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Pectins filled with LDH-antimicrobial molecules: Preparation, characterization and physical properties

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ABSTRACT

Nanohybrids of layered double hydroxide (LDH) with intercalated active molecules: benzoate, 2,4-dichlorobenzoate, para-hydroxybenzoate and ortho-hydroxybenzoate, were incorporated into pectins from apples through high energy ball milling in the presence of water. Cast films were obtained and analysed. X-ray diffraction analysis showed a complete destructuration of all nanohybrids in the pectin matrix. Thermogravimetric analysis showed a better thermal resistance of pectin in the presence of fillers, especially para-hydroxybenzoate and ortho-hydroxybenzoate. Mechanical properties showed an improvement of elastic modulus in particular for LDH-para-hydroxybenzoate nanohybrid, due probably to a better interaction between pectin matrix and nanohybrid layers. Barrier properties (sorption and diffusion) to water vapour showed improvement in the dependence on the intercalated active molecule, the best improvement was achieved for composites containing para-hydroxybenzoate molecules, suggesting that the interaction between the filler phase and the polymer plays an important role in sorption and diffusion phenomena. Incorporation of these active molecules gave antimicrobial properties to the composite films giving opportunities in the field of active packaging.

1. Introduction

Environmental legislation (Guideline CE 94/62) as well as consumer demand has recently resulted in an enormous interest in natural materials, making recyclability and biodegradability important issues for the introduction of new materials and products. Among natural polymers, pectins are particularly attractive. They are complex carbohydrates that occur in ripe fruits and certain vegetables. Fruits rich in pectin are the peach, apple, citrus fruits, currant, and plum (Coffin & Fishman, 1994; Suvorova, Tyukova, Smirnova, & Peshekhonova, 2003). Structurally the pectic polysaccharides are a heterogeneous grouping, showing substantial diversity with botanical origin. They are based on chains of linear regions of 1,4-α-D-galacturonosyl units and their methyl esters, interrupted in places by 1,2-α-L-rhamnopyranosyl units (Hill, Ledward, & Mitchell, 1998). Pectin is a secondary product of fruit juice, sunflower oil, and sugar manufacture. As food processing industry wastes, pectin is therefore a very good candidate for eco-friendly biodegradable materials. Poor water resistance and low strength, however, are limiting factors for the use of materials manufactured only from natural polymers, and hence they are often blended with other polymers (Alves, Costa, & Coelhoso, 2010; Kaczmarek, Bajer, Galka, & Kotnowska, 2007; Kaczmarek, Dabrowska, & Vukovic-Kwiatkowska, 2011; Kowalonek & Kaczmarek, 2010). An alternative way to overcome this problem is to modify natural polymers by incorporation of inorganic fillers, at the nanometric level, that can further extend their applications in more special or severe circumstances. Several nanocomposites have been prepared and analysed utilizing pectins and different inorganic fillers (i.e. ZnO; clays; halloysite, hydroxyapatite) and physical properties studied (Cavallaro, Donato, Lazzara, & Milioto, 2011; Jari, Tekla, Jaakko, Unto, & Ali, 2010; Junjie et al., 2011; Mangiacapra, Gorrasi, Sorrentino, & Vittoria, 2006; Shi & Gunasekaran, 2008). Interesting inorganic layered fillers are layered double hydroxides (LDHs) for which the possibility of substituting the internal anions, by simple of ionic exchange procedure, makes them ideal solids to be used as host of potentially active molecules having a negative charge. LDH can be prepared with simple procedures and high level of purity, they are also economic and eco-compatible (Bugatti et al., 2010, 2011; Costa, Leuteritz, Meinl, Wagenknecht, & Heinrich, 2011; Herrero, Martinez-Gallegos, Labajos, & Rives, 2011; Huang, Zhuo, Wang, & Wang, 2011; Kotal, Srivastava, Bhowmick, & Chakraborty, 2011; Manzi-Nshuti et al., 2009; Rives, 2001; Wang et al., 2011; Yuan, Zhang, & Shi, 2011). Nanocomposites based on LDH and pectins have been reported by Darder, Lòpez-Blanco, Aranda, Leroux, and Ruiz-Hitzky (2005). They were prepared by intercalation of anionic pectins into LDH based of Zn and Al. The biopolymer-LDH nanocomposites have been incorporated in

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carbon paste or PVC matrixes for the development of potentiometric sensors, being tested as active phases of such devices for the recognition of calcium ions. In the present paper we report the preparation and characterization of novel systems, formed by LDH intercalated with benzoate (Bz) and benzoate derivatives: 2,4-dichlorobenzoate (DCBz), p-hydroxybenzoate (p-OHBz) and o-hydroxybenzoate (o-OHBz), having antimicrobial properties, and dispersed into pectins from apple, for potential food packaging application, in particular dry foods and/or lyophilized products. The benzoate and benzoate derivatives are used as food preservatives and show toxicity at very high levels (CICAD, 2000; Joint FAO/WHO Expert Committee on Food Additives, 1961). The preparation and the analysis of thermal, mechanical and barrier properties of films obtained from pectins and the 5 wt.% of nanohybrids containing the four molecules with antimicrobial activity were carried out. It is well known that natural polymers, like pectins, generally do not melt on increasing the temperature, but undergo thermal degradation, so it is not allowed to prepare pectin based nanocomposites using the traditional melt mixing technique. For this purpose we utilized high energy ball milling to mix nanohybrids and pectin powders; such technique has been already successfully used to prepare nano bio-composites pectins-clays with improved mechanical ad barrier properties (Mangiacapra et al., 2006).

2. Experimental

2.1. Materials

Pectin from apples was purchased from Sigma Aldrich in powder form. The molecular weight is 30,000–100,000 and the degree of esterification about 70–75%, on a dry basis, total impurities $\leq$10% water, CAS Number: 9000-69-5. The nanohybrids were synthesized using a previously reported procedure through the urea method (Costantino et al., 2009). Starting from hydrolysis of urea it was obtained the hydrotalcite carbonate form (LDH-CO_3), then via anion exchange procedure the chloride form (LDH-Cl) and finally the nitrate form (LDH-NO_3). Benzoate and benzoate derivatives anions were intercalated between the LDH-NO_3 layers by ion-exchange procedure. The active molecules and the relative amount (w/w, %), evaluated by TGA analysis, are: Benzoate (Bz) 1.31%, 2,4-dichlorobenzoate (DCBz) 2.12%, para hydroxybenzoate (p-OHBz) 1.79%, and ortho hydroxybenzoate (o-OHBz) 1.6%.

2.2. Composites and film preparation

Samples based on pectin and hydrotalcite (vacuum dried for 24 h) at 5% (w/w) of nanohybrids were prepared by dissolving the powder of pectin and LDHs, in weight ratio 95:5 (pectin: LDH), in 30 ml of distilled water and left stirring at 50 °C for 15 min. Nanohybrids LDHs-Active molecules, the pectin powders and water, were milled at room temperature in a Retsch (Germany) centrifugal ball mill (model S 100), using a cylindrical steel jar of 50 cm^3 with 5 steel balls of 10 mm of diameter. The rotation speed used was 580 rpm and the milling time was 1 h. The mixtures obtained were evaporated slowly in Petri dishes. Films of pure pectin were obtained in the same described experimental conditions. All films, having the same thickness $\cong$200 μm, were dried in a vacuum oven at about 10^{-2} mmHg, at room temperature for 5 days.

2.3. Methods of analysis

Wide-angle mode X-ray diffraction patterns, with nickel filtered Cu Ka radiation, were obtained, in reflection, with an automatic Bruker D8 Advance diffractometer.

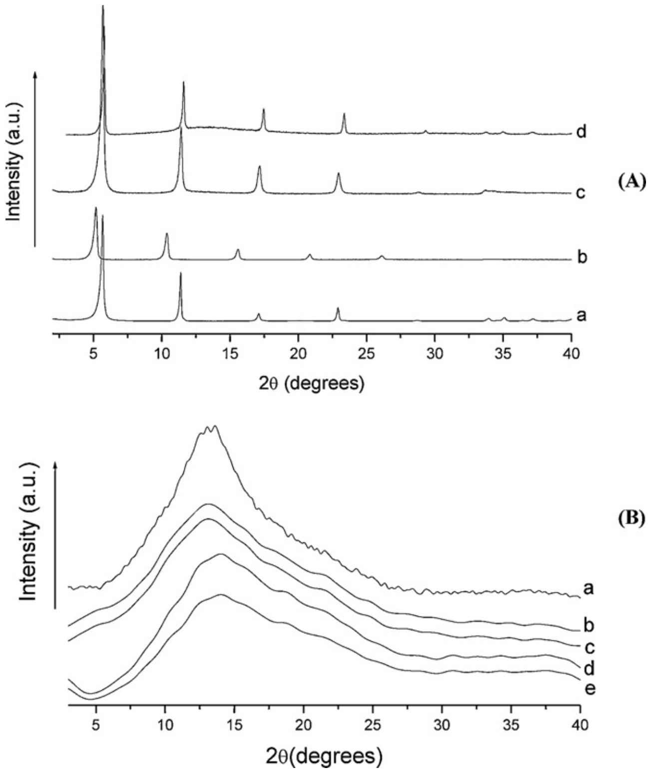


Fig. 1. X-ray diffraction patterns of (A): (a) LDH-Bz, (b) LDH-DCBz, (c) LDH-o-OHBz, (d) LDH-p-OH-Bz; and (B): (a) Pectin, (b) Pectin/LDH-Bz, (c) Pectin/LDH-DCBz, (d) Pectin/LDH-o-OHBz, (e) Pectin/LDH-p-OHBz.

Thermogravimetric analyses (TGA) were carried out from 30 to 900 °C (heating rate of 5 °C/min) under air flow, using a Mettler TC-10 thermo-balance.

Mechanical properties of the samples were evaluated at room temperature and ambient humidity (about 50%) using a dynamometric apparatus INSTRON 4301. Experiments were conducted at room temperature with the deformation rate of 2 mm/min. The initial length of the samples was 10 mm. Elastic modulus was derived from the linear part of the stress–strain curves, giving to the samples a deformation of 0.1%. Data was averaged on five samples.

Barrier properties of water vapour were evaluated using conventional McBain spring balance system, which consists of a glass water-jacketed chamber serviced by a high vacuum line for sample degassing and vapour removal. Inside the chamber, samples were suspended to a helical quartz spring supplied by Ruska Industries (Houston, TX) having a spring constant of 1.62 cm/mg. The temperature was controlled to 30 ± 0.1 °C by a constant temperature water bath. Samples were exposed to the water vapour at fixed pressures, P, giving different water activities $a = P/P_0$, where P_0 is the saturation water pressure at the experimental temperature. The spring position was recorded as a function of time using a cathetometer. The spring position data were converted to mass uptake data using the spring constant, and the process was followed to a constant value of sorption for at least 24 h. Data averaged on three samples.

3. Results and discussion

3.1. X-ray analysis

Fig. 1(A) shows X-ray analysis of all nano-hybrids. The basal peaks for nanohybrids are at $2\theta = 5.7^\circ$ for LDH-Bz, at $2\theta = 5.17^\circ$ for LDH-DCBz, at $2\theta = 5.68^\circ$ for LDH-o-OHBz and at $2\theta = 5.7^\circ$ for LDH-p-OHBz. Fig. 1(B) displays the X-ray diffraction patterns of: (a) pure pectin, (b) pectin/LDH-Bz, (c) pectin/LDH-DCBz, (d) pectin/LDH

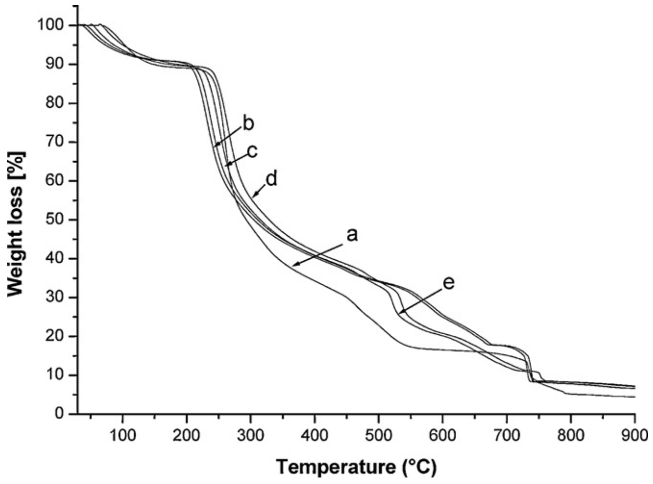


Fig. 2. TGA analysis of (a) Pectin, (b) Pectin/LDH-Bz, (c) Pectin/LDH-DCBz, (d) Pectin/LDH-o-OHBz, (e) Pectin/LDH-p-OHBz.

-o-OHBz, (e) pectin/LDH-p-OHBz. Pure pectin presents a broad peak located at about 13° of 2θ. Such structure is retained in all the composites. The absence of any other diffraction peak in the composites induces to affirm that, in the used milling conditions, complete delamination of LDH layers was reached for the four nanohybrids. We totally exclude that the pectin pattern could hide the peaks of LDH complexes, due to the much higher diffraction intensity of the crystalline nano-hybrids respect to the amorphous pectin.

3.2. Thermogravimetric analysis (TGA)

Fig. 2 reports the thermogravimetric analysis in air flow, to better simulate the ambient conditions of degradation, evaluated on all the nanocomposites. The aim was to determine both the content of the inorganic component in the composites and the degradation temperatures. Pure pectin was also submitted to TGA test. Pure pectin presents a characteristic three-step thermal degradation: the first one, occurring at about 80 °C, corresponds to the water loss and can be evaluated as 10% of the initial mass; then, it is followed by the second step, between 200 and 400 °C. In this temperature range, it has been reported that the degradation, covering about 60% of mass loss, is primarily derived from pyrolytic decomposition (Einhorn-Stoll & Kunzek, 2009a, 2009b). It consists in a primary and secondary decarboxylation. The third step between 500 and 700 °C corresponds to the oxidation region. In the nanocomposites we observe that the first step is slightly anticipated and reduced. This could be an indication that the composite samples have a lower amount of absorbed water in the same storage conditions as pure pectin, such water seems to be less bonded to the polymer. The second (after about 250 °C) and the third degradation steps appear delayed in all the composites. The presence of the nanohybrids helps the pectin to degrade at higher temperatures. We observe a degradation temperature at 50% of weight loss for pure pectin at 293 °C, and at 305 °C for pectin/LDH-Bz, at 310 for pectin/LDH-DCBz, at 314 °C for pectin/LDH-p-OHBz and at 328 °C for pectin/LDH-o-OHBz. Such improvement could be due either to the LDH layers that create a more tortuous path lowering the diffusion of oxygen, or with a protecting effect of LDHs increasing the thermal stability of the biopolymer. Such increasing of thermal stability is a confirmation of a strong interaction between the pectin and the inorganic phase.

3.3. Mechanical properties

The elastic modulus, E (MPa), of the milled pectin, and the pectin-nanohybrid composites, evaluated soon after the removal from the vacuum oven, are compared in Fig. 3. In general, the tensile modulus of a polymeric material has been shown to be remarkably improved when nanocomposites are formed with layered silicates. In the case of milled samples, considering that the mechanical degradation of the chains backbone, due to the milling action, can be assumed equal for the three samples, we can observe the effect of the LDH-hybrids into the pectin matrix. It is evident an increasing of E (MPa) in all the nanocomposites. The higher value of elastic modulus is reached for nanohybrid having p-OHBz as active molecule. More likely, for the pectin nanocomposites, the extent of the improvement of the modulus does not depend only upon the degree of exfoliation, but from the interaction with the host molecule. The higher modulus exhibited from composites with LDH/p-OHBz filler could be attributed to the stronger interactions between pectin matrix and nanohybrid layers via formation of hydrogen bonds, better favoured by the p-OHBz molecule.

3.4. Transport properties of water vapour

In order to determine how the nature of the inorganic phase in a hybrid composite affects the permeability, the transport properties were measured for all the samples using water vapour. In the present case we have biphasic isotropic systems for which we assume that the continuous phase is the only permeable one, in addition we can compare very similar fillers with the same type of dispersion. Measuring the increase of weight with time, for the samples exposed to the vapour at a given partial pressure, it is possible to obtain the equilibrium value of sorbed vapour, $C_{eq}(g_{solvent}/100\,g_{polymer})$. Moreover, in the case of Fickian behaviour, that is a linear dependence of sorption on square root of time, it is possible to derive the mean diffusion coefficient from the linear part of the reduced sorption curve, reported as C_t/C_{eq} versus square root of time, by Eq. (1) (Vieth & Amini, 1974):

$$\frac{C_t}{C_{eq}} = \frac{4}{d}\left(\frac{Dt}{\pi}\right)^{1/2} \qquad (1)$$

where C_t is the penetrant concentration at the time t, C_{eq} the equilibrium value, d (cm) the thickness of the sample and D (cm^2/s) the average diffusion coefficient. All the samples showed a Fickian behaviour during the sorption of water vapour at different activities. Using Eq. (1) it was possible to derive the diffusion coefficient, D, at every fixed vapour activity ($a = P/P_0$), and the equilibrium concentration of solvent into the sample, $C_{eq}(g_{solvent}/100\,g_{polymer})$. For polymer–solvent systems, the diffusion parameter is usually not constant, but depends on the vapour concentration, according to the empirical equation:

$$D = D_0 \exp(\gamma C_{eq}) \qquad (2)$$

where D_0 (cm^2/s) is the zero concentration diffusion coefficient (related to the fractional free volume and to the microstructure of the polymer); γ is a coefficient, which depends on the fractional free volume and on the effectiveness of the penetrant to plasticize the matrix (Gorrasi et al., 2003). Fig. 4 reports the sorption isotherms of the composites with the different nano-hybrids in the range of vapour activity (P/P_0) between 0.2 and 0.6. For comparison the curve of pure pectin is also displayed. The sorption curve of the pure pectin follows the classical dual sorption behaviour: at low activity (up to $a = 0.2$), a rapid increase in vapour concentration, followed by a linear dependence indicates that besides the normal dissolution process the sorption of the polar solvent occurs on preferential sites, in which the molecules are adsorbed and/or

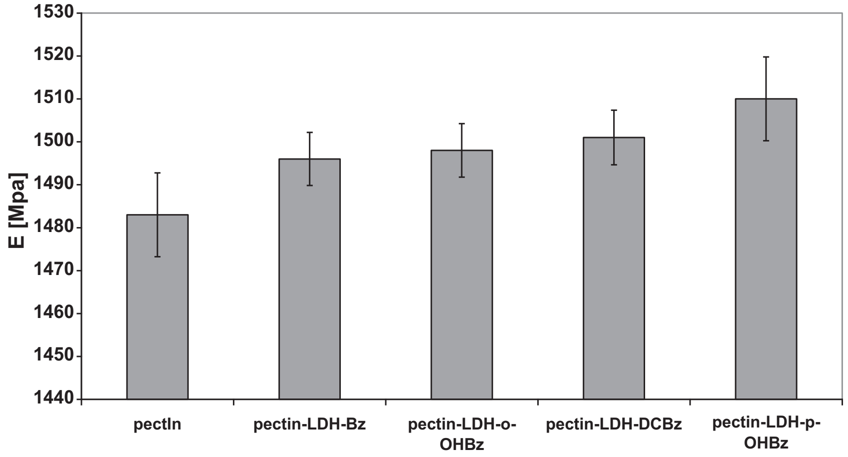


Fig. 3. Elastic moduli evaluated on pure pectin and nano composite films.

immobilized. It is generally assumed that these specific sites on the matrix have a finite capacity. At higher activities, the presence of water molecules determines the plasticization of the matrix, and we observe a transition in the curve, followed by an exponential increase in vapour concentration. The isotherms of the composites follow the same trend as pectin, although showing a higher water uptake in the whole investigated activity range. This behaviour is strictly related to the hydrophilicity of the inorganic lamellae, and determines a significant dependence of water sorption on the LDH content. The plasticization effect of water, above activity 0.4 is evident, according to Flory–Huggins mode of sorption. According to such mode of sorption there is preference for the formation of penetrant–penetrant pairs, so that the solubility coefficient continuously increases with activity. The first molecules sorbed tend to locally loose the polymer structure and make it easier for the following molecules to enter. These isotherms are observed when the penetrant effectively plasticizes the polymer, being a strong solvent or swelling agent for the polymer. Table 1 reports the equilibrium concentration of water vapour $C_{eq}(g_{solvent}/100\,g_{polymer})$ at activity 0.2, because we are sure to be in ideal conditions and all samples follow Henry's law, for all the analysed samples. Values for composites filled with LDH-Bz and LDH-DCBz are significantly higher than the pure pectin, this is due to the high hydrophilic nature of hydrotalcites and to the fact that the mechanism of sorption, particular at low activity, is mainly influenced by the availability of the hydrophilic sites to the water molecules. Sorption at $a = 0.2$ for LDH-o-OHBz is slightly higher than the pure pectin, and the same of the pure pectin for the sample filled with LDH-p-OHBz. Such trend is shown in all the investigated activity range. These results indicate a better interaction between active molecules having —OH groups and pectin matrix, that reduces the availability of hydrophilic sites to water molecules.

Table 1
Transport parameters extracted from the curves of Figs. 4 and 5.

Sample	C_{eq} (g/100 g) at $a = 0.2$	D_0 (cm^2/s)
Pectin	4.00	2.30×10^{-8}
Pectin/LDH-Bz	7.50	1.97×10^{-8}
Pectin/LDH-DCBz	7.81	3.10×10^{-9}
Pectin/LDH-o-OHBz	5.00	3.20×10^{-9}
Pectin/LDH-p-OHBz	3.98	1.35×10^{-9}

Fig. 5 reports the diffusion coefficients, D (cm^2/s), as function of C_{eq} (g/100 g) of sorbed water for all samples. It is observed an exponential dependence of the diffusion on concentration for all the samples, that allows us to extrapolate to zero vapour concentration and obtain the thermodynamic diffusion coefficient, D_0, according to Eq. (2). The numerical values of D_0 (cm^2/s) are listed in Table 1. They tend to decrease with LDH-hybrids, reaching the

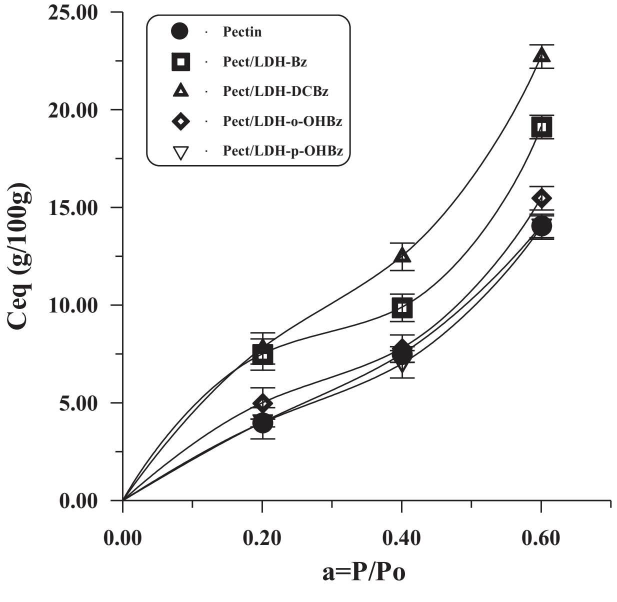


Fig. 4. Sorption isotherms of water vapour of pure pectin and composites with different Nanohybrids.

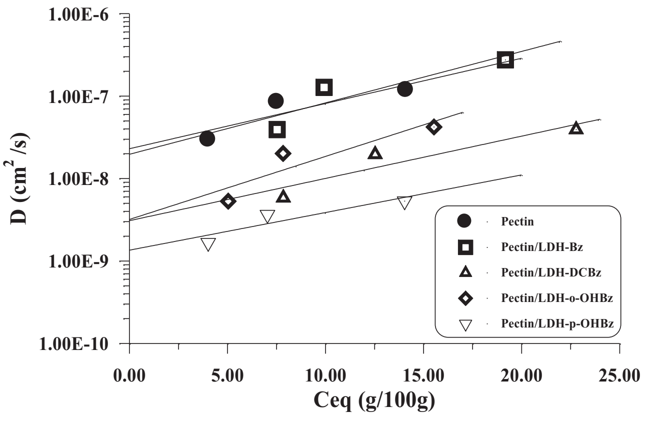
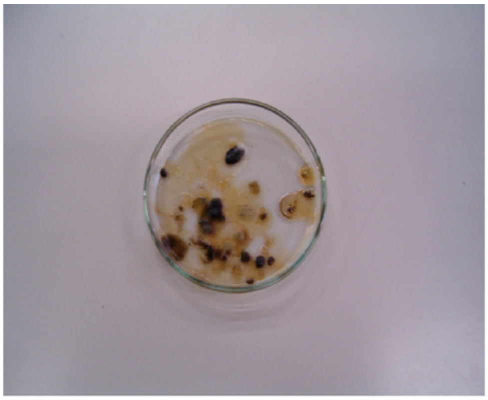
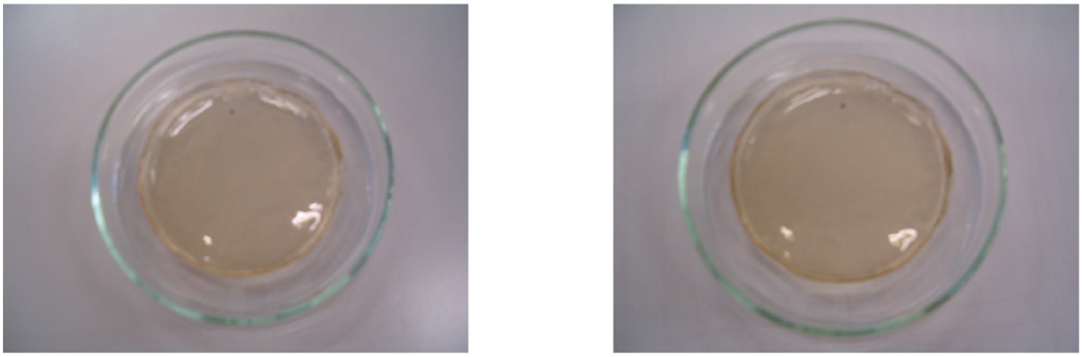


Fig. 5. Diffusion coefficients of water vapour as function of C_{eq}(g/100 g) for pure pectin and composites with different nanohybrids.

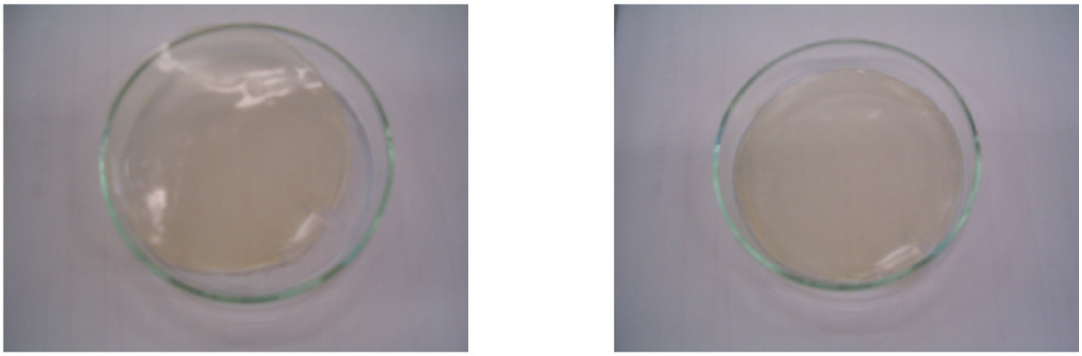


Pectin



Pectin/LDH-Bz

Pectin/LDH-DCBz



Pectin/LDH-p-OHBz

Pectin/LDH-o-OHBz

Fig. 6. Pictures from cast film of pectin and composites with nanohybrids after storage 12 months at ambient temperature.

minimum value for sample Pectin/LDH-p-OHBz. As already discussed, not only the amount of filler and degree of dispersion, but also the interaction with the continuous polymer phase has an important influence also on the kinetic parameter.

3.5. *Antimicrobial behaviour*

Antimicrobial activity of the nanocomposite films were examined by storing them at room temperature and humidity conditions along with the control pectin films. Fig. 6 shows pictures taken on pectin and nanocomposite films after 12 months of storage at room temperature (i.e. 20–30 °C) and environmental humidity (i.e. 30–60%). Mould formation has been noticed in the pectin films after 2 weeks of storage, but no such indication in the nanocomposite films even after 12 months. These results clearly suggest the potential of utilizing pectin films enriched with LDH intercalated antimicrobial compounds as novel packaging materials. Work is in progress, using different amount of antimicrobials, in order to evaluate a threshold value of inhibitory concentration.

4. Concluding remarks

Novel nanocomposites of apple peel pectins with 5 wt.% of nanohybrid fillers based on layered double hydroxide (LDH) containing molecules with antimicrobial activity: benzoate (Bz), 2,4-dichlorobenzoate (DCBz), para hydroxybenzoate (p-OHBz) and ortho hydroxybenzoate (o-OHBz) were prepared through high energy ball milling (HEBM) in the presence of water. Milled composites and water were cast in Petri dishes and films obtained and analysed.

- X-ray analysis showed the absence of the peak corresponding to the basal spacing of the LDH hybrids in the composite samples, suggesting the exfoliation of the filler in all cases.

- Thermogravimetric analysis showed that the presence of the nanohybrids helps the pectin to degrade at higher temperatures for a protecting effect of LDH on the biopolymer.
- Elastic moduli of nanocomposites are higher than that exhibited from pure pectin and is higher composites with LDH/p-OHBz, probably for a stronger interactions between pectin matrix and nanohybrid layers via formation of hydrogen bonds, better favoured by the p-OHBz molecule.
- Barrier properties to water vapour indicated the best improvement for composite with p-OHBz molecule, confirming that the interaction filler-continuous polymer phase has an important influence also on sorption and diffusion.
- Prepared films showed antimicrobial activity, indicating the potential application of prepared complexes in the packaging field and open new perspectives in using pectins-antimicrobials as coating agents for a wide number of packaging polymers.

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