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In vitro evaluation of the mixed xanthan/lignin hydrogels as vanillin carriers

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ABSTRACT

Various amounts of lignin from annual fiber crops (GL) exhibiting antioxidant properties were incorporated in xanthan to obtain hydrogel films. These mixed xanthan/lignin hydrogels were evaluated as matrices for vanillin release as active aroma ingredient. The new obtained biodegradable polymeric matrices, containing vanillin, have been characterized by the swelling/release experiments, FT-IR and AFM analysis. As a novelty, AFM microscopy was done on powder form. In FT-IR spectra after incorporation of the aroma, the shifting of the bands at 1618 and 1510 cm^{-1} (assigned to C=C stretching vibration) to higher wavenumbers was observed, indicating interactions between components. The comparison of all the results afforded by the various characterization methods leads to the conclusion that the 70X/30GL hydrogel (15% within 100 min) slower releases the vanillin aroma more than 90X/10GL (18% within 100 min) one because of stronger inter- and intramolecular interactions between matrix and active substance.

1. Introduction

Environmental legislation as well as consumers demand has recently resulted in a renewed interest in natural materials, making recyclability and biodegradability important issues for the introduction of new materials and products. One of the more promising approaches to overcome these problems is the use of annually renewable resources, for obtaining biodegradable materials useful for various applications in medical, agriculture, drug release and packaging fields.

Biopolymers directly extracted from biomass (e.g., proteins, polysaccharides and lipids) or produced by microorganisms (e.g., polyhydroxyalkanoates), as well as some produced by classical chemical synthesis (e.g., polylactic acid), have been used to develop new materials for food industry. Development of food packaging applications from biopolymers has lagged behind medical materials due to high cost, low strength and poor water resistance. Until recently, the most exploited routes to overcome these limiting factors involved the blending of natural and synthetic polymers together or incorporating of inorganic fillers [1]. As an alternative, hydrogels can also offer new opportunities for design of efficient biopolymer packaging materials with desirable properties.

Dry hydrogels from biomacromolecules exhibit a number of advantages for packaging films, particularly biodegradability and the possibility to incorporate cells, bioactive compounds and drugs. Furthermore, due to the chemical properties of functional groups along with the macromolecule backbone, hydrogels can be developed as 'smart' tailored devices able to respond to specific external stimuli (e.g., pH, the temperature, ionic strength and biological molecules of the surrounding medium) that act as triggers to modify over time the release rates of compounds loaded into them [2–4].

Appropriately formulated edible coatings can be utilized for most foods to meet challenges associated with stable quality, market safety, nutritional value and economic production cost. Fig. 1 [5] shows the potential benefits of using edible coatings with regard to the fresh product industry.

Xanthan gum has been used in a wide variety of foods (in many low fat food systems due to its water binding capacity) [8] for a number of important reasons, including emulsion stabilization, temperature stability, compatibility with food ingredients and its pseudoplastic rheological properties [9]. It has become one of the most successful hydrocolloids largely due to its high functionality, particularly in difficult environments such as acid, high salt and high shear stress. Its anionic character is due to the presence of both glucuronic acid and pyruvic acid groups in the side chain, therefore, offers a potential utility as a bioactive substances carrier because of its inertness and biocompatibility [10].

Xanthan gum is classified E 415 in the European List of Permitted Food Additives. According to JECFA (Joint WHO/FAO Expert Committee on Food Additives), it has the status of ADI-non-specified (Acceptable Daily Intake), i.e., no quantitative limitation is stated, and, as such xanthan gum is recognized as a non-toxic additive for human consumption.

Lignins are complex phenolic polymers occurring in higher plant tissues and are the second most abundant terrestrial polymer after cellulose. Due to their very complex structure, lignins are

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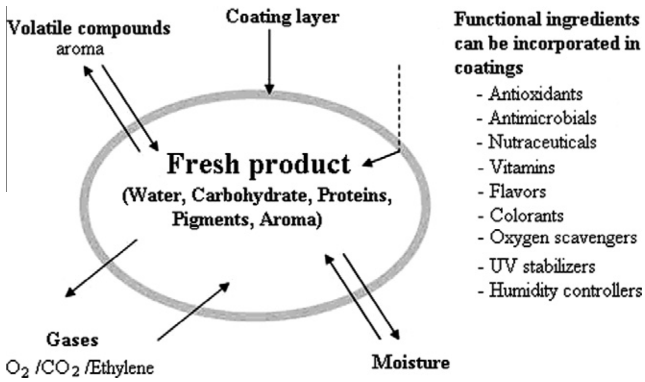

Fig. 1. Functional properties of an edible coating on fresh fruits and vegetables [adapted from 6,7].

amorphous polymers with rather limited industrial use. They are usually seen as waste products of pulp and paper industry and often used as fuel for the energy balance of the pulping process. The major problem identified with natural fibers during incorporation in hydrophobic polymers is their poor compatibility. To alleviate this problem, various fiber–polymer interface modifications have been proposed which results in improvement of performance of the resulting composite [11,12]. For the last decades, a great deal of research was devoted to the development of lignin-containing polymeric materials. A way of lignin use consists in the incorporation of small amounts of lignin in order to take advantage of lignin structure and to stabilize the material against photo- and thermooxidation [13,14]. Indeed, the lignins are hindered phenolic polymers, which can exert antioxidant properties [15].

Vanillin is one of the most popularly used flavoring components extracted from the seedpods of *Vanilla planifolia* and is widely used in foods, beverages, cosmetics and drugs, and more it has been reported to exhibit multifunctional effects such as antimutagenic, antiangiogenetic, anticolitis, antisickling and antianalgesic effects. Concentrations of vanillin used in food and beverage products range widely from 0.3 to 33 mM [16].

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is efficacious for the treatment of chronic hypoacidic gastritis and chronic non-acid gastritis. By the inhibition occurred in the central nervous system, vanillin also influences the craving to consume food. In this context, it is supposed that the vanillin is able to increase the concentration of the neurotransmitter serotonin in the brain [17]. Increased brain serotonin concentration, however, leads demonstratively to a reduced craving to consume food.

In our previous papers, we have studied the kinetics of swelling of the new obtained hydrogel films containing xanthan and three different types of lignin (aspen wood lignin (L), annual fiber crops lignin (GL) and lignin epoxy-modified resin (LER)) [18], which were characterized by UV and FT-IR spectroscopy, X-ray diffraction, DSC and TG/DTG measurements [19], following the effect of temperature on the swelling aptitude of the hydrogels, the dependence of their properties in different medium conditions function on the composition, etc. [18].

Here, the vanillin release from the biodegradable polymeric matrices characterized afterward by FT-IR analysis, atomic force and scanning electron microscopy (AFM and SEM) has been investigated.

1.1. Materials

In Table 1 are listed the materials used in this study and their characteristics.

1.1.1. Hydrogel preparation and purification

The hydrogels containing xanthan gum and annual fiber crops lignin were prepared in various mixing ratios of the two polymers in the presence of NaOH and epichlorohydrin (EPC) as was discussed in our previous paper [18]. Shortly, the xanthan and lignin were mixed with NaOH solution, then epichlorohydrin was added, and the mixtures were heated at 80 °C for 8 h. The hydrogels have been washed repeatedly with twice-distilled water until neither lignin nor epichlorohydrin was detected in the washing waters by UV spectroscopy.

1.2. Methods of investigation

1.2.1. Aroma loading and in vitro release studies

Because the flavor compounds in food are mostly volatiles, loading method was applied to produce a powdered flavor in order to prevent the flavor loss to prolong the product shelf life and make it convenient to use [20].

The aroma loading of the hydrogel matrices was carried out by mixing vanillin, with dried matrices in powdered form, and then a certain quantity of the appropriate solvent (maximum amount of liquid uptake during swelling) was added and left to swell at room temperature at least one hour, while the aroma penetrates and/or attached into matrices. The active ingredient concentration solution was 18 mg/mL. At the end, the aroma-loaded samples were freeze-dried using a Labconco FreeZone device.

In vitro release studies have been conducted by a standard dissolution setup [21].

The dissolution medium was twice-distilled water. During dissolution testing, the media was maintained at 37 ± 0.5 °C. Aliquots of the medium of 1 mL were withdrawn periodically at predetermined time intervals and analyzed at λ_{max} value of 228 using a HP 8450A UV–vis spectrophotometer. In order to maintain the solution concentration, the sample is carefully, totally, reintroduced in the circuit after analyzing.

The concentrations of the active ingredient were calculated based on calibration curves preliminary determined for aroma at specific maximum absorption wavelengths.

A simple, semiempirical equation using Korsmeyer and Peppas model was used to kinetic analysis of the data regarding the aroma release from studied matrices system which is applied at the initial stages (approximately 60% fractional release) [22]

$$M_t/M_\infty = k_r t^{n_r} \quad (1)$$

where M_t/M_α represents the fraction of the aroma released at time t; M_t and M_∞ are the absolute cumulative amount of aroma released at time t and at infinite time (in this case maximum release amount in the experimental conditions used, at the plateau of the release curves), respectively; k_r is a constant incorporating characteristics of the macromolecular matrix and the aroma. n_r is the diffusion exponent, which is indicative of the release mechanism. In the equation above, a value of $n_r = 0.5$ indicates a Fickian diffusion mechanism of the aroma from matrix, while a value $0.5 < n_r < 1$ indicates an anomalous or non-Fickian behavior. When $n_r = 1$, a case II transport mechanism is involved, while $n_r > 1$ indicates a special case II transport mechanism [23,24].

1.2.2. Infrared spectroscopy (FTIR)

FTIR–ATR analysis of the xanthan/annual fiber crops lignin samples was recorded on KBr pellets with a Bruker VERTEX 70 spectrophotometer with a spectral resolution 2 cm^{-1}. The spectra were recorded in the range of 4000–500 cm^{-1}, 64 scans.

1.2.3. Atomic force microscopy (AFM)

Tapping mode of scanning was used on powders (X/GL). The samples were examined with a SPM Solver PRO-M AFM (NT-MTD Co. Ze-