



Nanoscale, zero valent iron particles for application as oxygen scavenger in food packaging



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ABSTRACT

Oxygen scavengers which are based on oxidation of iron powder dispersed in a polymer matrix are established in the packaging industry. They protect foods from oxygen. The iron particles have a diameter of several micrometers, which is too high to allow thin layers in multilayer film structures. A promising alternative is a developed nanoscale oxygen scavenger which is subject of this study. The aim of this study was to evaluate the oxygen absorption rate and the oxygen absorption capacity of nanoscale iron at 100% relative humidity and at dry conditions.

Nanoscale oxygen scavengers (zero valent iron particles) were synthesized. Their reactivity was tested. Furthermore, they were blended with a silicone matrix. The nanoscale oxygen scavenger absorbed oxygen in wet (100% relative humidity) and dry conditions. At 100% relative humidity the reaction rate of the powder was two to three times higher compared to non-nanoscale iron powder. The absorption rate of the nanoscale iron dispersed in a silicon carrier was at least ten times higher at 100% relative humidity compared to a commercially available iron based oxygen scavenger in a polyethylene or polypropylene polymer matrix.

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1. Introduction

Oxygen causes quality loss at many food products such as cured boiled sausage, salami, milk, peanuts, beer, edible oils and wine (Bohner, Hosl, Rieblinger, & Danzl, 2014; Giovanelli, & Brenna, 2007; Jensen & Risbo, 2007; Kozak & Samotyja, 2013; Lisińska-Kuśnierz, 2001; Kuchel, Brody, & Wicker, 2006; Roman, Heyd, Broyart, Castillo, & Maillard, 2013; Rizzo, Torri, Licciardello, Piergiorganni, & Muratore, 2013; Sangerlaub et al., 2012; Saffert, Pieper, & Jetten, 2008; Saffert, Pieper, & Jetten, 2006; Zardin et al., 2016). Deterioration processes involved are autoxidation, light induced oxidation and aerobic microbial growth (Buchner, 1999). To reduce the access of oxygen, foods are packaged with barrier materials and the headspace of packagings is flushed with nitrogen or nitrogen/carbon dioxide mixtures (Buchner, 1999; Lange & Wyser, 2003). However, residual oxygen can remain in the

headspace, it can permeate from the environment into the packaging or it is gotten into packagings as solved oxygen in food (Chaix, Guillaume, & Guillard, 2014; Hintze, Becker, & Heiss, 1965). A strategy to reduce the oxygen permeability of plastic packagings and to absorb oxygen from packaged food and from packaging headspace is the application of oxygen scavengers. Oxygen scavengers (Brody, Strupinsky, & Pruskin, 1995) remove oxygen from the inner package environment and thus, in turn, from the food product itself through partial pressure actions.

Many studies showed the effectiveness of oxygen scavengers for different foods such as salami, milk powder, milk, juice, tortilla, olive oil, wine, almonds, beer, catfish and probiotic yoghurts (Antunez, Omary, Rosentrater, Pascall, & Winstone, 2012; Cecchi, Passamonti, & Cecchi, 2010; Giovanelli & Brenna, 2007; Gibis & Rieblinger, 2011; Mannon, 2007; Mueller, 2003; Mohan, Ravishankar, & Srinivasagopal, 2008; Miller, Nguyen, Rooney, & Kailasapathy, 2003; Perkins, Zerdin, Rooney, D'Arcy, & Deeth, 2007; Mexis & Kontominas, 2010; Realini & Marcos, 2014; Sangerlaub et al., 2012; Zerdin, Rooney, & Vermue, 2003)

A multitude of oxygen scavengers were developed and tested. They are subsumed into organic (e.g. polymers with double

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bounds) and inorganic (e.g. metal powders) systems. Organic systems include Nylon MXD6 (a mainly aliphatic polyamide resin which contains meta-xylylene groups) blended with Poly(ethylene terephthalate) (PET), ethylene methacrylate cyclohexenylmethyl, cyclo-olefin bonded chemically to a silicate backbone, low-density polyethylene filled with oxygen scavengers made of powdered activated carbon impregnated with sodium erythorbate, polybutadiene, gallic acid and others (Amberg-Schwab, Weber, Burger, Nique, & Xalter, 2006; Dombre, Guillard, & Chalier, 2015; Goldhan et al., 2007; Joven, Garcia, Arias, & Medina, 2014; Li, Tung, Paul, & Freeman, 2011; Müller, Sänglerlaub, Kramer, Huber, & Fritsch, 2011; Müller, Welle, Rieblinger, & Sänglerlaub, 2010; Piton & Rivaton, 1996; Singh, Sänglerlaub, Wani, & Langowski, 2012; Singh, Wani, & Sänglerlaub, 2011; Schneider, Orzinski, Embs, Fritsch, & Weber, 2006; Solis & Rodgers, 2001). Their oxidation is often catalysed, e.g. by cobalt compounds. Inorganic systems include polymers blended with iron powder, different iron compounds and sodium sulphite (Cruz, Camilloto, & Pires, 2012; Foltynowicz, Kozak, & Fiedorow, 2002; Gibis & Rieblinger, 2011; Galotto, Anfossi, & Guarda, 2009; Müller et al., 2010; Müller, 2013; Rooney, 1995; Singh et al., 2012, 2011). Oxygen scavengers differ in their absorption kinetics, absorption capacity, time-temperature behavior, reactivity at different relative humidities and costs.

One of the most important systems for packaging materials is the group of oxygen scavengers that contain iron powder (Chiang et al., 1997; Gibis & Rieblinger, 2011; Lehner, Schlemmer, & Sänglerlaub, 2015; Müller et al., 2010; Singh et al., 2012; Singh et al., 2011; Sänglerlaub et al., 2012). They are a mixture of a carrier polymer, iron powder with a particle diameter in the range of 10 to 30 micrometres and a catalyst such as sodium chloride (NaCl) (Chiang et al., 1997; Klein & Knorr, 1990; López-Cervantes, Sánchez-Machado, Pastorelli, Rijk, & Paseiro-Losada, 2003; Sänglerlaub et al., 2012; Galotto et al., 2009). In dry conditions metallic iron is inert even though it is a non-nobel metal. The reason for this property is that metallic iron forms on its surface a passivating layer in the thickness of several nanometres (Ohtsuka, 2012; McCafferty, 2010). At high relative humidity or in contact with liquid water the passivating layer reacts with water and becomes porous, which makes this layer permeable for water vapour and oxygen. Therefore, metallic iron below this porous layer is accessible for water vapour and oxygen and can react then with both. The oxidation is catalysed by electrolytes, e.g. NaCl. Galotto and Sänglerlaub reported that oxygen scavengers with iron powder start to react with oxygen at a relative humidity of 75% or higher (Galotto et al., 2009; Sänglerlaub et al., 2012). Results from Schindelholz indicate that reaction starts already at a lower relative humidity (Schindelholz, Risteen, & Kelly, 2014). He showed that steel in direct contact with NaCl had a low but detectable corrosion rate at 33% relative humidity. The corrosion rate increased at higher relative humidity (>53%) by factor 300 to 2500. In polymers with dispersed iron powder and NaCl the property of non-nanoscale NaCl is used to absorb water vapour above 75% relative humidity (deliquescence point) and to solve in the absorbed water (Ewing, 2005). The salt solution can then wet the surface of the metallic iron particles and catalyse the oxidation of iron by oxygen there. This behaviour explains the higher reaction rate of iron powder when the relative humidity is higher than 75% (Galotto et al., 2009; Klein & Knorr, 1990; Sänglerlaub et al., 2012).

An important property of oxygen scavengers is their reaction rate. A strategy to increase the reaction rate is the reduction of particle diameters. The area of spheres increases by factor 10 when the particle diameter decreases by factor 10. For example iron powder with a particle diameter of 10 nm instead of 10 μm will have a 1000 times bigger surface area. Due to the fact that the passivating layer of metallic iron is several micrometres thick and forms in dry conditions or at very low relative humidity such iron

powder is already active in conditions of dehydrated and dry foods. Crane assumed a passivating layer thickness of 3 nm (Crane, & Scott, 2012). In this case a sphere is fully oxidised when the diameter is 6 nm or less. At 20 nm diameter around 65 vol-% of the sphere is oxidised. The passivating layer consists of iron oxides or oxyhydroxides (Liu & Zhang, 2014). Also in humid conditions and in contact with electrolytes the reaction rate of nanoscale iron would be much faster than at iron powders with a diameter of several micrometres.

Nanoscale iron powder is available as 'zero valent iron' (ZV). In recent years it gained prominence in research because it catalyses and/or oxidises the decomposition of contaminants such as antibiotics, biocides, hexachlorobenzene, azo dyes and it can be therefore applied for water treatments and decontamination (Crane & Scott, 2012; Fang et al., 2011; Homem & Santos, 2011; Moon, Park, & Park, 2011; Shih, Hsu, & Su, 2011; Zha et al., 2014; Xu & Wang, 2011). Additionally it inactivates microbes (Diao & Yao, 2009). Several groups measured the diameters of zero valent iron particles. The smallest diameters were between 3 nm and 5 nm (Machado, Grosso, Nouws, Albergaria, & Delerue-Matos, 2014; Oropeza, Corea, Gómez-Yañez, Cruz-Rivera, & Navarro-Clemente, 2012).

For food packaging related applications *Mu* and *Busolo* did experiments with nanoscale iron. *Mu* prepared nanoscale iron from borohydride resulting in 110 nm particle size (Busolo & Lagaron, 2012; Mu et al., 2013). The nanoscale iron and iron with a particle size of around 20 μm was mixed with activated carbon, NaCl and calcium chloride in a weight ratio of 1:1:1:0.2. At 75% relative humidity and 25 °C nanoscale iron absorbed oxygen circa 9 times faster than conventional iron. The compound absorbed circa 220 cm^3 oxygen per one gram of iron, which is circa 280 mg per one gram of iron (density of oxygen at 25 °C, 1013 mbar: 1.3093 mg cm^{-3}). The oxygen absorption capacity was lower than the stoichiometric capacity of 430 mg oxygen per one gram iron. *Busolo* used an iron containing kaolinite (Busolo & Lagaron, 2012). The average iron particle diameter was 115 nm. The iron containing kaolinite and a HDPE-powder compound with the iron containing kaolinite were analysed. At 100% relative humidity the reaction rate was higher than at 50% relative humidity. Interestingly, zero valent iron modified bentonite and kaolinite are approved by the European Food Safety Authority (EFSA) as non-nanoform species (EFSA 2013a, 2013b).

1.1. Intention of the present study

For this study an oxygen scavenger based on nanoscale iron (nano iron) was synthesised. The intention of this study was to measure and to evaluate its oxygen absorption rate and its oxygen absorption capacity.

2. Materials and methods

2.1. Experimental plan

Table 1 shows the samples of this study. Samples were analysed in measuring cells with defined headspace. The weight of iron powder was similar or in the same range at all samples as well as the headspace-sample ratio. Nanoscale iron was analysed in cells with and without a petri dish of water with the aim to evaluate the influence of relative humidity on the reaction rate. Iron powder was mixed with NaCl because this electrolyte catalyses the oxidation and because it is applied at oxygen scavengers with iron powder. The concentration of NaCl was varied to 1 and 10% w/w to study the influence of its concentration on the reaction rate.

For comparison oxygen scavenger films containing the commercially available oxygen scavenger SHELFPPLUS[®] O₂ were provided by Fraunhofer IVV. The system SHELFPPLUS[®] O₂ is an oxygen scavenger

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