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Comparative time-course of lipid and myofibrillar protein oxidation in different biphasic systems under hydroxyl radical stress

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β-Mercaptoethanol (PubChem CID: 1567)

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ABSTRACT

This study aimed to investigate the relative reaction rate of protein and lipid oxidation in different biphasic model systems (linoleic acid; liposome; emulsion) containing myofibrillar protein (MFP at 1, 8 and 20 mg/mL) under hydroxyl radical stress. Protein oxidation markers exhibited significant changes in 2 h: reduced tryptophan fluorescence intensity, carbonyl formation, and extensive polymerization of myosin. In contrast, no detectable changes ($P > .05$) in lipid peroxide occurred within 2 h except for samples with 1 mg/mL MFP which showed an early TBARS formation. Of the three biphasic systems, the oxidative stability of lipids followed the order of emulsion > linoleic acid > liposome, indicating the steric role of proteins. In general, MFP was more susceptible to radicals than lipids, and a higher protein:lipid ratio was associated with a slower TBARS production and more rapid protein oxidation, suggesting a sacrificing role of MFP to protect lipids.

1. Introduction

Lipid and protein oxidations are a primary cause for quality deterioration in muscle foods. These two processes can be inter-related or occur independently; however, the relative susceptibility of lipid and protein to oxygen species in different food systems has not been well characterized. On one hand, the decomposition of lipid hydroperoxides generates alkoxyl and peroxyl radicals that may promote protein oxidation by abstracting hydrogen atoms from protein (Stadtman & Levine, 2003). Aldehydes produced from further chain reactions can initiate protein oxidation as well and are known to be involved in the generation of protein-lipid adducts (Li & King, 1999). On the other hand, protein radicals are able to react with double bonds in unsaturated lipids and susceptible side chain groups of other proteins (Elias, Kellerby, & Decker, 2008). In general, the characteristic oxidative stability of lipid and protein is influenced by their intermolecular packing with each other in an aqueous medium (Miyashita, Nara, & Ota, 1993). Therefore, the sequence of lipid and protein oxidation must be studied case by case.

Many formulated foods contain a lipid phase (e.g., triacylglycerols or phospholipids) dispersed in an aqueous medium. A triacylglycerol (TAG) is an ester derived from glycerol and three fatty acids. TAGs make up the bulk of edible oils and are one of the best sources of lipids to use for the evaluation of the potency of an antioxidant in emulsions (Decker, Warner, Richards, & Shahidi, 2005). In oil-in-water (O/W) emulsions, TAGs are dispersed in the form of small spherical droplets in an aqueous phase. Such a system is thermodynamically unstable, and an emulsifier is required to minimize the contact area between oil and water (McClements & Decker, 2000). Emulsifiers, such as amphiphilic proteins, phospholipids, and small molecule surfactants, are surface-active molecules capable of adsorbing to the surface of oil droplets during homogenization. The properties of the interfacial membrane formed by these emulsifiers in O/W emulsions could influence the rate of lipid oxidation (Jiang & Xiong, 2015; McClements & Decker, 2000).

Because of the abundant presence of unsaturated fatty acid components, phospholipids are considered to be a primary source of oxidative reactants responsible for rancidity in meat products. Moreover, with a high degree of unsaturation, phospholipids possess around 100 times more surface area than TAGs on a weight basis (Decker et al., 2005). Lecithin (phosphatidylcholine) is a common type of phospholipid, composed of a hydrophilic phosphoric acid with a choline “head”, and two hydrophobic fatty acids “tails”, joined together by a glycerol molecule. Lecithin is rich in egg yolk and soybean oil, and is widely utilized in food processing application as an emulsifier because of its strong amphiphilic nature (Dickinson & Yamamoto, 1996). Liposomes can be made from lecithin molecules that self-assemble in aqueous media into a spherical, enclosed structure (Sabın, Prieto, Ruso, Hidalgo-Alvarez, & Sarmiento, 2006). Namely, an aqueous solution core is

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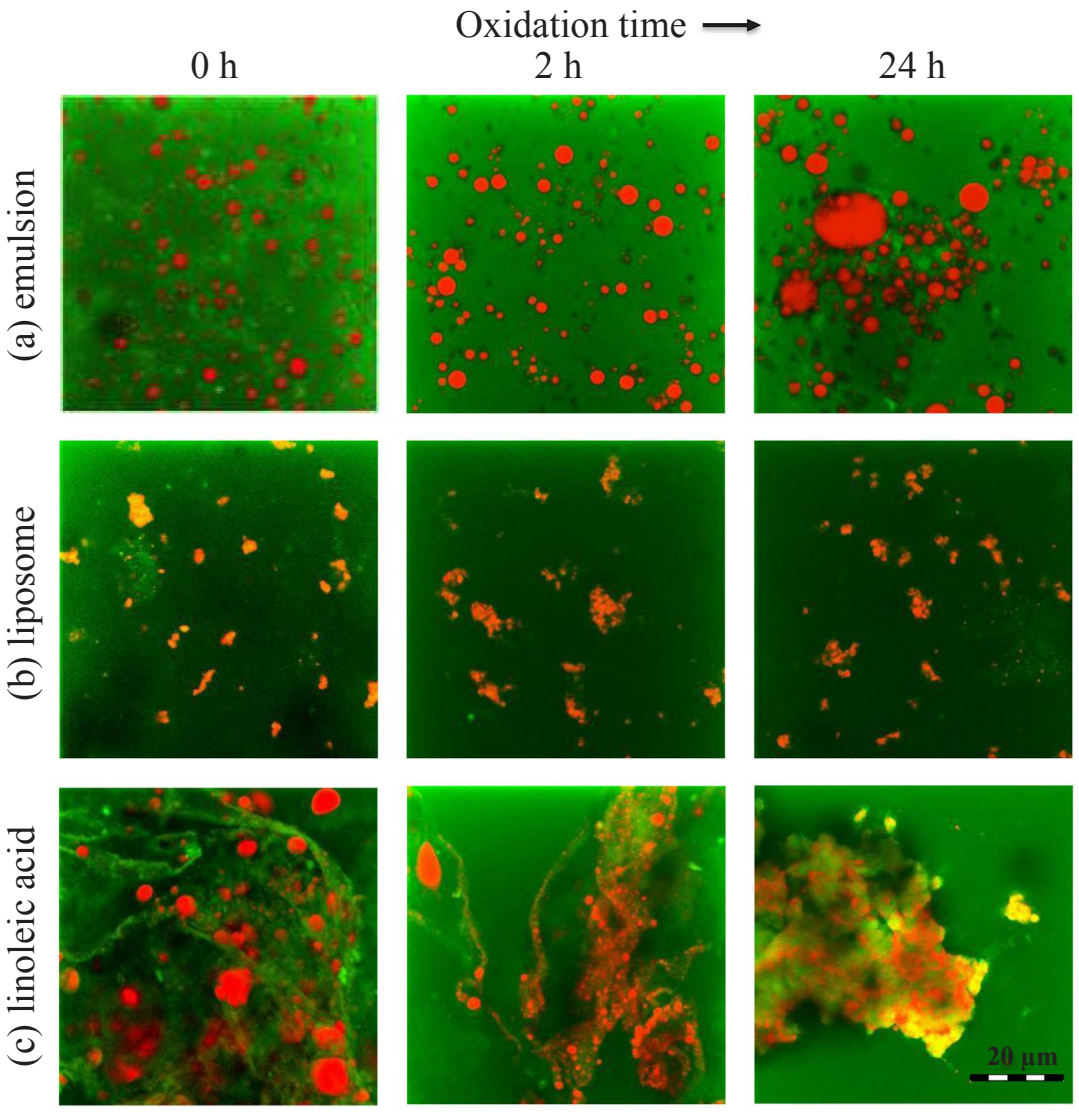

Fig. 1. Oxidation induced changes in microscopic images of (a) emulsion, (b) liposome, and (c) linoleic acid dispersion containing 20 mg/mL MFP. Oxidation was performed with a Fe^{2+}-recycling solution for 0 (control), 2, and 24 h. (Fat globules: red, protein network: green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

surrounded by a hydrophobic membrane, in the form of a lipid bilayer (hydrophobic tails line up against one another, forming a membrane of hydrophilic heads on both sides facing the water).

In biphasic model systems made of lipids and proteins, the distribution of proteins and lipids contributes to the susceptibility to reactive oxygen species (ROS). When fatty acids and proteins amorphously exist in an aqueous phase, it is thought that they physically have an equal probability to be modified by radicals. In contrast, the lipid bilayer in liposome systems and the protein membrane at the oil-water interface in an emulsion make lipids and proteins respond differently to ROS in an aqueous phase. It is believed that proteins or protein hydrolysates act as a physical barrier against liposome oxidation (Viljanen, Kivikari, & Heinonen, 2004; Zhang, Xiong, Chen, & Zhou, 2013). In protein-stabilized emulsions, the membrane formed around the oil droplets may deter radicals, thereby protecting the interior lipid core (Hu, McClements, & Decker, 2003; Jiang, Zhu, Liu, & Xiong, 2014). A number of recent studies have demonstrated the antioxidant effect of proteins and their apparent role in delaying lipid oxidation in liposome system, O/W emulsions, and other model systems (Cheng, Chen, & Xiong, 2014; Hu et al., 2003; Lethuaut, Metro, & Genot, 2002).

Both chemical (radical neutralization) and physical (steric) protection are to be considered when comparing the reactivity of lipids and proteins subjected to oxidants. The antioxidant activity of proteins is attributed to the cooperative effect of multiple properties, including radical scavenge, metal ion sequestration, and structural change of the food matrix (Díaz & Decker, 2004; Kaul, Sharma, & Mehta, 2008; Levine, Berlett, Moskovitz, Mosoni, & Stadtman, 1999). As the consumer's demand for 'all natural' foods continues to grow, the efficacy of proteins in the controlling of lipid oxidation makes them an attractive supplement and possibly substitute for synthetic antioxidants in fatty foods. However, more kinetic studies about protein oxidation and the exact mechanism of lipid and protein interaction warrant examination. Therefore, this study was designed to analyze the oxidative indicators in systems that have different ratios of MFP to lipids to investigate the comparative time-course of protein and lipid oxidation in different biphasic systems (oil/lecithin/free fatty acids).