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Article

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NANO FOOD PACKAGES: FROM FOOD PRESERVATION EFFICIENCY TO CONSUMER LEGAL PROTECTION

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Abstract
The paper explores some aspects related to the application of nanomaterials in food packaging. Therefore, the paper is structured into two sections. In the first section, aspects that could restrict/restrain the application of nanomaterials in food packaging industry in terms of environmental and human risks, the consumer's rights to be informed regarding the utilization of nano-packages and regulation issues in the field of large scale application of food nano-packages are discussed. In the second section, the efficiency of a nano-package based on Ag/TiO_2 to preserve for a longer time (6 days) the physical attributes of wheat bread (moisture, specific volume, porosity) by comparison with shorter ranges allowed by the common polyethylene bag (3 days) and non-packaging respectively (1 day) is demonstrated.

Keywords: food nano-packaging, bread packaging, consumers' rights

JEL Classification: I15, I18, D18, Q18

Introduction

Globalization, social changes, growth of the recorded number of foodborne diseases related to the consumption of microbiologically contaminated food (Mead et al., 1999) associated with losses of nutritional and sensorial value of food due physical-chemical changes that occur during food storage, increase the consumers' demands for safe food in terms of chemical-microbiological - sensorial qualities. It results in a trend triggering high pressure on researchers to identify and on producers to apply food storage techniques with improved antimicrobial and preserving properties. The packaging, an integral part of the food chain, plays an essential role in the preservation of food and in the adequate maintenance of its nutrients during storage for longer periods of time. The common plastic and paper packaging reached their limits due to the water and oxygen molecules retained in the package headspace that produce loss of physical-chemical nutritional parameters and accelerate the microbiological spoilage. Despite the development of new systems of

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preservation techniques (modified atmosphere, food coating, etc.) there is still a need for new methods to reduce or eliminate foodborne pathogens.

The benefits of nanotechnology, already recognized by medical, pharmaceutical and aerospace industries can be extended in the field of food packaging. The insertion of active nanoparticles into plastic or paper polymer matrices brings beyond the improving the performance of food packaging material by additionally functionalities (i.e. antimicrobial, antioxidant, reducing the humidity in the package headspace) which prolong the shelf life of food, the food economic and environmental advantages such as such as reduction to zero of any critical interaction with food matrices and with human health, reduction of the energy-inputs for production, transport and storage, increase of biodegradability and barrier protection to gases and light, reduction of volume of waste material to be disposed of in landfills, contribution to decrease CO_2 emissions (Brody, 2008; Lagaron et al., 2005; Lagaron et al., 2007; Aurora and Padua, 2010; Chaudhry et al., 2008; De Azedero, 2009; Moraru et al., 2003 and Sanguansri and Augustin, 2006). According to Silvestre, Duraccio and Cimmino (2011) bakery and meat products attracted the most nano-packaging applications and in beverages, carbonated drinks and bottled water dominate. Japan is the market leader in active nanoenabled packaging with 45% of current market, valued at US$ 1.86 bln in 2008 and projected to grow to US$ 3.43 bln by 2014 with an annual increase of 13%. In opposition, in Europe the industrial application of nanomaterials based on packaging are coming slowly due to the legislation restrictions, the lack of knowledge about acceptability to European consumers and the environment and health safety concerns rise up (Silvestre Duraccio and Cimmino, 2011).

Among the wide range of nanomaterials which proved their efficiency in prolongation the food shelf-life (Yamamoto, 2001; Jones et al., 2008) titanium dioxide (TiO_2), a well-known photocatalyst, is widely used as oxygen and water scavenger. The pairs of holes (h^+) and electrons (e^-) resulted following the excitation under light with input energy higher than the gap energy of TiO_2 crystal (3.2 eV for anatase; 3.03 eV for rutile) migrate to the surface and react with oxygen and water molecules from the package headspace (Gumiero et al., 2013). The incorporation of Ag in TiO_2 matrix confers additional functional value due to the antimicrobial properties of silver against to a wide range of microorganisms (Baker et al., 2005; Morones et al., 2005; Panácek et al., 2006; Gogoi et al., 2006; Lok et al., 2006; Pal, Tak and Song, 2007; Yoon et al., 2007; Wigginton et al., 2010; Duncan, 2011; Fabrega, Fawcett and Renshaw, 2009; Egger et al., 2009). The incorporation of photocatalyst into paper or plastic polymers designed for food packaging efficient exploits the Ag/TiO_2 photocatalytic and antibacterial properties. Gumiero et al. (2013) reported the successfully application of high density polyethylene (HDPE)-based on food packaging containing $CaCO_3$ and TiO_2 in preserving of structural and microbiological stability of a short-ripened cheese. Li et al. (2009) demonstrated the beneficial effects of Ag/TiO_2 based on polyethylene in quality preservation of Chinese jujube, the work of But and Bertoti (2012) generated encouraging results related to meat safety preservation, while the results of Peter et al. (2013a) display a high efficiency of a nanosensor based on TiO_2 for oxygen detection in damaged vacuum packages. Application of food packages based on nanomaterials at industrial level is strictly dependent on exploration of regulatory aspects which should be issue considering not only their efficiency in preserving the physical-chemical-microbiological-sensorial quality of food but also their potential and unforeseen risks on environment and human health.

In this review, the paper is structured in two sections. In the first part we focused on the aspects that could restrict/restrain the application of nanomaterials in food packaging industry in terms of environmental and human risks, the consumer's rights to be informed regarding the utilization of nano-packages and regulation issues in the field of large scale application of food nano-packages are discussed. In the second section, the efficiency of a nano-package based on Ag/TiO_2 to preserve for a longer time (6 days) the physical attributes of wheat bread (moisture, specific volume, porosity) by comparison with shorter ranges allowed by the common polyethylene bag (3 days) and non-packaging respectively (1 day) is demonstrated.

1. Risks and regulations

1.1 Human risks

The widespread application of nanomaterials at industrial scale results in emission release to all environment components (water, air and soil). Due to theirs special properties (high reactivity and specific area, small sizes) they can be widely spread and integrate in the environment lifecycle and having toxic effects. Zhang et al. (2007) and Zhu et al (2007) reported the accumulation of cadmium in viscera and gills of fish favoured by titanium dioxide nanoparticles (Silvestre, C., Duraccio, D., Cimmino, 2011) and revealed the toxicity of zinc oxide over the zebrafish. Morelli and Scarano (2003) demonstrated the accumulation of cadmium in phytoplankton.

Regarding the food consumer, the first concern is related to migration of nanomaterial from packaging into food followed by it ingestion. Scientific evidence report oxidative damage and inflammatory reactions induced by the nanomaterials which can cross the cellular barrier (Bouwmeester et al., 2009; Geiser et al., 2005; Li et al., 2003; Borm et al., 2006; Nel et al., 2006; Powers et al., 2006; Mroz et al., 2008).

1.2 Regulation issue; Consumers' rights

In approaching the regulation framework applicable to nanomaterials we will begin from the following statement, based on the aspects that will be developed below:

Currently there aren't any specific regulations of the European Union on nanomaterials, although they contain innovative compounds, fact which would entail the institution of a regulation of its own, adapted to this range of materials.

However, there is a regulation framework applicable to nanomaterials, which evolved from the point of view of concepts and principles on the use of such compounds in relation with food.

In this regulation framework we will enclose one of the major themes in the field of consumer protection: the obligation of the professional to inform the consumer (Apan, 2009, pp.577-590) which represents the keystone of the consumer protection policy. In the context of the challenges that globalization involves, the obligation to inform experiences a justified expansion of the professionals' obligations in their relations with consumers, in the case of food.

An additional element of the obligation to inform shall be analyzed *hic et nunc:* informing the consumer about the nanomaterials used in connection with food. For the consumers, the purpose of this is the detailed and clear information regarding the possible risks and/or benefits of nanomaterials.

(i) The field of regulation in which were included nanomaterials together with other materials is the one concerning *"the materials and objects intended to come in contact with food"*. At European Union level these were regulated through Regulation (EC) No 1935/2004 of the European Parliament and of the Council of 27 October 2004, hereinafter called Regulation (EC) No 1935/2004.

The domain was previously regulated through Council Directive 89/109/EEC of 21 December 1988 on the approximation of the laws of the Member States relating to materials and articles intended to come into contact with foodstuffs**,** hereinafter called Council Directive 89/109/EEC**,** which established the general principles for the elimination of differences that existed at that time between the national laws relating to the aforesaid materials and articles and provided for the adoption of directives implementing certain specific categories of materials and objects, called „special directives". Council Directive 89/109/EEC was abrogated through the entering into force of Regulation (EC) No 1935/2004, but the approach carried out through the provisions of the Directive was continued through the regulation that is the subject of this analysis.

The fundamental principle underlying this regulation, mentioned in point 3 of its preamble, is that any material or article intended to come into contact directly or indirectly with food must be sufficiently inert to preclude substances from being transferred to food in quantities large enough to endanger human health or to bring about an unacceptable change in the composition of the food or a deterioration in its organoleptic properties.

At the same time is was ascertained that there are two types of new materials and objects intended to come in contact with food, which are different from those traditional:

- intended to extend the shelf-life or to maintain or improve the condition of packaged food, called "*active materials and objects"*. They are designed to deliberately incorporate components that would release or absorb substances into or from the packaged food or the environment surrounding the food.
- monitor the condition of packaged food or the environment surrounding the food, called "*intelligent materials and objects"*. The names and definitions of active and intelligent materials and objects is offered by art.2(2), letter (a) and (b) of Regulation (EC) No 1935/2004.

Consequently, the efficient functioning of the internal market, ensuring an increased level of health protection and the protection of consumers' interests were the reasons that generated the inclusion in the scope of Regulation (EC) No 1935/2004 of the active and intelligent materials and objects that come in contact with food, namely nanomaterials, and setting the main requirements related to their use. Nevertheless, for the same reasons indicate *ut supra,* it should be noticed at European level the shift from the regulation relating to *materials and articles intended to come into contact with foodstuffs* through the community means that is the "directive" as "community act", to regulating the field through a "regulation". The effectiveness of the Regulation is well-known, being generated by the immediate entering into force in the Member States without needing transposition, the effectiveness is widely revealed in Craig,P., Burca, G., 2009 pp.166, 348-355.

Two categories of requirements are instituted through art. 3 and 4 of Regulation (EC) No 1935/2004, in the field of materials and articles intended to come into contact with foodstuffs, including active and intelligent materials: general and specific requirements.

The general requirements align with the requirements instituted through the entire European legal framework on food products, and their production must be carried out so that: it does not endanger human health, it does not produce unacceptable modifications to food products or change the composition of the food or cause a deterioration in the organoleptic characteristics thereof, all of these as a result of the transfer into the food product of the substances that exist in their composition, in quantities that can attract the above mentioned consequences.

The special requirements applicable to active and intelligent materials and objects comply with the provisions applicable to them from the Regulation (EC) No 1935/2004, in the following areas of regulation:

a) *active materials and objects* may change the composition or the organoleptic properties of the food only if the changes comply with the Community provisions applicable to food, such as the provisions of Directive 89/107/EEC [4] on food additives, or, if no Community provisions exist, with the national provisions applicable to food.

• *substances deliberately incorporated into active materials and articles* to be released into the food or the environment surrounding the food shall be authorized and used in accordance with the relevant Community provisions applicable to food, and these substances shall be considered as ingredients within the meaning of Article 6(4)(a) of Directive 2000/13/EC on ingredients, hereinafter called Directive 2000/13/EC, until the adoption of additional rules in a specific measure on active and intelligent materials and articles.

Also, special requirements applicable to active and intelligent materials and objects are instituted through art. 4 (4), (5), (6) of Regulation (EC) No 1935/2004 on the appropriate consumer information, without misleading them about the condition of the food, on the information through appropriate labeling of the active and intelligent materials and objects that come in contact with food, in order to allow the identification of the non-edible parts and the identification of their nature (active and/or intelligent).

Art. 15, (e) of the Regulation (EC) No 1935/2004, without prejudice to the provisions indicated *ut supra,* establish the labelling requirements for the active materials and objects that are not yet in contact with food at the time of their placing on the market.

Regulation (EC) No 1935/2004 establishes through art. 5(1), for certain groups of materials and articles listed in Annex I and, where appropriate, combinations of those materials and articles or recycled materials and articles used in the manufacture of those materials and articles, specific measures that may be adopted or amended in accordance with the procedure referred to in Article 23(2). The measures target a number of 14 goals from which we will list those relevant for this study, provided at letters (b), (e), (f) and (l):

(b) authorized substances incorporated in active or intelligent food contact materials and articles, or list(s) of active or intelligent materials and articles and, when necessary, special conditions of use for these substances and/or the materials and articles in which they are incorporated;

(e) specific limits on the *migration* of certain constituents or groups of constituents into or on to food, taking due account of other possible sources of exposure to those constituents;

(f) an overall limit on the migration of constituents into or on to food;

(l) additional provisions of labelling for active and intelligent materials and articles;

We point out that using nanomaterials as packaging in the food industry involves their contact with food. Once the nanomaterials enter in contact with food, a “migration” process of the compounds in nanomaterials takes place from the nanomaterials packaging into the food.

At points 1 and 17 of Annex 1 of the regulation are indicated “active and intelligent materials and objects” that are likely to be the object of special measures that are to be taken through Regulation (EC) 450/2009 of 29 May 2009 on active and intelligent materials and objects intended to come in contact with food, hereinafter called Regulation (EC) 450/2009.

(ii) Regulation (EC) 450/2009, as pt. 4 of its preamble reveals, represents a “specific” measure in the meaning of art.5 (1)(b) of the Regulation (EC) No 1935/2004, and establishes the specific rules for the marketing of the active and intelligent materials and objects intended to come in contact with food, rules that must be applied in addition to the general requirements established by Regulation (EC) No 1935/2004, in order to use them safely. Taking into consideration that the active and intelligent materials and objects may be made of one or several layers or parts, from different types of materials such as plastic, paper, carton, coatings and lacquer, the rules provided by the regulation shall be applied without prejudice to the community regulations or national laws that regulate such materials.

Regulation (EC) 450/2009 maintains the conceptual framework given by art.2 (2) (a) (b) of Regulation (EC) No 1935/2004 under the aspect of the definitions of “active materials and objects”; “intelligent materials and objects”, but at the same time it broadens it by defining in art.3 the notions of “component”, “releasing active component”, “released active component”.

Component means an individual substance or a combination of individual substances which cause the active and/or intelligent function of a material or article, including the products of an in situ reaction of those substances; it does not include the passive parts, such as the material they are added to or incorporated into;

Releasing active component are those active materials and articles designed to deliberately incorporate components that would release substances into or onto the packaged food or the environment surrounding the food;

Released active substances are those substances intended to be released from releasing active materials and articles into or onto the packaged food or the environment surrounding the food and fulfilling a purpose in the food;

The broadening of the conceptual framework through these new definitions has the purpose to clarify it in order to put together a community list of substances that may be used in active and intelligent components. Art.5 of Regulation (EC) 450/2009 provides the principle according to which *only the substances that are included in the community list of authorized substances may be used in the components of active and intelligent materials and objects.* In order for them to be included in the community list, the substances from which are composed the components of the active and intelligent materials and objects must meet the requirements of art. 3 and, if necessary, those of art.4 of Regulation (EC) No 1935/2004, requirements developed *ut supra*, at point (i) under the provided conditions for the use of active and intelligent material and object.

Exceptionally, certain categories of substances may be used as components of the active and intelligent materials and objects without having to be included in the community list, if they are in one of the following cases: they are released active substances or substances added to or incorporated into active materials and articles in order to have a technological effect in the food.

For both these categories of substances respecting the conditions mentioned at art.9 of Regulation (EC) 450/2009 is mandatory, and namely the amount of released active substance shall not be included in the value of the measured global migration, where a *global migration limit* (GML) is established throughout a specific community measure for the material that comes into contact with the food in which the component is incorporated.

Exceptionally there are other substances that can be used as components of the active and intelligent materials and objects without having to be included on the community list, namely substances used in components that do not come in direct contact with food or with the environment in which the food is kept and which are separated from the food through a functional barrier, on condition they comply with the conditions set out in Article 10 and that they do not fall within either of the following categories:

- substances classified as "mutagenic", "carcinogenic", or "toxic to reproduction" in accordance with the criteria set out in sections 3.5, 3.6 and 3.7 of Annex I to Regulation (EC) No 1272/2008 of the European Parliament and of the Council;
- substances deliberately engineered to particle size which exhibit functional physical and chemical properties that significantly differ from those at a larger scale.

Released active substances are considered to be ingredients in the meaning of art.6 (4)(a) of Directive 2000/13/EC and they are the object of the respective Directive.

(iii) Regulation (EU) No 1169/2011 of the European Parliament and of the Council of 25 October 2011 on the provision of food information to consumers, hereinafter called Regulation (EU) No 1169/2011.

The regulation provides the basis for the assurance of a high level of consumer protection in relation to food information, taking into account the differences in the perception of consumers and their information needs whilst ensuring the smooth functioning of the internal market.

This Regulation establishes the general principles, requirements and responsibilities governing food information, and in particular food labelling. It lays down the means to guarantee the right of consumers to information and procedures for the provision of food information, taking into account the need to provide sufficient flexibility to respond to future developments and new information requirements.

The Regulation defines in art.2 (2) (t) that 'engineered nanomaterial' means any intentionally produced material that has one or more dimensions of the order of 100 nm or less or that is composed of discrete functional parts, either internally or at the surface, many of which have one or more dimensions of the order of 100 nm or less, including structures, agglomerates or aggregates, which may have a size above the order of 100 nm but retain properties that are characteristic of the nano scale

The Regulation defines the concept of 'food information' meaning information concerning a food and made available to the final consumer by means of a label, other accom-panying material, or any other means including modern technology tools or verbal communication, and the concept of 'mandatory food information' means the particulars that are required to be provided to the final consumer by Union provisions.

Consumer information is carried out mainly through 'labelling' which means any words, particulars, trademarks, brand name, pictorial matter or symbol, written, printed, stencilled, marked, embossed or impressed on, or attached to the packaging or container of food.

The Regulation establishes that correct information practices on food for consumers, which should not be misleading, as well as the mandatory character of certain information on food, establishing a list of mandatory particulars regarding food and additional mandatory particulars for specific types or categories of food.

Within the detailed provisions on mandatory particulars, art.18 presents "the list of ingredients" which contains the express provision that all ingredients present in the form of engineered nanomaterials shall be clearly indicated in the list of ingredients. The names of these ingredients are followed by the word "nano" between brackets; hence consumer information regarding the presence of 'engineered nanomaterial' in foods is regulated.

Responsibility with respect to food information falls on the operator under whose name or business name the food is marketed or, if that operator is not established in the Union, the importer into the Union market.

(iv) Commission Delegated Regulation (EU) No 1363/2013 of 12 December 2013 amending Regulation (EU) No 1169/2011 of the European Parliament and of the Council on the provision of food information to consumers as regards the definition of "engineered nanomaterials", hereinafter called Regulation (EU) No 1363/2013.

The premise for the modification of Regulation (EU) No 1169/2011 is the need to adapt the definition of engineered nanomaterials given by the Regulation to the definition found in the Commission Recommendation of 18 October 2011 on the definition of nanomaterials, which reflects the technological progress made up to the date of its issuance.

The Recommendation from 2011 defines 'Nanomaterial' as being a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50 % may be replaced by a threshold between 1 and 50 %. By December 2014, the definition set out in points 1 to 5 will be reviewed in the light of experience and of scientific and technological developments. The review should particularly focus on whether the number size distribution threshold of 50 % should be increased or decreased.

Therefore, the definition given to nanomaterials in art.2 (2)(t) of Regulation (EU) No 1169/2011 is replaced by the definition given in the Recommendation of 2011, indicated *ut supra.*

Regulation (EU) No 1363/2013 provides a derogation in which food additives covered by the definition set out in the first paragraph shall not be considered as engineered nanomaterials, if they have been included in the Union lists referred to in Article 4 of Regulation (EC) No 1333/2008 by Commission Regulations (EU) No 1129/2011 and (EU) No 1130/2011, hence they are excluded from the applicability of the nanomaterials definition given in the Commission's Recommendation of 2011.

We have indicated at pt. (i) that *active materials and objects* may change the composition or the organoleptic properties of the food only if the changes comply with the Community provisions applicable to food additives.

Or in accordance with art.4 of Regulation (EC) No 1333/2008 of the European Parliament and of the Council of 16 December 2008, only food additives included in the Community list in Annex II may be placed on the market as such and used in foods, in food additives, in food enzymes and in food flavourings under the conditions of use specified therein, and only following an assessment of the safety of the food additive. The lists comprise food additives that were authorized for use in foods before the entering into force of Regulation (EC) No 1333/2008, after examining their conformity with the dispositions of this regulation. All these authorized additives currently make the subject of a re-evaluation program carried out by the European Food Safety Authority. Re-evaluation of approved food additives shall be carried out in accordance with the priorities stipulated by the respective regulation and divided on groups of food additives according to the main functional class they belong to, and cover all the aspects relating to nanotechnologies. From the preamble of Regulation (EC) No 1363/2013 results that 30 food colours have already been evaluated. None of the colours are produced in nano-form. For calcium carbonate (E170) and vegetable carbon (E153) the Authority recommended to lay down the particle size in the specifications. Other additives that could be in a nano-form will be evaluated by: (a) 31 December 2015: Titanium dioxide (E171), Iron oxides and hydroxides (E172), Silver (E174) and Gold (E175).

It possible that some food additives included in the European Union lists set through Regulation (EC) No 1129/2011 Regulation (EC) No 1130/2011 to be contained in the form of "engineered nanomaterials" in the final foods. However it was appreciated that indicating such additives in list of ingredients, adding after them the word "(nano)" could create confusion among consumers as it could be understood that these additives are new, when they have been used for decades in food, in this form. Therefore, consumer information regarding the presence of engineered nanomaterials in food shall be carried out by the operator under whose name or business name the food is marketed or, if that operator is not established in the Union, the importer into the Union market, only for the food additives that were not included on the EU lists that comprise the food additives that were authorized and are subject of a process of progressive evaluation.

Consequently, consumer information regarding nanomaterials related to food is crucial, and an adequate standard of information was established through the pre-cited regulations. As neither the effects of the long-term exposal of the human body to nanomanterials nor effects of their accumulation in the human body are unknown at this date, it was launched the "risk assessment paradigm" in the study carried out by Restuccia et al. (2007).

However, the consumer cannot decide upon the advantages and disadvantages of consuming food containing nanomaterials only based on the information he is offered by the operator.

The EU concerns regarding the development/restrain of food nano-packages have been generated following to experimental studies that demonstrate the efficiency of such food nano-packages in food preservation. Just in demonstration purpose the paper presents a study that proves the efficiency of an Ag/TiO_2 based on nano-package in preserving some physical attributes of wheat bread during storage.

2. The objectives and methodology

2.1. Objectives of research

The paper presents the influence of packaging on physical parameters of wheat bread. In this end, some physical attributes (moisture, specific volume, porosity) of wheat bread samples packed in polyethylene bag (HDP-P) and nano-polyethylene bag (Ag/TiO_2-P) were monitored for 6 days and discussed by comparison with those of un-packed bread considered as control.

2.2. Methodology of research

2.2.1. Preparation and characterization of Ag/TiO_2 nanocomposite

The sol-gel procedure was used for Ag/TiO_2 nanocomposite preparation as described by Peter et al., 2013b. X-ray diffraction (XRD) and transmission electron microscopy (TEM) methods were employed to show the homogenous crystalline structure of nanocomposite while the atomic absorption spectrometry method indicated the value 0.21 ± 0.01% of Ag concentration in Ag/TiO_2 matrix.

2.2.2. Bread preparation

Wheat flour was used with the following specifications: moisture 14.1 g/100 g, protein 12.3 g/100 g, fat 1.3 g/100g, sugar 76.3 g/100 g, ash 0.55g/100 g, wet gluten 33.86 g/100 g, dough extensibility 0.119 m. The basic formulation was (per 100 g flour weight): baking yeast (5 g/100 g), salt (1 g/100 g) and water (70 g/100 g). All ingredients were mixed for 20 minutes at 120 rpm and the dough was allowed to rest for about 30 minutes at room temperature. Pieces of dough of 300 g shaped by hand were put into rounded baking tins, proofed at 30^oC for 60 minutes followed by baking for 60 min at 250^oC (MATINA oven). After baking, the bread loaves were allowed to cool at the ambient temperature (25^oC) for 3 h.

2.2.3. Bread samples packaging

The experiment was conduct considering three preserving modalities: (i) Bread stored in Ag/TiO_2 nano-package (Ag/TiO_2-P), (ii) Bread stored in polyethylene package (HDP-P) and (iii) un-packed bread. The nano-package (Ag/TiO_2-P) was prepared as follows: a suspension made of 5 g of Ag/TiO_2 nanocomposite (anatase-phase crystal structure with particle size in range of 25-50 μm) and 2 ml of C_2H_5OH was manually coated onto one side of 270 x 240 x 0.1 mm high-density polyethylene layer (Griff Paper and Film, USA) using a bar coater at room temperature. The rugged structure of plastic layer assured the nanocomposite anchorage. The Ag/TiO_2 film was air dried for 10 minutes to allow solvent's evaporation and then covered by the second polyethylene layer. The air between layers was removed by suction in order to achieve a compact structure. Polyethylene package (HDP-P) was prepared by dispersion of 2 ml C_2H_5OH onto one side of polyethylene layer with the same characteristics as above mentioned, followed by alcohol evaporation, overlapping of the second polyethylene layer and air removing.

2.2.4. Storage conditions and sampling frequency

Samples of bread weighting approximately 250 g left in open atmosphere, sealed in HDP-P and Ag/TiO_2-P respectively were stored for 6 days in a summer environment described by the following average parameters: 25.8°C, 275.5 lx (PU 150 Luxmeter) of natural light intensity, UV factor of 5.5 (Weather Online, 2012) and 31.2% of relative humidity. Samples of each type were submitted daily for moisture, specific volume and porosity measuring. Each bread loaf was sliced and three alternative slices were extracted as sample. The crust and crumb were carefully separated using a sharp blade and analysed.

2.2.5. Analysis of bread physical parameters

2.2.5.1. Moisture content

The moisture content was analysed according to SR 91:2007 by drying the sample at 105°C until the constant weight and calculated with equation:

$$\text{Moisture}\,(\%) = \frac{m_1 - m_2}{m_1} 100 \tag{1}$$

where:

m_1 – the initial weight of sample, g
m_2 – the final weight of the sample, g

2.2.5.2. Specific volume

The correlation that exists between the weight and density of rapeseeds displaced by the analysed sample accuracy weighted (SR 91:2007) was used to measure the specific volume of crumb and crust samples. The equation used to determine the specific volume was:

$$V\,(cm^3/100g) = \frac{m_1 + m_2 - m_3}{m_1 \cdot \rho} 100 \tag{2}$$

where:

m_1 – the weight of sample, g
ρ – the density of rapeseeds, g/cm^3
m_2 – the weight of the container filled with rapeseeds, g
m_3 – the weight of the container with sample and filled with rapeseeds, g.

2.2.5.3. Porosity

The pycnometer method was used to measure the porosity of crust and crumb samples. The porosity was calculated with the equation:

$$\varepsilon\,(\%) = (1 - \frac{V_S}{V_b}) \cdot 100 \tag{3}$$

where:

V_b – the bulk volume of the sample, cm^3
V_s – the sample volume (calculated based on V_b and the picnometric density of bread sample), cm^3

2.2.6. Statistically processing of experimental data

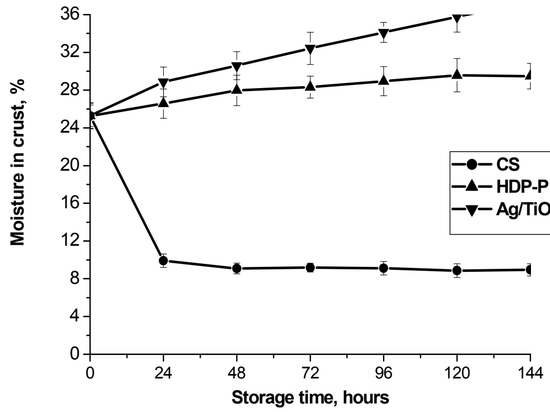
Three analyses in three replicas were performed for all parameters and the results are presented as means ± relative standard deviation (RSD%). All RSD% values were statistically tested using the STATISTICA 7.0 software. The Gaussian distribution of the RSD(%) results subsequently obtained (not shown) suggested that those results are not significantly affected by the work errors.

3. Experimental results

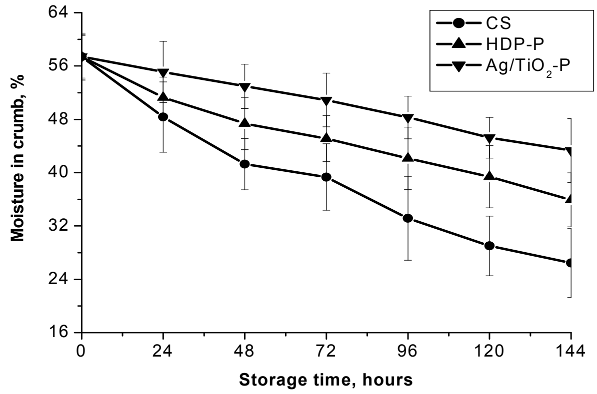
The experimental results indicate that physical changes occur both in the crumb and the crust of bread during storage, regardless of the fact that the bread is stored in open atmosphere or in different packages (figures no. 1-3).

3.1. Moisture evolution in bread crust and crumb during storage

Initially, the humidity of the crumb (50.10%) is higher than that of the crust (25.28%) in all cases (figures 1a and 1b).



a. Crust



b. Crumb

Figure no.1: Evolution of moisture content in crust (a) and crumb (b) during storage (mean±RSD%)

After 144 hours of storage, the moisture level in the CS decreases considerably both in crust and crumb by comparison to HDP-P and Ag/TiO_2-P, due to the water evaporation under the high vapour gradient between the components of bread and the environment. Humidity decreases with a lesser extent in the crumb (by 2.17 times) than in the crust (by 2.82 times), so that after 144 h the values of moisture became 26.45% in the crumb and 8.95% in the crust. Bread packaging reduces the evaporation rate from the crust, due to the low permeability of HDP-P and Ag/TiO_2-P for water and air. The gradient of dryness between the crust and the internal region of the bread led to moisture migration from the crust to the crumb, but the permanent high humidity present in the package headspace blocks the loss of moisture in the crust. Thus, after 144 hours in storage, the moisture decreases in the crumb and increases in the crust in both packages, but at visibly different rates, because of the superior barrier properties of Ag/TiO_2-P. In term of moisture, there was a decrease by 1.54 times in the crumb (from 57.4% to 35.92%) and an increase by 1.16 in the crust (from 25.28% to 29.48%) of samples in HDP-P at the end of storage range. Humidity dropped by 1.32 times in the crumb (from 57.4% to 43.32%) and went up by 1.47 times (from 25.28% to 37.37%) in the crust of the Ag/TiO_2-P sample. The moisture level in the crumb tends to reach the level of moisture in the crumb in both packages, as the water activity of bread reaches equilibrium with the relative humidity of the ambient environment. After 144 hours in storage, the humidity of the crust and of the crumb of the HDP-P sample was 35.91% and 29.48% respectively. The humidity of the crust and of the crumb of the Ag/TiO_2-P sample, at 37.37 % and 43.32 % respectively, was significantly higher.

3.2. Evolution of porosity and specific volume of bread crust and crumb during storage

In general, an inversely proportional relationship exists between the porosity (figure nr. 2) and the specific volume (figure nr. 3) of bread samples.

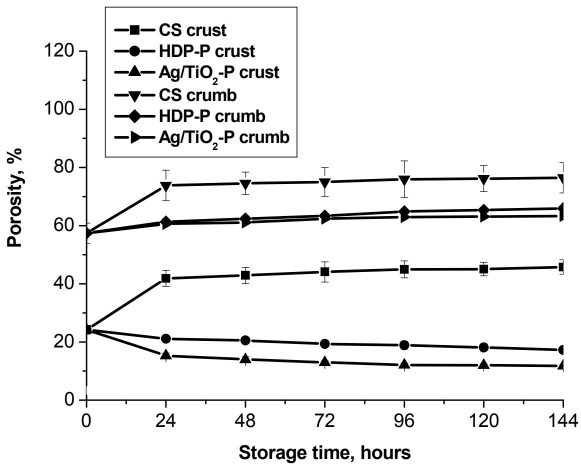


Figure no. 2: Evolution of bread porosity in crust and crumb versus storage time (mean±RSD%)

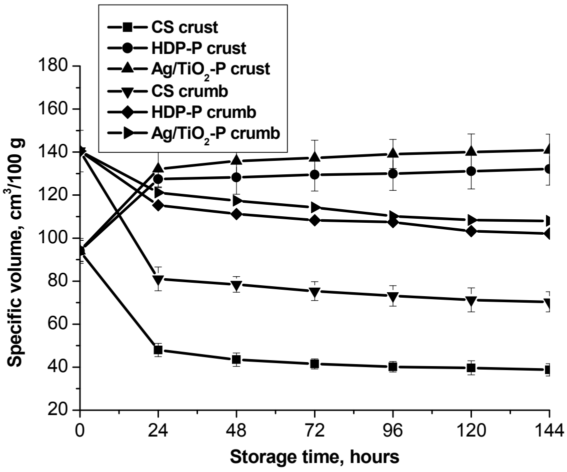


Figure no. 3: Evolution of bread specific volume in crust and crumb versus storage time (mean±RSD%)

The initial values of porosity and specific volume are higher in the crumb (57.40% and 140.52 cm^3/100g) than in the crust (24.20% and 94.04 cm^3/100g). After 144 hours of storage, the porosity of the crust in CS increases more (by 1.89 times) than the porosity of the crumb (by 1.33 times) while the specific volume decreases more in the crust (by 2.42 times) than in the crumb (by 1.99 times). The number of pores increases as the bread losses moisture but in the same time the walls of the pores become more fragile. The porosity of the crumb of HDP-P sample increased by 1.14 times (from 57.4 % to 65.91%) with reducing its specific volume by 1.37 times from 140.52 cm^3/100g to 102.16 cm^3/100g. A decrease of porosity in the crust by 1.40 times (from 24.2% to 17.26%) was accompanied by a 1.40 times increase of its specific volume (from 132.12 cm^3/100g to 94.04 cm^3/100g). The crust porosity of sample Ag/TiO_2-P decreased by 2.054 (from 24.2% to 11.78%) while its specific volume went up by 1.49 times (from 140.96 cm^3/100g to 94.04 cm^3/100g). In the crumb of the same sample, a growth by 1.1 times (from 63.32% to 57.4%) in porosity occurred with the reduction by 1.30 times (from 140.52 cm^3/100g to 107.97 cm^3/100g) of its specific volume. It is interesting to notice that in opposition with the CS, the porosity of crust samples stored in HDP-P and Ag/TiO_2-P decreases. This may happen because crust pores are covered by the gel resulted after the water dissolution of the soluble low-weight compounds usually present in the crust (dextrines, water-soluble pentosans). This process did not occur in CS due to the low humidity of environment.

Considering above presented results we can conclude that Ag/TiO_2 nanomaterial based on package shows a higher efficiency in preserving for a longer period the physical properties of wheat bread in terms of moisture, porosity and specific volume compared with HDP-P and CS. If in case of CS the sharp drop in humidity after 24 h of storage, both in crust and crumb, has negative impact on elasticity, specific volume and porosity of samples, the slow rise of humidity in crust accompanied with the slow reducing of humidity in crumb of samples stored in Ag/TiO_2-P maintains for a longer range the physical attributes of bread.

Our previous work (unpublished) indicates also a high efficiency of Ag/TiO_2 based on package in preserving the chemical attributes of bread (proteins, sugars, fats) as well as microbiological safety in terms of low profile of yeasts, moulds, *B. subtilis* and *B. Cereus*.

Detailed studies are required in order to optimize the amount of Ag/TiO_2 used to prepare the nano-package in relation with the preservation range of physical-chemical-microbiological-sensorial parameters of bread. The releasing of Ag and TiO_2 from the nano-package matrix to bread also should be further investigated to avoid the chemical contamination of bread.

Conclusions

There is no doubt that application of nanomaterials in food packaging sector has substantially benefits both in terms of food safety and financial costs but industrial application has a number of important issues to consider. The possible migration of nanoparticles from packaging materials into food, their toxic effects on humans and on environment are of great importance and they are treated with due attention by the European Union. This is why the next directions should be reinforced: (i) a clear and coherent legislation in the field of food packaging based on; (ii) monitoring the producer in applying the regulations in the field, namely complying with the quality of food packaging and sanctioning them if they breach these regulations; (iii) provide the consumers with the detailed and clear information regarding the possible risks and/or benefits that are involved by using nanomaterials.

Together with the consolidation of this course of action as background, it is achieved consumer awareness on nanometrials in food packaging and hence their interest for information in this field. The correlation between the producer's obligation to inform the consumer and consumer's interest for information on the benefits and risks of using nanomaterials as food packaging, represents the means through which consumer protection gains extra efficiency.

If it is obvious that the laboratory research on the use of nanomaterials as food packaging must be continued, just as important is to develop the means of consumer information and even consumer advice on this subject. The theme of setting-up so-called "consumer information centres" within consumer associations, universities, local authorities dealing with social issues, is applicable in this field as well, even more as the use of nanomaterials as food packaging is a particularly specialized, unfamiliar field, in which the professionals' "voices", not numerous, whether chemists, legal advisors or sociologists need to be heard by consumers.

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