Mass Transfer in Novel “Food Contact Materials”: Scales and Stakes

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Research and development efforts were in the last decades mainly dedicated to the huge development of convenient versatile petrochemical plastics, related additives, recycling processes etc. Future packaging will have to respond to the evolution of societal needs and concerns in term of health, quality, environment, cost, sustainability, worldwide raw materials availability, information etc. The present paper will focus on reasonable hypothesis on food packaging technologies development scenarios. It could be anticipated that concepts such as eco–friendly, biodegradable, active and nano-engineered materials will develop. Some examples will be briefly presented and discussed by focusing on subsequent research lines of thinking likely to facilitate the use of biopolymer for food packaging. Controlling mass transfer between the food, the food contact material (FCM) and the external atmosphere is the major key factor for the development for these new packaging solutions when considering adequacy to foods requirements and safety rules. The mass transfer control can be achieved by adjusting the FCM matrix nature and structure at different scales (macro/micro/nano). The knowledge and modeling of solute, gas, vapor and nanoparticles transfer in the packaging material can facilitate the development of efficient packaging. This approach was performed to develop different packaging food systems such as modified atmosphere packaging based on gas selective bio–materials, antimicrobial bio–packaging based on controlled release of volatile active molecules or nanocomposites packaging combined with high pressure food treatments.

Key words: active packaging, biodegradable, mass transfer, nanotechnologies

1. Introduction

Food packaging R&D efforts were, in the last decades, mainly devoted to barrier materials (new polymers, complex and multilayer materials) or new design for marketing purposes, supported by the huge development of versatile petrochemical polymers. New food packaging technologies, such as active and intelligent packaging, are now developing as a response to consumer trends towards mildly preserved, fresh, tasty and convenient packed food products [1].

In addition, changes in retailing practices, such as globalize markets resulting in longer distribution distances, present major challenges to the food packaging industry acting as driving forces for the development of new and improved packaging concepts that extend shelf–life while maintaining and monitoring food safety and quality. Using active and intelligent packaging solutions are also expected to allow the reduction of thermal treatments and/or to the use of the cold storage, thus resulting in potential significant energy saving. Simultaneously, and apart from the already engaged weight reduction of conventional materials, development of new sustainable, recyclable and/or biodegradable packaging materials is also a major driving force to increase the overall presence of eco–friendly packaging solutions across the food chain. New bio–plastics based materials are entering the market and numerous industrial projects for their production are announced. These bio–plastics are designed to provide a better environmental impact than conventional plastic.

Modern concepts of packaging are expected to develop by combining renewable materials with active and intelligent systems provided by the latest innovative technologies (e.g. nanotechnologies). This could be achieved by a change of paradigm from the actual use of a small numbers of “commodity” materials to the design of tailor–made “specialty” materials driven by the foods requirements and safety in addition to logistics, costs,
and environmental issues. Controlling mass transfer between the food, the food contact material (FCM) and the external atmosphere is the major key factor for the development of these new packaging solutions when considering either adequacy to foods requirements and to safety rules. The mass transfer control is generally achieved by adjusting the FCM matrix nature and structure at different scales, i.e. by polymer cross-linking, polymer assembling, polymer blending, composites or multilayer materials. Nano-engineered materials were recently introduced as promising materials to improve/control conventional and biodegradable material mass transfer properties. The present paper will focus on novel FCM: bio-plastic, active and nano-engineered materials.

2. “Bioplastics” for food packaging: examples of application of wheat gluten based materials based on their specific functional properties

New materials, based on natural resources and designed in order to present a better environmental impact than conventional plastic materials are generally called “bio-plastics” [2,3]. As far as polymer origin (renewable/ fossil), polymer synthesis (chemical or “natural-made”) and/or material end life (conventional /biodegradable or compostable) can be considered; there is no clear definition for the “bio-plastics”. The different way to obtain bioplastics (commercially available or under development) are presented on Fig. 1 with two main groups: chemical and “natural-made” polymers. The actual production of bioplastics is still below 350 000 tons/year (i.e. less than 0.2% of the total year production of plastic), with about 50% of “natural-made” polymers (mainly starch/polyesters blends, Fig. 1) and 50% of chemical polymers (mainly polylactic acid, Fig. 2) but the demand for FCM application is increasing very rapidly.

One of the two main groups of bioplastics (Fig. 1) refers to “chemical synthesis” polymers which are also sometimes called “artificial biopolymers”. They can be i) bio-sourced (renewable origin) and biodegradable or compostable (e.g. polylactic acid (PLA)), ii) bio-sourced and non–biodegradable (e.g. bio-polyethylene, bio-polypropylene) or iii) petrol based (fossil origin) but biodegradable (e.g. polybutylene succinate adipate). These polymers are synthesized by conventional chemical polymerization of monomers issued either from fossil oil cracking or from renewable resources “deconstruction” (e.g. products of the “plant biorefinery”). This way benefits from the possibility to designed tailor-made polymers with controlled properties but their environmental impact benefits is sometimes controversial.

The second group of bio-plastics refers to “natural-made” polymers naturally engineered by vegetal or microbial cells (crop plants, industrial microorganisms), which are extracted, purified and eventually modified (Fig. 1). These polymers are renewable. They benefit from the high yields of natural fabrication with excellent carbon and energy balance. In addition, functional prop-
erties (e.g. mass transport properties) are often original and far from conventional plastic properties, thus paving the way for new applications such as active or intelligent materials. The formulation of bioplastic materials based on “extractible” agro-polymers implies the use of polyesters, polysaccharides or proteins. Commercial water-resistant starch–based bioplastics are produced by using fine molecular blends of biodegradable synthetic polymers and starch [3]. The polyester forms the continuous phase leading to materials presenting an acceptable barrier and mechanical properties. Microbial polyesters (e.g. polyhydroxyalkanoates (PHA’s)) are excreted or stored by micro-organisms cultivated on starch hydrolysates or lipidic mediums. The use of thermoplastics proteins was investigated [4,5] but commercial applications are still expected.

Wheat gluten proteins based packaging materials were demonstrated to be of great interest because of their high gas permeability and permselectivity values that are able to create unique low oxygen and low carbon dioxide atmosphere, adapted to the preservation of fresh fruits and vegetables, especially CO₂ sensitive commodities [6,7]. Combinations of wheat gluten proteins with fiber-based materials such as paper have been studied to overcome their poor mechanical properties [8,9].

The increasing relative humidity (RH) effect was attributed to a modification of the wheat gluten network structure and polymeric chain mobility, related to a change from a glassy to a rubbery state [6,10]. The increase of CO₂ permeability was more pronounced than O₂ permeability. This phenomenon was explained by a selective sorption of CO₂ due to the specific interactions setting up between carbon dioxide and the water plasticized protein matrix, especially high content amide groups of wheat gluten protein [11].

At high RH value, adsorption of water should provide a better accessibility to active sites of CO₂ sorption located on the mobile polymeric protein chains. As a consequence, gas permselectivity was highly affected by RH and rise from 1.9 to 7.9 and 1.5 to 7.5 for composite and nanocomposite materials, respectively.

Charles et al. [12] developed a mathematical predictive model, called “transferomatic”, based on Fick diffusion. It was used to determine solute, gas, vapor and nanoparticles transfer in the packaging material and to predict short to long-term transfer in foods (model or real) packaging system. This model was validated with different packaging food systems such as modified atmosphere packaging based on gas selective bio–materials as illustrated by Fig. 2 for modified atmosphere packaging (MAP).

Passive MAP experiments (without antimicrobial release) were conducted on parsley with uncoated control paper and coated paper (Fig. 3). As expected for a highly porous material, O₂ and CO₂ partial pressures at the steady state obtained when using control paper were close to air composition (21 and 0 kPa, respectively). Such an atmosphere was detrimental to the quality of the product. After only 4 days of storage, more than 50% of ascorbic acid and chlorophyll were lost, and leaves were
fully yellow. Wheat gluten composite material generated a headspace atmosphere containing lower O₂ (11 kPa) and higher CO₂ (4 kPa) content. This steady atmosphere clearly improved quality attributes of parsley during storage by maintaining high chlorophyll content (directly linked to green color of herb) and ascorbic acid during 8 days of storage. A critical level of 60% of initial vitamin C content was reached after only 3 days of storage with uncoated paper against more than 8 days for composite material. The use of composite materials for MAP of parsley led to equilibrium atmosphere favorable for maintaining quality of parsley, by slowing down oxidation reactions and physiological reactions responsible for product degradation. Similar results were obtained with mushrooms or other fruits or vegetables.

3. Active packaging: unique potentialities of bio–polymers for a controlled release of antimicrobial agent

Active packaging deliberately incorporates active agents intended to release or to absorb substances into, onto or from the packaged food or the environment surrounding the food, as defined in the food contact material framework regulation 1935/2004 [1]. Such new packaging technologies are appointed to play a major role in response to consumer’s demand for more convenient, safe and mildly preserved products with longer storage duration. In addition, markets globalization results in longer distribution distances and presents major challenges to the food packaging industry, acting as a driving force for development of packaging concepts that extend shelf-life while maintaining food quality and safety. This concept is developing throughout Europe for enhancing the competitiveness of food and packaging industry with a huge potential market. Japan and the USA take share of more than 50% and 22% of the global active and intelligent (A&I) packaging market, respectively, against only 15% for EU. The use of active modified atmosphere packaging (active MAP), by using volatile emitter or absorber, for the preservation of fresh or minimally processed fruits and vegetables constitutes one of the most challenging application.

A promising application of agro–polymers materials is their use as a vector of antimicrobial agent. This relies on the ability of biobased polymers to entrap active compounds and release them in a controlled way, according to a moisture and temperature triggering effect [13]. Protein based materials have been demonstrated to be efficient antimicrobial packaging for their ability to control, in a relevant way, the release of volatile extracts of various essential oils (allylisothiocyanate, carvacrol, cinnamaldehyde or eugenol) [14]. It has been shown that the release of carvacrol from paper coated with wheat gluten is RH–dependent with or without addition of nanoparticles of montmorillonites (MMT). Release of volatile compound, carvacrol, was assessed at 25°C, on all materials, as a function of time and using a two steps gradient of relative humidity. Composite material lost more than 70% of carvacrol within 20 days of storage at 60% RH. This means that only 30% of active agent would be available for being released toward the food during its

| Packaging                  | Paper (control) | Paper coated with gluten |
|----------------------------|-----------------|--------------------------|
| O₂⁻¹ (kPa)                 | 19 ± 1          | 11 ± 2                   |
| CO₂⁻¹ (kPa)                | 0.5 ± 0.2       | 4 ± 1                    |
| Remaining asc. acid (%)²   | 30 ± 3          | 61 ± 4                   |

¹ Concentration in the atmosphere at steady state
² Percentage of the initial content: 2.4 ± 0.1 mg/g of fresh parsley

Fig. 3 Preservation of ascorbic acid and color of parsley under MAP using control paper and wheat gluten coated paper as packaging.
storage within packaging. Once placed at 100% of RH, this 30% was entirely released within 8 days. In the presence of MMT introduced in the wheat gluten network (nanocomposite material), only 20% of carvacrol was released during the 20 days of storage at 60% of RH. Consequently 80% of the volatile active agent remained available for being released during the period in which food is packaged. Once placed at 100% of RH, this 80% was entirely released within 13 days (from day 22 to 35). It can be concluded from these results that the release of carvacrol from wheat gluten coated paper is RH-dependent with or without MMT. Such a behavior is highly interesting for both limiting volatile active agent losses before using the material as food packaging, and for triggering the active agent release in the presence of the food.

In the framework of the European Project “Novel Q” (Novel Processing Methods for the Production and Distribution of High Quality and Safe Foods), it has been demonstrated that antimicrobial bio–sourced packaging materials may contribute to combine environmental protection and food quality improvement. PLA–based materials containing a natural antimicrobial agent, allyl isothiocyanate (AITC), previously encapsulated in cyclodextrins (CD) was demonstrated to be an efficient optimized antimicrobial system for inhibiting Botrytis cinerea growth during at least 10 days at 22°C. Results are presented in Table 1 [15]. Combining mild high pressure (HP) treatment (around 300 MPa) and use of active film was proven to be more efficient for inhibiting B. cinerea growth than either a HP pasteurization–like treatment (800 MPa) or antimicrobial packaging used alone, even though the quantity of active compound released from the film was lower than the minimal quantity required to obtain inhibition at atmospheric pressure. This synergy between pressure and antimicrobial agent can be used to reduce quantity of active agent used in antimicrobial film and/or to reduce intensity of the HP treatment.

4. Nano-engineered materials for food packaging and safety issues

Recently, combinations of wheat gluten proteins with nanofillers such as MMT have been demonstrated to be an efficient way to overcome the drawback of moisture

| HP intensity (MPa) | 0.1 | 300 | 600 | 800 |
|-------------------|-----|-----|-----|-----|
| Control (HP treatment alone) | +   | +   | +   | +   |
| HP with additional AITC | +   | +   | -   | -   |
| HP and active pack. PLA/CD_{AITC} | +   | -   | -   | -   |

Fig. 4 Nano-engineered gluten material: effect of MMT concentration on structure characterized by X-ray diffraction and transmission electron microscopy, and on permeability (water vapor permeability, CO₂, O₂ and aroma compounds permeability) (adapted from [17]).
sensitivity by reducing the water vapor permeability and water swelling [16,17]. Figure 4 illustrates this effect on water sensitivity and shows that introduction of MMT does not affect O₂ and CO₂ permeability.

O₂ and CO₂ permeability values were not significantly affected by the presence of MMT in the wheat gluten network. Since permeability is known to be governed by two mechanisms, diffusion and sorption, it was assumed that introduction of MMT did not change solubility nor diffusivity of O₂ and CO₂.

O₂ and CO₂ permeability of nanocomposite (gluten+ MMT) material increased when increasing RH [17]. This phenomenon was also observed on pure wheat gluten films [6], suggesting that the wheat-gluten based coating layer is the key element of gas barrier properties of the studied materials.

In the European project “Novel Q” the effect of high-pressure thermal (HP/T) treatments on food/packaging interactions was assessed in a variety of cases, including migration and scalping of novel biodegradable and nanocomposite materials in food simulating liquids (FSL). Three materials were studied, namely linear low density polyethylene (LLDPE), polylactide (PLA) and a wheat gluten/montmorillonite (WG/MMT) nanocomposite [18–20]. Food/packaging interactions were studied after two HP/T treatments intended to perform pasteurization (800 MPa, 5 min, 40°C) and a sterilization (800 MPa, 5 min, 115°C) treatment, as well as subsequent storage for 10 days. Specific migration of an additive (Uvitec OB) was assessed for LLDPE and PLA, whereas other adapted tests were carried out for WG/MMT, i.e. overall migration, protein migration and nanoparticles migration. HP/T treatments did not significantly modify the migration or scalping in the conditions studied but for the release of nanoparticles from WG. Furthermore, the increase in the melting point of LLDPE allowed the sterilization of LLDPE whereas it melted when submitted to a conventional thermal sterilization.

5. Conclusion

It can be concluded that there is still an important need for improved knowledge on how ‘agro–polymers science and engineering’ can facilitate the development of efficient packaging for food. An essential step in the application of biodegradable packaging by the food industry is to increase knowledge on structure/properties and mainly the structure/mass transport relationship of agro-polymers matrix. It can be reasonably expected that the next projects and studies will be focused on developing integrated studies of bio–materials process–structure–properties relationships based on the latest innovative developments for complex materials characterization, production processes of composite bio–materials, and mathematical modeling tools to calculate how the structure–functions relations at different scales will determine the end properties.

To make certain that the developed packaging materials will optimally fulfill food industry, compounds producers, packaging converters, food retailers, waste management, legislative as well as consumers requirements, future projects should adopt a holistic approach to prepare the ground for addressing the long-term stake of developing biopolymers based food packaging.

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