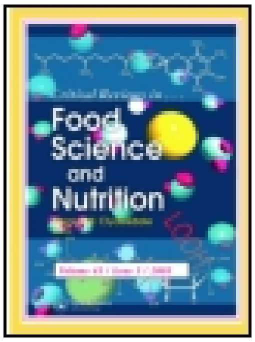


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INNOVATIVE APPLICATIONS OF FOOD RELATED EMULSIONS

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**Abstract**

Research on oxidative stability of multiple emulsions is very scarce. Given that this is a relevant topic that must be ascertained before the successful application of multiple emulsions in foods (especially when a combination of highly unsaturated oils is used as a lipid phase), this review mainly focus on various aspects of the multiple emulsions.

Fat replacement in meat products using emulsions is critically discussed along with innovative applications of natural antioxidants in food based emulsions and multiple emulsions based on bioactive compounds/encapsulation as well as confectionery products.

Keywords

food, emulsions, innovative applications, meat, antioxidants, confectionery products



 

## 1. INTRODUCTION

Chronic diseases such as obesity, cardiovascular diseases (CVD), hypertension, diabetes and cancer show an alarming growing trend worldwide (WHO, 2003). Greece shows worrying levels of them: 64% of the adults and 32% of children under six years are overweight or obese according to the last National Health Survey Ydria (2015) and recent Eurobarometer research, 18% of the population are at high cardiovascular risk. Scientific evidence that nutrition and changes in eating habits are among the most important risk factors in the development of chronic diseases which has led consumers to a growing concern about the consumption of healthier foods in recent years.

Due to the implications of dietary fat on health, lipids are one of the most studied functional ingredients regarding the development of healthier products, both in quantitative and qualitative terms (Jiménez-Colmenero, 2007).

A wide literature is available about bulk oil whilst very little is known about oil oxidative and microstructural stability when it is present as droplets dispersed in a complex aqueous media. (Kiokias and Varzakas, 2014). Overall, food emulsions offer good examples of food products that can rapidly degrade by lipid oxidation reactions (Alamed et al., 2009).

An increasing body of research evidence nowadays focuses on oil-in-water emulsions as they form the basis of many innovative food products and their properties define the quality of the final product to a great extent. (Nikovska, 2010). Therefore, a better understanding of the endogenous and exogenous factors which regulate the functional properties and the parameters that modulate their oxidative and microstructural stability of o/w food emulsions would elucidate


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their lipid oxidation mechanisms during the formulation, production, and storage of relevant products such as dressings, mayonnaise etc. (Kiokias & Oreopoulou, 2006).

Furthermore, although there are many studies focusing on the oxidative stability of conventional emulsions, especially O/W ones (Di Mattia et al., 2011, Sorensen et al., 2011; Ramful et al., 2011), research on oxidative stability of multiple emulsions is very scarce (Poyato et al., 2013; O'Dwyer et al., 2012). Given that this is a relevant topic that must be ascertained before the successful application of multiple emulsions in foods (especially when a combination of highly unsaturated oils is used as lipid phase), this review mainly focus on various aspects of the multiple emulsions.

## 2. FAT REPLACEMENT IN MEAT PRODUCTS USING EMULSIONS

Global patterns of food consumption show an increasing trend in meat consumption. The consumption of meat and meat products in Greece involves the highest percentage of the total food expenditure (22%). Per capita meat consumption in Greece was record in 2012, with 86.9 kg, whereas the consumption of processed meat products reached 15.5 kg per capita. Because of their composition (proteins with high biological value and micronutrients such as B group vitamins, iron, zinc, selenium), together with their high consumption, meat and meat products contribute to a significant extent to the dietary intake of various nutrients that are essential for optimal growth and development (Jiménez-Colmenero et al., 2012). However, they have been often associated with negative health aspects since they also contributed to the intake of fats, saturated fatty acids (SFA), cholesterol, salt, nitrites and other compounds which can exert a negative effect on human health. Therefore, an inadequate intake of meat in terms of quantity, quality or circumstances can lead to health disorders. In particular, red meat and processed meat products have been associated with an increase in the risk of developing of several chronic diseases, mainly CVD and various types of cancer (WCRF/AICR, 2007; WHO, 2003).

Meat industry has not been indifferent to these health concerns and the negative image of meat and meat products that consumers have developed in recent years. As a result, in the last decade there has been a growing interest in meeting consumer demands by producing healthier meat and processed meats. Numerous reviews can be found dealing with the developing of healthier meat and processed meats by several strategies, mainly focused on either the reduction of unhealthy compounds such as nitrites, SFA and salt; or the incorporation of health-promoting (functional) ingredients such as monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids, fibre, probiotics, minerals, vitamins and antioxidants (Jiménez-Colmenero et al., 2001; Toldrá & Reig, 2011; Jiménez-Colmenero, 2007; Weiss et al., 2010, 2013; Decker & Park, 2010; Zhang et al., 2010; Olmedilla-Alonso et al., 2013). These changes in composition can be achieved mainly by modification of the composition of animal tissues *in vivo* through nutritional and genetic strategies, or by modification of the formulation of meat products during processing (Jiménez-Colmenero et al., 2001; Scollan et al., 2006; Moloney, 2006; Jiménez-Colmenero et al., 2012; Olmedilla-Alonso et al., 2013; Toldrá & Reig, 2011).

Numerous studies have dealt with the reduction of fat content and/or the modification of meat fatty acid composition, which is mainly achieved through reformulation strategies in the case of processed meats (Jiménez-Colmenero, 2007). The use of leaner meat cuts and fat replacers or substitutes led to the production of low fat meat products (Keeton, 1994; Weiss et al., 2010). The improvement of the fatty acid profile is usually achieved by partial replacement of animal fat (pork or beef) with vegetable or marine oils (Jiménez-Colmenero, 2007; Weiss et al., 2010), obtaining a fatty acid profile closer to recommendations from international organizations (WHO, 2003; FAO, 2010) for prevention of diet-related chronic diseases, i.e. lower content of SFA, higher content of MUFA or PUFA, improved PUFA/SFA (> 0.4) and n-6/n-3 (< 4) ratios.

Miklos et al. (2014), claimed thar enzymatic modification triacylglycerols (TAGs) can be converted to diacylglycerols (DAGs) resulting in changes of the physical and chemical properties of the fat. They presented results that suggest future opportunities for the application of DAGs to improve the quality of meat products.

Oils such as olive, linseed, corn, cottonseed, sunflower, canola, soya bean, and fish oil have been used to obtain healthier meat products (Jiménez-Colmenero, 2007); but fatty acid profiles closer to health recommendations are obtained when a lipid combination is used (Paneras et al., 1998; Delgado-Pando et al., 2010 a, b; 2011). Marine oils (fish and algae) are excellent sources of long chain n-3 PUFAs, with percentages of EPA+DHA around 30% and 40% for fish and algae oils, respectively (Delgado-Pando et al., 2010). They have been used to increase the content of these fatty acids in food products, including meat products (Cáceres et al., 2008; Delgado-Pando et al., 2010; 2011). The incorporation of linseed oil, one of the richest sources of α-linolenic acid, lead to an increase in PUFA levels and PUFA/SFA ratio together with a decrease of n-6/n-3 ratio in meat products (Pelser et al., 2007; Valencia et al., 2008; Delgado-Pando et al., 2011). Other oils such as olive, high-oleic sunflower oil, and more recently, avocado oil have been used to increase MUFAs in meat products (Jiménez-Colmenero, 2007; Rodriguez-Carpena et al., 2012). Avocado oil, with almost 55% oleic acid and 10% linoleic acid (Carvajal-Zarrabal et al., 2014), can also be a good source of compounds with high antioxidant capacity such as polyphenols, carotenoids and chlorophylls (Wang et al., 2010). Although a negative impact on color and texture has been reported when used as the only back-fat replacer in pig patties (Rodríguez-Carpena et al., 2012), it is likely that this oil could be used in combination with others to optimize both fatty acid composition and sensory characteristics of the resulting meat products. In this study, the combination of several oils rich in MUFAs (olive, avocado or high-oleic sunflower oils) and PUFAs (linseed, fish or algae oils) is proposed to obtain a fatty acid profile according to health recommendations. These combinations will be incorporated as the lipid phase in the formulation of multiple emulsions. According to Choi et al (2009), low-fat meat batters with reduced pork fat content (10%) and 10% vegetable oil plus rice bran fiber had improved characteristics relative to the regular fat control.

## 3. MULTIPLE EMULSIONS BASED ON BIOACTIVE COMPOUNDS/ENCAPSULATION

Among the different technological procedures used for animal fat replacement in meat products by reformulation, pre-emulsion technology has been widely used to stabilize the non-meat fats incorporated (Jiménez-Colmenero, 2007; Delgado-Pando et al., 2010; Cofrades et al., 2013). These pre-emulsions, that are oil-in-water emulsions where a non-meat protein (such as sodium caseinate or soy protein isolate) is usually used as emulsifier, are used as fat ingredients. A body of literature has examined the composition and processing factors that modulate the microstructural stability of protein stabilized emulsions (Bot et al., 2003; Kiokias and Bot, 2006). During the last decade, that protein-based emulsions have offered the basis for the development of novel industrial products such as dairy spreads, creamers and fresh cheese types (Kiokias et al., 2004).

The main advantages of pre-emulsions are that oils remain stabilized in a protein matrix throughout the product's lifetime, reducing the chances of oil separation from the meat structure (Djordjevic et al., 2004). Jiang and Xong (2015) describe the steric effects along with chemical roles (radical scavenging and metal ion chelation) of proteins and their structurally modified derivatives as potential interface-building materials for oxidatively stable meat emulsions. A very recent review paper (Kiokias et al. 2015) presents recent findings about the factors ("compositional" such as: pH, presence of transition metals; or processing such as temperature, droplet size) that determine the oxidative stabilisation in emulsions where proteins constitute the stabilising interface. Emphasis is given to "endogenous" factors, such as those of compositional (e.g. protein/lipid phases, pH, presence of transition metals) or processing (e.g. temperature, droplet size) nature.

Water-in-oil-water (W1/O/W2) multiple emulsions are multi-compartmentalized systems consisting of a water-in-oil (W1/O) emulsion dispersed as droplets within a continuous aqueous phase (W2) (Garti, 1997; McClements, 2012). Although there are different methods to prepare these emulsions, a double emulsifying process is one of the most frequently used, since this process gives quite stable, well-defined systems with reproducible particle sizes (Jiménez-Colmenero, 2013). W1/O/W2 multiple emulsions have many potential advantages over oil-in-water emulsions such as encapsulation and controlled release of bioactive compounds, the masking of unpleasant flavors, as well as the developing of reduced-fat products without involving major changes in physico-chemical and sensory properties compared to full-fat products, since the overall disperse phase volume and droplet size distribution should not change (McClements et al., 2007; Dickinson, 2011). Furthermore, multiple emulsions also allow the replacement of animal fat normally present in some foods with an improved fatty acid composition (Jiménez-Colmenero, 2013). However, despite these advantages that can be very useful in the design of functional foods and their great potential in food applications, most of the studies have dealt with the design, formation, structure and properties of multiple emulsions themselves, while the application of multiple emulsions in new food developments is very scarce. Therefore, more studies are needed to determine how they will behave in a real food matrix and the consequences that their addition will have on physico-chemical, sensory or microbiological properties of real foods (Jiménez-Colmenero, 2013). As mentioned before, only a few studies address the utilization of W1/O/W2 multiple emulsions as ingredients in the development of food products, and many of them are focused on the development of reduced-fat or fortified dairy products (Lobato-Calleros et al., 2006, 2008, 2009; Márquez & Wagner, 2010; Giroux et al., 2013). As authors are concerned, there are only two very recent studies dealing with the development of multiple emulsions applied as fat ingredients in meat product reformulation to reduce fat and improve the fatty acid composition (Cofrades et al., 2013; Bou et al., 2014). However, both studies used olive oil as lipid phase instead of a combination of lipids to obtain a healthier fatty acid profile. Furthermore, the encapsulation of bioactive compounds, one of the main advantages of this system, was not addressed.

One possible explanation for the scarce application of multiple emulsions in novel food products development may be that these systems are thermodynamically unstable (Bot et al., 2003). To be used as food ingredients they should be prepared beforehand and subjected to storage processes such as chilling, like any other food ingredient (Cofrades et al., 2013). Moreover, multiple emulsions should be stable to the most common processing conditions used in food industry such as chilling, frozen, heating or dehydration, since they may affect the quality of the resulting products (McClements, 2012). Thermal processing is one of the most common processes used in food industry. In the meat sector, comminuted cooked meat products (gel-emulsion systems) are a commercially important group of meat products. There are only two studies evaluating the thermal stability of multiple emulsions to be incorporated into meat products as pork backfat replacers, and they have reported that although heating (70 ºC/30 min) reduced the stability of the multiple emulsions, they showed enough stability to be used as fat ingredients (Cofrades et al., 2013; Bou et al., 2014). Furthermore, when bioactive compounds are encapsulated in double emulsions, it is important to know how the processing conditions usually used in food industry may affect both the encapsulation stability and the bioactivity of the compound. A few studies have dealt with this aspect. In this regard, Bonnet et al. (2009) studied the magnesium release from multiple emulsions subjected to heat treatments usually used in milk pasteurization and sterilization, reporting higher release with increasing temperature and incubation time.

As mentioned above, multiple emulsions are thermodynamically unstable systems (Kiokias et al., 2008). The main mechanisms of destabilisation proposed for water-in-oil-in-water multiple emulsions are: coalescence of the inner water droplets, coalescence of oil droplets, coalescence of the inner water droplets with the external water phase and diffusion/migration of water and water soluble compounds between internal and external water phases (Dickinson, 2011, Kiokias and Bot, 2005).

An image of a whey-protein stabilised model emulsion containing sunflower oil is presented in Fig. 1 (Kiokias et al., 2004). As shown, there, the emulsion clearly gets more aggregated upon heating (85°C) and acidification (pH = 4.5), which is intentional to achieve a semi-solid structure for certain type of products. According to the authors, the oil or fat droplet size distribution of protein-stabilized o/w emulsion gels is an important characteristic because it reflects the quality of the initial emulsification process, and its development probes emulsion stability over time with respect to (partial) coalescence Furthermore, the average droplet size is expected to influence the texture (firmness, elasticity, etc) of the emulsion gel in a similar way as filler particles affect the mechanical properties of other ‘filled’ protein gels (Tesch & Schubert, 2002; Dimakou et al., 2007).

A recent study (Gao et al. 2014), has demonstrated a superior stability against both coalesence and creaming, through a novel strategy of facilitating the formation of protein particles and small molecular weight surfactant complexes.

In addition, Destribats et al. (2014) have investigated a new class of food-grade particles, whey protein microgels, as stabilisers of triglyceride-water emulsions. The sub-micron particles stabilized oil-in-water emulsions at all pH with and without salt.

Furthermore, when a water soluble bioactive ingredient is entrapped in W1, both trapping and retention of the encapsulated material is a key factor to be addressed. Leakage of W1 and the bioactive compounds that are entrapped in it can result from several of the destabilization mechanisms described above. An extensive research work has been carried out to improve stability and to insure high encapsulation efficiency and controlled release of the bioactive compounds encapsulated in multiple emulsions (Dickinson, 2011; Benichou et al., 2007; Carrillo-Navas et al., 2012; Matos et al., 2014; Hatterm et al., 2014). The incorporation of polymers to the external water phase as texture modifiers and/or as emulsifiers is among the strategies that have been addressed. The addition of different polysaccharides such as xanthan, locust bean gum or gelatin into the W2 has been reported to reduce creaming of multiple emulsions (Benna-Zayani et al., 2008). Furthermore, the use of blends of proteins and polysaccharides as hydrophilic emulsifiers in W2 may lead to the formation of protein-polysaccharides complexes and strong and thicker interfacial films. As a result of the formation of these complexes, a significant increase of the stability of multiple emulsions can be observed, together with better encapsulation efficiency and encapsulation stability (Jiménez-Alvarado et al., 2009; Carrillo-Navas et al., 2012; Benichou et al., 2007). The formation of protein-polysaccharides complexes is depending on several factors such as protein/polysaccharide ratio, pH, ionic strength, and characteristics of the polymers such as molecular weight, net charge, structure and molecular flexibility (Benichou et al., 2002). Strong electrostatic complexes between anionic polysaccharides (xanthan or pectin), and proteins such as whey protein isolate, usually used as hydrophilic emulsifier in multiple emulsions, mainly take place below the protein isoelectric point. However, this kind of anionic polysaccharides will not be addressed in this study, given that we propose these multiple emulsions as fat ingredients in meat systems with pH values close to neutral. Regarding this, it has been reported that non-ionic polysaccharides such as galactomannans (guar gum, konjac) are able to strongly interact with whey protein isolate and form complexes absorbed at the oil-water interface of multiple emulsions at a wide range of pH values (Benichou et al., 2007). However, the performance of these multiple emulsions for encapsulation and controlling the release of bioactive compounds has not been evaluated. Inulin is a polysaccharide mainly composed of fructose units with β-(1,2) links to glucose at the end of the chain. This non-digestible polysaccharide has interesting technological and nutritional properties. This is currently used in several food systems as it can enhance the rheological and textural properties, improving the stability of foams and emulsions (Álvarez & Barbut, 2013). However, its ability to improve the stability of multiple emulsions has not been addressed. Furthermore, this polysaccharide has been used as fat replacer in different foods such as meat and dairy products (Meyer et al., 2011; Álvarez & Barbut, 2013). Inulin has been reported to be chemically stable in water solution at a wide range of pH values, decreasing its stability only at pH $\leq$ 4. In neutral and alkaline environments inulin degradation did not occur, even when this polysaccharide is subjected to thermal treatment as high as 100ºC for 60 min (Glibowski & Bukowska, 2011). In this study, the use of non-ionic polysaccharides, such as guar gum or konjac or inulin, is proposed to improve the stability of the multiple emulsions and to obtain high encapsulation rates together with high encapsulation of quercetin and gallic acid.

## 4. INNOVATIVE APPLICATIONS OF NATURAL ANTIOXIDANTS IN FOOD BASED EMULSIONS

Further to the above-indicated, a very important and widespread category of bio compounds with functional properties in food emulsions comprise the natural antioxidants. The use of antioxidants is the most common strategy to prevent lipid oxidation in food products. Thus the replacement of synthetic antioxidants by a “safer natural” antioxidant has been increasingly advocated, nowadays. Kiokias et al., (2008) have reviewed the antioxidant potential of several natural antioxidants, with a focus on several, widely spread in nature, vitamins such carotenoids (provitamin-A), tocopherols (vitamin-E), and ascorbic ascorbic acid (vitamin-C).

Polyphenolic compounds have been widely used in foods due to their high antioxidant potential and their beneficial effects on human health, as pure compounds or taking part of aqueous extracts or essential oils (Giménez et al., 2011; Sánchez-Escalante et al., 2011; Montero et al., 2005; Giménez et al., 2013; Arancibia et al., 2014). In emulsified systems, the initial step of lipid oxidation takes place at the interface between the oil and water phases (McClements & Decker, 2000). Multiple emulsions have two oil-water interfaces, in contrast with conventional emulsions where there is a single oil-water interface. The efficacy of antioxidants in emulsified systems is determined by their polarity but also by their molecular size, mechanism of action and the presence and type of emulsifiers (Shahidi & Zhong, 2011). Different results were obtained when a *Melissa officinalis* water extract rich in rosmarinic acid and BHA were tested in O/W and W/O/W emulsions (Poyato et al., 2013). Contrary to what might be expected according to the polarity of these antioxidants, the aqueous extract was more effective in O/W emulsions; whereas the lipophilic antioxidant (BHA) inhibited lipid oxidation more effectively in the case of W/O/W emulsions when it was dispersed in W1. In this study, two phenolic antioxidants with different polarity (Di Mattia et al., 2009) are proposed: gallic acid and quercetin (Figure 2). Gallic acid is a hydroxybenzoic acid present in many fruits and vegetables with significant biological activities such as antioxidant, antifungal, anti-inflammatory and anticarcinogenic (Daneshfar et al., 2008). Quercetin, as aglycones and glycosides, is one of the most abundant flavonoids in vegetable and fruits. Quercetin has a high radical scavenging capacity, since the three most important structural features for radical scavenging activity of flavonoids are present in its structure: orto-hydroxyl groups on B-ring, a hydroxyl group in position-3 and a double bond at position 2,3 conjugated with the 4-carbonyl group in C-ring (Edenharder & Grünhage, 2003). Furthermore, a number of other biological activities have been reported for this phenolic, such as cardioprotection, anti-inflammatory, antimicrobial or anticancer (Adewole et al., 2007). The antioxidant activity of gallic acid and quercetin has not been evaluated in multiple emulsions, but several studies can be found where they have been incorporated to O/W emulsions. According to Di Mattia et al (2009) the partition of quercetin in the aqueous phase of an olive O/W emulsion was about the half of that obtained for gallic acid at the same concentration for a similar interfacial area. However, gallic acid inhibited the formation of both primary and secondary oxidation products, in spite of its high polarity that favor its partition in the water phase (Di Mattia et al., 2010). Both gallic acid and quercetin were able to decrease the interfacial tension at the oil-in-water interface (Di Mattia et al., 2010). Regarding quercetin, a significant reduction in lipid oxidation has been reported when this flavonoid was incorporated in 20% olive oil and 10% cottonseed oil-in-water emulsions emulsified by Tween (Di Mattia et al., 2011; Kiokas & Varzakas, 2014).

Concerning their mechanism, and similar to the general mechanism of antioxidant activity for phenolic antioxidants, olive oil phenolics (ArOH) can inhibit autoxidation of lipids (RH) by trapping intermediate peroxyl radicals in two ways (Kiokias et al., 2008):

$$\mathrm{ROO} + \mathrm{ArOH} \Rightarrow \mathrm{ROOH} + \mathrm{ArO} \quad \textbf{(1)}$$

$$\mathrm{ROO} + \mathrm{ArO} \Rightarrow \mathrm{ROO\text{-}ArO} \quad \textbf{(2)}$$

First the peroxyl radical abstracts a hydrogen atom from the phenolic antioxidant to yield a hydroperoxide and phenoxy-radical *(reaction1)* that subsequently undergoes radical coupling to give peroxide products (*(reaction 2)*) The rate of oxidation of a lipid inhibited by a phenolic antioxidant requires consideration of the *following reactions 3-5.*

$$\mathrm{ArO} + \mathrm{ROOH} \Rightarrow \mathrm{ROO} + \mathrm{ArOH} \quad \textbf{(3)}$$

$$2\mathrm{ArO} \Rightarrow \mathrm{Non\ redical\ products} \quad \textbf{(4)}$$

$$\mathrm{ArO} + \mathrm{RH} \Rightarrow \mathrm{ArOH} + \mathrm{R} \quad \textbf{(5)}$$


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Furthermore, quercetin has been found to be more effective in inhibiting lipid oxidation in different highly unsaturated oil-in-water emulsion systems than other natural antioxidants such as catechin, β-carotene or α-tocopherol (Di Mattia et al., 2010; Kiokias & Varzakas, 2014; Huber et al., 2009).

Further to phenolic compounds, a body of literature has focused on the antioxidant effect of natural carotenoids (terpenoid type compounds) against the oxidative deterioration of oil-in-water emulsions).

Kiokias and Gordon (2004) discussed the in vivo antioxidant activity of dietary carotenoids along with literature evidence of any reported prooxidant effects. Kiokias and Oreopoulou (2006) have observed that certain natural carotenoid mixtures inhibited the azo-inititated oxidation of sunflower oil-in-water emulsions (operated rapidly under low $pO_2$) in terms of both primary and secondary oxidation products.

Furthermore, Kiokias et al. (2009) reported that, several carotenoid extracts (paprika, annatto and marigold preparations) containing mainly polar carotenoids, added at an active concentration of 1 g $l^{-1}$, exerted a strong activity against hydroperoxides and TBARs during the accelerated oxidation (60ºC) of homogenised protein-based emulsions.

Carotenoids act with a different antioxidant mechanism than the phenolic compounds (Kiokias et al, 2009). They have been reported to act as radical scavengers due to the extensive system of conjugated double bonds in their molecule that makes them very susceptible to radical addition. According to this particular mechanism, β-carotene (as an example) is capable of scavenging peroxyl radicals (reaction-6). The resulting carbon centred radical (ROO-β-CAR$^{\bullet}$) reacts rapidly and reversibly with oxygen to form a new, chain-carrying peroxyl radical (ROO-β-CAR- OO $^{\bullet}$, reaction-7). The carbon centred radical is resonance stabilized to such an extent, that when the oxygen pressure is lowered the equilibrium of reaction 2 shifts sufficiently to the left, to effectively lower the concentration of peroxyl radicals and hence reduce the amount of autoxidation in the system (Kiokias and Gordon 2004). Furthermore, the β-carotene radical adduct can also undergo termination by reaction with another peroxyl radical (reaction-8).

$$\beta\text{-CAR} + \text{ROO} \rightarrow \text{ROO-}\beta\text{-CAR} \quad \textbf{(6)}$$

$$\text{ROO-}\beta\text{-CAR} + O_2 \leftrightarrow \text{ROO-}\beta\text{-CAR-OO} \quad \textbf{(7)}$$

$$\text{ROO-}\beta\text{-CAR} + \text{ROO} \rightarrow \text{inactive products} \quad \textbf{(8)}$$

The physical location of antioxidants in oil-in-water emulsions can have significant influence on their free radical scavenging activity and ability to inhibit lipid oxidation (Raikos et al. 2014). Kirilan et al (2014) have suggested that surfactant micelles could increase the antioxidant activity of tocopherols by changing their physical location.

A few studies (Losada-Barreiro et al., 2013; 2014) have investigated the effects of temperature and surfactant volume fraction on the distribution of two representative antioxidants the water insoluble α-tocopherol and the oil insoluble caffeic acid in a model food emulsion composed of stripped corn oil, acidic water and the nonionic surfactant Tween 20.

Further to phenolic compounds, Liu et al. (2015) concluded that the stability and antioxidant capacity of β-carotene in oil-in-water emulsions could be improved by the presence of different antioxidants (in particular α-Tocopherol).

Relkin et al (2014) has reported that the ability of spray dried protein-stabilized emulsions for long-term vitamin protection appeared to be related to matrix structure-forming properties and, particularly to absence or presence of high energy crystals capable of vitamin expelling from the core of lipid droplets to their external phase.

## 5. INNOVATIVE APPLICATIONS OF ADDITIVES IN FOOD BASED EMULSIONS

Emulsions can be stabilized by applying emulsifiers, thickeners, or weighing agents. For water-in-oil (w/o) emulsions, stabilization strategies are restricted to (a) small droplets production to retard sedimentation, (b) interfacial tension reduction and stable interfacial layer formation to prevent aggregation and adsorption layer rupture, and (c) solutes addition to the disperse aqueous phase as osmotic agents to counteract capillary pressure and coalescence. Several studies have shown that emulsion stability can be improved by confectionery emulsifiers such as polyglycerol polyricinoleate (PGPR) and lecithins (Knoth *et al*., 2005a,b; Norton *et al*., 2009; Norton and Fryer, 2012; Killian & Coupland, 2012; Ushikubo & Cunha, 2014, Varzakas et al., 2014).

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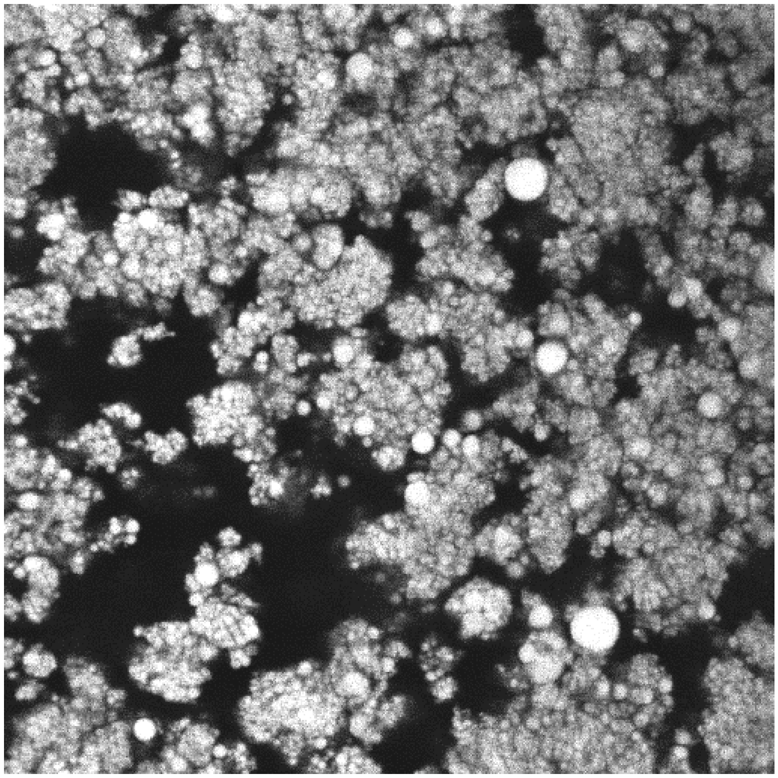

**Figure 1: Fat-stained CSLM pictures of whey-protein stabilised model emulsions containing sunflower oil, prepared under thermal homogenization. The emulsion clearly gets more aggregated upon heating and acidification (Kiokias et al., 2004).**