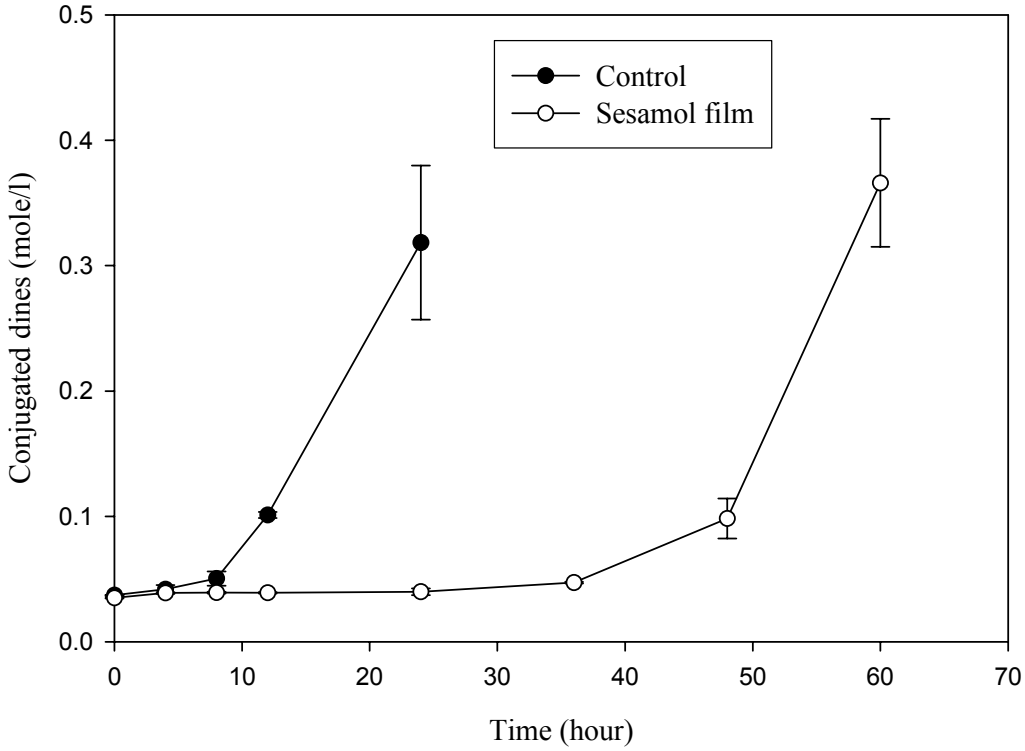


Figure 61 Generation of conjugated dienes in linoleic acid stored with sesamol film at 40°C

Experiment was done at 40°C in dark place. Linoleic acid stored with the film contain no antioxidant was used as control.

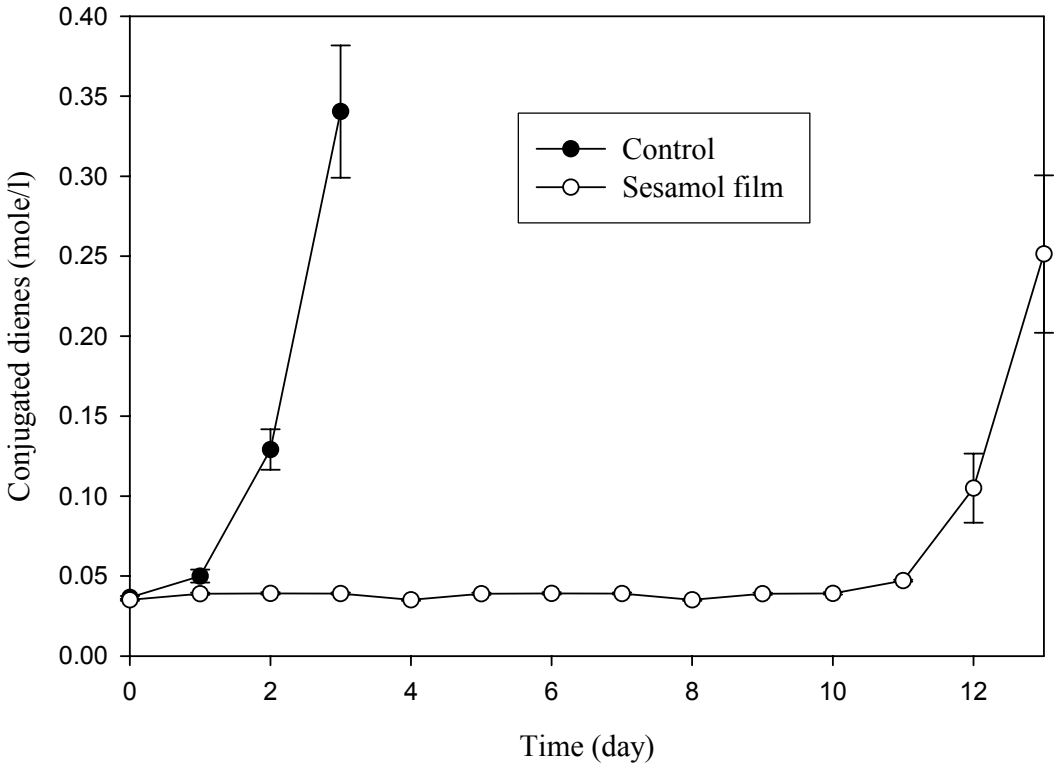


Figure 62 Generation of conjugated dienes in linoleic acid stored with sesamol film at 23°C

Experiment was done at 23°C in dark place. Linoleic acid stored with the film contain no antioxidant was used as control.

11.4 Results of breakfast cereal in storage

Film A (contain no antioxidant), Film B (containing 646.1±18.3 ppm sesamol), Film C (containing 1605.5±29.2 ppm BHT) and a control film were used to pack a breakfast cereal made of oatmeal. The sesamol containing film was compared with the BHT containing film in order to investigate the possibility to replace BHT (synthetic antioxidant) with sesamol (natural antioxidant). The concentration change of hexanal,

which was a good indicator of lipid oxidation [22], was measured from the breakfast cereal packaged with the above three films stored at 23ºC (room temperature) after one year (Figure 63). The effect of treatments was: cereal packed with the BHT film and the sesamol film had 85% and 59% less hexanal than cereal packed with the control film (no antioxidant), respectively. The internal sensory evaluation also showed that a strong rancid odor was smelled from the control film packed cereal. The rancid odor was not smelled from the BHT film and the sesamol film packed cereal (sensory data not shown here). The results on the cereal product verified the result that sesamol released from film inhibited lipid oxidation of linoleic acid. Wessling et al. (2000) also found that BHT was released from LDPE film and extended the shelf life of a cereal food, while alpha-tocopherol was not release from LDPE film and did not extend the shelf life of the cereal food [49]. All above results verified that volatile antioxidants such as sesamol and BHT extended shelf life of the cereal product. The sesamol packed cereal had more hexanal than BHT because that much less sesamol was incorporated in the film than BHT. The above result indicated that sesamol can be a good substitute for BHT for the antioxidant packaging application.

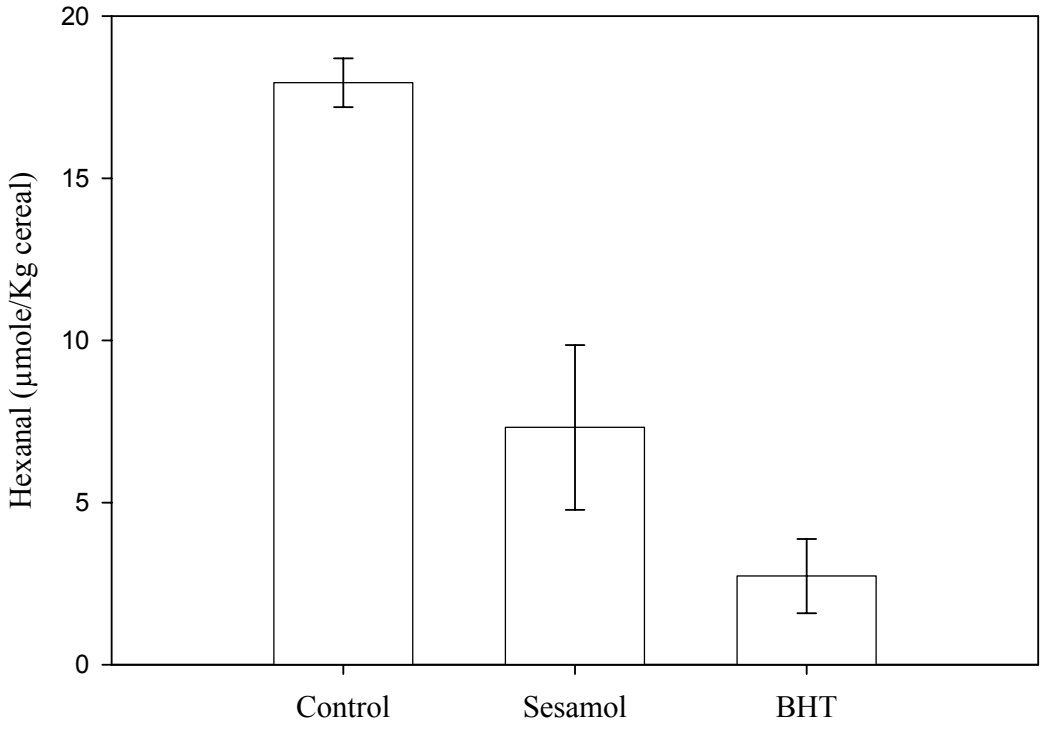


Figure 63 Hexanal concentration in generic cereal stored at 23°C for 1 year in dark place

In conclusion, the encouraging results from the simulated food (the linoleic acid) and the real food (the oatmeal cereal) support our assumption that sesamol can be incorporated into polymer film and extend the shelf life of food. The volatility of active compound is an important factor affecting the target release rate for the controlled release packaging. Sesamol as a natural antioxidant can be the substitute for the synthetic antioxidant BHT. In the future, the packaging film containing much higher concentration of sesamol will be produced and tested. The packaging film containing other volatile natural antioxidants such as carvacrol, will also be produced and test in a similar manner.

12 FOOD FACTOR

Experiments were done to evaluate the shelf life of the food products which were packed with the tocopherol containing films in order to prove the concept of target release rate, and to verify the results from the simulated food (linoleic acid). The tested food items included the peanut, the cheese spread and the peanut butter. The purpose of this study on real food products was two folds: the first purpose was to evaluate the effectiveness of tocopherol containing pouches on inhibiting oxidation of the food products. The second purpose was to evaluate the effect of food factor on the target release rate. A cereal product was also tested with the sesamol containing film and the result was discussed in Chapter 11.

12.1 Results of peanut test

Three different films were produced at the Pliant Company (Chippewa falls, WI) as shown in Table 12. The first film was the control film without any antioxidants added. The second film (Film A) was a polymer blend of LDPE and PP (50:50) with 3000 ppm of tocopherol. The third film (Film B) was 100% PP containing 3000 ppm of tocopherol. These films were laminated onto aluminum foil and then fabricated into pouches.

Table 12 Films used in peanut test

No.	Film Name	Film Composition	Added Tocopherol	Extractable Tocopherol
1	Control	100% LDPE	0 ppm	0 ppm
2	A	50% LDPE 50% PP	3000 ppm	2878.9±92.3ppm
3	B	100% PP	3000 ppm	2770.59±72.49ppm

Two types of peanuts (the dry peanut and the oil roasted peanut) were filled into the pouches and then heat sealed. The pouches were stored at three different temperatures (60, 40 and 23°C). Samples were taken periodically for chemical analysis (measurement of hexanal using GC) as well as sensory evaluation to determine the progress of lipid oxidation and shelf life of the food.

As shown in Figure 64 and Figure 65, the concentration of hexanal (µmole/ Kg peanut) was excessively high even initially, especially in the dry roasted peanuts. Rancid odor was also confirmed by the sensory evaluation. The result indicated that the peanuts were oxidized even before packaging.

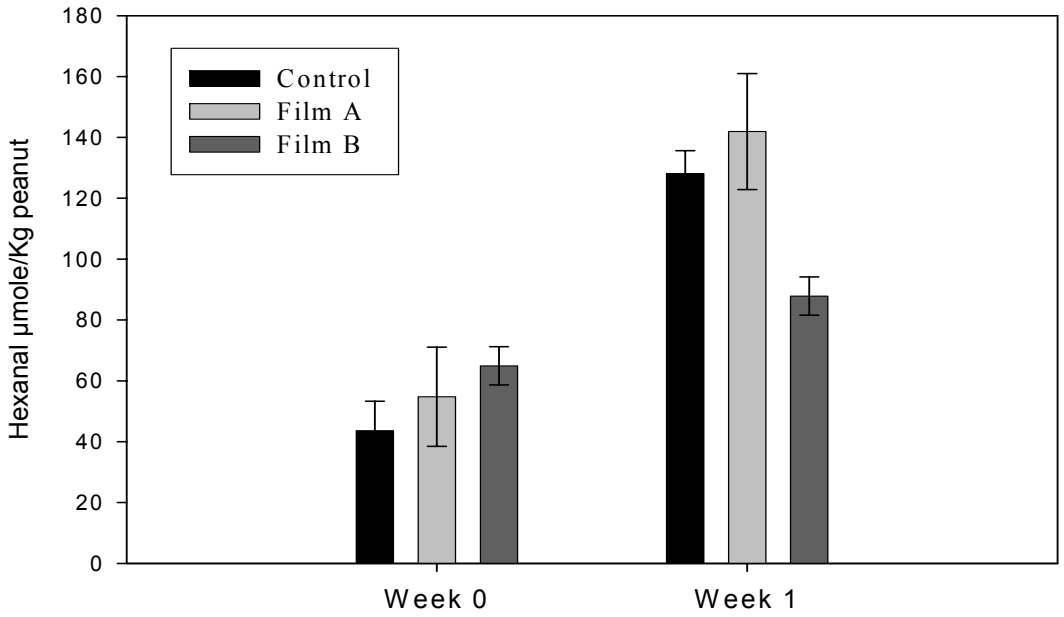


Figure 64 Hexanal concentration in MRE dry peanut at 60°C

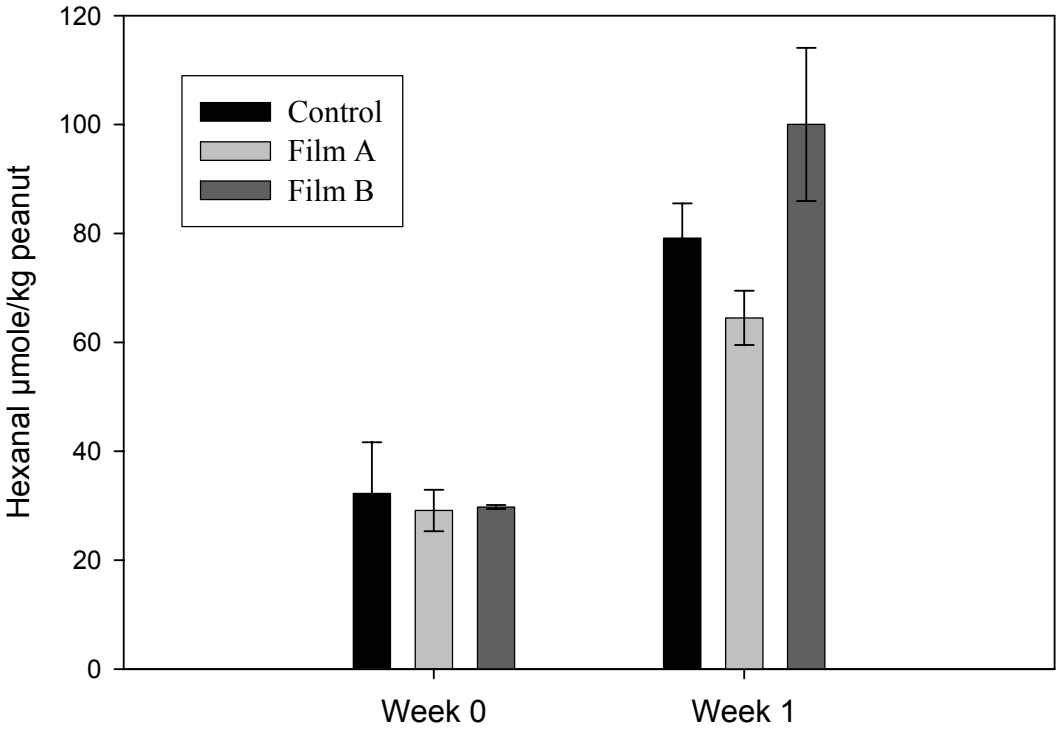


Figure 65 Hexanal concentration in MRE oil peanut at 60°C

The above data showed that the peanut provided by the Food Company (Houston, TX) had an unacceptable level of oxidation to begin with, although it still met the military specifications. Tightening the specifications or finding vendors who can provide peanut of good quality will help solve this problem. The current military specifications for peanut do not include instrumental quantification of oxidation (such as concentration of hexanal), and thus oxidized peanuts are sometimes not rejected. However, the controlled release antioxidant packaging cannot provide benefits for these previously oxidized products.

The above results showed that the initial oxidation of the food (food factor) was an important factor determining the shelf life and the target release rate for CRP.

12.2 Results of cheese spread test

Cheese spread, with a high fat content and semi-solid consistency, provides an ideal food matrix to study the release of tocopherol from packaging film into food.

Two laminated films (the control film without tocopherol and the test film with 3000 ppm tocopherol) were produced at Pliant Company. The structures of the films were listed in Table 13.

Table 13 Films for packing cheese spread

Film	Structure
Control (current MRE cheese spread laminate)	PET/adhesive/EVA/adhesive/foil/adhesive/LDPE
Tocopherol (3000 ppm) containing film (GLAM-083)	PET/adhesive/foil/adhesive/75% PP/25% LDPE

Cheese spread was packed at Portion Pac (Georgia, USA), the current and only supplier of this product to the military. The MRE pouches were stored at different temperatures (60°C and 40°C) and the samples were taken periodically for each temperature (60°C: every week, 40°C: every 2 weeks) for chemical analysis (measurement of hexanal using GC) as well as sensory evaluation to determine the progress of lipid oxidation and shelf life of the food.

12.2.1 Sensory evaluation of cheese spread

The sensory evaluation of the cheese spread was conducted by Natick Soldier Systems Center (Natick, USA). The results in Table 14 and Table 15 showed that cheese spread

packed with tocopherol film generally had better (higher) sensory scores than the control film packed cheese spread. It was clearly showed that release of tocopherol form film into cheese spread prevented the browning (darker color) of cheese spread (Figure 66). The reason why The lipid oxidation products (free radicals, hydroperoxides and aldehydes) can react with free amine groups of proteins and with free amino acids, forming yellow intermediary products which can polymerize into macromolecules of brown color. Release of tocopherol can inhibit the formation of lipid oxidation products, and therefore inhibit the formation of browning reaction of lipid oxidation products and proteins in the cheese spread [80-82].

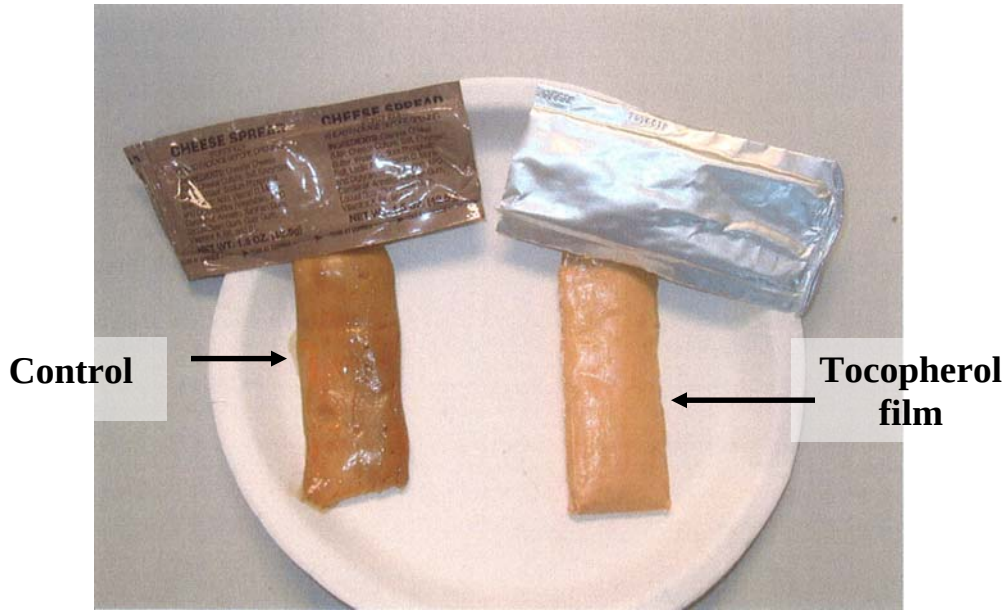


Figure 66 Releasing of tocopherol from film inhibited browning of cheese
The samples of cheese spread were stored at 40°C for 6 month.
Courtesy of Natick Soldier Systems Center and Pliant Company

Table 14 MRE cheese spread sensory results at 60°C

Week	Appearance		Odor		Flavor		Texture		Overall acceptance	
	Control	Tocopherol	Control	Tocopherol	Control	Tocopherol	Control	Tocopherol	Control	Tocopherol
0	6.64	6.64	6.36	6.58	6.55	6.27	6.55	6.09	6.41	6.23
1	4.45	6.23	6.18	6.59	5.65	6.25	4.86	6.06	4.86	6.18
2	4.70	5.90	5.70	5.98	4.88	6.28	4.78	6.25	4.98	6.09
3	5.44	5.50	5.22	6.11	5.22	5.44	4.71	5.06	4.81	5.42

Courtesy of Natick Soldier Systems Center and Pliant Company.

Table 15 MRE cheese spread sensory results at 40°C

Month	Appearance		Odor		Flavor		Texture		Overall acceptance	
	Control	Tocopherol	Control	Tocopherol	Control	Tocopherol	Control	Tocopherol	Control	Tocopherol
0	6.64	6.64	6.36	6.58	6.55	6.27	6.55	6.09	6.41	6.23
3	3.86	5.36	4.86	6.07	4.71	5.41	4.00	5.00	3.79	5.57
6	3.69	5.83	5.38	6.26	4.84	5.59	4.16	5.55	4.08	5.57

Courtesy of Natick Soldier Systems Center and Pliant Company.

12.2.2 Results of hexanal concentration in cheese spread

The result (Figure 67) showed that cheese spread stored at 40°C did not generate high concentration of hexanal. There was no significant difference between the control film (no tocopherol) and the tocopherol film packed cheese spread. The possible explanation is that cheese spread contains mostly saturated fat. Under certain oxidation pathway, hexanal was not generated from cheese spread (personal communication with Dr. Karen Schaich). Therefore, in order to get a whole picture of food lipid oxidation, other analytical methods such as SAF test should also be included in the future study.

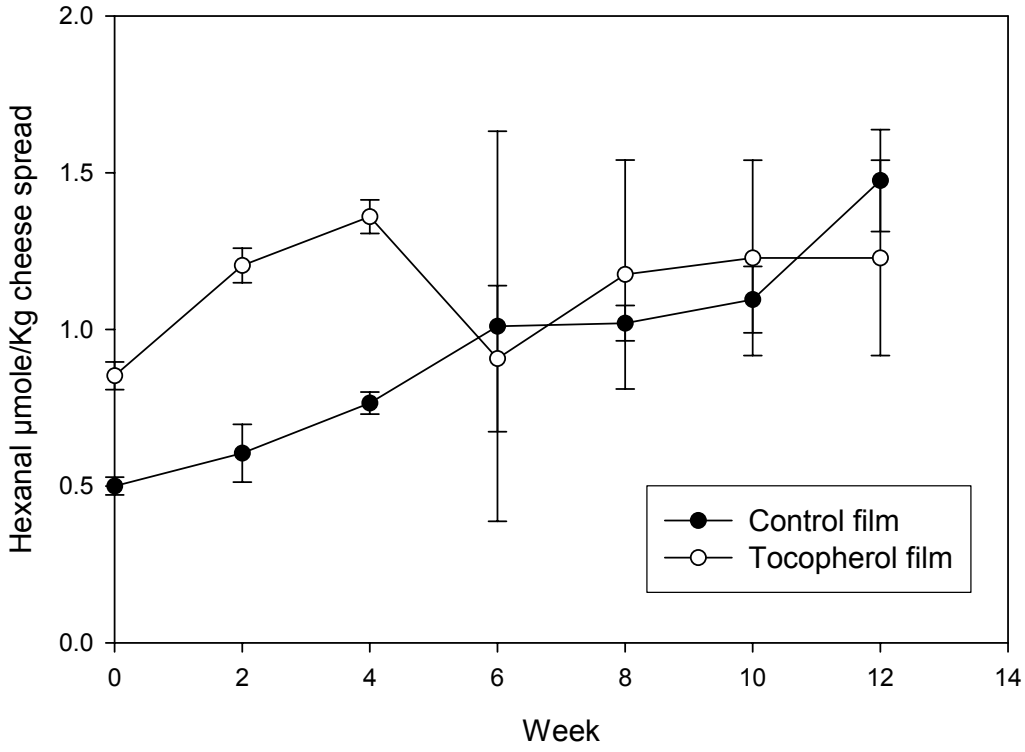


Figure 67 Hexanal concentration in cheese spread over time at 40°C

12.2.3 Release of tocopherol from film into cheese spread

In order to find out how we can determine the target release rate for the real food system, it is necessary for us to build a data base on actually tocopherol released into real food and build a connection with the tocopherol release kinetics and the food quality, especially during the food storage. In the cheese spread experiment, the release of tocopherol from packaging film into cheese spread over time was investigated. To simplify the analysis, tocopherol remained inside the packaging film was measured by using solvent extraction. The total amount of tocopherol in the film at time 0 was known, therefore, the amount of tocopherol released from film into the cheese was calculated based on the mass balance.

Figure 68 shows the tocopherols remained in the films (packing the cheese) during storage at 40°C. Figure 69 showed the possible release of tocopherol from films into cheese which was calculated based on data in Figure 68. It was likely that over one third of the tocopherol was released form the film into the cheese after 12 weeks. From sensory analysis, it seemed that the release of tocopherol from film (1238 ppm of tocopherol over 12 weeks) helped to slow down the browning of cheese. This encouraging result seemed to support our hypothesis that release of active compounds at certain rates (the target release rate) help to enhance food quality.

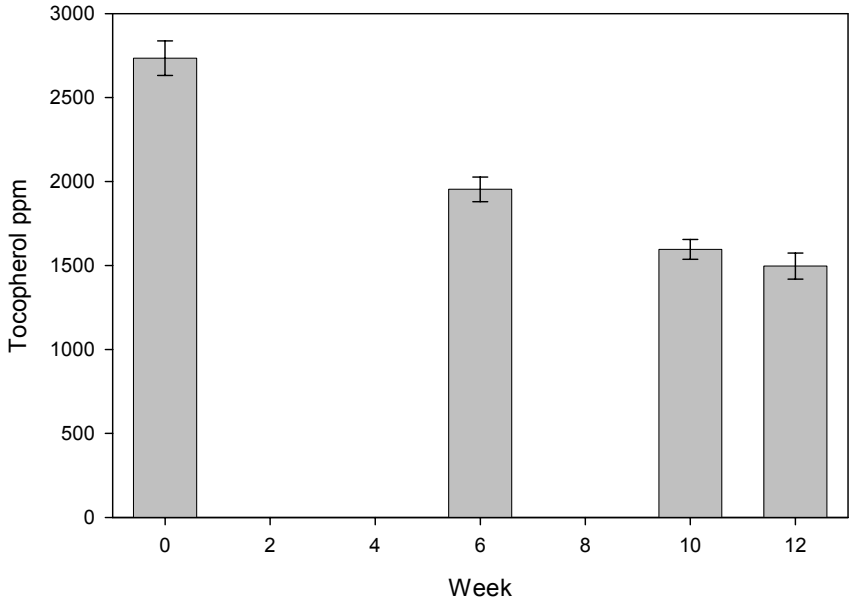


Figure 68 Tocopherol retained in films (cheese spread) during storage at 40°C

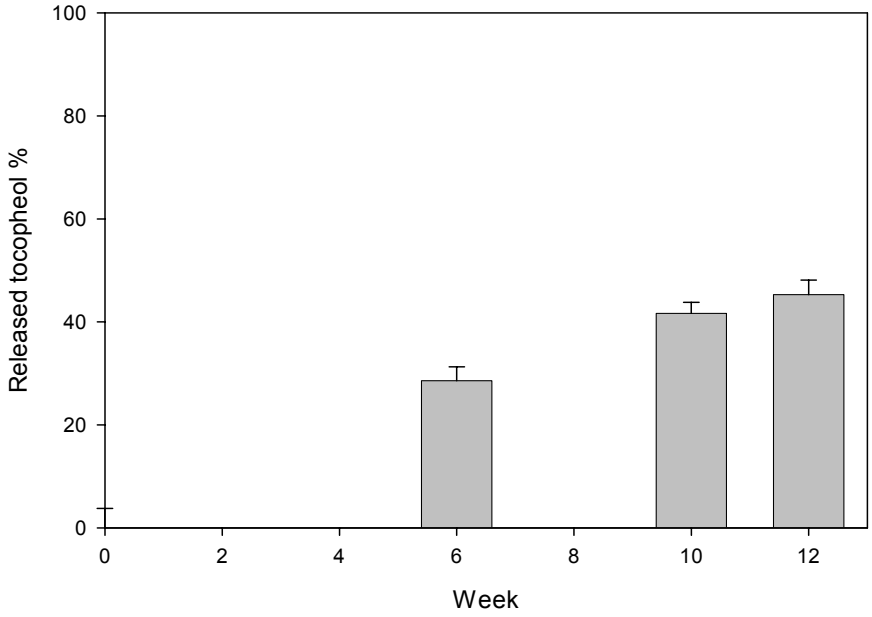


Figure 69 Tocopherol released from films into cheese spread during storage at 40°C

12.3 Results of peanut butter test

Peanut usually contains high amount of naturally presented tocopherol [75]. The peanut butter (containing tocopherol in the food composition) was packed with control films (no antioxidant). The packed peanut butter was used to investigate the effect of initial load of antioxidant in food on determination of the target release rate.

12.3.1 Change of hexanal in peanut butter during storage

Figure 70 showed that hexanal concentrations (related to rancid odor) were very low at 8 weeks; the hexanal concentrations at 60 and 40°C were still not high enough to yield rancid odor. Monitoring the hexanal should continue for a longer period of time.

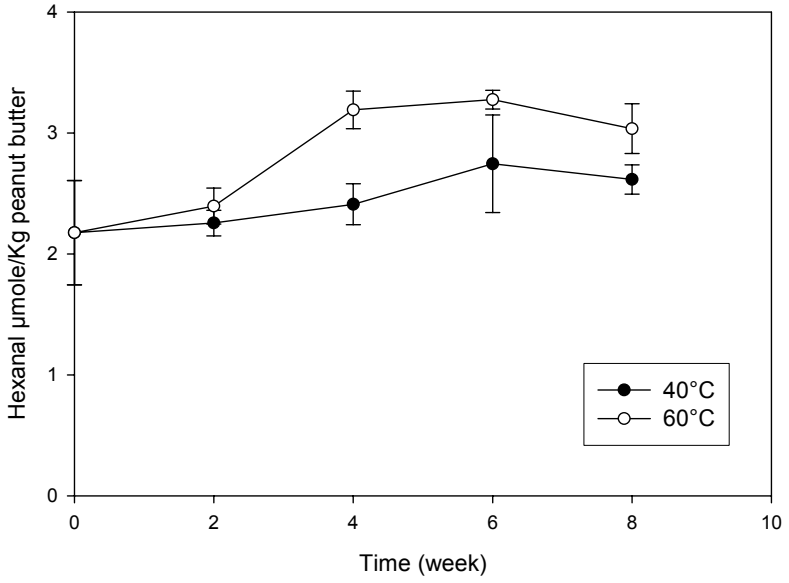


Figure 70 Hexanal in peanut butter stored at 40 and 60°C

12.3.2 Tocopherol degradation in peanut butter

The peanut butter was packaged with laminated film with alumina foil layer. The peanut butter initially contained above 400 ppm tocopherol which came from the peanut. As shown in Figure 71, tocopherol was degrading during storage at 60°C. At beginning, the degradation of tocopherol was fast, and slowed down after a while. However, there were about 200 ppm tocopherol remained after 8 weeks. The chemical analysis and the sensory test all demonstrated that there was little change in the quality of peanut butter. The possible reason was that tocopherol concentrations were still high enough to provide the protection against the lipid oxidation. In controlled release packaging application, this probably means that tocopherol release may not be necessary at this stage. Similar trend was also found at 40°C.

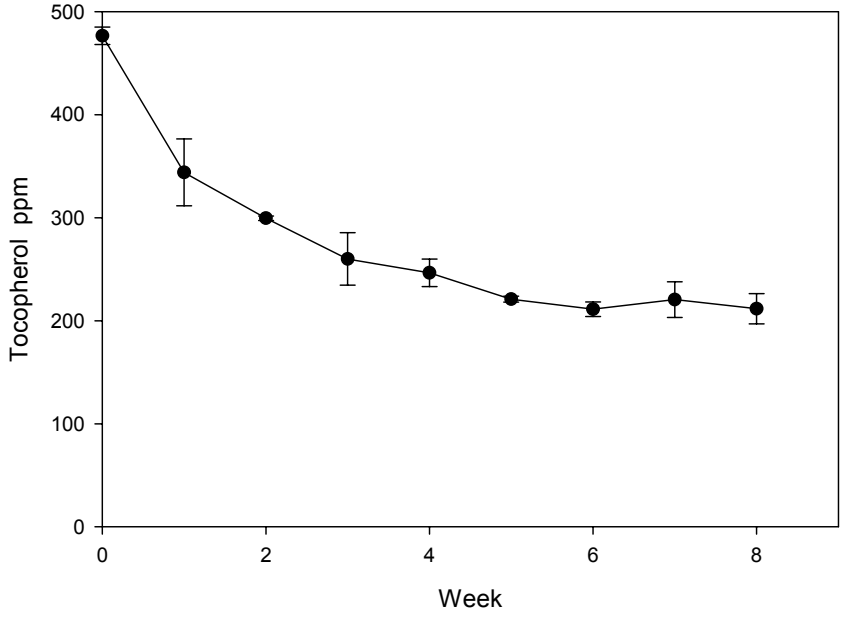


Figure 71 Tocopherol degradation in peanut butter at 60°C

12.4 Discussion and conclusion on real food tests

Shelf life study with real food products were conducted involving two antioxidants. The volatile antioxidant sesamol was released from the packaging film to the breakfast cereal (solid food). The non-volatile antioxidant tocopherol was released from the packaging film to the cheese spread (semi-solid food). Sesamol, as a volatile antioxidant, showed effectiveness on solid type of food (cereal box). Tocopherol, as a non-volatile antioxidant, showed effectiveness to reduce browning of cheese spread.

The major factors affecting the target release rate were summarized as below: First, volatility of the active compounds affects the target release rate. Second, food contact is a limiting factor affecting the target release rate. Third, food formulation, especially initial tocopherol load (peanut butter with 400 ppm initial tocopherol loading was investigated as an example) affects the stability of the food product and therefore affects the target release rate.

All the above experiments were our initial attempt for the purpose of defining and determining the target release rate. Preliminary results, especially the results from the breakfast cereal and the cheese spread were encouraging. They seemed to support our concept of the target release rate and provided some approaches to determine target release rate in the future work. Further study with real food products is absolutely necessary in order to continue our endeavor to determine the target release rate and for the development of the controlled release packaging.

13 PHYSICAL PROPERTY OF POLYMER FILM

Physical properties of packaging films were determined in this study. The purposes were three folds. The first purpose was to characterize the properties of packaging films. The second purpose was to investigate the possible effect of added active compounds on the physical properties of film. The third purpose was to provide useful means of control on the production of film and the quality of film for the future production of controlled release packaging films in the industry.

Based on the conceptual framework for controlled release packaging (Figure 15), we have considered different variables such as polymer type and morphology. We have found that polymer type contribute the most (60% to 70%). Based on that, in the film delivery mode experiment, we blended two types of polymer LDPE and PP together with different ratio try to achieve different release rates of tocopherol (Table 16). The purpose of blending of different polymers is to prove the concept that polymer composition affects the release rates of tocopherol. Therefore we are looking more at the overall trends rather than the particular release rate of one polymer.

Considering the commercialization of CRP, the common packaging materials were preferably tested during our study. The prime resins such as Dow PL1840 are very consistent between batches. The resin companies take samples from each lot and measure rheological properties, etc. to ensure consistent quality. Therefore, the properties of the resin and film are consistent between batches. However, there will be some difference between different grades of LDPE for example; but these differences will be small in comparison to the effect of resin type, i.e. difference in release rates between two LDPE

resins will be small in comparison to a LDPE and a PP. As long as we pick LDPE resins with the same density, our release properties should be very similar (personal communications with Dr. Brad Finnigan, Polymer scientist, Pliant Co., Ltd.). Some of the data on the physical properties of the synthetic polymer resins used in our research are summarized in Table 17.

13.1 Physical properties of polymer films with tocopherol

13.1.1 Mechanical properties

The effect of blending ratio and added tocopherol on film thickness, tensile strength and transparency was investigated and results were summarized in Table 18. The results showed that changing polymer composition and adding tocopherol (3000 ppm) did not cause significant variation in film thickness. Polymer blend films generally significantly lowered transparency than single polymer film (LDPE and PP). Adding tocopherol also caused significant changes in film transparency for the same polymer composition. PP film with and without tocopherol showed much higher tensile strength than LDPE film. Blending PP into LDPE increased the tensile strength of films. Adding tocopherol into the films generally reduced the tensile strength of films probably because tocopherol acted as a plasticizer in the film. Since changing the polymer composition and adding tocopherol changed physical properties of films, therefore, it was suggested that the tocopherol film should be laminated with aluminum layer in order to counteract the compromise of physical properties.

Table 16 Production formulations for tocopherol containing films

No.	Film Name	Film Composition	Added Tocopherol	Extractable Tocopherol
1	A	100% LDPE	3000 ppm	2706±57 ppm
2	B	75% LDPE 25% PP	3000 ppm	2937±48 ppm
3	C	50% LDPE 50% PP	3000 ppm	2970±66 ppm
4	D	25% LDPE 75% PP	3000 ppm	2970±42ppm
5	E	100% PP	3000 ppm	2859±12 ppm

Table 17 Density, Tm, Tc and Tg of resin pellet (raw material)

	LDPE resin pellet	PP resin pellet
Density g/cc	0.92	0.89
Tm °C	109	161
Tc °C	98	119

Table 18 Physical property of polymer films

Analysis/Test type	Control (no tocopherol)					Tocopherol (3000 ppm)				
	Film A	Film B	Film C	Film D	Film E	Film A	Film B	Film C	Film D	Film E
Film thickness (mm)	0.0770^{aA} (±0.0039)	0.0804^{aB} (±0.0039)	0.0813^{aC} (±0.0025)	0.0762^{aD} (±0.0025)	0.0804^{aE} (±0.0039)	0.0787^{bA} (±0.0025)	0.0787^{bB} (±0.0025)	0.0770^{bC} (±0.0039)	0.0754^{bD} (±0.0053)	0.0779^{bE} (±0.0064)
Toughness (MPa)	9456.61^{aA} (±93.17)	11054.19^{bC} (±280.68)	11960.71^{cE} (±271.34)	15595.98^{dG} (±474.67)	15547.12^{dI} (±396.40)	8794.68^{eB} (±112.01)	10131.26^{fD} (±139.04)	10827.91^{gF} (±285.04)	13271.89^{hH} (±238.83)	15203.80^{iI} (±61.84)
Young's modulus (MPa)	1.38^{aA} (±0.12)	3.67^{bB} (±0.27)	5.51^{cD} (±0.22)	8.90^{dE} (±0.33)	9.68^{dG} (±1.16)	1.25^{eA} (±0.07)	2.76^{fC} (±0.15)	5.12^{gD} (±0.54)	7.78^{hF} (±0.33)	9.71^{iG} (±0.25)
Maximum force (MPa)	56.63^{aA} (±0.41)	64.70^{bC} (±1.59)	66.71^{bE} (±1.35)	84.39^{cG} (±5.61)	83.72^{cI} (±0.75)	52.47^{dB} (±0.58)	58.45^{dD} (±1.42)	61.00^{eF} (±1.31)	71.97^{fH} (±2.87)	79.49^{gJ} (±1.50)
Transparency (%)	87.8^{aA} (±0.2)	76.2^{bB} (±2.3)	77.6^{bC} (±0.9)	76.6^{bD} (±0.6)	83.4^{cE} (±0.3)	87.8^{dA} (±0.9)	72.6^{eB} (±1.2)	76.4^{fC} (±2.6)	74.6^{eD} (±2.2)	77.5^{fF} (±1.0)

Standard deviations were reported in brackets. Different letters denoted statistically significant differences ($p \leq 0.05$)

13.1.2 Thermal properties

The objective was to study the effect of film processing (extrusion) and the addition of tocopherol on the thermal properties of synthetic polymer and polymer blend by using DSC and DMTA.

DSC analysis was carried out using two instruments. The first one was TA instrument Q2000 (Analyzer Inc., USA). The second one was Mettler DSC823 (Figure 72). The scanning rate was 10°C/minute under nitrogen purge. The DMTA analysis was performed using TA instruments Q800 with the film tension clamps. Samples (film strips) were subjected to 0.1% strain at 10Hz. The heating rate was 2°C/minute (Figure 73).

Three types of films were prepared at different blending ratios (w/w) of synthetic polymer resins of LDPE/PP with ratio of 100/0, 75/25, 50/50, 25/75 and 0/100, using a single screw extruder (Davis-Standard, LLC., Pawcatuck, CT, USA) as shown in Figure 12 and Figure 13 in chapter 2. The tocopherol was mixed with above synthetic polymer resins at a concentration of 3000 ppm, and the mixture was extruded at temperature of 221°C and a screw speed of 70 rpm. The films containing no tocopherol were also prepared for each blending ratio as the controls.

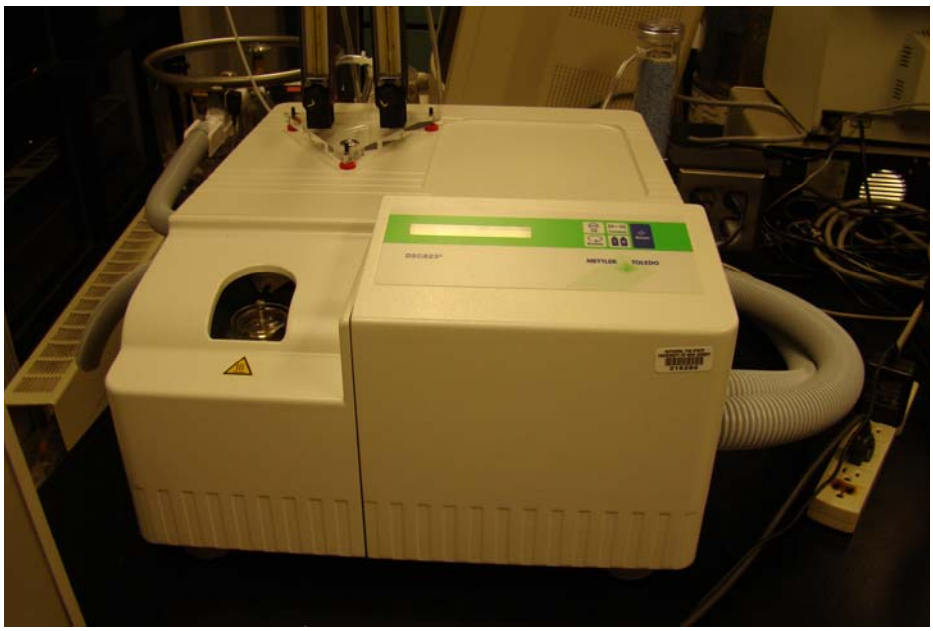


Figure 72 A DSC used in this study

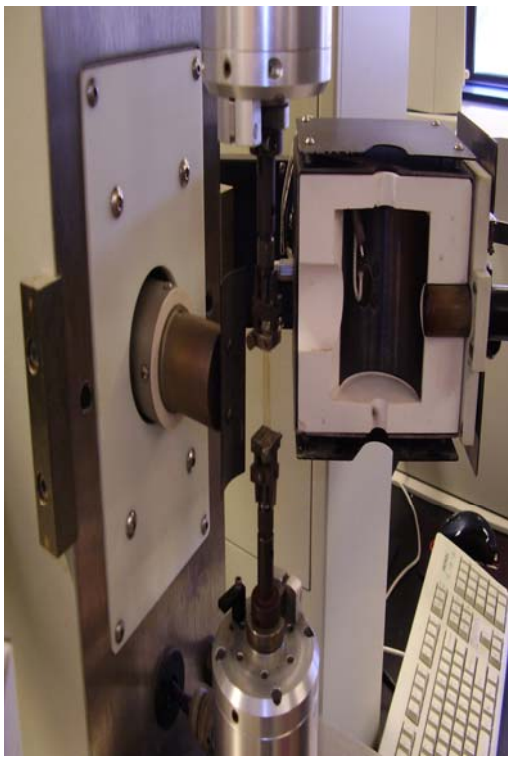


Figure 73 Using DMTA to measure Tg

Plastic film production by extrusion is a process commonly used in food packaging industry. As shown in Figure 13, the synthetic polymer resin pellets (commercial grade) were heated inside the barrel of an extruder and melted into viscose polymer flow. The polymer melt was then pushed out of a die (narrow slot) and cooled into thin layer (with uniformed thickness) of films. Therefore, the film production by extrusion is by and large a physical processing (melting and cooling) which involves little chemical changes. The rational for using extrusion method to produce the tocopherol containing films are three folds. First, it will be easy to scale up in the future commercial production of the tocopherol containing film since the extrusion is the major commercial film production method. Second, using commercial extrusion method can produce polymer film with more uniform properties. Third, high shear generated by screw of extruder will enhance the mixing of polymer melt and tocopherol and enhance the uniform distribution of tocopherol inside the polymer matrix. Fourth, commercial grade synthetic polymers (i.e. LDPE, PP) have consistent and repeatable properties from batch to batch.

Table 19 summarized the properties, including density, melting temperature (Tm), crystallization temperature (Tc), and glass transition temperature (Tg) of polymer films made by extrusion (with and without tocopherol). For single polymer LDPE and PP, the measured data were similar to reported data from references (Table 20). The data also were identical to that of manufacture's specification on this type of LDPE and PP (Table 20).

Table 19 Density, Tm, Tc and Tg of polymer blend films

	LDPE control	LDPE tocopherol	Blend control	Blend tocopherol	PP control	PP tocopherol
Density g/cc	0.9266	0.9224	0.9089	0.9102	0.8888	0.8890
Tm (°C)	109.1	109.0	109.1 / 159.7	108.7 / 159.4	160.4	159.4
Tc (°C)	98.7	98.6	99.0 / 116.1	98.4 / 116.5	119.4	116.5
Tg (°C)	-106.5	-110.4	-108.6 / 20.0	-119.3 / 24.5	22.1	23.1

Table 20 Density, Tm, Tc and Tg of resin pellet from literature

	LDPE	PP
Density g/cc	0.92 (*)	0.90(*)
Density g/cc	0.91-0.939(**)	0.87-0.89(**)
Tm °C	110	161
Tg °C	N/A	13-19

* Data adopted from manufacturer's specification sheets.
** Data cited from 'Polymer data handbook' (Mark, J. E., Polymer data handbook, Oxford University Press Inc., 1999)and Obinata [6]

The density of LDPE was slightly higher than PP. The polymer blend of LDPE and PP (50% each) had the density between that of LDPE and PP.

The Tm and Tc data (measured by DSC) were shown in Figure 74 to Figure 79. The melting point and crystallization point (Tm and Tc) of LDPE (109.1°C and 98.7°C) were much lower than that of PP (160.4°C and 119.4°C). The polymer blend of LDPE (50%) and PP (50%) had two Tm (Tc) corresponding to those of LDPE and PP. The above results suggested that the polymer blend produced was a physical mixing of LDPE and PP. LDPE and PP did not seem to react with each other to form new polymers under the current extrusion conditions. Film extrusion did not significantly change the physical properties of synthetic polymer before and after extrusion.

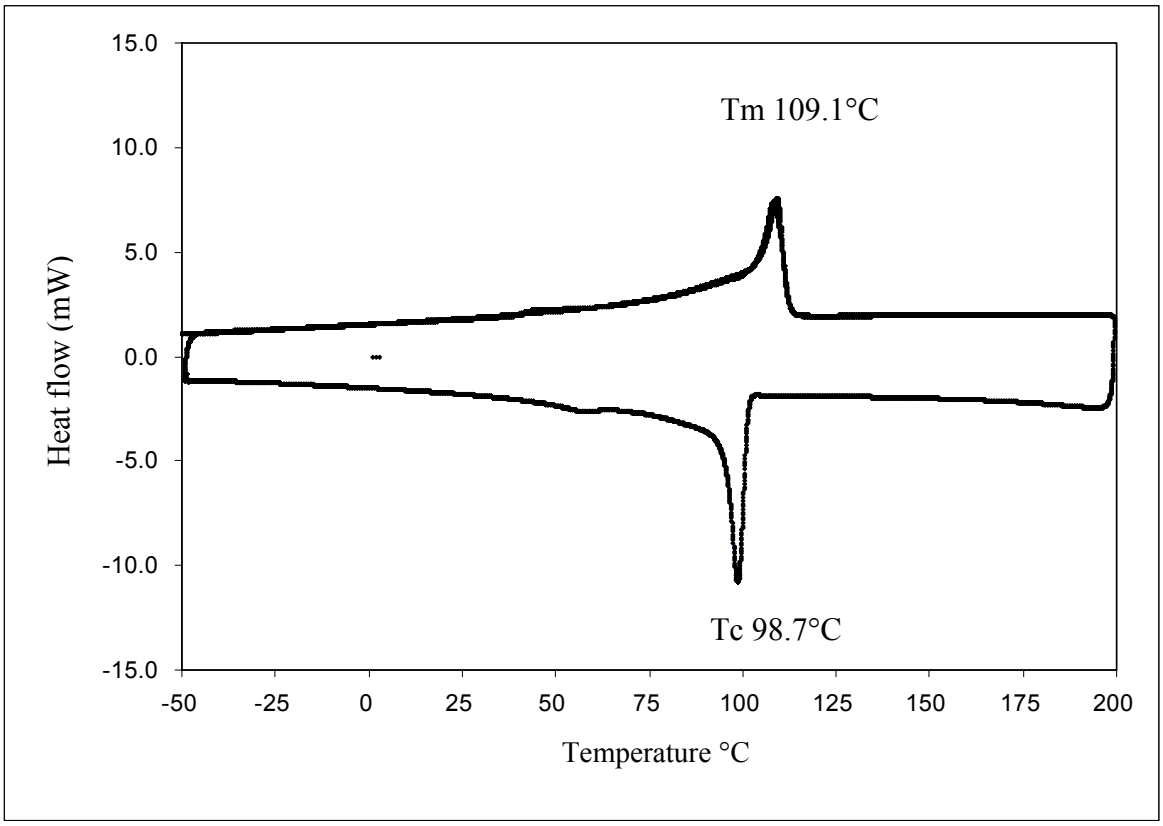


Figure 74 DSC plot of LDPE control film (no tocopherol)

Data was measured using DSC Q2000. First scan was cooling and second scan was heating.

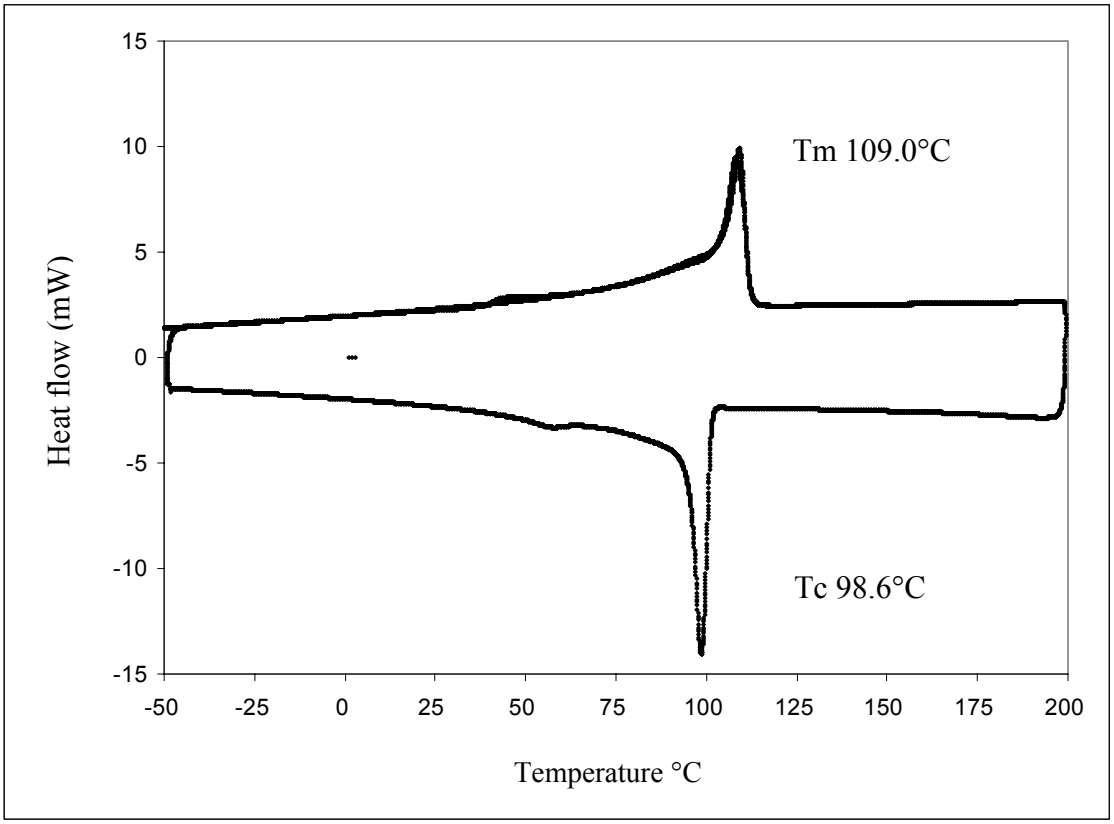


Figure 75 DSC plot of LDPE film with 3000 ppm tocopherol

Data was measured using DSC Q2000. First scan was cooling and second scan was heating.

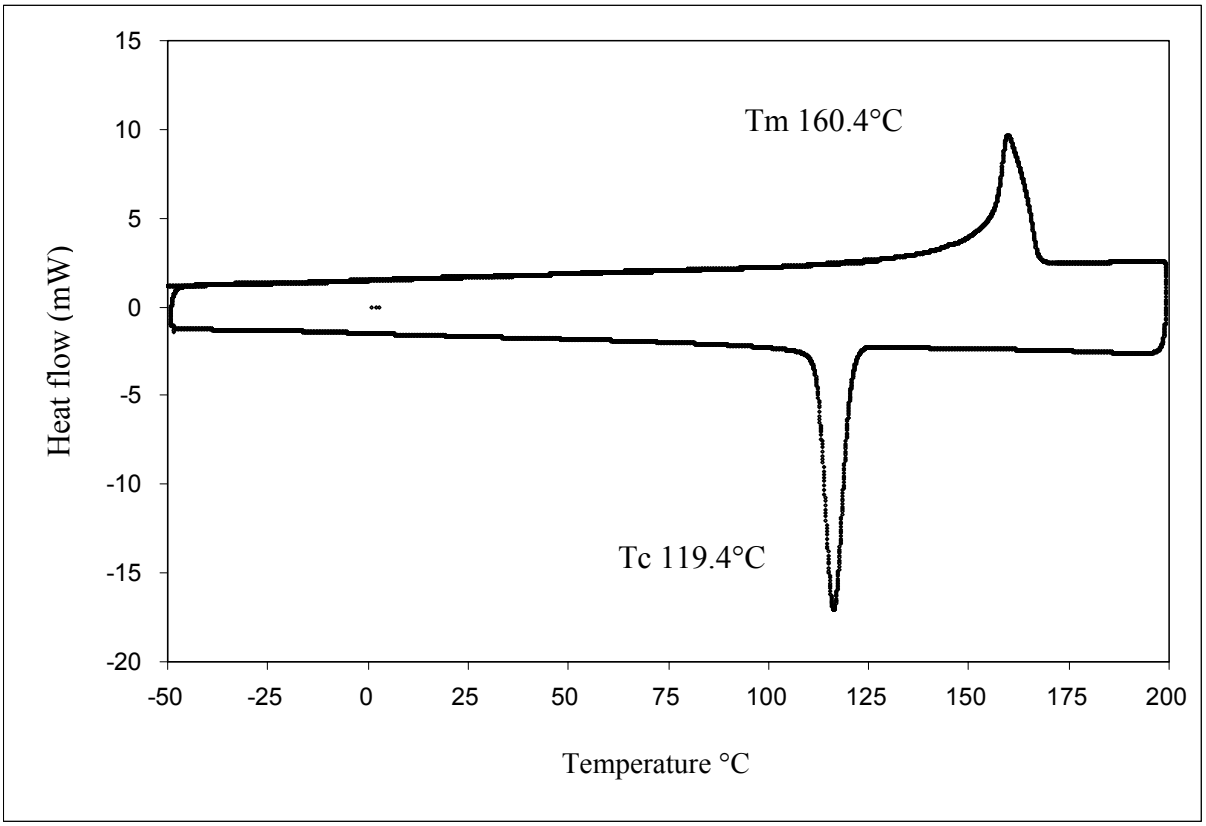


Figure 76 DSC plot of PP control film (no tocopherol)

Data was measured using DSC Q2000. First scan was cooling and second scan was heating.

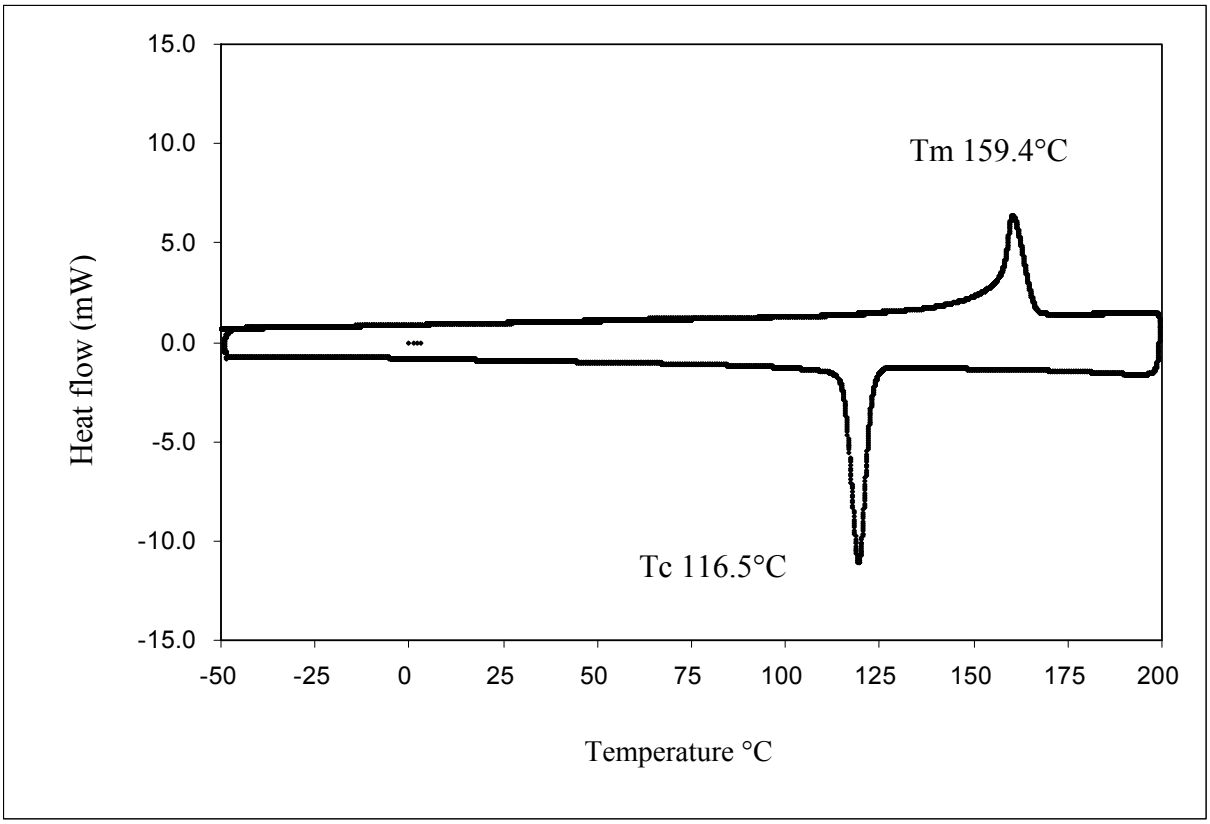


Figure 77 DSC plot of PP film containing 3000 ppm tocopherol

Data was measured using DSC Q2000. First scan was cooling and second scan was heating.

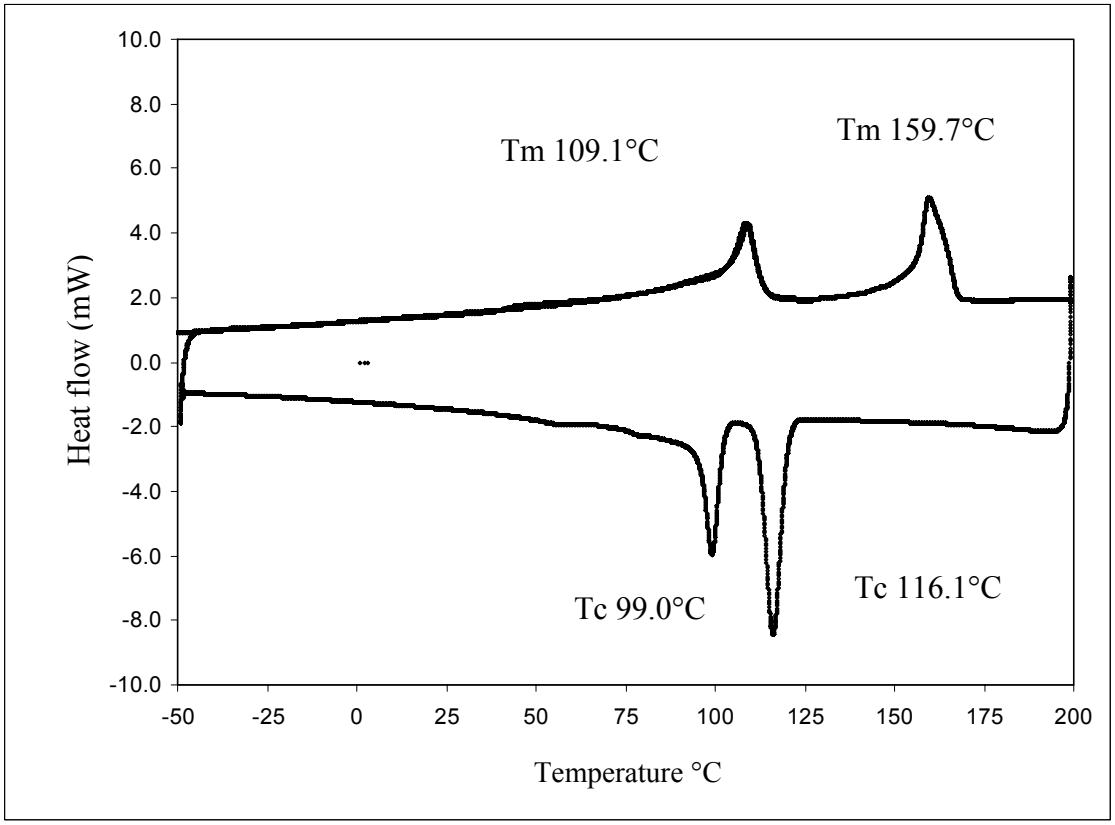


Figure 78 Polymer blend film of LDPE and PP (50:50) with no tocopherol

Data was measured using DSC Q2000. First scan was cooling and second scan was heating.

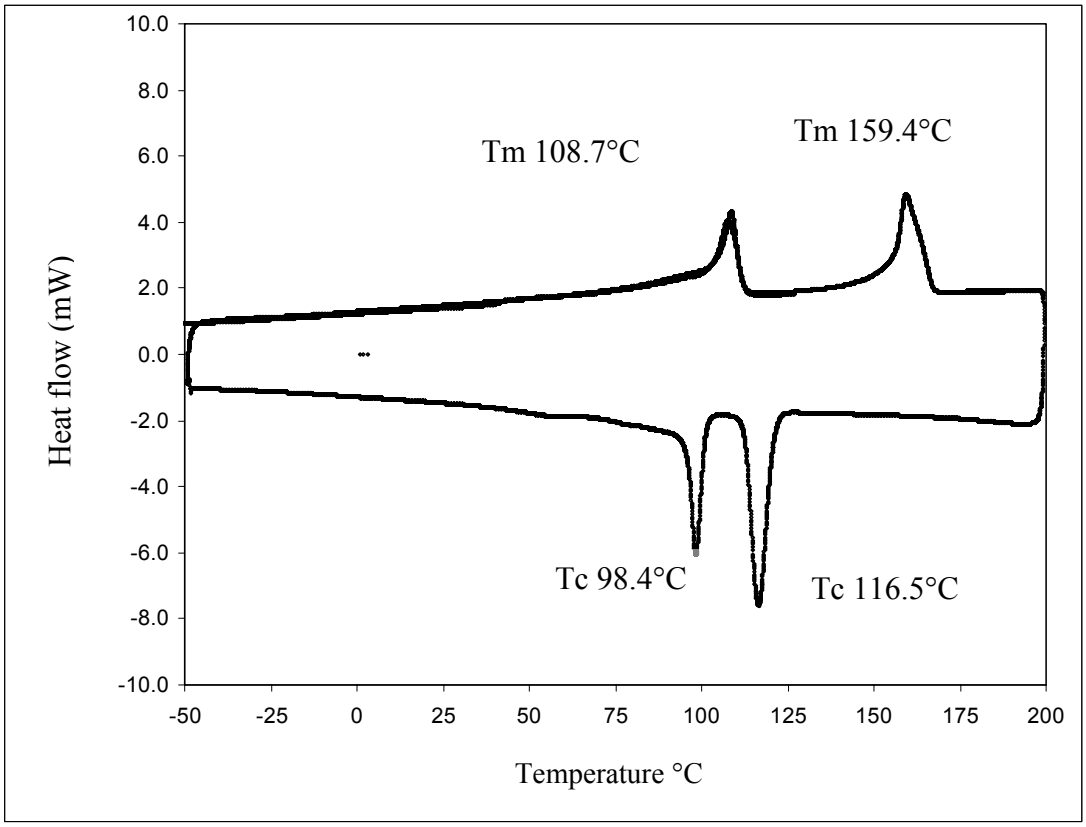


Figure 79 Polymer blend of LDPE and PP (50:50) with 3000 ppm tocopherol

Data was measured using DSC Q2000. First scan was cooling and second scan was heating.

We measured Tg (glass transition temperature) by using two types of DSC instruments (a Mettler DSC in Food Science, Rutgers University and a TA instrument DSC Q2000). However, in both cases, the Tg for LDPE and PP could not be measured. It was assumed that the sensitivity of the instruments which we used might not be good enough to detect the glass transition of LDPE and PP.

The above same films were then analyzed by the DMTA (TA instrument Q800) with film tension clamps. As shown in Figure 80, Figure 81 and Figure 82, the glass transition temperatures of LDPE, PP and LDPE /PP blend were measured. The glass transition temperature for LDPE control film was -106.5°C, LDPE tocopherol film was -110.4°C. The glass transition temperature for PP control film was 22.1°C. The glass transition temperature for PP film containing tocopherol was 23.1°C. The measured data were very close to the reported data from literature (Table 20). The polymer blend of LDPE and PP (50:50) had the two glass transition temperatures corresponding to that of LDPE and PP. The result suggested that the polymer blend was a physical mixing of LDPE and PP. The LDPE and PP did not seem to react with each other to form new polymers under the current extrusion conditions. Film extrusion did not significantly change the physical properties of the synthetic polymers before and after extrusion. The addition of tocopherol reduced the Tg of LDPE from -106.5°C (control) to -110.4°C (tocopherol). Tocopherol might act as a plasticizer and enhance the mobility of the polymer chains.

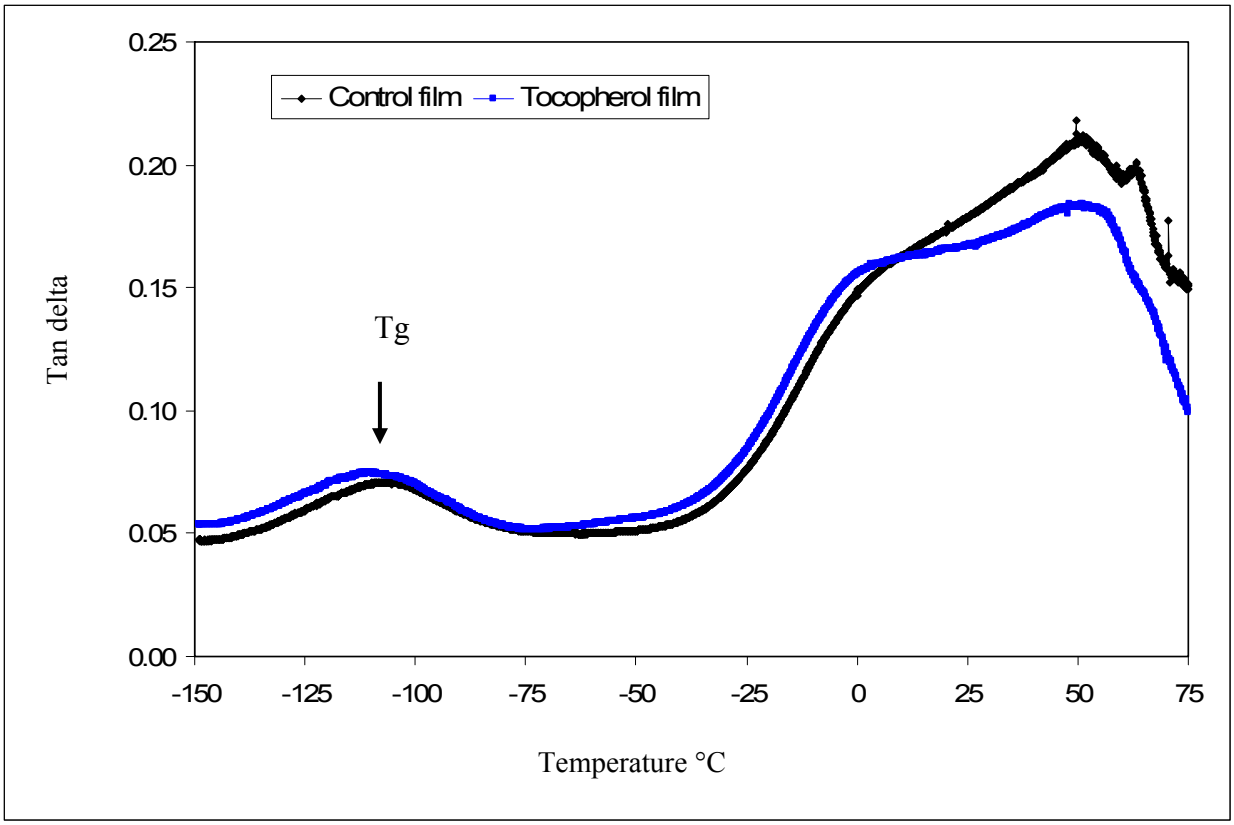


Figure 80 DMTA plot of LDPE films (control film and tocopherol film)

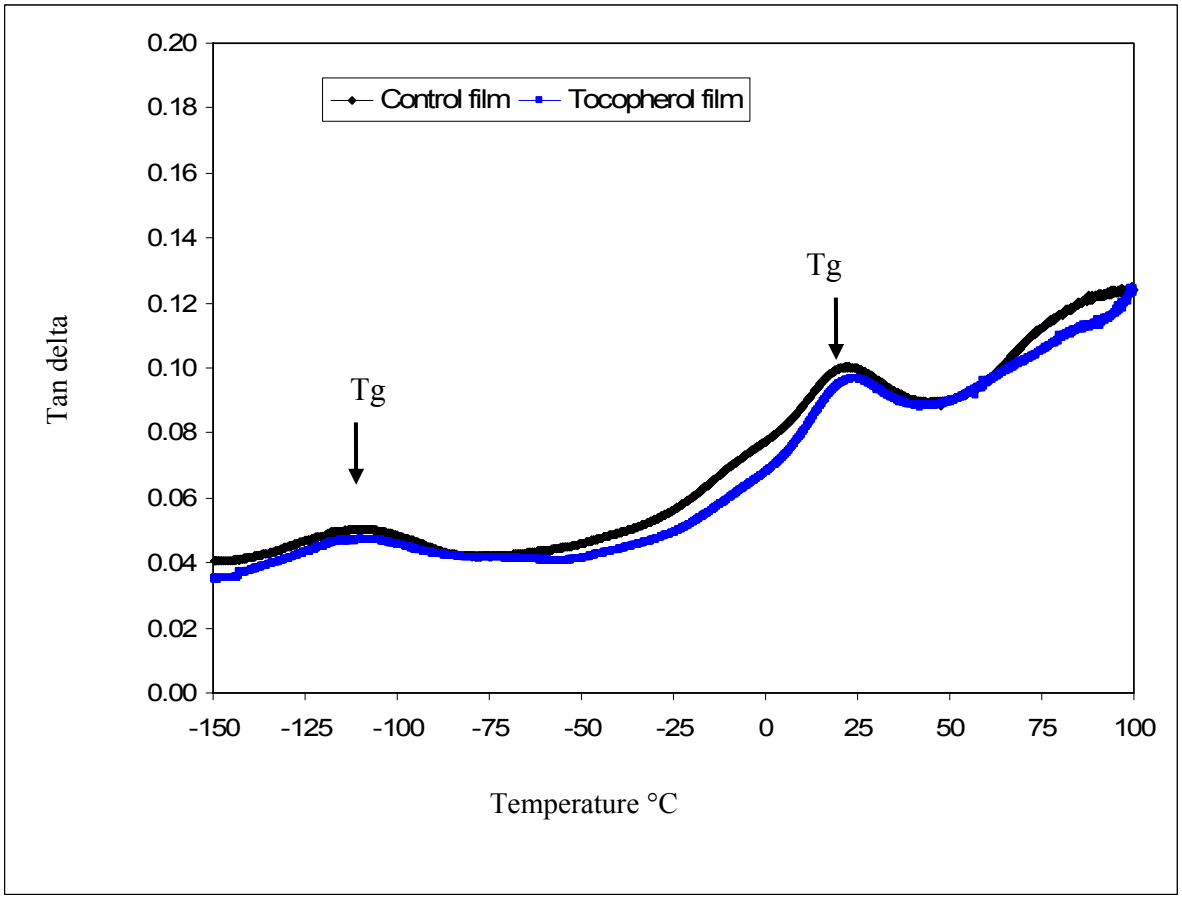


Figure 81 DMTA plot of LDPE/PP (50:50) blend films (control and tocopherol film)

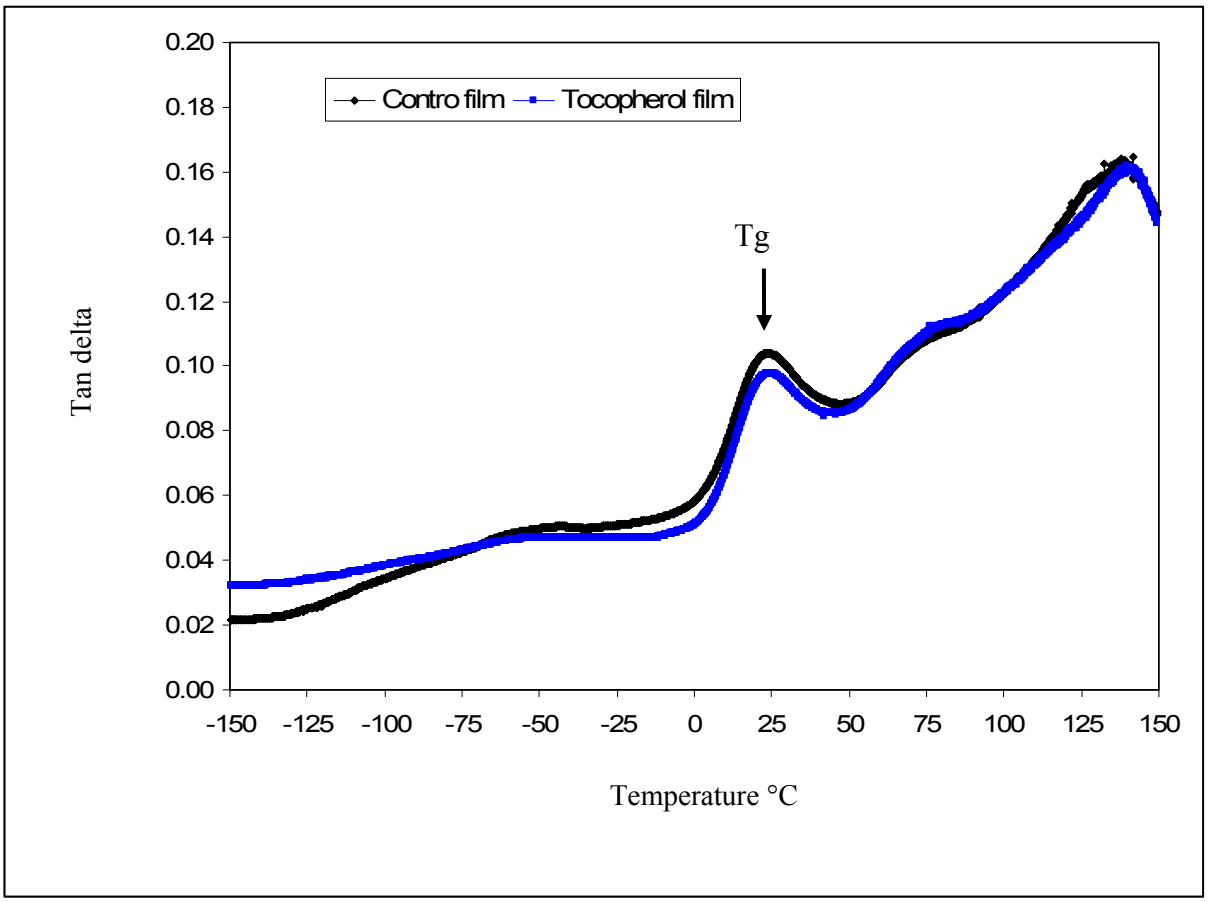


Figure 82 DMTA plot of PP films (control film and tocopherol film)

We also measured the properties of resin pellets (raw materials) using the DSC (Mettler DSC823) to compare with films made from the same polymer. The results (Figure 83 and Figure 84) showed almost identical plots for the resin pellet and for the film made from same resin (both LDPE and PP). The result suggested that normal extrusion process currently used to produce the controlled release films had minor effect on film physical properties.

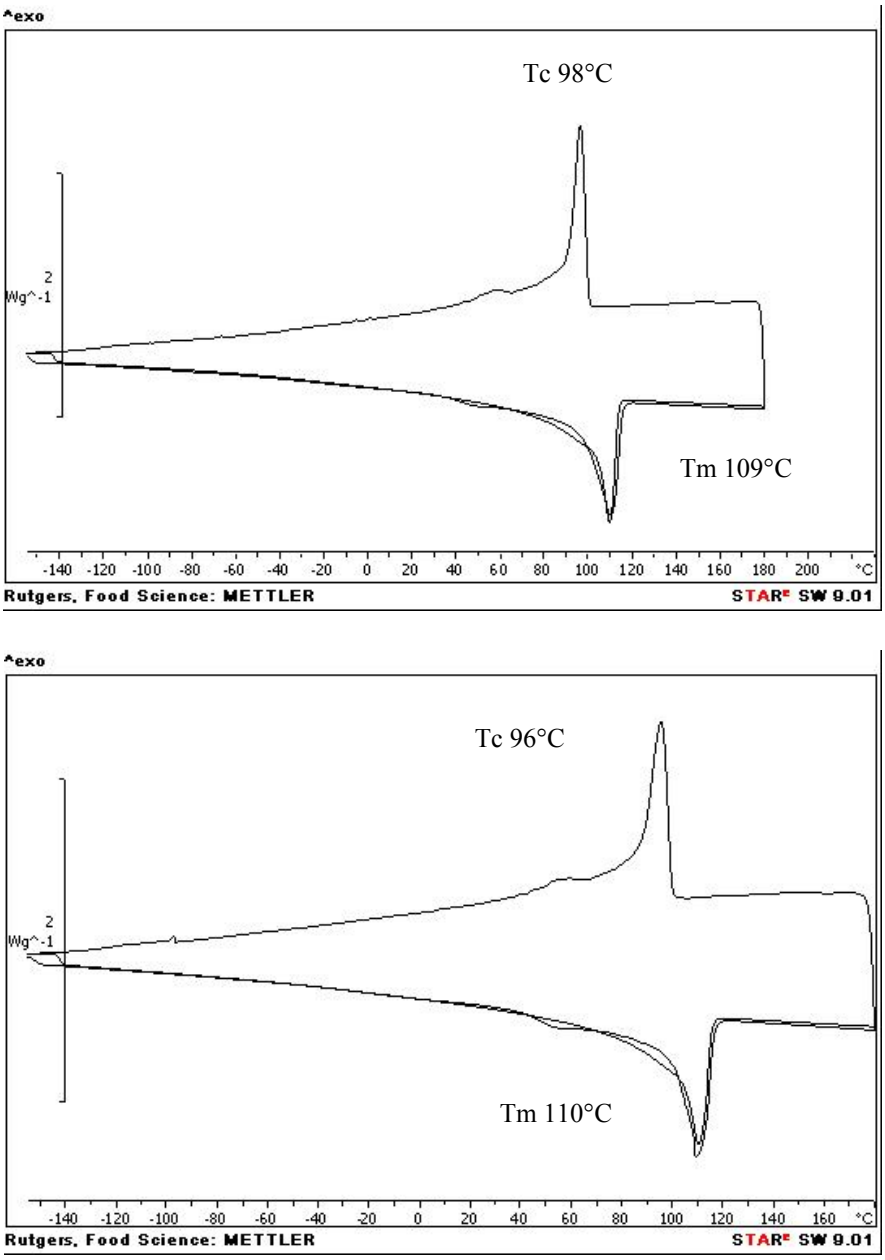


Figure 83 DSC plots of LDPE resin pellet and the film made from the same resin

Data was measured using DSC 823 (Dept. Food Science, Rutgers University). First scan was heating, second scan was cooling and third scan was re-heating. The up plot was for the resin pellet and low plot was for the film made from the same resin.

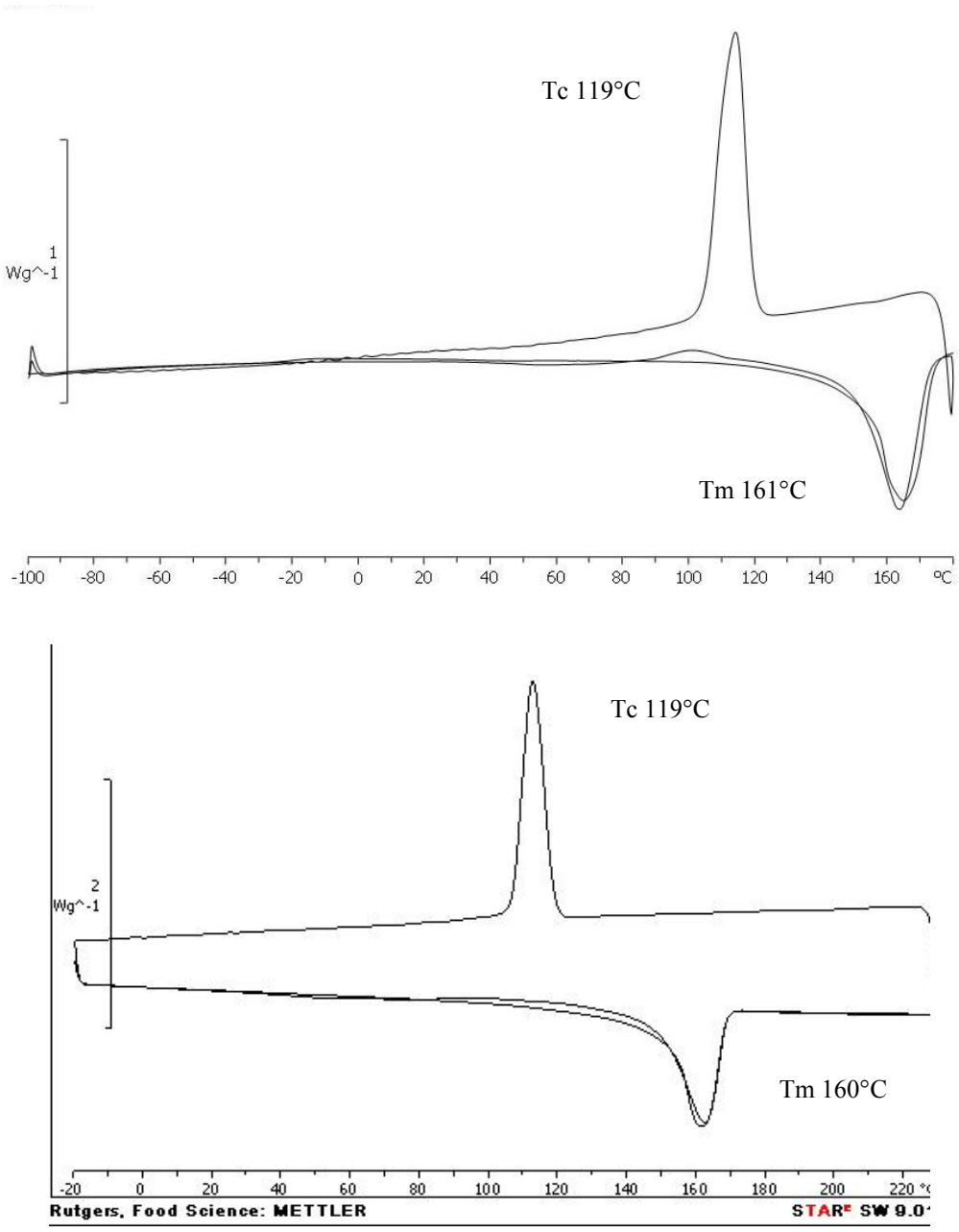


Figure 84 DSC plots of PP resin pellet and the film made from the same resin

Data was measured using DSC 823 (Dept. Food Science, Rutgers University). First scan was heating, second scan was cooling and third scan was re-heating. The up plot was for the resin pellet and low plot was for the film made from the same resin.

In summary, first, extrusion did not significantly change film physical properties (density, Tm, Tc and Tg) as compared with the synthetic polymer resin pellet (raw material). The LDPE and PP did not seem to react with each other to form new polymers under the current extrusion conditions. Second, addition of tocopherol did not significantly change film physical properties (density, Tm, Tc and Tg) compared with the control (no tocopherol). Third, our data showed that polymers we used to produce packaging films had physical properties which were consistent with reported data from literature. Fourth, the above results and our other data seemed to support that the film properties including thermal properties and release of tocopherol were controllable and repeatable as long as we make films using the same processing conditions and the same materials.

13.2 Physical properties of films with sesamol

The effects of the polymer compositions and the addition of sesamol and BHT on the thickness, major tensile properties, and transparency of the films were examined (Table 21). The film thickness, ranging from 73.7 to 76.2 μm, was not significantly affected by both the LDPE/PP blending ratio and the addition of sesamol and BHT. The values of tensile strength, Young's modulus, and toughness are different between film A and Film B/C because different polymers were used to produce the films. However, adding sesamol and BHT did not significantly change the tensile strength, Young's modulus, and toughness of films when compared with control films (without sesamol and BHT).

Table 21 Mechanical and optical analyses on films with and without sesamol

Analysis/Test type	Control (no antioxidant)		Sesamol and BHT		
	Film A	Film B/C	Film A	Film B	Film C
Film thickness (μm)	76.2 (±2.5)	75.4 (±1.5)	73.8 (±2.9)	76.2 (±2.5)	73.7 (±2.5)
Toughness (MPa)	11533.56 (±1171.70)	13375.09 (±736.88)	10153.62 (±295.01)	14200.95 (±387.20)	14021.86 (±523.98)
Young's modulus (MPa)	4.99 (±0.79)	7.41 (±0.60)	4.22 (±0.35)	7.94 (±0.55)	7.83 (±0.97)
Maximum force (MPa)	59.31 (±2.80)	67.99 (±6.01)	53.99 (±0.91)	70.37 (±3.48)	68.98 (±3.93)
Transparency (%)	76.3 (±0.9)	38.3 (±1.4)	76.3 (±0.8)	40.9 (±1.2)	36.9 (±1.5)

14 FUTURE WORK

14.1 Predict shelf life based on accelerated shelf life testing (ASLT)

Since a food is a complex matrix consisting of many different components, it is highly desirable to predict the degree of interactions between a polymer films and a food based on the results of studies which use food simulants. Therefore, it may be of interest to study the behavior of active compounds (in the packaging film) in contact with the real food and compare with the result which is measured by using the food simulant. For example, in our study, food simulants such as ethanol and linoleic acid were used. We also used accelerated test conditions such as the high temperatures. It was a common practice to use accelerated shelf life testing (ASLT) to predict the shelf life of the food product by determining the oxidation stability of lipids [22]. Therefore, it would be very important to know that to what extend the food simulant can be used to predict real food products. Is there any factors can be applied in order to extrapolate the data obtained from food simulants to real food products. What are the accelerating factors should be used to predict food shelf life at the room temperature based on the data obtained from the higher temperatures.

14.1.1 A predictive mode used by FDA

To evaluate the release of chemical compounds (such as additives) from packaging material into food, FDA recommended that a test temperature of 40°C for 10 days should be used to predict the room temperature (20°C) applications. This accelerated testing protocol was based on the studies showing that migration levels at 40°C for 10 days were roughly equivalent to levels after extended time periods (6-12 months) at 20°C (68°F) [83].

Migration data obtained at different temperatures that exhibited the fickian behavior could be extrapolated by means of the Arrhenius plot to predict the additive migration at another temperature. If no apparent change in polymer morphology, such as glass transition or polymer melting occurred, the diffusion coefficients (D) at a certain temperature for a certain system (additive/polymer/food simulating liquid) could be obtained by plotting D (Log scale) against 1/T (K). For example, additive migration for 2 hours at 121°C can be estimated to obtain the total migration expected for the retort conditions.

Our results showed that the diffusion coefficient (D) is a material property related to release rates of active compounds. Since we can predict D based on different conditions such as temperature, we will be able to build film which has a similar D under certain conditions. Therefore, it is possible for us to produce the film which can release active compounds at target release rate. Future work will be needed to build math model to describe the correlation between D and the target release rats under different conditions.

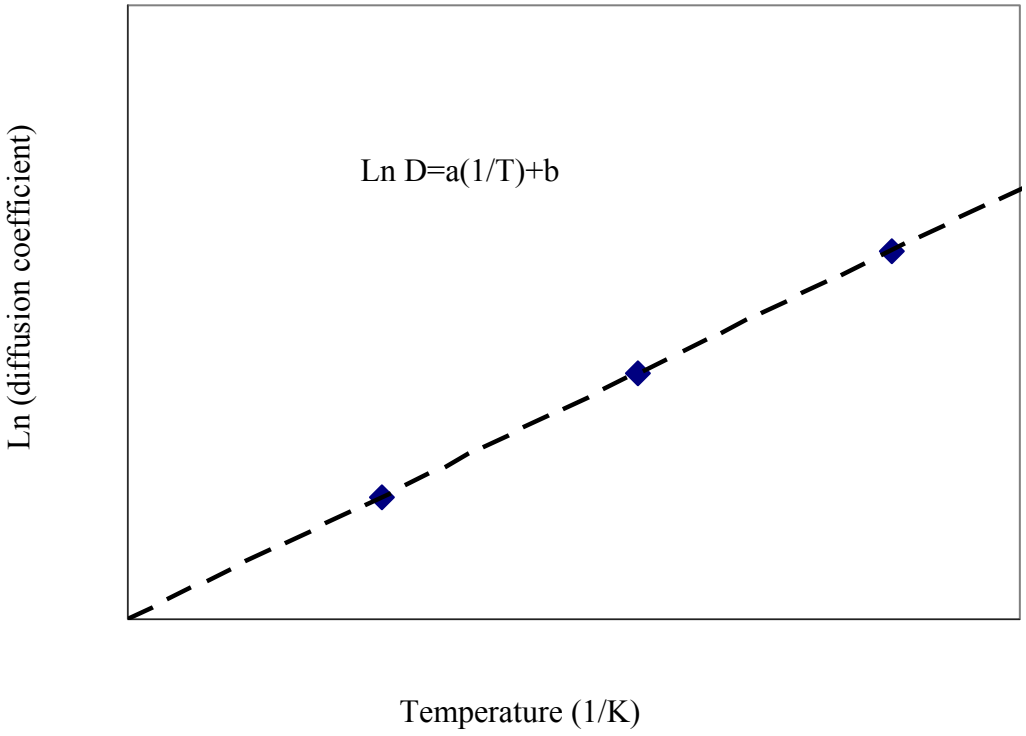


Figure 85 Predict diffusion coefficient based on temperature

14.1.2 Migration of tocopherol to real food as compared with food simulant

Wessling (1999) investigated the release of the antioxidant (alpha-tocopherol) from polymeric film when contacting with several liquid food products and liquid food simulants [51]. In their study, the foodstuffs investigated covered a wide range of compositions, from water-based to fatty. Data showed that food compositions and properties of the foodstuffs influenced the release of alpha-tocopherol from the packaging material (polymer matrix).

For example, Wessling's result found that alpha-tocopherol was retained to a much higher degree in PP than in LDPE for both the food simulant and the real liquid food (Table

22 and Table 23). It suggested that tocopherol released faster from LDPE than PP. This result was in accordance with our results with polymer films of LDPE and PP [37]. This difference between the materials might be explained by their difference in glass transition temperature (Tg). The storage temperature in Wessling's experiment was held at temperature near Tg of PP (about 20°C). Thus, PP had a rather rigid structure at this temperature, and it slowed migration of the alpha-tocopherol within the polymer matrix.

Results in Table 22 and Table 23 also demonstrated that the food compositions affected the release of active compounds. For LDPE film, there was a fast release of tocopherol into the fatty liquid food and the ethanol containing liquid food. The release increased with the higher fat content or the higher ethanol concentration in food. As for fat-containing foods, release of tocopherol into the water-in-oil emulsions was slower than the oil-in-water emulsions. This was because tocopherol was hydrophobic. In an oil-in-water emulsion (milk and cream), the outer water phase slowed down the migration of alpha-tocopherol. For water-in-oil emulsions (mayonnaise or margarine) the oil phase facilitates the migration of tocopherol. For the ethanol solutions, the release of tocopherol from the film was dependent of the ethanol concentration. For solutions with concentrations of 60% ethanol and higher, there was a complete release of tocopherol from the film over time. Therefore, factors which might enhance the release of alpha-tocopherol from polymer matrix were high fat content, the type of emulsions (water-in-oil emulsion vs. oil-in-water emulsion), the ethanol content, and etc.

The result also showed that the release rates of tocopherol followed the order of 95% alcohol, the fatty foods, and the high water food. Therefore, using a 95% alcohol was a good food simulant for fatty food. For LDPE film, the accelerating factor of 3 to 4 might be

appropriate for fatty liquid food products with good packaging and food contact. For PP film, the accelerating factor of 1 might be appropriate for fatty liquid food products with good packaging and food contact. Accelerating factors for the low fat food and less food / packaging contact will be determined via future investigation.

Table 22 Alpha-tocopherol content in the LDPE film at 40°C in contact with the various foods and food-simulating liquids

Storage time (weeks)	Mayonnaise	Cream	Low-fat milk	Orange juice	95% v/v ethanol	White wine
0	100 (±2.2)a	100 (±2.2)a	100 (±2.2)a	100 (±2.2)ab	100 (±2.2)a	100 (±2.2)a
1	69 (±3.5)b	91 (±2.0)b	91 (±2.5)b	96 (±0.9)ab	20 (±1.0)b	92 (±2.5)a
2	46 (±2.0)c	81 (±0.5)c	93 (±0.6)b	107 (±0.2)a	2 (±1.5)c	95 (±4.3)a
3	51 (±0.0)c	79 (±0.9)c	NA	103 (±0.9)a	NA	107 (±1.5)a
4	43 (±2.0)cc	77 (±1.3)cb	80 (±2.3)cb	95 (±1.5)ba	1 (±0.6)ce	103 (±1.5)a

1 Mean values in the same column, with different following superscript (a±c), are significantly different ($P < 0.05$) according to Tukey's pair wise comparisons.

2 Mean values for week 4, with different following subscript (a±e), are significantly different ($P < 0.05$) according to Tukey's pair wise comparisons.

3 NA ± not analyzed due to analytical difficulties.

Data was adapted from Wessling [51].

Table 23 Alpha-tocopherol content in the PP film at 4°C in contact with the various foods and food-simulating liquids

Storage time (weeks)	Mayonnaise	Cream	Low-fat milk	Orange juice	95% v/v ethanol	White wine
0	100 (±2.8)ab	100 (±2.8)a	100 (±2.8)a	100 (±2.8)a	100 (±2.8)a	100 (±2.8)a
1	96 (±1.5)ab	104 (±1.0)a	87 (±1.5)b	99 (±4.1)a	99 (±2.0)a	99 (±0.7)a
2	88 (±1.2)b	100 (±1.5)a	89 (±0.7)bc	105 (±2.9)a	93 (±3.0)a	91 (±0.9)c
3	95 (±1.5)ab	97 (±1.4)a	90 (±1.2)bc	NA	97 (±1.0)a	95 (±0.7)b
4	101(±5.2)aa	104 (±3.0)a	99 (±0.3)aa	101 (±1.5)aa	100 (±0.7)aa	93 (±1.0)bc

1 Mean values in the same column, with different following superscript (a±c), are significantly different ($P < 0.05$) according to Tukey's pair wise comparisons.

2 Mean values for week 4, with different following subscript (a±b) are significantly different ($P < 0.05$) according to Tukey's pair wise comparisons.

3 NA ± not analyzed due to analytical difficulties.

Data was adapted from Wessling [51].

14.1.3 Migration of additive to solid food with good contact

Silva et al. investigated the release of a model active compound (diphenylbutadiene) from the packaging film (LDPE) into a solid food product (minced pork meat) [84]. The diffusion coefficients were calculated for the applied test conditions using a mathematical model based on Fick's law. The results showed that migration increased with fat content in the meat and the storage temperatures (Figure 86). Analysis of migration data corresponding to minced pork meat containing different amounts of fat, stored for 10 days at 25°C, showed a correlation between release rates of the active compound and the fat content in meat. Similar result was also found for other types of meat products (chicken and pork neck).

A simplified mathematical model was applied to calculate the diffusion coefficients in the polymer matrix. For minced pork meat, the diffusion coefficients derived from mathematical modeling were ten times higher for the storage at 25°C (1.88×10^{-9} cm^2 s^{-1}) than for the storage at 5°C (1.2×10^{-10} cm^2 s^{-1}) [84].

Similar release patterns were also found in our results based on the food simulants (95% alcohol). The results demonstrated that it was possible using math model to predict the diffusion coefficient based on the factors such as food compositions (fat contend) and temperatures.

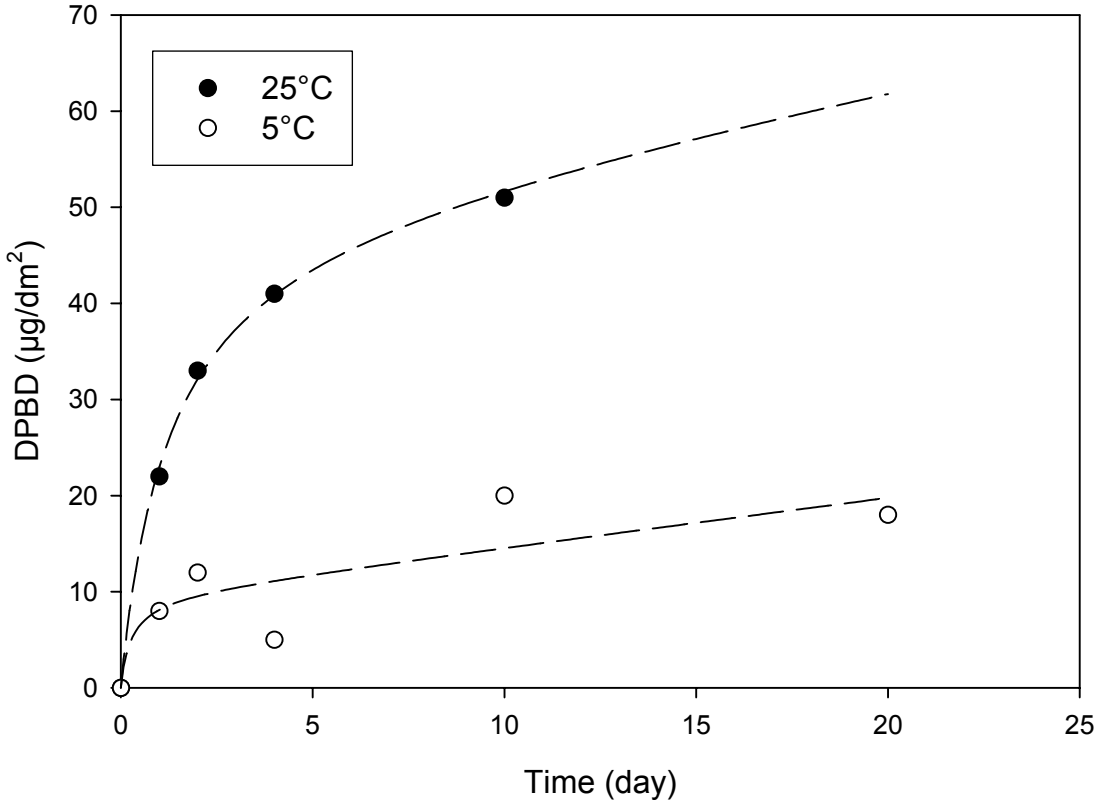


Figure 86 Release of model active compounds from LDPE to meat
Adapted from Silva [84].

14.1.4 Accelerating factors for lipid oxidation of food oil

Kaya et al. carried out the accelerated shelf life testing on sunflower oil and vegetable oil. Their results showed that they were able to make linear regression plot of the induction period (log scale) against the temperature [72]. Similar results were found by our research group (see Chapter 10). They confirmed that they could extrapolate the accelerated shelf life testing (high temperature and short term storage) to low temperature long term storage based on above plot (linear regression). The temperature coefficient (Q10) was 2.0 for the sunflower oil and 2.1 for the olive oil. The shelf life of sunflower oil

was estimated to be 10.6 month at 20°C. The shelf life of sunflower oil was estimated to be 20.8 month at 20°C.

In summary, for the release of compounds from polymer film, FDA recommended that migration levels at 40°C for 10 days were roughly equivalent to extended time (6-12 months) at 20°C. Therefore, our release data using 95% ethanol at 40°C could be useful to predict the actual release at room temperature storage for about one year. The release in food simulant was good prediction for fatty food (liquid), especially for PP which had the slow release properties. For solid food (meat) similar approach for liquid food can be taken as been demonstrated by meat products. For the lipid oxidation, accelerating factor (Q10=2 to 3) might be applied. Data on accelerating factors for food product without good food-package contact, and for low fat food products are still needed in the future study.

14.2 Using syringe pump to determine target release rate

The efforts will be continuously made to define and determine the target release rate using the syringe pump method. A kinetic model will be built based on the above concept to put the food factor and the environmental factors into the model. Other factors including mixing, oxygen concentration, initial antioxidants load, and concentration of metals, etc. will be further investigated.

14.3 Modeling tocopherol degradation kinetics

Tocopherol degradation kinetics in real food will be further investigated to validate our results from the food simulant (linoleic acid). Some preliminary results on the real food products have been discussed in Chapter 13.

Based on the results from the real food, a mechanism model to describe and predict the tocopherol degradation based on the chemistry of lipid oxidation and antioxidants will then be proposed. The food factor and the environmental factors such as temperature, mixing, oxygen concentration, and initial antioxidants loading will also be incorporated into the model. This model will enable us to predict the consumption rate of antioxidants for different food under different conditions. The target release rate will then be determined by matching the consumption rate of the antioxidant.

14.4 Modeling the release kinetics of tocopherol form packaging films

Currently, the release kinetics of tocopherol from the packaging films (migration of tocopherol from polymer matrix) was determined by using the inert food simulant (95% ethanol). As discussed in chapter 8, the migration of tocopherol into 95% ethanol seemed to obey the Fick's law. However, in real food system, the released tocopherol will participate in the free radical chain reactions to prevent lipid oxidation. Therefore, a model to describe the release kinetics of tocopherol from the packaging films into the reactive food simulant will be more useful to deal with real food application.

The release kinetics of tocopherol from packaging films into reactive food simulant such as linoleic acid or vegetable oil might be determined using a math model proposed by Dr. Donghwa Chung (Personal communication with Dr. Chung). Figure 87 was the math model based on the principles of mass balance.

$$\left[\frac{dm}{dt}\right]_a = \left[\frac{dm}{dt}\right]_r + \left[\frac{dm}{dt}\right]_d$$

In the above model, m = mass of tocopherol, $[dm/dt]_a$ = accumulation rate of tocopherol in linoleic acid, $[dm/dt]_r$ = release rate of tocopherol from the film, and $[dm/dt]_d$ = degradation rate of tocopherol in linoleic acid.

Figure 87 A math model to determine the release rate of tocopherol from the CRP film into linoleic acid

(Courtesy of Dr. Donghwa Chung)

14.5 Determine the range of target release rates by storage conditions

Besides the two approaches to determine target release rate (syringe pump approach and matching tocopherol degradation, see details in previous chapters), the concept of target release rate may also be defined by different storage conditions (courtesy of Dr. Donghwa Chung, 2007) as shown in Figure 88. Food or food simulant was stored at storage conditions from mild to extreme. Examples of the extreme conditions are higher temperature, exposure to open air (unlimited oxygen) and constant shaking. Examples of mild conditions are refrigerated temperature, static (no shaking), and low oxygen concentrations.

Figure 88 shows a hypothetic example to demonstrate the approach to determine target release rate based on storage conditions. Experiments are conducted using a syringe pump under a severer storage condition, including 40°C, 100 rpm shaking, and air-exposing. The maximum cumulative concentration of tocopherol in linoleic acid is set to 300 ppm. For example, if the release rate is set at 100 ppm/day, tocopherol is delivered only for three days. Results (red line) show that the slow delivery of tocopherol is more effective in retarding the onset of lipid oxidation than the initial instant addition of 300 ppm tocopherol within the range of release rate from 40 to 100 ppm/day. The results (red line) also show that there was an optimum release rate that can be targeted for the most effective use of tocopherol under the given condition. The black line represents the mild conditions in the Figure 88. The range between two optimum release rates obtained from the two extreme storage conditions could be considered as a range of target release rates for the storage of linoleic acid. Therefore, it is suggested that the concept of target release

rate must be carefully considered in developing antioxidant packaging to maximize its effectiveness.

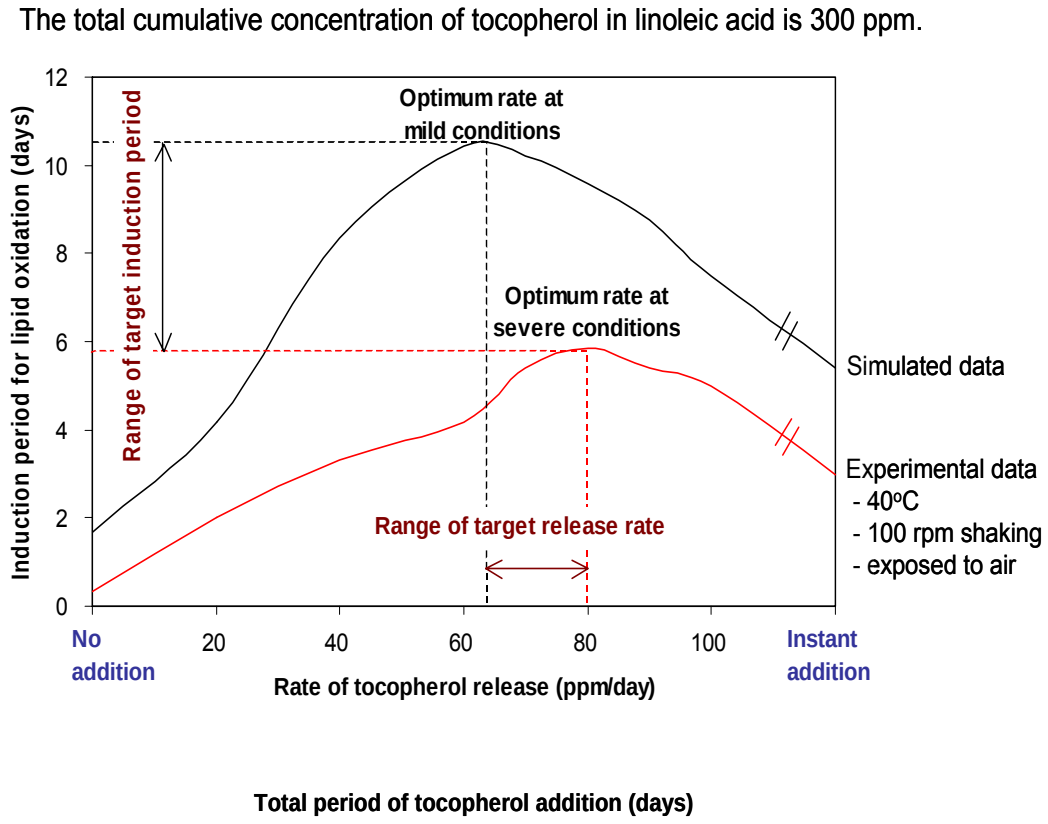


Figure 88 An approach to determine target release rate based on storage conditions (Courtesy of Dr. Donghwa Chung)

14.6 Testing films with different release rates on food products

After we build the math models to determine the target release rate, we need to validate the models with real food products. The food products to be tested include MRE menu items such as peanut butter, cheese spread, and chicken breast. Target release rate will be determined for each food product. Then packaging films which can provide the above target release rates will be manufactured in packaging companies such as Pliant

Company. The above food products will be packed and tested to determine the shelf life as compared with the normal packaging. The data generated from the above real food product tests (including lipid oxidation, tocopherol degradation) will help to build a math model to determine the target release rate.

14.7 Exploring different active compounds

Besides tocopherol and sesamol, other natural active compounds bearing anti-oxidant and anti-microbial activities will be investigated. Examples are plant extracts such as rosemary extracts, thyme extracts, and oreganol extracts. We will study the possibility of incorporate the above active compounds into the polymeric films and the effectiveness of releasing the above active compounds from the packaging film to the food in order to enhance the food safety and quality.

14.8 New technology such as micro-encapsulation

In order to develop the packaging films which can provide the required release rates (the target release rate), some new technologies may be useful and need to be tested. For example, we can use micro-encapsulation technology to reduce the possible evaporation of volatile active compounds and slow down the release of active compounds into food. The antioxidants can be first encapsulated and release in a more controllable manner. For example, Yoo successfully encapsulated alpha-tocopherol with sodium alginate and achieved the controlled release properties[85]. The emerging food nano-technology also provides exiting opportunity for improving the controlled release packaging. We are

purposing to use nano-composite or nano-device in the controlled release packaging films which may be one of the final solutions for “controlled release”.

14.9 Application of target release rates in other fields

Besides controlled release packaging, the concept of target release rate is also important for the application of other controlled release technologies. For example, in pharmaceutical industry, controlled release technology is one of the most important areas developing fast in recent years. The important benefits are improving drug effectiveness, reducing side effect and improve convenience [86]. There are basically two types of controlled drug release: the temporal control and the distribution control. The temporal control means to deliver the drug over an extended time during treatment. In controlled release over time, the drug devilry systems (such as encapsulation) aim to deliver drug over time during the treatment, which is highly beneficial since some drugs are metabolized and eliminated out of human body after administration and caused the drug concentration dropping below the effective range. As shown n Figure 89, two delivery methods for a drug were used. One was instant injection at 6 hours interval for 4 times. The second one was controlled release using a polymeric delivery system. With the controlled release system, the rate of drug released match the rate of drug elimination and therefore, the drug concentration was within the effective concentration window for the 24 hour period of treatment. This controlled release rate was the target release rate for this drug during this period of time.

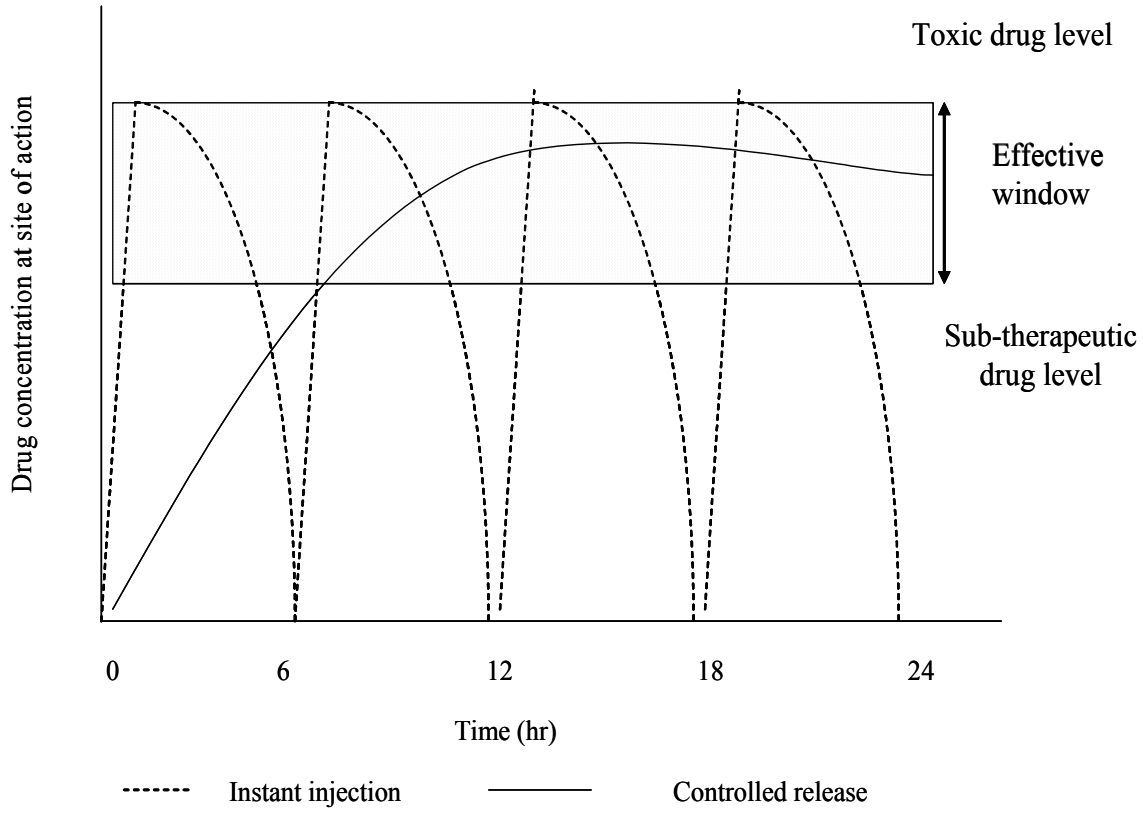


Figure 89 Instant addition and controlled release of drug

Adapted from Uhrich [86]

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Publications

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