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Biobased packaging for improving preservation of fresh common mushrooms (*Agaricus bisporus* L.)

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Freshness of common mushrooms was related to the internal atmosphere composition during modified atmosphere packaging (MAP) experiments at 20 °C and 80% RH with stretchable polyvinylchloride (PVC) film, paper, and the same paper coated with a wheat gluten solution. MAP with the stretchable film led to a detrimental deterioration of mushrooms after only one day of storage: dark brown blotches appeared and almost 30% of mushrooms exhibited open veil. This was due to the formation of condensed water at the inner surface of the material and onto mushrooms combined to a high O_2 partial pressure (16 kPa) in the headspace. Wheat gluten (WG) coated paper was the most effective to improve the shelf-life of mushrooms since it allowed the preservation of a fair colour, unbroken veils, and an acceptable texture during 3 days. This beneficial effect was attributed to the combination of a medium CO_2 (9.5 kPa) and low O_2 (2.5 kPa) partial pressure, without condensation. The main drawback of using WG-coated paper was its high water vapour permeability that led to an important weight loss (3.8 wt.% on day 3). However it did not affect the overall quality of mushrooms within the storage duration.
Industrial relevance: Even with the development of micro-perforated materials that provide the largest range of O_2 and CO_2 permeability values, several limitations are still encountered for synthetic MAP applications such as

- an insufficient perm-selectivity ratio that remains lower than 6 (value of 1 for micro-perforated material): generated atmosphere cannot reach both low O_2 and low CO_2 partial pressures and then are not adapted to CO_2-sensitive fresh produces.
- unattractive water condensation at the inner surface of the packaging that might occur due to a low water vapour permeability, favouring the development of microorganisms.
- their non biodegradability.

Previous studies reported a high selectivity ratio and a high water vapour permeability for biodegradable materials made from crops proteins (wheat gluten, for instance) that appeared well adapted for fresh fruits and vegetables preservation. However, despite low cost and such interesting functional properties, these materials exhibited poor mechanical properties and cannot be used as packaging material. Combination with other materials, such as cellulosic fibres, appeared to one way to get round this major drawback without losing its biodegradability. Indeed paper exhibits an environmental-friendliness potential (recyclability, sustainability, biodegradability, and compostability) and a high versatility in food packaging.
By choosing common mushrooms, known to be sensitive to high CO_2 content, and a stretchable PVC film, commonly used to over-wrap mushrooms in tray (on European market), we demonstrate that this material was greatly less effective than a new biobased material (wheat gluten film coated onto paper) developed in collaboration with Smurfit Worldwide Research Center. This work confirms the interest in developing functionalised paper based packaging material with agro-based polymers adapted to the storage of fresh fruits and vegetable storage in ambient temperature.

1. Introduction

Worldwide production and consumption of fresh cultivated mushrooms have undergone an important rise during the last 10 years. Nevertheless, its high respiration rate (RR) and rapid post-harvest degradation still remains an economical issue. After only 1 day of storage

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at ambient temperature, cap is opened and coloured, stem is elongated, and texture becomes soft and spongy, resulting in a depression of its commercial value (Gormley, 1975; Lopez Briones et al., 1992). Refrigeration, which induces a decrease in respiration of fresh commodities (Burton & Noble, 1993; Escriche, Serra, Gomez, & Galotto, 2001; Varoquaux, Gouble, Barron, & Yildiz, 1999), can be an issue if applied throughout the post-harvest handling and distribution chain. Such conditions without disruption are not always appropriated to the European market and consumers' trends, since sales and home storage mainly occur at an ambient temperature, 20 °C. Therefore the solution for extending the shelf-life of this highly perishable commodity still constitutes a scientific and economical challenge.

Several works reported some beneficial effects of gas concentration on the storage potential of fresh white mushrooms (*Agaricus bisporus* L.), at a temperature ranging from 0 to 18 °C (Burton, Frost, & Nichols, 1987; Gonzalez-Fandos, Olarte, Gimenez, Sanz, & Simon, 2001; Lopez Briones, Varoquaux, Bureau, & Pascat, 1993; Roy, Anantheswaran, & Beelman, 1995) and all agreed on optimal recommended atmosphere with low content of O_2 (less than 10%) and limited CO_2 content (5% maximum). Although this atmosphere both low in O_2 and CO_2 could be easily produced and maintained in controlled atmosphere (CA) storage, such conditions are quite difficult to reach in modified atmosphere packaging (MAP) techniques because it implies high gas permeability values and high perm-selectivity of packaging materials, i.e. a high ratio between CO_2 and O_2 permeability (Al-Ati & Hotchkiss, 2003; Exama, Arul, Lencki, Lee, & Toupin, 1993; Guilbert, Gontard, & Gorris, 1996; Mujica Paz & Gontard, 1997). Most of plastic films commercially available exhibit too low gas permeabilities for allowing gas exchanges and permitting a slow respiration. When macro or micro-perforated, this drawback is overcome, but the perm-selectivity dropped from average values of 4 to 6 to a value close to 1, whatever environmental conditions (Yam & Lee, 1995).

New opportunities for MAP development are coming from hydrophilic materials, such as agropolymer based films or synthetic films made of polyether–polyester (Hydrel®, Dupont-Teijin Films) or polyether block amide (Pebax®, Elf Atochem). To the contrary of common synthetic materials, barrier properties of hydrophilic films change in high moisture condition, which occurs when fresh fruits and vegetable are packaged inside. This behaviour is more pronounced in agropolymer based film than in hydrophilic synthetic materials (Barron, Varoquaux, Guilbert, Gontard, & Gouble, 2002), e.g. CO_2 permeability and perm-selectivity ratio of wheat gluten film ranged from 88 amol/(m.s.Pa) and 5 at 0% relative humidity (RH), to 55,580 amol/(m.s.Pa) and 30 at 100% RH, respectively (Gontard, Thibault, Cuq, & Guilbert, 1996; Mujica Paz & Gontard, 1997). In addition, CO_2 and O_2 permeabilities of wheat gluten films increase concomitantly with the rise in respiration (similar activation energy; Mujica Paz & Gontard, 1997) when increasing temperature; it should lead to a self-adjustment of the gas composition in the headspace of MAP in case of temperature abuse.

Wheat gluten and hydrophilic synthetic materials (polyether block amide) have been comparatively tested for MAP applications on fresh white mushrooms stored at 10 °C and over 92% RH (Barron et al., 2002). Both materials generated a steady state atmosphere poor in O_2 and CO_2, but wheat gluten film was more efficient than the synthetic one to eliminate CO_2 from packaging (only 2.5 kPa at the steady state against 13 kPa with the synthetic film) and to maintain freshness of mushrooms. Thus, agropolymer based materials, such as wheat gluten, appeared to be an interesting sustainable alternative to conventional plastics in the context of 'eco-friendly' and biodegradable materials development. However, films made from wheat gluten exhibited poor mechanical properties that can be improved by combining these proteins with fibre based material, such as paper (Gastaldi, Chalier, Guillemin, & Gontard, 2007).

The objective of the present study was to evaluate the ability of such composite wheat gluten-paper material to improve preservation of fresh products at ambient temperature (20 °C) as often encountered in European market and home storage, and 80% RH to simulate RH conditions used in the assessment of materials gas permeation. MAP experiments were performed on fresh white mushrooms, *Agaricus bisporus* L., and compared to a commercial stretchable film commonly used for over-wrapping pre-packed mushrooms. Several freshness parameters of common mushrooms were evaluated and related to the in-package atmosphere, according to gas and water vapour permeabilities of packaging materials and conditions of use.

2. Material and methods

2.1. Packaging materials

A paper made from bleached cellulosic fibres (50° Schopper-Riegler) was provided in sheet form by Smurfit Worldwide Research Center and is hereinafter referred as 'uncoated paper'. To obtain a coated paper, hereinafter referred as 'WG-paper', a wheat gluten solution was coating onto this paper according to a method adapted from Gastaldi et al. (2007). Vital wheat gluten (80% of protein) was supplied by Amylum Aquitaine (France). Coating solution was prepared by melting equal part of an aqueous preparation of gluten (gluten concentration and sodium sulfite at 40% and 0.08% (w/v), respectively) and an acetic acid solution at 2% (v/v), under stirring. A first depositing of this solution was realized thanks to a spiral bar with a threading of 510 µm (Unicoater 409, Erichsen, Rueil-Malmaison, France) and the material was dried at 120 °C for 30 s on a Nobel wood type tray dryer. The overall operation was then repeated once, but coating was done perpendicularly to the first one. Coating weight of the WG-paper was then of 20.69 ± 2.19 g protein m^{-2}. A polyvinylchloride (PVC) stretchable film (Elite C, Globalplastic) used to over-wrap pre-packed mushrooms in trails was considered as a standard film.

All materials were placed in a desiccator with suitable saturated salt, depending on expected relative humidity, and kept in adequate constant temperature chamber during 5 days prior to thickness evaluation (50% RH and 20 °C) and gas permeation measurements or MAP experiments (80% RH and 20 °C). A micrometer (Braive instruments, Liege, Belgium) was used to take ten thickness measurements at random positions around each material, and results were averaged.

2.2. Gas permeability

Gas permeation toward oxygen or carbon dioxide was assessed according to an isostatic and dynamic method (Chalier, Peyches-Bach, Gastaldi, & Gontard, 2007; Gontard et al., 1996). Materials were placed in a permeation cell, i.e. between two stainless steel chambers. The inferior and superior chambers were each spread by a 40 mL min^{-1} flux of permeant (O_2 or CO_2) and vector gas (He), respectively. The permeability cell was coupled to a gas chromatograph (GC 3800, VARIAN, Les Ulis, France) which allowed to online analyze the evolution with time of permeant gas concentration in the superior chamber of the cell thanks to an automatic valve. Gas chromatograph was equipped with a filled column (Porapak Q, Chrompak) of 2 m length and 0.32 m diameter, which allowed to separate O_2 and CO_2, with a thermal conductibility detector (TCD) and automatic injector. A minimum of three replicates for each material and each permeant were measured. The measured gas (O_2 or CO_2) permeability of the film was determined at the steady state as following in the international system units:

$$P_x - \frac{\Delta Q \times e}{\Delta t \times A \times (P_2 - P_1)} \quad (1)$$

where P is the permeability and subscript x refers to O_2 or CO_2, ΔQ is the quantity of gas that pass through the film, e is the thickness of material, Δt is the time for which permeation occurs, A is the film area exposed and $(p_2 - p_1)$ is the difference in pressure exerted by the gas on each side of the film. P_x has a constant value for a specific combination of gas and polymer at a given temperature and relative humidity. Gas