COATINGS FROM NATURAL MACROMOLECULES, WITH GAS BARRIER PROPERTIES TAILORED IN SITU, AND RELATED PREPARATION METHOD

The invention concerns lake compositions based on natural macromolecules (gelatin, chitosan, pectine etc.) with possible additions of vinyl polymers, metal-alkoxides etc., characterized by a barrier effect modulated in situ, in particular as a function of the relative humidity in the exterior ambient.
COATINGS FROM NATURAL MACROMOLECULES, WITH GAS BARRIER PROPERTIES TAILORED IN SITU, AND RELATED PREPARATION METHOD

The present invention relates to coatings basically from natural macromolecules, with gas barrier properties that may be tailored in situ, intended as coatings for plastic substrates, especially films, sheets, and tri-dimensional objects, for many different applications, in particular the food and biomedical fields. More specifically, the invention concerns natural matrices (gelatin, chitosan, chitin, pectin, gluten, casein, zein, whey protein, carrageenan, guar gum, xanthan gum, alginate, starch, cellulose in its different forms) that can be blended with inorganic substances (metal alkoxides) and synthetic polymers (polyvinyl alcohol, polyvinyl acetate, ethylenvinyl alcohol, ethylenvinyl acetate) to generate, through a well-defined and controlled process, hybrid structures as transparent coatings, characterized by very high barrier property against gases (oxygen in particular) and strong adhesion to the plastic substrate.

BACKGROUND OF THE INVENTION.

Safety and security are nowadays two major forefront topics, especially within those fields linked to the human health, such as the food and medical ones. In this direction, enormous efforts are continuously being performed in order to guarantee the best conditions in terms of hygiene and security of foodstuffs and medical devices. It is therefore easy to understand the pivotal role of the primary package in protecting the contained item against detrimental external factors like the microbiological contamination, the permeation of gases and vapors, which may contribute to accelerate some adverse reactions. For this reason, packaging materials are requested to possess the best performance in terms of barrier properties. This is especially true for the plastic packaging, since they exhibit poor general barrier properties when compared to glass and metal materials. Among the different routes pursued to enhance the barrier properties of plastics, depositing thin layers is one of the most valuable. This is because such layers, called coatings, are capable of improving the barrier properties of
the plastic substrate even though applied as very thin layers (i.e., with thickness ranging from some hundred nanometers to few microns). At present, the most widely coatings used are those based on polyvinyl alcohol (PVOH), ethylenvinyl alcohol (EVOH), polyvinylidene chloride (PVDC), and acrylates. For all these solutions (marketed by specific trade marks) exist many references within the patent literature, and citing all of them would be a hard task. It is however worth noting that in all cases such coatings are obtained by a synthetic process on monomers of fossil origin. Only recently have been reported new solutions where the hydrocarbon structure is blended to an inorganic component.

PRIOR ART.

PCT Publication (WO/2007/042993) describes the method to obtain a laminate structure based on a plastic film and a hybrid coating, i.e. made of an organic component (polyvinyl alcohol) and an inorganic matrix (metal alkoxide). The final structure is characterized by very high barrier properties against oxygen even at high external moisture conditions. Similarly, EP Patent 1 348 747 A1 discloses a method to obtain barrier coatings at high and low hygrometric conditions. In this case, the coating is made of polyvinyl alcohol, a metal alcoholate and a organosilane. US Patent 2002/0197480 describes instead a laminate structure including a gas barrier plastic film and a hybrid coating made of a polyvinyllic resin, a Si-alkoxide hydrolyzed, and polyethylene oxide. Such a structure is claimed to have excellent gas barrier properties even at high humidity conditions. JP Patent 7126419 provides details on the obtainment of a laminate structure with excellent barrier properties against gases and water vapour, together with high resistance to humidity and heat. Such a structure is composed by three layers: a plastic polymer as a substrate, a metal alkoxide (or its
hydrolyzed), and tin chloride. Also this structure is defined as hybrid due to the simultaneous presence of organic and inorganic matrices. JP Patent 62295931 describes materials and procedures to produce an inorganic coating having excellent gas barrier properties, obtained from an aqueous or either alcoholic solution of a metal alkoxide deposited onto thermoplastic resins such as PVC, PS, PP o PVA. PCT Publication (WO/2005/053954) describes a hybrid coating obtained by using a metal alkoxide and a synthetic polymer containing carboxylate groups (-COO) partially neutralized. Such a structure exhibits very low gas permeability values regardless the external relative humidity conditions, even after retort process.

Even with many merits, barrier coatings described in the literature are not exempt from some negative aspects, which dictate, especially for some specific applications, lack of universality. In particular:

- coatings are exclusively obtained using synthetic polymers originating from fossil fuels; in a few cases, an inorganic component (prevalently represented by a metal alkoxide) is also added;

- it has never been either cited nor reported the possibility of modulating the gas barrier performance in response to well defined external stimuli (namely temperature, pH, relative humidity). Indeed, whole prior art describes excellent barrier properties, which are kept constant regardless the external relative humidity and temperature conditions.

Nevertheless, for specific applications such a behaviour represents a negative feature.

**SUMMARY OF THE INVENTION AND BRIEF DESCRIPTION OF THE DRAWINGS**

First aim of this invention is to provide coatings having gas barrier properties with special features unknown to the prior art, thus able to afford some advantages in respect to the
solutions nowadays available, overcoming in this way the aforementioned lacks of the prior art.

Other aim is to provide specific preparation methods, involving specific manufacturing and economic advantages.

Further goal is to provide specific applications, which would allow exploiting efficiently the functional properties of the invention, with special emphasis to the biomedical/pharmaceutical and food packaging fields.

The most important features of the invention are recited in the claims which are considered herein incorporated. Aspects and advantages of the invention will more clearly appear from the following description of the preferred embodiments which refer to figures 1-7, diagrams of the performances of the products and methods according to the invention. In particular, Figure 1 shows the basic mechanism governing the possibility of modulating in situ the gas barrier property of the bio-coating which is subject of the present invention. Figures 2-4, highlight the oxygen barrier properties, in terms of oxygen transmission rate (OTR), of three different coatings obtained by using three different starting bio-macromolecules to produce the bio-coatings then deposited onto a 20 μm oriented polypropylene. Figure 5 depicts the effect on the OTR arising from a slight addition of ethylenvinyl alcohol to the original pectin-based coating formulation. Figure 6 illustrates the effect on the OTR of a 20 μm oriented polypropylene due to the addition of a small amount of a metal alkoxide represented by the formula $M^1(OR)^1$ ($M^1 = Si$) to the starting formulation of a chitosan-based bio-coating. Finally, in Figure 7 are summarized the OTR results obtained after the deposition of a coating onto a 12 μm polyethylene terephthalate film. More specifically, the coating is made by
blending the structuring component (ethylvinyl alcohol) and a metal alkoxide (TEOS), both in percentage of (8%), i.e. higher than the bio-macromolecule chitosan (1%).

**DETAILED DESCRIPTION OF THE INVENTION.**

This invention provides methods for obtaining coatings of natural origin with innovative properties and their applications on substrates. According to a feature of the invention, an optimal adhesion to the substrates is reached thanks to the selection of specific natural macromolecules belonging to the categories of proteins and polysaccharides. Among proteins, this invention foresees the following molecules: gelatin (porcine, bovine, fish), gluten, casein, whey protein. The use of pigskin gelatin as a protein is more favourable. Among polysaccharides, this invention envisages the use of the following molecules: chitosan, chitin, pectin, carrageenan, guar gum, xanthan gum, alginates, starch, and cellulose in its different forms. Preferably, pectin and chitosan are used as polysaccharides. Possibly, to obtain the coating subject of this invention, molecule of not natural origin may be used, such as ethylvinyl alcohol (EVOH) and polyvinyl alcohol (PVOH) as structuring agent, preferably the first one, and a metal alkoxide as reinforcing agent. In this last case, the tetraethyl orthosilicate (TEOS) is preferred. The solvent will be always represented by water.

Among the many benefits arising from the new matrices, we only refer to those related to their characteristics and properties which are better than those of films without the invention (uncoated) and also existing synthetic coatings.

Indeed, when applied as a coating, the matrix of the invention:

1) exhibits gas barrier properties that can be deliberately modified *in situ* in response to specific external stimuli, such as relative humidity and temperature. Surprisingly, the
targeted barrier property recovers its original value as the trigger is switched off. This feature makes the invention unique in the field, since the gas barrier coatings described in the prior art show barrier properties that can be properly defined static, i.e. characterized by values that do not change over time as a response to external triggers, such as the environment surrounding the packaging of a food item or of a syringe for medical purposes. The possibility of controlling the gas barrier property by means of a mechanism “ON-OFF” – type is deemed of utmost importance for all those applications requiring the control of the permeation rate of gas and vapours across the packaging;

2) exhibits strong adhesion to the substrates even in absence of any of the common physical-chemical pre-treatment normally used to activate the surface (corona discharge, plasma, flame treatment, chemical primers);

3) increases the transparency of the films acting as a substrate; this is a very important feature, especially from an aesthetic point of view;

4) according to the invention, the coating obtained can be defined as a ‘green coating’, since it accounts mostly of bio-macromolecules. This aspect appears of primary importance since it falls in the concept of ‘packaging optimization’, which is based on the opportunity of using the common plastic packaging materials to a minor extent without compromising the final performance of the ultimate package, rather achieving the final goal of dumping a less amount of wastes into the environment. The concept of ‘packaging optimization’ answer the continuously increasing request for new solutions with a low environmental impact during the waste disposal operations.

Coatings produced according to this invention answer this request accordingly.
According to a first feature of the invention, said matrices comprise:

- as natural molecules of protein origin:

1. gelatin, from pigs, cows or fishes, the pigskin one being to be preferred, characterized by a Bloom value ranging between 30 e 250;
2. wheat gluten, with a protein content between 70% and 85%, starch content between 7% and 12%, lipids content less than 6%, cellulose content between 0.3% and 1%, ash content less than 1%, moisture content less than 10%;
3. casein, with protein content not less than 85%;
4. zein from corn;
5. whey proteins;

- as natural molecules of polysaccharide origin:

1. pectin, obtained from citrus of apples, with a degree of esterification (DE) between 7 and 75 and with degree of amidation (DA) between 15 e 65;
2. chitosan, with degree of deacetylation (DD) between 0.70 and 0.95;
3. cellulose and its derivatives, i.e.: carboxymethyl-cellulose (CMC), methyl-cellulose (MC), hydroxypropyl-cellulose (HPC), hydroxypropylmethyl-cellulose (HPMC);
4. alginates;
5. carrageenan;
6. guar gum;
7. xanthan gum;
- as a structuring agent, it can be possibly used polyvinyl alcohol, with hydrolysis degree between 80% and 100%. Preferably, ethylvinyl alcohol may be used, with hydrolysis degree between 80% and 100% and ethylene/vinyl ratio between 0 and 0.38. Its role is to provide ductility to the final coating structure;

- as a reinforcing agent, the metal alkoxide represented by the general formula $M^1(OR)^1$, with $M^1$ is a atom selected among Si e Al, and $R^1$ states for an alkyl group to be selected between methyl and ethyl. Alternatively or in combination to this component, also inorganic fillers may be used in the form of micrometric or nanometric platelets that, properly exfoliated, act as a physical obstacle to the molecules permeation across the final structure of the coating. To this purpose, clays like mica, cloisite, bentonite, vermiculite, kaolin, and dellite may be used. Generally speaking, such inorganic components have to be used when high resistance to the external relative humidity is required, thus avoiding that the barrier properties do not change by varying this parameter;

- as a catalyst, the bi-carboxylic oxalic acid (COOH)$_2$ has been selected, which makes it possible the metal alkoxide hydrolysis takes place;

- as a solvent of the whole reaction, only distilled water.

According to another aspect of the invention, the natural component (protein or polysaccharide) content will be in the range 0.1% - 20% ($\%_w$) when used alone. If both biomacromolecules are used, the specific amounts will be defined according to the following relationship:

$$y = f(X_{prot.})$$

(1)
Equation 1 indicates that the amount of polysaccharide (y) to be used will always depend on the amount of protein (x). In one preferred embodiment the amount of polysaccharide is:

$$f(x_{prot.}) = \frac{\sqrt{x-1}}{x} \pm 0.2\%$$  \hspace{1cm} (2)

The other components would be used according to the specific quantities reported hereinafter:

- structuring agent: from 0.1 to 20% (\text{\%/w}) of the total water solution;
- reinforcing agent: it will be added to the water solution so that the molar ratio between metal alkoxide and solvent (water) will be always between 1:15 e 1:7.2;
- catalyst: it has to be used in a concentration ranging between 0.001 M and 0.1 M.

The complement to 100\% will be given by the solvent (H2O).

The easier and rapider method, thereby the preferred one, according to the invention to obtain the starting matrix (in the form of slurry) is as follows:

1. In a first tank is prepared the natural component. As a function of the selected bio-macromolecule, the dissolution process will be performed at room or high temperature. The pH value of the solution will be then adjusted depending on the starting bio-macromolecule.

2. At the same time, but in another tank, is prepared the water solution containing the structuring agent (if it is requested) at 90\°C for 2 hours at a speed of 500 rpm. Later on, the water solution will be immediately cooled as long as 30\°C will be reached.

3. In a third tank has to be prepared the reinforcing agent, which is put in an acid water solution according to the stoichiometric ratios aforementioned. This step has to be
carried out at room temperature, at a speed of 1000 rpm. This hydrolysis process has to be considered complete after 4 hours. Such a frame time is significantly lower than what is reported in the prior art, thus allowing an optimization of the process to be achieved.

4. The so prepared matrices will be at this point blended according to this specific order: the natural component has to be added to the tank containing the structuring agent. This mix will be kept stirring at 500 rpm for 1 hour. Only after this time will be added the reinforcing component. This final blend (natural component + structuring component + reinforcing component) will be stirred for 1 hour more at 500 rpm.

5. According to this invention, steps 2, 3 and 4 will be omitted if the final coating is obtained from only natural macromolecules (i.e., protein or polysaccharides).

The treatment sub 1) assures:

- if a protein is used as a natural macromolecule, the total denaturation of the structure, which in turn loses its tertiary conformation. In this way, early inaccessible sites are now available to form new bonds or interactions between the protein and other molecules. The pH adjustment is necessary to bring the protein to its isoelectric point, in order to make effective the electrostatic interactions with other charged molecules;
- if a polysaccharide is used as a natural macromolecule, the dissolution of the molecule within the solvent, which takes place by thermal treatment for some polysaccharide.

The treatment sub 2) assures the total dissolution of the structuring agent (ethylen vinyl alcohol or polyvinyl alcohol), through the breakage of the hydrogen bridges between different –OH groups along the skeleton of the molecule.
The treatment *sub 3*) assures the partial hydrolysis of the reinforcing component, making it possible the replacement of part of the alkoxid groups with the alcoholic groups to form the silanol (Si-OH) species.

The step *sub 4*) guarantees the interaction between the different matrices blended together. Such an interaction is characterized by intermolecular forces, especially hydrogen bonds.

The so obtained starting matrix (in the form of a sol), has to be obtained onto the plastic substrate, according to the invention. The method of deposition strictly relies on the specific substrate. For example, if the sol has to be deposited onto plastic films, the preferred way of deposition is the coating technique, which allows applying very thin layers in dry form. In this case, the sol will be placed in a large tank at controlled temperature (25°C) and continuously transferred into a smaller basin (60 litres) by means of a dedicated pumps system. In this place, the sol is in turn moved to a rectangular basin of approximately 20 liters, where a metal engraved roll picks the sol up and spreads it on the plastic film, according to a well defined amount fixed by the number of engraves on the roll. The wet-coated plastic film undergoes at this point the drying effect of an array of infra-red lamps, immediately followed by a long slit where hot air (90°C) is fluxed through, so that the residual humidity within the coating is pushed out. In this way, any potential phenomena of blocking in the rolls are avoided. The operation speed has to be $\geq 150 \text{ m min}^{-1}$, which is always higher than those reported in the prior art. Nevertheless, the coating according to this invention will result perfectly dried even at this speed.

In all those cases where the coating has to be applied onto surfaces different from flexible plastic films, one preferred method is the nebulization. For other items, the dipping method
may represent the best way for the deposition of the coating.

The bio-polymeric matrix as described within this invention can find a wide variety of applications. Among them, those preferred are: 1) packaging of food items; 2) packaging of bio-medical devices. In both cases, the coating of this invention is intended as a replacement of the coatings commonly used so far.

In particular, the most characterizing feature of this invention relates to the possibility of modulate in situ the barrier property against gases of the coating once it has been deposited onto the plastic substrate, thanks to external triggers that modify the structure of the coating enabling to change the rate of permeation of gases and vapors. More specifically, in this invention the selected trigger is represented by the humidity of the surroundings. According to the procedure described previously, it is possible to develop coatings able to ‘sense’ more or less intensively the change in the values of the external relative humidity. The basic principle is illustrated in Figure 1, where increasing the relative humidity of the external environment the physical structure of the coating changes. In particular, it starts to ‘open its web’ due to the swelling phenomenon, which brings an increase in the intermolecular space and thus of the free volume of the matrix. As a final result, the matrix self will be more permeable to the gaseous species. Such a mechanism enables tailoring in situ (i.e., when the coating has been right deposited on the substrate) the permeability of the coating depending on the specific application. It is worth pointing out that the coating of this invention is able to recover its physical original structure when the trigger (humidity) gets off, i.e. the modulation of the permeability property is reversible. At the boundary of this arrays of solutions there are two distinct types of coatings: those which do not change their permeability properties up to very
high humidity conditions (~ 80% RH) and those that, conversely, start ‘sensing’ the changes in humidity values at ~ 20% RH. Of course, the different behavior of the coatings will depend on the formulation, namely on the type of biopolymer used and if it has been/it has not been used the structuring and/or the reinforcing agent. From a chemistry point of view, the tendency is to use molecules with hydrophilic groups in order to enhance the sensitivity to the external humidity. On the contrary, molecules with more hydrophobic group will be preferred if the resistance to humidity is the targeted goal. It has to be noticed that the coating deposited onto the plastic substrate not only improved its barrier properties against gas like oxygen, but brought relevant benefits as far as other functional properties are concerned. Among them, the best transparency of the final structure with respect to the uncoated substrate has to be mentioned. In addition, the excellent adhesion of the coating to the substrate even at high relative humidity values deserves to be mentioned. This aspect is very important since it governs the delamination phenomena that can possibly take place once the coated substrate is coupled to another polymer usually through the lamination process (by means of an adhesive). The reason for such high adhesion properties lies in the use of biopolymers. Indeed, the established polarity of the majority of the functional groups along the macromolecule backbone as well as the presence of charged groups makes it possible to achieve this desired ultimate property.

Examples

The examples described below emphasize the surprising characteristics and properties of the edible matrix according to the invention. In all the examples, reference is made to six different coating formulations, as shown in Table 1, deposited onto different plastic substrates
commonly used in the food and biomedical packaging fields.

<table>
<thead>
<tr>
<th>Bio-molecule</th>
<th>Formulations</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Protein</strong></td>
<td></td>
<td>Gelatin (5%)</td>
<td>Not used</td>
<td>Not used</td>
<td>Not used</td>
<td>Not used</td>
<td>Not used</td>
</tr>
<tr>
<td><strong>Polyssaccharide</strong></td>
<td></td>
<td>Not used</td>
<td>Pectin (5.0%)</td>
<td>Chitosan (5.0%)</td>
<td>Pectin (5.0%)</td>
<td>Chitosan (5.0%)</td>
<td>Chitosan (1.0%)</td>
</tr>
<tr>
<td><strong>Structuring (EVOH)</strong></td>
<td></td>
<td>Not used</td>
<td>Not used</td>
<td>Not used</td>
<td>0.1%</td>
<td>Not used</td>
<td>8%</td>
</tr>
<tr>
<td><strong>Reinforcing (TEOS)</strong></td>
<td></td>
<td>Not used</td>
<td>Not used</td>
<td>Not used</td>
<td>Not used</td>
<td>1.0%</td>
<td>8%</td>
</tr>
<tr>
<td><strong>Solvent</strong></td>
<td></td>
<td>95.0%</td>
<td>95.0%</td>
<td>95.0%</td>
<td>94.9%</td>
<td>94.0%</td>
<td>83%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

The following analyses have subsequently been performed:

- **Thickness.** The thickness of the coating has been drawn by the mathematical equation:

\[
G \text{ (gm}^{-2}) = d \text{ (gc}^{-3})L \text{ (mm)}
\]

which relates with each other three different parameters: grammage (G), density (d) and thickness (L).

From the above relationship it is easy to obtain the thickness as follows:

\[
L = Gd^{-1}
\]

In practice, it is done by determining G by difference (the weight of 1 dm² of coated film - the weight of 1 dm² of uncoated film) and knowing that the density of the coating is equal to 1.05 gc⁻³. When possible, the thickness has been measured by a micrometer (Dialmatic Digital Indicator, Maplewood, NJ, 07040) to the nearest 0.001 mm at 10 different random locations.
- **Oxygen Transmission Rate (OTR).** Such analysis has been performed according to the Standard Method ASTM D1434-88, by using a permeabimeter OPT 5000 (Dansensor, Denmark). Measurements have been done at controlled thermo-hygrometric conditions: (T = 23°C; RH gradient = 0%, 50%, and 80%). Results from 10 replicates are expressed in ml m⁻² 24h⁻¹.

- **Transparency.** Transparency was determined according to ASTM D 1746-88 by using a spectrophotometer (Lambda 650-High performance-Perkin Elmer). In particular, the transparency of both uncoated and coated films was measured in terms of specular transmittance, i.e. the transmittance value obtained when the transmitted radiant flux includes only that transmitted in the same direction as that of the incident flux in the range 540–560 nm. The final values are expressed as a percentage (%) of the total incident radiation.

Table 2 summarizes the results obtained from the oxygen transmission rate and transparency analyses.

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**Tabella 2. OTR and transparency of the six different formulations reported in the examples.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Formulation</th>
<th>OTR* (ml m⁻² 24h⁻¹)</th>
<th>Transparency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>54.2</td>
<td>90.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.13</td>
<td>87.9</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.03</td>
<td>88.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.2</td>
<td>86.7</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.2</td>
<td>88.8</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0</td>
<td>81.3</td>
</tr>
</tbody>
</table>

*23 °C; 0% UR
Transparency uncoated OPP = 91%
Transparency uncoated PET = 82%
Example 1. It is herein described the oxygen barrier property of a 2.0 \( \mu \text{m} \) thick coating totally obtained from a bio-macromolecule, namely gelatin from pig skin. As it can be see from Figure 2, this type of coating does not exhibit excellent barrier properties at dry conditions (i.e., 0% RH), though it has a pretty good resistance to the water vapor, which is the reason for the limited increase of the OTR values at higher relative humidity conditions. The explanation accounts for the chemical structure of the gelatin molecule, which is composed by a sequence of amino acids, among them those hydrophobic like phenylalanine, valine, leucine, isoleucine, and methionine are responsible for the humidity resistance. Therefore, is can be understood as the selection of the starting polymer plays a fundamental role in the definition of the ultimate properties of the coating. In particular, such a kind of coating (i.e., having these specific properties) can find application when is not required a total barrier to gas while maintaining a relatively constant barrier property as the external humidity increases. Finally, it has to be noticed as the coating deposition does not affect the transparency of the plastic substrate (OPP 20 \( \mu \text{m} \)).

Example 2. It illustrates the oxygen barrier property of a 2.0 \( \mu \text{m} \) thick coating totally obtained from pectin as a bio-macromolecule. As depicted in Figure 3, at 0% RH the barrier property of such a molecule is higher than gelatin. However, the effect due to the external relative humidity is greater, since the increase in the OTR values moving from 0% to 80% RH is more marked. This type of coating might be used when is required a total barrier to oxygen permeation at external anhydrous conditions. Further application could be the packaging of sliced vegetables, which require the possibility of modulating the exchange of \( \text{O}_2 \) and \( \text{CO}_2 \) with the external environment as a function of the respiration kinetic. Also this kind of
coating does not affect the transparency of the plastic substrate.

**Example 3.** This example aims at highlighting the characteristics of another bio-macromolecule, chitosan, in terms of barrier property against oxygen. As reported in Figure 3, this biopolymer exhibits intermediate OTR values at dry and wet conditions compared to gelatin and pectin. As a consequence, this kind of coating might by profitably used in the medical field, for the packaging of specific devices which requires, for safety reasons, the use of ethylene oxide. In particular, the efficacy of the ethylene oxide-based treatment strictly depends on the hygrometric conditions within the sterilization chamber (usually an autoclave). The best recognized performance are at RH ~ 40-60%. Such a bio-coating would allow the permeation of the sterilizing gas across the plastic substrate and its removal once the bactericide effect took place and this because of the medium-high relative humidity conditions. Once the trigger ceases, i.e. the relative humidity values are brought back to the original conditions, the coating would recover its physical properties, which make it possible its function as a barrier against gases. Also in this case, the chitosan-based coating does not modify the original transparency of the substrate.

**Example 4.** It is here highlighted the effect arising from the addition of a small amount (0.1 wt%) of ethylenvinyl alcohol as a structuring agent within the formulation according to the Example 2, where the bio-macromolecule used is pectin. As displayed in Figure 5, the structuring agent leads to a more performing coating, in the sense that it is able to withstand higher relative humidity values. The final result is a more pronounced capability of maintaining high oxygen barrier properties even at the highest external humidity conditions. The transparency of the final structure appears also in this case excellent.
Example 5. Figure 6 shows what happens when adding a small amount (1.0%) of the reinforcing agent (TEOS) to the formulation according to the Example 3. The OTR values of a 20 μm polypropylene film are kept at excellent values also at high humidity conditions, due to the role of TEOS as water resistant component. Also in this case the final structure has an excellent transparency.

Example 6. This last example contains the relevant aspects arising from the simultaneous use of the natural, synthetic organic and inorganic components to produce the high gas barrier coatings. The composition of such a solution is reported in Table 1 (last row). Figure 7 reports the oxygen barrier properties of a 12 μm polyethylene terephthalate (PET) after the deposition of a 2 μm hybrid coating. As it can be seen, the major benefit is given by very low oxygen barrier properties even at 50% relative humidity. These properties, however, are roughly maintained at also 80% RH, due to the synergic effect of the three different components. One potential application of this type of coating could be the packaging of food items stocked at high relative humidity values (for example, meat products in the refrigerators of the markets) requiring a high protection against oxygen permeation. Although the more complex structure of this coating, the final optical properties (in terms of transparency) of the substrate are not affected also in this case.

Even though this invention has been described with reference to specific and preferred examples, it has to be intended as not limited to the above examples, rather as a body that can be changed and improved through modifications that to be handled by the mean technician in the field, fall within the domain of this invention.
CLAIMS

1) Coatings basically from natural macromolecules, having gas barrier properties, characterized by the possibility of modulating these barrier properties in situ, as a function of the external relative humidity acting as a trigger.

2) Coatings according to claim 1, wherein said natural macromolecules are deliberately selected among: gelatin, chitosan, chitin, pectin, gluten, casein, zein, whey protein, carrageenan, guar gum, xanthan gum, alginates, starch, and cellulose in its different derivative forms.

3) Coatings according to claim 1, wherein the basic composition made of natural macromolecules may also contain organic synthetic and/or inorganic components selected among the following: vinyl polymers, metal alkoxides, inorganic clays, catalyst, and solvent.

4) Coatings according to claim 3, wherein the vinyl polymer is the ethylendivinyl alcohol having hydrolysis degree between 80% and 100%.

5) Coatings according to claim 3, wherein the metal alkoxides have general formula:

\[ M^1 \text{(OR}^1) \]

where \( M^1 \) is an atom selected between silicium and alluminum, \( R1 \) being an alkyl group (methyl or ethyl group).

6) Coatings according to claim 3, wherein the inorganic filler are mica, cloisite, bentonite, vermiculite, kaolin, dellite.

7) Coatings according to claim 3, wherein the catalyst is the bi-carboxylic acid oxalic \((\text{COOH})_2\) in concentration ranging between 0.001 e 0.1 M.

8) Coatings according to claim 3 wherein the solvent has to be always water.

9) Coatings according to at least one of the previous claims, wherein in the case of use of natural macromolecules (protein or polysaccharide) the natural component has to used in
amount ranging between 0.1% wt e 20% wt when used alone, whereas if used simultaneously (protein and polysaccharide), the amount of polysaccharide to be used (\(y\)) is function of the amount of the protein (\(x\)) and is defined by the following expression:

\[
y = f(x_{prot.}) = \frac{\sqrt{x-1}}{x} + 0.2\%
\]

10) Coatings according to claims 1 and 8, wherein the amount of vinyl polymer (also called structuring agent) is between 0.1% and 20% of the total weight of the starting water solution, and the molar ratio metal alkoxide: water is between 1:1 e 1:7.2.

11) Method to prepare coatings according the previous claims, characterized by the following steps wherein:

a) is prepared a water solution of the natural component, using distilled water as sole solvent;

b) is prepared a water solution of the vinyl component;

c) is prepared an acidic water solution of the metal alkoxide;

d) solutions a) – c) are mixed together, previously blending a) e b), which were kept in contact for at least one hour; later on, solution c) is added to the so obtained blend a) + b) in order to obtain the final water solution that can be directly applied onto different substrates (preferably plastic films) in the form of thin coatings.
FIG. 1 - Schematic representation of the effect of the external relative humidity on the barrier properties of the biocoating according to the invention.

FIG. 2 - Oxygen Transmission Rate (OTR) values at different relative humidity condition (0%-50%-80%-0%) of a 20 μm oriented polypropylene (OPP) film coated with a 2.0 μm Gelatin biocoating. OTR of uncoated OPP = 1800 ml m⁻² 24h⁻¹.
FIG. 3 - Oxygen Transmission Rate (OTR) values at different relative humidity conditions (0%-50%-80%-0%) of a 20 μm oriented polypropylene (OPP) film coated with a 2.0 μm pectin biocoating. OTR of uncoated OPP = 1800 ml m⁻² 24h⁻¹

FIG. 4 - Oxygen Transmission Rate (OTR) values at different relative humidity conditions (0%-50%-80%-0%) of a 20 μm oriented polypropylene (OPP) film coated with a 2.0 μm chitosan biocoating. OTR of uncoated OPP = 1800 ml m⁻² 24h⁻¹
FIG. 5 - Oxygen Transmission Rate (OTR) values at different relative humidity conditions (0%-50%-80%-0%) of a 20 μm oriented polypropylene (OPP) film coated with a 2.0 μm Pectin/EVOH biocoating. OTR of uncoated OPP= 1800 ml m⁻² 24h⁻¹

FIG. 6 - Oxygen Transmission Rate (OTR) values at different relative humidity conditions (0%-50%-80%-0%) of a 20 μm oriented polypropylene (OPP) film coated with a 2.0 μm Chitosan/TEOS biocoating. OTR of uncoated OPP= 1800 ml m⁻² 24h⁻¹
FIG. 7 - Oxygen Transmission Rate (OTR) values at different relative humidity conditions (0%-50%-80%-0%) of a 12 μm polyethylene terephthalate (PET) film coated with a 2.0 μm Chitosan/PVOH/TEOS biocoating. OTR of uncoated OPP= 1800 ml m⁻² 24h⁻¹
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C09D105/00 C09D189/00

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>WO 03/082995 A (AHLSTROEM OY [FI]; AHLSTROM RESEARCH &amp; SERVICES [FR]; DOMARD ALAIN [FR]) 9 October 2003 (2003-10-09) page 10; examples</td>
<td>1,3,7-9</td>
</tr>
</tbody>
</table>

X Further documents are listed in the continuation of Box C. X See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search 22 April 2010

Date of mailing of the international search report 04/05/2010

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk

Tel. (+31–70) 340-2040, Fax: (+31–70) 340-3016

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Vaccaro, Eleonora
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>DE 198 34 228 A1 (FEW CHEMICALS GMBH [DE]) 3 February 2000 (2000-02-03) claims; examples</td>
<td>1,3,7-9, 7-9</td>
</tr>
<tr>
<td>X</td>
<td>WO 97/23390 A (TETRA LAVAL HOLDINGS &amp; FINANCE [CH]; BERLIN MIKAEL [SE]) 3 July 1997 (1997-07-03) claims</td>
<td>1-4,7-9</td>
</tr>
<tr>
<td>X</td>
<td>ARVANITIOYANNIS ET AL: &quot;Edible films made from hydroxypropyl starch and gelatin and plasticized by polyols and water&quot; CARBOHYDRATE POLYMERS, APPLIED SCIENCE PUBLISHERS, LTD. BARKING, GB, vol. 36, no. 2-3, 1 July 1998 (1998-07-01), pages 105-119, XP005001941 ISSN: 0144-8617 the whole document</td>
<td>1-3,7-9</td>
</tr>
<tr>
<td>Patent document cited in search report</td>
<td>Publication date</td>
<td>Patent family member(s)</td>
</tr>
<tr>
<td>----------------------------------------</td>
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</tr>
<tr>
<td>AU 2003229861 A1</td>
<td>13-10-2003</td>
<td></td>
</tr>
<tr>
<td>BR 0308991 A</td>
<td>04-01-2005</td>
<td></td>
</tr>
<tr>
<td>CA 2480643 A1</td>
<td>09-10-2003</td>
<td></td>
</tr>
<tr>
<td>CN 1646645 A</td>
<td>27-07-2005</td>
<td></td>
</tr>
<tr>
<td>EP 1490446 A1</td>
<td>29-12-2004</td>
<td></td>
</tr>
<tr>
<td>FR 2837829 A1</td>
<td>03-10-2003</td>
<td></td>
</tr>
<tr>
<td>JP 2005527710 T</td>
<td>15-09-2005</td>
<td></td>
</tr>
<tr>
<td>MX PA04009565 A</td>
<td>13-12-2004</td>
<td></td>
</tr>
<tr>
<td>RU 2293751 C2</td>
<td>20-02-2007</td>
<td></td>
</tr>
<tr>
<td>US 2005084677 A1</td>
<td>21-04-2005</td>
<td></td>
</tr>
<tr>
<td>ZA 200407849 A</td>
<td>01-07-2005</td>
<td></td>
</tr>
<tr>
<td>JP 2003064205 A</td>
<td>05-03-2003</td>
<td></td>
</tr>
<tr>
<td>DE 19834228 A1</td>
<td>03-02-2000</td>
<td>NONE</td>
</tr>
<tr>
<td>DE 69624837 D1</td>
<td>19-12-2002</td>
<td></td>
</tr>
<tr>
<td>DE 69624837 T2</td>
<td>27-03-2003</td>
<td></td>
</tr>
<tr>
<td>DK 868362 T3</td>
<td>14-04-2003</td>
<td></td>
</tr>
<tr>
<td>JP 2000502620 T</td>
<td>07-03-2000</td>
<td></td>
</tr>
<tr>
<td>US 6495223 B1</td>
<td>17-12-2002</td>
<td></td>
</tr>
</tbody>
</table>