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Development of low-density polyethylene antioxidant active films containing α-tocopherol loaded with MCM-41(Mobil Composition of Matter No. 41) mesoporous silica

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ABSTRACT

Antioxidant active packaging films are always prepared to help protect fatty food safety. In this study, a new LDPE (Low-Density Polyethylene) film containing α-tocopherol adsorbed on MCM-41 mesoporous molecular sieve was prepared by extrusion. The synthesized MCM-41 were thoroughly characterized before and after loading with α-tocopherol by powder X-ray diffraction, nitrogen adsorption isotherms, infrared spectroscopy, and thermogravimetric analysis. Physical properties of the new films including tensile strength, oxygen and water barrier properties were studied. In particular, the effect of loading α-tocopherol onto MCM-41 on the migration behavior of α-tocopherol from active films was investigated. Migration test were performed at 40 °C, using 95%(v/v) ethanol as fatty food simulants on LDPE films with pure α-tocopherol and the assembly of α-tocopherol and MCM-41. The results showed that, after being adsorbed on MCM-41, the releasing period of α-tocopherol in LDPE were prolonged by about 36%, and the diffusivity of the antioxidant decreased by 53%. Moreover, DPPH radical scavenging assay proved the effectiveness of the antioxidant in the new film. These demonstrated that the new kind of active film can be potentially used for controlled release antioxidant food packaging application.

1. Introduction

Antioxidant packaging have been investigated for a very long time, since lipid oxidation may cause a lot of quality problems which are not just on lipids but also on other components of food during storage and transportation (López-de-Dicastillo et al., 2012). Lipid oxidation of packaged food can be partly excluded by adding antioxidants to the packaged food, however, in order to make sure sustain release of antioxidant in a relatively long term and avoid food safety problems concerned by consumers, controlled release antioxidant active packaging, on the basis of active packaging, has been introduced and investigated. Controlled release packaging (CRP) means that active compounds release from packaging materials in a controlled manner which offers a prolonged delivery of active compounds at predictable and reproducible release rate (Koontz et al., 2010). Controlled release of antioxidants in food packaging films can be realized by the modification of structure and composition of packaging polymers (Gemili, Yemenicioğlu, & Altınkaya, 2010; LaCoste, Schaich, Zumbrunnen, & Yam, 2005; Zhu, Lee, & Yam, 2012). Moreover, the use of encapsulation technique has also been proved to be an effective method to control the release of active compounds, such as complexation by beta-cyclodextrin (Barba, Eguinoa, & Maté, 2015; Chen & Liu, 2016; Koontz et al., 2010; Liu et al., 2015; Siró et al., 2006) and incorporation into a mesoporous matrix (Gargiulo et al., 2013; Heirlings et al., 2004; Ruiz-Rico et al., 2015).

Since the development of ordered mesoporous molecular sieves in 1992 (Beck et al., 1992; Kresge, Leonowicz, Roth, Vartuli, & Beck, 1992), they have received noteworthy attentions from researchers. MCM-41 mesoporous molecular sieve was firstly proposed to be used in controlled drug-delivery system for its ability to accept and deliver organic compounds in 2001 (Vallet-Regi, Ramila, Del Real, & Perez-Pariente, 2001). Until now, considerable research has been conducted on ordered mesoporous silica materials including MCM-41 and SBA-15 (Santa Barbara-15) (Berlier et al., 2013; Datt, El-Maazawi, & Larsen, 2012; Manzano et al., 2008; Qu, Zhu, Huang,

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et al., 2006; Szegedi, Popova, Goshev, Klébert, & Mihály, 2012; Szegedi, Popova, Goshev, & Mihály, 2011; Vallet-Regı, Doadrio, Doadrio, Izquierdo-Barba, & Pérez-Pariente, 2004; Yu & Zhai, 2009). Several advantages of these materials account for this phenomenon: stable mesoporous structure, regular and adjustable nano-pore size, and high surface area (Qu, Zhu, Lin, et al., 2006). As to the controlled release of antioxidant, the pore size of mesoporous materials determines the size of antioxidant molecule that can be adsorbed, and controls the antioxidant release rate according to pharmaceutical research (Horcajada, Rámila, Pérez-Pariente, & Vallet, 2004; Vallet-Regí, Balas, & Arcos, 2007). Natural antioxidants, such as tocopherol, catechin, rosemary extract and quercetin, etc(Barbosa-Pereira et al., 2013; de Abreu, Rodriguez, & Cruz, 2012; Graciano-Verdugo et al., 2010; Granda-Restrepo et al., 2009; Lopez-de-Dicastillo, Alonso, Catala, Gavara, & Hernandez-Munoz, 2010; Nerín et al., 2006; Wessling, Nielsen, & Leufven, 2000; Zhang & Zhao, 2014; Zhu, Schaich, Chen, & Yam, 2013) have been extensively studied because of the toxic potential of synthetic antioxidants. α-Tocopherol with the size of about $2.4 \times 0.7 \times 0.4\ nm^3$ (Fig. 1), as one of them, has been added to LDPE, linear low-density polyethylene (LLDPE), polypropylene (PP) and other polymeric materials and investigated the migration behavior in foods and food simulating liquids (Gargiulo et al., 2013; Heirlings et al., 2004; Koontz, 2008; Koontz et al., 2010; Koontz, Marcy, O'Keefe, & Duncan, 2009; Lopez de Dicastillo, Ares Pernas, Castro Lopez, Lopez Vilariño, & Gonzalez Rodriguez, 2013; Siró et al., 2006; Wessling, Nielsen, Leufven, & Jagerstad, 1998). As a new approach to control the release kinetics of antioxidant, SBA-15 has been applied in the research of antioxidant active packaging on the one hand to protect α-tocopherol during extrusion and on the other hand to ensure a sufficient release of the antioxidant in a controlled manner, while the results showed the adsorption of α-tocopherol onto SBA-15 only made a small difference in the migration rate of α-tocopherol (Heirlings et al., 2004). Lately, Gargiulo et al(Gargiulo et al., 2013) has attempted to overcome this issue by loading the active compound onto functionalized SBA-15, and nearly 60% decreases in diffusivity has been found due to the reduced pore size and interactions between the antioxidant and functionalized carrier. Accordingly, in general, SBA-15 possesses large pore size of 4.6–30 nm (Zhao, Wan, & Zhou, 2012), normal MCM-41with pore size of 2–4 nm, by contrast, may be more suitable for control the release kinetics of α-tocopherol in terms of the pore size influence of unmodified mesoporous silica materials. Moreover, it has been demonstrated that as long as the pore size allows the drug to get into the matrix, the higher the surface area, the higher the amount of drug adsorbed, meanwhile, lager pore volumes may result in greater drug loading rate (Vallet-Regí et al., 2007). Specifically, MCM-41 has larger pore volume and surface area, which are both determining factors of loading amount.

Thus, the aim of this work is to develop a new kind of antioxidant active packaging film containing α-tocopherol adsorbed onto MCM-41 mesoporous silica sieve, which were chosen by taking the size of active compound molecule into consideration, to finely control the release of the antioxidant from packaging materials.

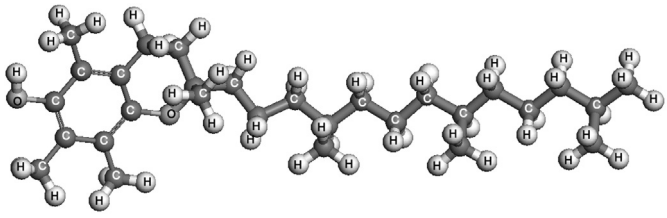

Fig. 1. Molecular structure of α-tocopherol.

Meanwhile, some properties of the new film were investigated to analyze the changes that may caused by the addition of the assembly.

2. Materials and methods

2.1. Materials

Analytical grade sodium metasilicate nonahydrate, hexadecyl trimethyl ammonium bromide (CTMABr), sulfuric acid, absolute ethanol and methanol of HPLC grade were received from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 95% Ethanol was prepared by dilution of absolute ethanol in ultrapure water which was obtained from Aquaplore ultra-pure water system provided by Shanghai Ultrapure Instrument Co., Ltd (Shanghai, China). (+)-α-Tocopherol of 98% purity and 2,2-Diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma-Aldrich (St. Louis, USA). Low-Density Polyethylene (LDPE) resin were obtained from Exxon Mobil Corporation (Texas, USA).

2.2. Samples

2.2.1. Synthesis of MCM-41 mesoporous molecular sieve

The MCM-41 was prepared according to a method previously reported using CTMABr as surfactant and sodium silicate as silica source (Beck et al., 1992) with some alterations. Typically, 25 g sodium metasilicate nonahydrate dissolved in 30 mL deionized water and 6.4 g CTMABr heated in 20 mL deionized water were mixed with vigorously stirring for 0.5 h after the later cooling to room temperature. Then, the pH value of the mixture was adjusted to 10 using sulfuric acid (5 M). After magnetic stirring for about 80 min, the resulting gel mixture was heated to 373 K for 3 days. The product was filtered and washed with deionized water until the pH value reached 7. Then, it was dried in an oven at 373 K overnight. Finally, the dried product was heated to 550 °C for 5 h.

2.3. Adsorption of α-tocopherol on MCM-41 mesoporous molecular sieve

2.5 mmol α-Tocopherol was dissolved in 10 mL absolute ethanol, and 0.5 g MCM-41 was added into the solution. After stirring for 3 h, the mixture was filtered using sintered glass filter, and then dried in vacuum oven at 40 °C for 3 days.

2.4. Preparation of LDPE antioxidant active packaging films

The films were prepared through two-step process. First, 1% α-tocopherol, pure and adsorbed on MCM-41, were mix granulated with LDPE resin using a 16 mm twin-screw extrusion line. Then, the granules were made into films by flat extrusion on a LabTech LCR-300 one layer single screw extrusion flat film and sheet chill roll line (Bangkok, Thailand) at 170 °C at a screw speed of 30 rpm. Films containing no α-tocopherol were also prepared as control. The resulting films were L (LDPE), LA (LDPE with α-tocopherol) and LMA (LDPE with α-tocopherol adsorbed on MCM-41). The thickness of these films were measured as 89 ± 4, 114 ± 3, and 114 ± 2 μm using a micrometer. Different type of film samples were separately vacuum packaged in AL/LDPE bags and stored at room temperature before analysis.

2.5. Instrumental analysis

2.5.1. Characterization techniques of additives

In order to characterize the structure of MCM-41 and MCM-41 loaded with α-tocopherol, the isotherms of nitrogen adsorption/