

Biodegradable starch/clay nanocomposite films for food packaging applications

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Abstract

Novel biodegradable starch/clay nanocomposite films, to be used as food packaging, were obtained by homogeneously dispersing montmorillonite nanoparticles in different starch-based materials via polymer melt processing techniques. Structural and mechanical characterizations on the nanocomposite films were performed. The results show, in the case of starch/clay material, a good intercalation of the polymeric phase into clay interlayer galleries, together with an increase of mechanical parameters, such as modulus and tensile strength.

Finally the conformity of our samples with actual regulations and European directives on biodegradable materials was verified by migration tests and by putting the films into contact with vegetables and simulants.

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Keywords: Nanocomposite; Biodegradable; Food contact; Migration tests; EU directives

1. Introduction

In the past 20 years, the production and the use of plastics in the world have been enormously increased, worsening the problem of the waste disposal. The growing interest in environmental impact of discarded plastics has directed research on the development of plastics that degrade more rapidly in the environment, leading to a complete mineralization or bioassimilation of the plastics (Aminabhavi, Balundgi, & Cassidy, 1990; Crosby, 1981; Doi, 1990). Biopolymers should be used in those applications where biodegradability and/or the derivation of natural resources gives added value, particularly, where valuable petroleum-based plastics are used for applications with a short life time.

Nevertheless, the used packaging materials, such as shopping bags, are still easily visible in the environment in many countries. So biodegradable materials offer a possible alternative to the traditional non-biodegradable polymers, especially in short life-time application and when their recycling is difficult and/or not economical.

The term “biodegradable” materials is used to describe those materials which can be degraded by the enzymatic action of living organisms, such as bacteria, yeasts, fungi and the ultimate end-products of the degradation process, these being CO₂, H₂O, and biomass under aerobic conditions and hydrocarbons, methane and biomass under anaerobic conditions (Doi & Fukuda, 1994).

Thus, there is a considerable interest in replacing some or all of the synthetic plastics by biodegradable materials in many applications. Some of the natural polymers (PHB and its copolymers (Gilbert, 1985)) and aliphatic polyesters (polycaprolactone (Huang, Shetty, &

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Wang, 1990), polylactic acid (Jarowenko, 1977)) are biodegradable, but their cost compared of that of petroleum-based commodity plastics prevents a larger commercial usage and finds applications only in niche sectors.

Among the biomaterials present today in the market, those derived from renewable resources such as starch-based products are the most widespread and economic biomaterials. Some examples are: Materbi from Novamont-Italy and Biopar from Biop. Germany. The starch is normally blended with biodegradable aliphatic polyesters, such as Ecoflex from BASF Germany or Bionolle from Showa Highpolymers Japan.

Starch is a semicrystalline polymer stored in granules as a reserve in most plants. It is composed of repeating 1,4- α -D glucopyranosyl units: amylose and amylopectin. The amylose is almost linear, in which the repeating units are linked by α (1–4) linkages; the amylopectin has an α (1–4)-linked backbone and ca. 5% of α (1–6)-linked branches. The relative amounts of amylose and amylopectin depend upon the plant source. Corn starch granules typically contain approximately 70% amylopectin and 30% amylose (Lambert & Poncelet, 1997). The ratio of the two components characterises materials with very different properties. In the food packaging sector, starch-based material has received great attention owing to its biodegradability, wide availability and the low cost (less than 1 euro per kg). Several studies are concentrated on the development of starch-based materials, for the above-mentioned reasons (Pelissero, 1990). Unfortunately, the starch presents some drawbacks, such as the strong hydrophilic behaviour (poor moisture barrier) and poorer mechanical properties than the conventional non-biodegradable plastic films used in the food packaging industries.

Recently the application of the nanocomposite concept has proven to be a promising option in order to improve mechanical and barrier properties.

In this work nanocomposite films were obtained by homogeneously dispersing functionalised layered silicates (clay minerals) in thermoplastic starch via polymer melt processing techniques. These films were made by using different starch matrices, such as neat potato starch and a mixture of potato starch with a biodegradable polyester. The structure and mechanical characteristics of the nanocomposites were investigated. Moreover, food-contact tests with some vegetables and simulants have been performed in order to study the possibility of utilising these materials in the food packaging sector. In fact, plastic materials are not inert and, where direct contact between the packaged product and the plastic container occurs, there can be migration of substances into the product. The amount of any component that migrates into food depends on the original concentration of the particular

component in the polymer and its solubility as well as the temperature, mechanical stresses and contact time. It is extremely difficult to measure the migration directly into a food, as most foodstuffs have complicated compositions. The migration behaviour of the plastic material is easily measured by so-called food simulants such as ethanol and water (Plee, Borg, Gati-neau, & Fripiat, 1985).

The extractability of a compound from the plastic can be determined by placing the plastic in contact with the food or food simulant under defined conditions of temperature, time and static/dynamic mode. At the end of the test, an appropriate analytical technique is applied to determine the amount of compound present in the food/simulant and hence, the degree of migration can be calculated. The overall interaction of plastic packaging materials with foodstuffs is best described by global migration, which is the sum of all the specific migrations of plastic constituents and foodstuffs (Rutkowska & Dereszewska, 1998; Selke, 1996).

2. Materials and methods

2.1. Materials

The materials used for the preparation of our nanocomposite films are potato starch (supplied by Avebe, the Netherlands) and a purified clay (Montmorillonite) with cation-exchange capacity (CEC) of 128 meq/100 g furnished by Laviosa (Livorno) – Italy. Moreover, biodegradable polyesters (Ecoflex SBX 7000 from BASF, Germany) were also added to the starch phase to obtain the matrices of the last two samples.

Films were made through casting by BIOP – Biopolymer Technologies AG, Dresden – Germany, using granulate produced by a twin-screw extruder.

Compounding occurred with a mass flow of 2 kg/h and a screw speed of 30 rpm at 90 °C. Blending occurred with a slot die, a die gap of 0.5 mm and a screw speed of 125 rpm at 130 °C.

In Table 1, the list of nanocomposite films and the recipes used to prepare them are shown.

2.2. Techniques

The structural characterization employed the MAS NMR solid state technique in order to evaluate the dispersion of the clay into the starch matrix.

Magic angle spinning nuclear magnetic resonance (MAS NMR) experiments were performed on a Bruker AMX-200 spectrometer at 52.14 MHz. The samples were powdered and packed into 4 mm zirconia rotors and sealed with Kel-F caps. ^{27}Al experiments were performed with a selective pulse ($\pi/2$) duration of 3.5 μs ,

Table 1
Nanocomposite film samples

Recipe	Mass flow (kg/h)	Clay (%)	Sample codes
A*	4	0	PS
A*	4	4	PS/C
A**	5	0	PS/PE
A**	5	4	PS/PE/C

A* = (65 - x)% Potato starch, dry/x% Laviosa No. 12/20% Water/15% Glycerol.

A** = (52.4 - x)% Potato starch, dry/x% Laviosa No. 12/21.6% Water/12% Glycerol/14% prepolymer, dry Blend mixing a with biodegradable polyester (Ecoflex SBX 7000).

recycle time 1 s. Spectra were obtained with 512 points in the time domain, double zero filled and Fourier-transformed with a size of 1024 data points; the spin rate was 8 kHz. Chemical shifts were referenced to external standard $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ aqueous solution. To achieve an acceptable signal to noise ratio, 20,000 scans were performed.

Mechanical analysis was performed on both samples series by using an Instron tensile machine mod. 4301. The used machine parameters were: sample rate 25,000 pts/s, crosshead speed 10,000 mm/min, F 1 KN. The mechanical test was carried out at room temperature. The samples were conditioned for 24 h in a desiccator under vacuum at different relative humidities.

A SpectrAA 200 was used for this work, together with flame burner and with the Varian GTA-100 graphite furnace atomizer. Flame AA was used for iron and magnesium determinations and Graphite Furnace AA for silicon determination. An air/acetylene flame was used for iron and magnesium. In the case of silicon, for the determination of trace levels of this metal, it was essential to use the plateau type graphite tube, which was also pyrolytically coated. Nitrogen was used as the inert gas because it not only offers advantages for most elements in terms of sensitivity, but also provides a good protection for the graphite. The hollow cathode metal lamps were used at opportune wavelength, the silicon lamp at 251.6 nm, the iron lamp at 372 nm and the magnesium lamp at 202.6 nm. Water was distilled in a borosilicate vessel and then further purified through a Millipore Milli-Q system. Metal atomic absorption standard solutions with metasilicate, iron metal and magnesium metal as solutes, in 1000 ppm solutions, were used to prepare the working standard for the programmable sample dispenser. The final concentration of nitric acid in all the solutions was 0.5% v/v. A new rational calibration procedure was selected on the SpectrAA in order to assess the amount of silicon, iron and magnesium in the samples. Peak height-measurement mode was used. Although no standard reference material was available, there were

no apparent problems in carrying out this analysis on the GTA-100.

2.3. The contact-tests

Every polymeric film was acclimatized to 50% (w/w) humidity before the contact tests. The vegetable samples (lettuce and spinach) were cut into small samples while the polymeric films were manufactured as bags: the vegetables were packed into bags for the contact-tests. Subsequently the closed bags were placed in an electrical furnace and they were heated to 40 °C for 10 days. After this process, every bag was slowly cooled to the ambient temperature. The polymeric-films were newly acclimatized to 50% (w/w) humidity and they were subsequently characterized. The vegetable samples were digested by the method reported below.

Three grammes of sample, placed in china cup, were weighed and heated in a furnace at 105 °C to constant weight. Then, the sample was cooled in a dry atmosphere for 40 min and weighed. The sample was carbonised by a small flame, put into a muffle at 550 °C for some hours and cooled in a dry atmosphere for 40 min. The obtained ash was dissolved in hydrochloride acid solution and put in a hot water bath and finally filtered.

Then it was analysed by the described atomic absorption equipment to measure the silicon, iron and magnesium release.

3. Results and discussion

3.1. Preparation of nanocomposite films

Films under investigation were made by casting since film blowing appeared to be difficult. A rather stable film blowing process could be achieved in the laboratory, but the melt toughness was low and films became brittle and sticky straight after production. The latter is due to the high water content. The prepared films were analysed by polarised optical microscopy (POM) and environmental scanning electron microscopy (ESEM) in order to study the crystallinity content and the degree of dispersion of the second component in the starch matrix, respectively.

The ESEM photos are shown in Fig. 1(a)–(d) and the results are summarised in Table 2.

From these analyses the following can be easily deduced:

- the starch crystallinity drops to a very low content when a second phase is added to the starch matrix;
- the ESEM investigations showed a homogeneous dispersion of the components in all the examined samples and, only in the case of PS/PE/C sample, is a separation of polyester phase observed.

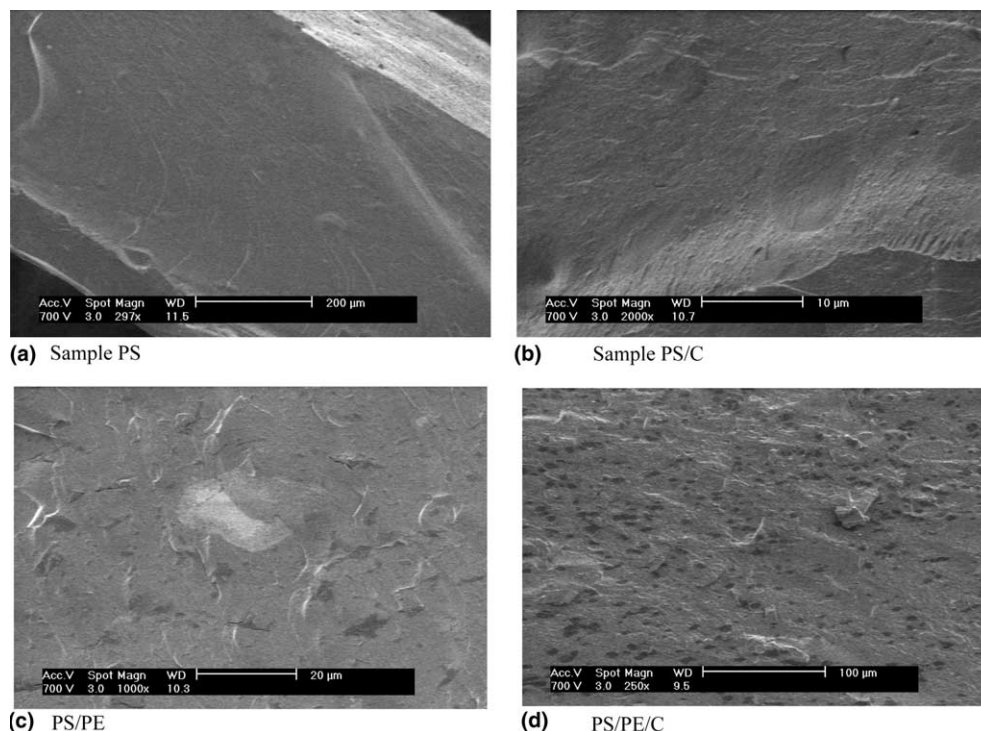


Fig. 1. (a) ESEM Micrograph of surface of sample PS. (b) ESEM Micrograph of surface of the anocomposite PS/C. (c) ESEM Micrograph of surface of sample PS/PE. (d) ESEM Micrograph of surface of the nanocomposite PS/PE/C.

Table 2
POM and ESEM analysis of the calander films

Sample	Composition starch:clay:water:glycerol	POM	ESEM
PS	65:0:20:15 + 0.1% tixosil	Starch cryst. >50%	Homogeneous, nearly no clusters
PS/C	61:4:20:15	Starch cryst. 1%	Very homogeneous, nearly no clusters
PS/PE	52.4:0:21.6:12 + 14% prepolymer + 0.1% tixosil; blend Ecoflex	Starch cryst. 1%	Homogeneous, some tixosil clusters; rough structure from polyester
PS/PE/C	48.4:4:21.6:12 + 14% prepolymer + 0.1% tixosil ; blend Ecoflex	Starch cryst. \ll 1%	Very homogeneous, nearly no clusters; phase separation from polyester

3.2. Characterisations

3.2.1. Structural analysis

The recent developments in solid-state NMR, especially for quadrupolar nuclei, have considerably increased the potential of this technique for the elucidation of the molecular structure of materials.

This is especially true for nanocomposite materials. The organization of the different nanocomposite constituents, however, may not result in a well-defined 3-dimensional periodicity, thus making diffraction methods inapplicable. A typical example is provided by aluminium-pillared clays: the clay layers are less than 1 nm thick (although they are much more extended in the other two directions), and they are held apart by inorganic polymers with a diameter in the nanometric range (Sheperd,

1982). There is usually a well-defined periodicity in the direction perpendicular to the layers (*c*-axis), but not in the *a* and *b* directions. For some time after the discovery of these materials, X-ray diffraction failed to resolve the structure of the Al-containing pillars. One of the early successes of one-pulse ^{27}Al NMR was to conclusively demonstrate that the pillars consist of tridecamers with formula $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ having the so-called “ ϵ -Kegging” structure (Tucker & Johnson, 2004).

For solid samples, the technique of magic angle spinning (MAS) was designed to average signal anisotropy. Sharp MAS NMR signals are indeed observed for nuclei with spin $I = 1/2$, which are only submitted to chemical shift and dipole–dipole interactions but, in the case of ^{27}Al ($I = 5/2$), additional quadrupole interactions are present and are not completely averaged out by MAS.

As a result, ^{27}Al NMR spectra provide information, essentially on the first coordination sphere of the Al (III) ion. It is possible to distinguish between tetrahedral ($^{\text{IV}}\text{Al}$) and octahedral ($^{\text{VI}}\text{Al}$) coordination. Thus, for ^{27}Al , transition is independent of quadrupolar interactions of first order but it is affected by second order quadrupolar effects. Large variations of the quadrupolar coupling constant provoke distortion of the peak shape because of the increasing influence of second-order terms. The sideband pattern is also modified. The quadrupole coupling constant is the product of the quadrupole moment by the electrical field gradient at the nucleus, so the peak shape is very sensitive to change in symmetry of the coordination shell and in the distribution of electrical charges.

In Fig. 2 ^{27}Al NMR MAS spectra of organo-modified clay (a), PS/C (b) and PS/PE/C (c) are, respectively, shown.

As it is possible to observe in the organo-clay spectrum (see Fig. 2(a)), two signals attributable to Al (IV) and Al (VI) coordination are clearly visible. As far as the line centred at 50 ppm relative to $^{\text{IV}}\text{Al}$, tetrahedral coordination is less intensive and more broad than that at 5 ppm relative to the octahedral coordination. A

quantitative determination of the tetrahedral site by integration of the relative peak was not possible, due to the broadness of the signal.

The spectrum of the sample PS/PE/C (see Fig. 2(c)) is almost similar to that of organo-clay. Two peaks, centred at 50 ppm ($^{\text{IV}}\text{Al}$) and at 10 ppm ($^{\text{VI}}\text{Al}$), are identifiable. The peak relative to octahedral coordination is slightly shifted to higher value and the signal appears broad. Finally, in the case of the PS/C sample (see Fig. 2(b)), the ^{27}Al NMR MAS spectra present significant differences from the clay spectra. In fact, in the spectra, a very broad peak is present, characterized by different and complicated sidebands. The maximum of this peak is centred around -20 ppm, while relative maxima at 50, 20 and -50 ppm can also be observed.

The lack of symmetry of the octahedron coordination strongly increases the quadrupole coupling constant, whereas the symmetries of the tetrahedral sites are not so distorted. Then, as shown in the clay spectra, the amounts of the Al tetrahedral sites are smaller than the octahedral ones. As a matter of fact, we could assess that the variations observable in the PS/C spectra could be attributable to a variation of symmetry and charge distribution around Al (VI) that influences the position and the shape of the relative signal. These variations could be due to a massive presence, in the polymeric matrix, of interlayer spacing, as verified by other characterizations performed on this sample.

3.2.2. Mechanical characterization

Tensile properties, such as Young's modulus, strength at break and strain at break have been evaluated from the experimental stress–strain curves obtained for all prepared nanocomposite films. The analysis has been effected on the sample series stored at different percentages of relative moisture in order to simulate different conditions of storage and to investigate the influence of the water presence on the final performance of films. The mechanical parameters measured for the nanocomposites are shown in Table 3. In particular, the samples were conditioned in a drier under vacuum at 15%, (see Table 3(a)) and 60% (see Table 3(b)) relative humidity. In comparison, the same materials without conditioning (see Table 3(c)) were also tested. As to be observed from these values, the sample coded as PS/C is characterized by the highest Young modulus and stress at peak than the other samples in all humidity conditions. This result also accords with the structural analysis in which it was underlined that the PS/C sample is characterized by a good intercalation of starch phase into the clay layers.

Moreover, the adding of a biodegradable polyester to the mixture (PS/PE sample) decreases the Young's modulus, increasing the strain at break with respect to the other samples.

The presence of clay nanoparticles seems to produce an increase of mechanical parameters of starch (PS sam-

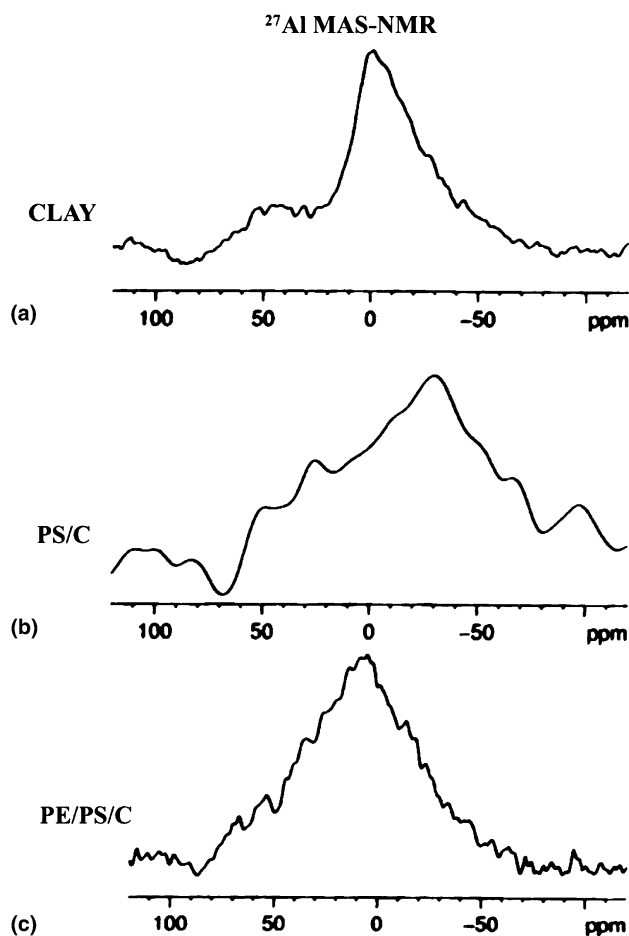


Fig. 2. ^{27}Al MAS NMR spectra of clay, PS/C and PS/PE/C.

Table 3
Mechanical analysis of all examined samples

Sample codes	Clay (%)	Young modulus (MPa)	Stress at peak (MPa)	Strain at break (%)
<i>Mechanical properties of the materials conditioned at 15% relative humidity</i>				
PS	0	979	19	3
PS/C	4	1135	22	4
PS/PE	0	682	7.5	2
PS/PE/C	4	374	7.8	38
<i>Mechanical properties of the materials conditioned at 60% relative humidity</i>				
PS	0	610	9	9
PS/C	4	830	10	2
PS/PE	0	150	3.6	21
PS/PE/C	4	137	4.7	58
<i>Mechanical properties of the materials without conditioning</i>				
PS	0	217	6	25
PS/C	4	450	6	10
PS/PE	0	160	5	22
PS/PE/C	4	75	4	60

ple), while the adding of nanopowder to the PS/PE matrix causes a decrease both of modulus and stress in all operative conditions and, at the same time, an increase of the strain.

Moreover, from Table 3 it seems that water strongly affects the modulus of the starch blends. A comparison of blends PS and PS/C shows the reinforcing effect of the clay particles. Similar effects are measured for the tensile strength. By mixing a second polymer with starch, the modulus is reduced due to the low modulus of the polyester as can be concluded from a comparison of blends PS and PS/PE/C. Ecoflex will decrease the modulus even more and no reinforcing effect of the clay is found as can be concluded from a comparison of blends PS/PE and PS/PE/C. PS and PS/C are in fact too stiff and brittle for making flexible films. More glycerol will make the blend less brittle. It can be concluded that: (a) the amount of plasticiser or polyester should be high enough to avoid embrittlement; (b) that the clay will reinforce the starch blend if it is dispersed properly (dispersed and exfoliated/intercalated); (c) that the water stability is to some extent affected by the presence of clay. Therefore, the use of a polyester in starch requires a two step process:

Step 1: Gelatinisation of starch. Water should be present in order to 'facilitate' gelatinisation;

Step 2: Mixing of gelatinised starch and the polyester before film blowing. Amount of water should be minimised in order to get a less sticky and a separable film.

The addition of the polyester negatively affects the reinforcing effect of the clay particles, because, in the present samples, probably no exfoliated clay is obtained. This can be avoided by mixing clay with starch, leading to an exfoliated clay prior to the mixing with a second polymer. Water, furthermore,

strongly affects the mechanical properties. Fluctuations of the relative humidity will give a fluctuation in properties.

3.3. Contact tests and conformity to EU directives of nanocomposites

The aim of this part of the work was to verify the conformity of our experimental nanocomposite films with the recent regulations and European directives. In fact, until a few years ago only few notes were related to the to compostable and biodegradable materials and, precisely because of this, the 94/62 EC Directive (adopted by European Parliament on 20 December 1994) came about in order to harmonize the national measures concerning the management of packaging and packaging waste, to provide a high level of environmental protection and to ensure the functioning of the internal market.

In this directive, a very brief part is dedicated to compostable and biodegradable materials. In the item three, *compostability* is defined as an organic recycling and it is pointed out that compostability can take place only under controlled conditions and not in landfills. Moreover, in the enclosure two, *biodegradable packaging* is defined as a material that must have a physical, chemical, thermal and biological degradation so that, decomposing ultimately into carbon dioxide and water, it could be used in compost.

In October 1999, the European Committee for Standardization (CEN), under European Commission mandate has elaborated a draft of a European Standard (prEN 13432) indicating *the requirements for recoverable packaging through composting and biodegradation*.

Finally, on June 28th 2001, the Commission approved the EN 13432 normative that now the European countries must respect.

The EN 13432 normative requirements are that the film constituents have to be known, if expected to become harmful to the environment during the biological treatment process, in excess of the limits given:

3.3.1. Volatile solids

Packaging materials shall contain a minimum of 50% of volatile solids which exclude largely inert materials. Our nanocomposites respect this normative because the amount of inert (nanopowder) is 4% by weight.

3.3.2. Heavy metals and other toxic and hazardous substances

The concentration of any substance listed in Table 4, present in packaging, materials and whole packaging, shall not exceed the value given in that table. EDAX analyses have shown that, in our samples, the presence of these elements is negligible.

More important is to establish if the eventual metal particles can migrate during contact with food. So an analysis on some vegetables (lettuce and spinach), after contact with our starch-based biodegradable films was performed.

In fact, the EC normative on food contact materials requires that they shall be safe and shall not transfer their components into the foodstuff in unacceptable quantities. The transfer of constituents of the food contact materials into the food is called migration. To ensure the protection of the health of the consumer and to avoid adulteration of the foodstuff, two types of migration limits have been established in the area of plastic materials: an overall migration limit (OML) of 60 mg (of substances)/kg (of foodstuff or food simulants) that applies to all substances that can migrate from the food contact material to the foodstuff and a specific migration limit (SML) which applies to individual authorised substances and is fixed on the basis of the toxicological evaluation of the substance. The SIVIL is generally established according to the acceptable daily intake (ADI) or the tolerable daily intake (TDI) set by the Scientific Committee on Food (SCF). To set the limit, it is assumed that, every day throughout his/her lifetime, a person of 60 kg eats 1 kg of food packed in plastics containing the relevant substance at the maximum permitted quantity.

Table 4
Maximum element content of packaging material and whole packaging

Element	Dry substance (mg/kg)	Element	Dry substance (mg/kg)
Zn	150	Cr	50
Cu	50	Mo	1
Ni	25.0	Se	0.75
Cd	0.5	As	5
Pb	50	F	100
Hg	0.5		

Table 5

Fe, Mg and Si content of the neat vegetables and of vegetables after contact with nanocomposite films (all the concentrations are expressed in 1 mg /100 g)

Samples	Fe	Mg	Si
Lettuce	2.2	45.7	0.28
Spinach	3.3	55.2	0.3
PS	2.4	14.8	1.3
PS/C	3.7	77.1	1.9
PS/PE	1.4	31.9	1.3
PS/PE/C	2.1	43.1	1.6

The results of this analysis are shown in Table 5.

From the findings it can be deduced that the contact of the different films with both the vegetables (lettuce and spinach) does not produce a strong increase of Fe and Mg in the vegetables, while the higher Si contents observed could be easily attributable to the fact that clay nanoparticles are mainly composed of this element.

Thus, we can affirm that the produced films are not responsible of any increase of element content and thus can be in contact with vegetables.

Finally a test measuring the overall migration limit (OML) after contact with common simulants, used for the vegetables, was also performed on the starch-based films. Particularly, the chosen simulant for vegetables was distilled water.

The samples were immersed in distilled water at 40 °C for the 10 days.

The test was performed on two series of films:

1. as received,
2. after drying under vacuum and kept in a plastic bag.

The results of the tests on the two series of film samples were different: as a matter of fact, all the samples previously dried (series 2) did not lose material and the weight remained constant even after ten days in water. On the contrary the samples not conditioned (series 1) presented a weight loss of around 15% (see Table 6).

These results indicate that, only after drying of the films, does a water-resistant material appear and probably the 14–16% of weight loss of samples not conditioned is due to the water release.

Table 6
Codes and weight losses of samples after simulant contact

Samples code	Weight loss on dried samples (%)	Weight loss on samples as received (%)
PS	0.0	15
PS/C	0.0	15
PS/PE	0.1	14.6
PS/PE/C	0.1	16

Thus, only the dried films satisfy the fixed limit of global migration of 60 mg/kg required for plastic materials

4. Conclusion

Biodegradable starch/clay nanocomposite films were prepared by homogeneously dispersing Montmorillonite nanoparticles via polymer melt processing techniques.

From the obtained results the following conclusions can be drawn:

- A complete intercalation of the polymeric matrix into clay interlayer galleries in the case of starch/clay sample by MAS NMR structural analysis was observed, not detectable for the other nanocomposites.
- A reinforcing effect of the clay particles on the modulus and the tensile strength of the starch was observed, while the addition of the polyester phase seems to negatively affect the reinforcing effect of the clay particles.
- Finally, the conformity of our prepared starch/clay nanocomposite films with actual regulations and European directives on biodegradable materials was assessed, demonstrating that these materials can be utilised in the food packaging sector owing to their low overall migration limit.

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