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Peculiarities of vanillin release from amino-functionalized mesoporous silica embedded into biodegradable composites

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ABSTRACT

Mesoporous silica nanoparticles are among the most promising nanovectors for controlled release of active compounds. In this work we design a mesoporous silica-based delivery system in which the release of the active compound is controlled by specific pore/wall interactions and can also be triggered by an external stimulus, such as the simple addition of water into the surrounding releasing medium. Due to its reversibility in presence of water, imine bond formation between amino groups and aldehydes has been proposed as a valuable approach to reach this scope. The amino-group is provided by the amino-functionalized mesoporous silica which has been obtained through the functionalization of Santa Barbara Amorphous (SBA)-15 with aminopropyltrietoxysilane. Whereas the aldehyde is represented by the active compound itself: the natural antimicrobial vanillin. The obtained particles have been embedded into PCL-based films. The amino-functionalization of mesoporous silica has been confirmed through NMR analysis and X-ray diffraction. Imine bond formation and evolution has been followed by ^{13}C NMR before and after the contact of mesoporous silicas with water. Release kinetics of vanillin show that the diffusion of vanillin from films containing the functionalized mesoporous silica is delayed by about 20% and 75% with respect to films containing free vanillin, in water and in ethanol respectively. The most significant feature of the system is the stepwise behavior which shows that the release of the amount of vanillin bound to the NH_2 groups of functionalized SBA is triggered only after the addition of water to the surrounding ethanolic solution. These findings give an important insight into the use of pristine and functionalized mesoporous silicas for the development of polymer films for active responsive packaging materials.

1. Introduction

Active packaging is a widely accepted term indicating packaging systems that directly and positively interact with the enclosed food by delaying or inhibiting those phenomena responsible for food quality decay [1].

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Emerging and challenging materials in food and food packaging research are represented by those corrective systems which exhibit a responsive behavior as a result of a specific trigger or change occurring in the food product, package headspace or the outside environment with the aim to maintain food safety or to promote food quality [2].

The combination of active, corrective and biodegradable packaging represents an interesting solution to promote both the shelf life extension of packaged foodstuff and to reduce environment pollution related to the accumulation of plastic waste. The biodegradable poly-ε-caprolactone (PCL) has been used in combination with polysaccharides, such as starch and chitosan, to obtain films with increased mechanical properties and improved water vapour barrier properties, potentially able to extend the shelf-life of fruits and vegetables [3,4]. Besides its use as passive material, PCL has been also used for the development of active packaging containing the natural biocide cinnamaldehyde which has shown good in vitro antimicrobial activity against *S. enterica* and *L. monocytogenes* [5]. Generally these systems do not respond to a specific trigger and their activity is primarily based on passive diffusion of selected components such ad antimicrobials or antioxidants from polymers. Whereas, in the design and development of corrective materials, the capability to control the release of the active compound (AC) is highly desirable [6]. To this aim, it has been shown that the simultaneous presence of active molecules and nanoparticles in the bulk of the polymer matrix certainly influences the release rate and diffusion of AC from the film to the outer environment. The use of commercial Cloisite30B, Layered Double Hydroxide and NanoBioTer AC11 in the bulk of PCL-based films has been recently investigated, thus showing that the presence of such particles affects, through a complex dynamics of weak interactions established on the filler surface, the release of hydroxytyrosol, benzoate and thymol [7–9].

However, a more effective and challenging approach is the use of porous inorganic (nano)particles as nanoscale container to encapsulate active compounds and control their release, also in the field of food packaging. Among nanocarriers, mesoporous silica and natural clay in tubular form [10–13] are particularly attractive materials since the release of molecules embedded in the internal lumen can be controlled by pore architecture, pore size and specific molecule/pore wall interactions [14]. Moreover, surface-functionalized and end-capped ordered mesoporous silica are considered potentially interesting for the engineering of stimuli-responsive systems since the opening/closing of the gatekeepers can be controlled by various external stimuli [15].

Within this context, our idea was to implement this strategy and find an easy route to obtain a dynamic system of high applicative interest in the field of food, food packaging and cosmetics. The aim of the authors has been the design of a mesoporous silica-based delivery system in which the release of the active compound is controlled by specific pore/wall interactions and can also be triggered by an external stimulus, such as the simple addition of water into the surrounding releasing medium. Due to its reversibility in presence of water, imine bond formation between amino groups and aldehydes has been proposed as a valuable approach to reach this scope. In this work the amino-group is provided by the amine-functionalized mesoporous silica which has been obtained through the functionalization of Santa Barbara Amorphous (SBA)-15 with aminopropyltrietoxysilane. Whereas the aldehyde is represented by the active compound itself; our attention has been focused on vanillin which exhibits antimicrobial and antifungal activity and has been recently used for the development of paperboard coatings [16] and of active film effective against food-contaminating bacterial and fungal pathogens [17] and in food applications such as smoked chicken breast [18], crab stick [19] and butter cake [20]. It is particularly interesting also because recent studies demonstrated that vanillin is an efficient inhibitor of cancer cell migration and metastasis in a mouse model, and thus it is potentially used in different and much broader application fields [21].

Only few recent papers report on the dynamic covalent behavior of the reversible imine bond formation/hydrolysis between vanillin and amino groups of chitosan [21,22]; no data on the imine bond formation between vanillin and amino groups of functionalized mesoporous silica have been published so far. In the present work for the first time amino-functionalized SBA15 particles loaded with vanillin have been developed and embedded into PCL-based flexible films with the aim to exploit the potential of the imine bond reversibility to control and trigger vanillin release for potential food packaging applications. Three aspects have been mainly investigated, namely the amino-functionalization of mesoporous silica, the imine bond formation and hydrolysis, and the release kinetics and diffusion of vanillin in liquid media from both functionalized mesoporous silica and PCL-based composites.

2. Experimental section

2.1. Materials

Poly(ε-caprolactone) (PCL) pellets were purchased by Perstorp (Capa™ 6800, CAS 24980-41-4). Santa Barbara Amorphous (SBA)-15 mesoporous silica was purchased from ACS Material (Stock # SBA-15-8-20 g, maximum dimension of the single particles is about 1 μm, pore Diameter 8–9 nm). (3-Aminopropyl)triethoxysilane (CAS 919-30-2, MW = 221.37 g/mol, d = 0.946 g/mL at 25 °C), vanillin (CAS 121-33-5, Mw = 152.15 g/mol, d = 1.056 g/cm^3), hydrochloric acid, toluene and ethanol were purchased from Sigma Aldrich. All chemicals were used as received but SBA which, as declared by the supplier, contains residual amount of template was subjected to thermal treatment to remove it.