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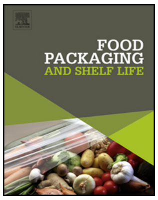

Research paper

Flexible hybrid coatings with efficient antioxidation properties

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Diethoxydimethylsilane (PubChem CID: 62322)
Triethoxyphenylsilane (PubChem CID: 13075)
Hydrochloric acid (PubChem CID: 313)
L-(+)-Ascorbic acid (PubChem CID: 54670067)
Ethanol (PubChem CID: 702)
2,4,6-Tris(2-pyridyl)-s-triazine (PubChem CID: 77258)
Ferric Chloride (PubChem CID: 24380)
Iron Chloride heptahydrate (PubChem CID: 152378)
Acetic acid (PubChem CID: 176)
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ABSTRACT

In this work, the feasibility of a transparent sol gel coating on polyamide-polyethylene (PA/PE) substrate with antioxidant properties as active food packaging was investigated. Stable water-based silicon alkoxide formulations, containing lipophilic vitamin E as natural antioxidant, were obtained adding ascorbic acid as catalyst. Comparative blank sols were prepared without antioxidant guest molecules. The sol formulations of tetraethyl orthosilicate and a mixture of alcoxysilane containing organic moieties as phenyl and methyl group were stable and easy to process *via* dip coating on Polyamide/Polyethylene substrates. Organic functionalities were essential to incorporate the lipophilic guests and to achieve an optimal adhesion on the polymeric substrate. The presence of stable coating was evaluated through Electron Microscopy and Optical Emission Spectroscopy analyses, while the surface roughness and optical absorption were measured by noncontact laser profilometry and by UV/vis spectra. The loaded antioxidant amount was estimated right after the coating deposition by spectroscopic UV measurements in ethanol, as its subsequent release within 14 days. The estimated antioxidant release was 10% and 40% of the loaded amount for the hydrochloric-sol and the ascorbic acid catalysed sol, respectively. The antioxidant efficacy of coatings was evaluated through the Ferric Reducing Antioxidant Power (FRAP) assay showing a significant difference in antioxidant efficacy between the vitamin E containing sols and their blank ones. Those results were confirmed by FRAP analysis even four months after the deposition.

1. Introduction

In the last decade, active packaging has received increasing attention, being one of the most promising evolutions of traditional passive packaging (Prasad & Kochhar, 2014), so that nowadays new safety regulations are rising in that field (*e.g.* European Regulation (CE) No. 450/2009). The traditional packaging aims to establish a barrier between the atmosphere surrounding the food and the external environment, whereas the active packaging carries out the barrier function together with playing an active role in extending the shelf-life of the product (De Abreu, Cruz, & Losada, 2012; López-de-Dicastillo, Catalá, Gavara, & Hernández-Muñoz, 2011). Indeed, active packaging solutions have been proposed in order to slow down food spoilage (Rodriguez, Nerin, & Batlle, 2008), improve food safety (López-de-Dicastillo et al., 2011; Rodriguez et al., 2008), or enhance sensory and taste properties of foods and beverages.

Active packaging solutions hence provide not only an economic gain, but mainly an improvement in food quality in terms of

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preservation against microbial degradation and contamination and in terms of biochemical changes (maintenance of organoleptic and nutritional properties) which affect food colour, texture, and flavour (Melone, Altomare, Cigada, & De Nardo, 2012

An active package acts in two main ways, depending on the needed function: by reacting with undesired species trough absorbing or scavenging mechanisms (López-de-Dicastillo et al., 2011) or by releasing desired substances (Dias et al., 2013). Among active packages, those with antioxidant properties raise great interest, because they work to reduce oxidative processes, which are one of the main causes of food spoilage (Gómez-Estaca, López-de-Dicastillo, Hernández-Muñoz, Catalá, & Gavara, 2014; in't Veld, 1996; Kubow, 1992; Mills, 2005). Antioxidants are classified by their mechanism of action: free radical scavengers (such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and catechins), oxygen scavengers, and reducing agents (such as ascorbic acid and sulphites), singlet oxygen quenchers (such as tocopherols and carotenoids), and chelators (such as citric acid and EDTA) (Tian, Decker, & Goddard, 2012).

These can be further classified depending on their natural or synthetic origin. Nowadays, natural antioxidant contained in essential oil or plant extracts (Chen, Lee, Zhu, & Yam, 2012; Dias et al., 2013; López-de-Dicastillo et al., 2012; Puoci et al., 2008; Qader et al., 2011) are more commonly used to overcome health problems, like suspected risks of mutagenic and carcinogenic effects, connected with the assumption of the most common synthetic antioxidants (Tian et al., 2012), such as BHA, BHT, *tert*-butylhydroquinone (TBHQ), and propyl gallate (PG) (Qader et al., 2011).

To give effective antioxidant properties, active molecules are incorporated into (Barbosa-Pereira et al., 2013; Chen et al., 2012; Jamshidian et al., 2012) or coated onto food packaging materials. Including the antioxidant molecules by extrusion process or during the polymerization implies high temperatures or reactive environment, and consequently potential losses of volatile compounds, thermal degradation of antioxidant molecules, or losses of antioxidant power (Gómez-Estaca et al., 2014). Moreover, changes in the pristine polymer properties due to the guest molecule can occur.

An easier way to expose the antioxidant molecule on the package can be obtained by applying a coating. A versatile method commonly used to create surface films and coatings is sol-gel process (Hench & West, 1990): it allows obtaining highly transparent coatings on different substrates, combining the advantages of a low cost procedure and low process temperatures. The sol-gel method is based on the hydrolysis of metal alkoxides, mainly silicon alkoxides, and their subsequent polycondensation. The reaction proceeds through basic or acid catalysis; from hydrolysis reaction the so-called "sol" is obtained: it is a metastable liquid colloidal solution constituted by hydrolysed alkoxides. *via* polycondensation of hydrolysed alkoxides, the sol evolves in gel.

Sol gel functionalization is used to change surface properties like wettability (Budunoglu, Yildirim, Guler, & Bayindir, 2011), UV light (Parejo, Zayat, & Levy, 2006), chemical resistance (Zheng & Li, 2010), scratch resistance (Toselli, Marini, Fabbri, Messori, & Pilati, 2007), and so on. The specific coating property is due to an organic functionality, and the hybridization is obtained by employing organo-modified silicates (Mackenzie & Bescher, 1998; Schubert, Huesing, & Lorenz, 1995; Wen & Wilkes, 1996). The hybridization often provides good flexibility to silicate materials (Budunoglu et al., 2011). Moreover the use of organo-modified silicates promotes the adhesion of the inorganic matrix to organic surfaces (Toselli et al., 2007).

In this work, new active coatings for food packaging with antioxidant properties were prepared and characterized. Employing the sol-gel process, a liposoluble antioxidant molecule was encapsulated in a hybrid organic-inorganic matrix. The coating was applied on polyamide/polyethylene (PA/PE), a very versatile material for food packaging. The selected antioxidant was vitamin E (α-tocopherol), one of the most powerful natural oxygen quencher. The process is water-based and the tested catalysts are hydrochloric acid and a natural not toxic acid, ascorbic acid, feasible for food industry applications. Moreover, ascorbic acid is a natural antioxidant compound. Optimized coatings were analysed in terms of their antioxidant power and the kinetics of release of vitamin E in ethanol, by mean of the FRAP test and UV spectrophotometry, respectively.

2. Materials and methods

2.1. Reagents and materials

Tetraethyl orthosilicate 98% (TEOS), diethoxydimethylsilane 97% (DMDES), and triethoxyphenylsilane 98% (PTES) were purchased by Aldrich and used as silica source. (±)–αTocopherol (Vitamin E, Sigma, synthetic >96% HPLC) was used as antioxidant. Deionized water was used as solvent. The hydrolysis reactions were catalysed by hydrochloric acid (Aldrich, ACS reagent, 37%) or L-(+)-ascorbic acid (ABCR, 99%). Ethanol (99,8%) and 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ, 98%) were purchased by ABCR, while $FeCl_3$ (99%), sodium acetate tri-hydrate, and acetic acid (99,7%) by Sigma-Aldrich. All chemicals were used without further purification. Polyamide/polyethylene (PA/PE) substrates, standard thickness 220 μm, were used to prepare the hybrid thin coatings.

2.2. Sol synthesis

Sol-gel derived silica hybrid coatings were synthesized using two different acid catalysts, HCl and L-(+)-ascorbic acid according to the following procedure. The antioxidant compound was 2% [w/w], over the final nominal silica amount. The (±)-α-tocopherol was dissolved in PTES before water addition, in order to support its hydrophobic nature and overcome phase separation problems. Secondly, the solvent with the catalyst (hydrochloric or ascorbic acid) was added under vigorous stirring, leading to hydrolysis in one hour. In the two last steps, TEOS was added and after 30 min of continuous stirring, DMDES was mixed up. The final TEOS, DMDES, and PTES molar ratio was 15:2.2:1. For each sol containing antioxidant guest molecule, a comparative blank sol was prepared following the same synthetic procedure (see composition details in Table 1). Sols were named HA in the presence of hydrochloric acid

Table 1
Composition details of the prepared solutions.

	TEOS M	PTES M	DMDES M	(±)-α-Tocopherol mg/100 ml	Ascorbic Acid mg/100 ml	Hydrochloric Acid 37% M
HA	0.6	0.04	0.09	–	–	0.01
HA-VE				101.6	–	0.01
AA				–	250	–
AA-VE				101.6	250	–