Chitosan films as pH-responsive sustained release systems of naturally occurring antifungal volatile compounds

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一、 簡述論文概要及重大發現

殼聚醣作為多醣類，因其高生物相容性，常作用於藥物載體上的研究，並且在不同的科學或工業領域都有許多的發展，而本篇特別的地方在於作者透過殼聚醣薄膜本身所具的氨基和醛類的羰基進行鍵結，形成席夫鹼（Schiff base），將其應用在食品保鮮上，席夫鹼在化學中使用廣泛，通常用於保護有機合成中的官能基或產生的配位化合物，易於操作，合成條件溫和，反應時間短，並且此鍵結對於酸鹼度具有敏感性，可以透過人為控制酸鹼值的情況下，去進行水解反應，將具有抗真菌能力的醛類重新釋放出來，來達到抑制真菌生長的效果。

二、 對論文內容的提問

雖然可以透過控制酸鹼度的方式，去促進水解反應，將醛類釋放出來達到抗菌效果，但甚麼時候該釋放，該釋放多少，都還尚未可知，在講求方便性跟需要大量使用的食品工業上感覺過於麻煩。

三、 論文的缺點和評論

作者在鍵結合成方面設計得很巧妙，透過酸鹼值控制醛類釋放的部分，意味著在正常中性狀態下可以穩定的被保存，如果是用在特定感染部分進行處理的話感覺會有更好的效果。

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ABSTRACT

Reversible imine bonds have been used as a strategy to develop pH-dependent antifungal systems based on grafting benzaldehyde and citral onto the surface of chitosan films. Formation of imine bonds was confirmed by ATR-FTIR and XPS. Aldehyde unit incorporation respect to glucosamine units of chitosan polymer was estimated by elemental analysis. The rate and extent of imine bond hydrolysis depended on the pH of the media and the chemical structure of the aldehyde. The release of the aldehydes was monitored by gas chromatography observing acidic media favours the release. Imine bond obtained from benzaldehyde was more prone to be hydrolysed than citral. Chitosan films grafted with benzaldehyde and triggered at acidic pH controlled *in vitro* growth of common fruit and vegetable spoilage and pathogenic fungi. The films developed could be applied in the design of food packages intended to prevent postharvest fungal spoilage.

1. Introduction

Polymers based on dynamers offer new possibilities in polymer chemistry to create functional materials with unique properties. In this framework, the concept of component exchange in reversible polymers allows the development of polymers consisting of a static molecular skeleton decorated with dynamic chain substituents attached through reversible covalent bonds that can be decorporated under an external trigger. These polymers can be formed as films or coatings giving rise to materials with new functions (Lehn, 2005; Liu et al., 2017).

In general, reversible covalent bonds present greater strength and their reversibility is more controllable than that in reversible connections based on non-covalent interactions. These features make those bonds very attractive for the creation of new functional materials with controlled release properties which action is triggered by external stimuli. Among dynamic covalent bonds, Schiff bases are imines formed by the condensation reaction of a carbonyl group with a primary amino group giving rise to an imine bond (C=N). Schiff bases are greatly spread in chemistry and are commonly used for protecting functional groups in organic synthesis or to create coordination compounds. Moreover, they are easy to perform, requiring mild conditions for synthesis with short reaction times, which meets the criteria of "Click Chemistry" (Kolb et al., 2001). Hydrolytic cleavage of C=N bonds is favoured at acid pH, therefore, it makes Schiff base sensitive to pH, giving rise to the possibility of using Schiff base structure to create stimuli-responsive systems (Xin & Yuan, 2012).

Chitosan is a biopolymer obtained by deacetylation of chitin, which forms part of various natural structures, such as the shell of crustaceans and insects. Chitosan has a linear structure consisting of β-(1-4)-D-glucosamine and *N*-acetyl-D-glucosamine, arranged randomly along the chain (Muxika et al., 2017). Chitosan has been highly studied during more than 20 years as biopolymer to carry and release active molecules of diverse interest in different scientific and industrial fields such as pharmacy, medicine, agriculture, health care, textile and food industry (França et al., 2018; Paul & Sharma, 2000; Qu & Luo, 2020; Shi et al., 2021). Chitosan has a great potential to be used for creating stimuli-responsive polymer-aldehyde conjugates based on imines since it has primary amine groups that can be used to reversibly attach active biomolecules having carbonyl groups.

Recently, a few researchers have employed the reversibility of imines to create aldehyde-chitosan conjugates with antimicrobial properties. Marin et al. (2015) and Demitri et al. (2016) developed aldehyde-imino-chitosan conjugates in a homogeneous solution of chitosan, they cast the solution into films studying their antimicrobial properties. Chabbi et al. (2020) also synthetized aldehyde-chitosan conjugates in homogeneous liquid media and were beyond studying the release of the aldehydes in buffered water.

In this work, the reversibility of the imine bond has been employed to

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