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Biodegradable nanocomposites obtained by ball milling of pectin and montmorillonites

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Abstract

Two composites of apple peel pectin with 3% of either a natural or an organically modified montmorillonite clay, were prepared using a new alternative method, that relies on solid-state mixing at room temperature high energy ball milling(HEBM). This technique involves an efficient mixing of the organic and inorganic components by mechanical grinding. The milled powders were cast by water as films and characterized. The absence of the peak, corresponding to the basal spacing of the clay, in the X-ray diffractograms of the composite samples allowed us to suggest that the dispersion of the clay inside the pectin matrix takes place with the exfoliation of the clay sheets. The physical properties such as thermal degradation, elastic modulus, sorption and diffusion of water vapour and oxygen were analysed. It was found that they all were improved in the nanocomposites, in particular in the sample containing the natural sodium montmorillonite.

Keywords: Pectin; Ball milling; Biodegradable polymer; Nanocomposites

1. Introduction

Environmental legislation as well as consumer demand has recently resulted in a renewed interest in natural materials, making recyclability and biodegradability important issues for the introduction of new materials and products. One of the more promising approaches to overcome these problems is the use of annually renewable resources, for obtaining biodegradable polymers useful for various applications in medical, agriculture, drug release and packaging fields.

Among natural polymers, pectins are white, amorphous, complex carbohydrates that occur in ripe fruits and certain vegetables. Fruits rich in pectin are the peach, apple, currant, and plum (Coffin and 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 (Mitchell, Hill, & Ledward 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.

Plasticized blends of pectin and poly(vinyl alcohol) or high amylase starch provide strong, flexible films, which can be used as water-soluble pouches for detergents and insecticides or medical delivery system devices (Fishman, Coffin, Konstance, & Onwulata, 2000; Fishman, Coffin, Onwulata, & Konstance 2004).

An alternative way to overcome this problem is to modify natural polymers by incorporation of inorganic fillers that can further extend their applications in more special or severe circumstances.

In the last few years, great attention has been devoted to hybrid organic-inorganic systems, and, in particular, to those in which layered silicates are dispersed at a nanometric level in a polymeric matrix (Giannelis, 1996). Such nano-hybrids

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composites possess very unusual properties, very different from their microscale counterparts. They often show improved mechanical and oxidation stability, barrier properties, decreased solvent uptake, self-extinguishing behaviour and, eventually, tuneable biodegradability (Le Baron, Wang, & Pinnavaia, 1999).

Generally, in order to obtain nanocomposites, intercalation of polymer chains between silicate layers is done by using one of the following two approaches: (1) introduction of suitable monomers in the silicate galleries and subsequent polymerization or (2) direct incorporation of polymer chains between the silicate layers from either solution or melt (Giannelis, 1996; Le Baron et al., 1999; Alexandre and Dubois, 2000). Natural polymers like pectins, generally do not melt on increasing the temperature, but undergo thermal degradation. Therefore all the methods of clay incorporation in the melt are excluded. On the other hand, the use of solvents alone can often result useless for obtaining the clay exfoliation. Also the solvent elimination from the final product, due to the gelation property can represent a very expensive and delicate stage.

In this paper we propose a new alternative method for the preparation of nanocomposites, which involves a solid-state mixing at room temperature (ball milling) (Sorrentino et al., 2005). Essentially, clay dispersion was promoted by the energy transfer between milling tools (generally balls) and polymer/clay mixture, which in turns results grinded and intimately mixed.

Among the available techniques used for nanocomposites preparation, ball milling has the considerable advantage of not requiring the use of high temperature or solvent treatments.

In this paper we report the preparation and the physical (thermal, mechanical/barrier) properties of new nanocomposites obtained from natural pectins and two different commercially available clays (a sodic montmorillonite and an organically modified one) by using high energy ball milling (HEBM) technology.

2. Experimental

2.1. Materials

The apple peel Pectin were purchased by Fluka. It is a powder sample with high molecular weight (30,000–100,000) and a high degree of esterification (70–75%) on a dry basis.

Two different commercial montmorillonite were used as filler: a not modified Montmorillonite (Nanofil 757) and an organophilic clay modified with Stearyl-dietoxamine (Nanofil 804); both were kindly supplied by Sud Chemie, and used as received.

2.2. HEBM experiments

During a ball milling process, the energy supplied during each impact determines, in principle, polymer particles size reduction, clay agglomerates size reduction, chemical reactions, phase transformations, clay dispersion into the polymeric network and heat dissipation (Benjamin, 1970; Magini et al., 1993; Padella et al., 1998). Each of these events has different effect on final properties of the polymer mixture. It means that operating conditions such as: process time, number and mass of balls, cooling liquid temperature and engine regime must be accurately selected in order to obtain a nano-metric dispersion having good mechanical and barrier properties.

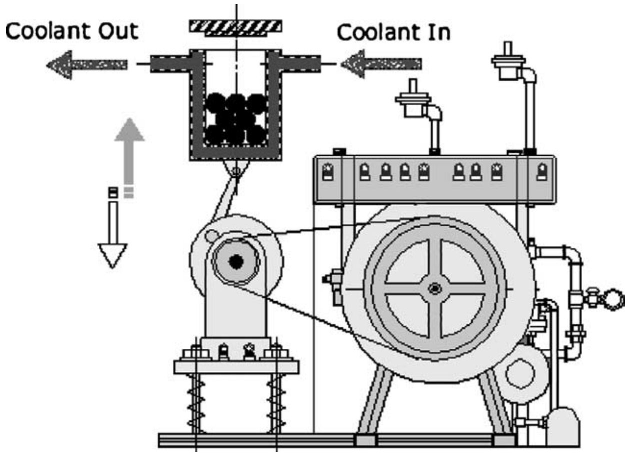

Fig. 1. Schematic representation of the homemade ball milling apparatus.

In our case, the montmorillonite and the pectin powders were mixed in the proper weight ratio in a stainless steel vial. In the vial 50 g of tungsten carbide balls were added. The vial was then hermetically closed and placed on a homemade apparatus (Fig. 1), where the powder was milled for a time of 15 min. To avoid excessive heating of the apparatus as well as of the milled powders, every 5 min of active milling action was followed by an equivalent period of rest. The vial was equipped with an external jacket, where a cooling liquid circulation helps to avoid excessive heating of the milling system.

2.3. Film preparation

Sample films were prepared by dissolving unfilled and nanocomposites pectin powder (400 mg) in 40 ml distilled water and stirring at 70 °C for 30 min.

The resulted solutions were cast in plastic Petri dishes (diameter 6 cm) and dried in a vacuum drying for 3 days at room temperature. After that, the films were removed from the Petri dishes and stored in a dessicator at room temperature for 5 days.

In the following films obtained from casting of unfilled milled pectin will be named ‘Pectin’, film obtained from pectin filled with the unmodified clay (Nanofil 757) will be coded as ‘PN757’, finally film obtained from pectin filled with organically modified clay (Nanofil 804) will be coded as ‘PN804’.

Particular attention, especially with ‘PN804’, was dedicated to keep the viscosity of the solution sufficiently high in order to prevent pectin/clay segregation during film casting.

3. Methods

Thermogravimetric analyses (TGA) were carried out from 25 to 900 °C (heating rate of 10 °C/min) under either air flow or nitrogen, using a Mettler TC-10 thermo-balance.

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

The mechanical properties of the samples were evaluated from stress–strain curves obtained using a dynamometric apparatus INSTRON 4301. The experiments were conducted at room temperature with the deformation rate of 2 mm/min. The initial length of the samples was 10 mm. Elastic moduls was derived from the linear part of the stress–strain curves, giving to the sample a deformation of 0.1%.

The transport properties (sorption and diffusion) were measured by microgravimetric method, using a quartz spring balance having an extension of 1.62 cm/mg. The permeant was water vapor. Sorption was measured as a function of vapor activity $a = P/Po$ where P is the actual pressure (in mmHg) of the experiment, and Po the saturation pressure at 30 °C for water (32 mm Hg).

A Hiden Isochema system, IGA-001, equipped with a controlled environment cell, has been used to perform gas sorption tests at low and high—pressures (from 0.2 to 3 bar).

The sample pan was kept at a constant temperature (25 °C) by means of a water jacket. Before performing sorption tests, the samples were first desiccated into the micro balance at 25 °C under vacuum for 24 h.

4. Results and discussion

4.1. X-ray analysis

Several techniques are used to detect the degree of intercalation/exfoliation of inorganic fillers into polymers, such as X-ray and microscopy (SEM, TEM, AFM). The simultaneous characterization using X-ray and microscopic techniques guarantees that the inorganic phase is present (also when it is completely exfoliated and/or present at very low concentrations); however all our tests started with a X-ray characterization of the samples and concluded with a thermogravimetric analysis in order to ensure a constant composition of all analyzed samples.

Fig. 2 shows, in the interval $2\vartheta = 3-10°$, the X-ray diffractograms of the pristine clay (Nanofil 757) (a), the organically modified clay (Nanofil 804) (b), the film of the powder of pectin and nanofil 804 after 5 min of milling (c), the two nanocomposites obtained after 15 min of milling and subsequent casting process, PN757 (d) and PN804 (e), and finally the composites obtained from casting of PN804 powder after an energetic centrifugation of the aqueous solution. The pattern of the clay Nanofil 757 (a) shows the typical peak at $2\vartheta = 6.5°$ corresponding to the basal spacing of the clay platelets of 1.36 nm.

As expected, the XRD of the organic modified clay (Nanofil 804) (b) shows an expansion of the d spacing due to the intercalation of the organic molecules into the clay galleries. In this case, the main peak is located at $2\vartheta = 4.78°$ corresponding to a basal spacing of 1.84 nm.

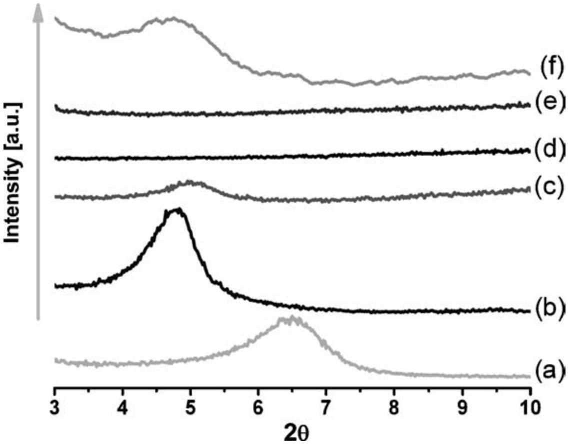

Fig. 2. X-ray diffraction of (a) nanofil 757, (b) nanofil 804, (c) film obtained from pectin powder milled with nanofil 804 for 5 min, (d) film obtained from pectin powder milled with nanofil 757 for 15 min (PN757), (e) film obtained from pectin powder milled with Nanofil 804 for 15 min (PN804), (f) film obtained from Pectin powder milled with Nanofil 804 for 15 min, dissolved in water and centrifuged.

The characteristic peak of the clays starts to decrease gradually in intensity during the milling process. As shown by curve (c) in Fig. 2, an inadequate milling time (5 min in that case) can be evidenced by the presence of a residual peak characteristic of the Nanofil 804. However, the minimum milling time is different for each polymer/clay/milling tools system. In our case, about 10 min are strictly necessary for the complete disappearance of the basal peak in the Pectine/Nanofil 804 system, whereas the Pectine/Nanofil 757 require only 5 min. For comparison purpose, however, both the pectin clay systems were milled for the same time (15 min).

Both the nanocomposites (samples PN757 and PN804) do not show any peak in the range 3–10° corresponding to the basal spacing of the clay. This is a clear indication that, with our processing conditions, we obtained a complete destruction of lamellar morphology of the clay particles with a consecutive dispersion in the polymer matrix.

Is interesting to note that the film resulting from cast process of a dilute solution, prepared and centrifuged, presents again the peak characteristic of the Nanofil 804. It seems to confirm that lamellar morphology destruction is reversible. In other words, during milling carried out with our processing conditions, the clay particles divide preferentially along the basal plane (i.e. in individual sheets) rather than normal to the basal plane. In Fig. 2(f), however, the broad shape and the lower intensity of the peak confirms a more disordered structure with respect to the pristine clay.

This is also an evidence of the fact that the organic modifier is not wholly removed from the clay for milling action.

In Fig. 3, the X-ray diffractograms of the pristine pectin (a), as well as the milled one (b) are shown at higher angles.

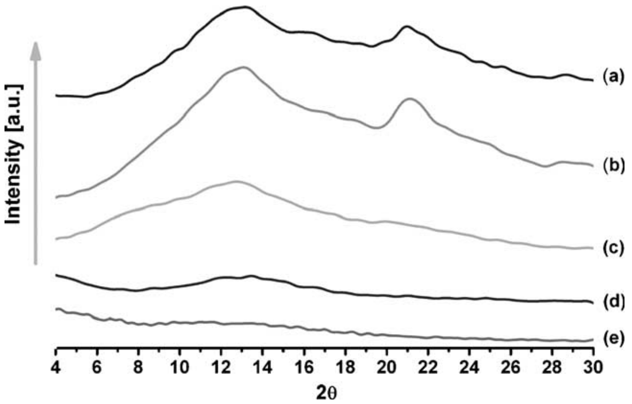

Fig. 3. X-ray diffraction of (a) untreated pectin powder, (b) milled pectin powder, (c) PN804 sample, (d) untreated pectin after film casting, (e) pectin sample.

The curves present two peaks located at about 13 and 21°. The similarity of the curves demonstrates that the milling process did not affect by itself the crystallinity of the pectin. After casting process, the X-ray evidences an amorphous morphology, as shown in curve (e). The casting procedure affects the crystallinity of the two nanocomposites in a similar way. As a matter of fact also in this case the two pectin samples, as evident in curves (c) and (d), present an almost amorphous scattering. Only the first peak at 13°, very broad and of low intensity, appears in the diffractograms. The clay addition does not seem to influence the final level of the sample crystallinity after the casting process.

4.2. Thermogravimetric analysis

The starting materials, clays and pectin, as well as the nanocomposites were analysed by thermogravimetric analysis to determine both the content of the inorganic component in the composites and the degradation temperatures.

Fig. 4 shows the residual mass for the two types of clay used as filler as a function of the temperature. In the case of sodium Momtmorillonite we observe a slight weight loss at 80 °C, due to the evaporation of absorbed water in the clay. The degradation occurs in a wide temperature interval, showing an accelerated drop at about 650 °C. The residual mass after degradation in air is 85%. The thermogram of the organically modified Nanofil 804 does not show the evaporation of absorbed water in the sample. The thermal decomposition occurs in two stages, an accentuated one at a temperature of 280 °C, and a further decrease of weight between 600 and 650 °C. This second stage is very similar to the previous, whereas the first has to be attributed to the organic molecule intercalated in the pristine clay. The residual mass after degradation in air is 68%. It means that the organic surfactant added by supplier never overcomes 35% in the nanoclay.

All the pectin samples, either pure or composites, present a characteristic three-step thermal degradation as shown in Fig. 4. In the pure pectin the first step, occurring at about 80 °C, corresponds to the water loss. It is followed by the second step, between 200 and 400 °C. In this temperature range it was reported that the degradation is primarily from pyrolitic decomposition consisting in a primary and secondary decarboxylation involving the acid side group and a carbon in the ring (Shim, Hajaligol, & Baliga, 2004; Waymack, Belobe, Baliga, & Hajaligol, 2004). The third step between 500 and 700 °C corresponds to the oxidation region.

In the nanocomposites we observe that the first weight loss at 80 °C, due to sorbed water, is slightly lower compared to that shown by pectin. This is a first indication that the composite samples had a lower quantity of absorbed water in the same storage conditions as pure pectin. Moreover the introduction of the inorganic components into the pectin material produced only a slight increasing (3–5 °C) of the evaporation temperature. The second degradation stage is very similar for either pure or composite samples, whereas the third stage is delayed of 30 °C in the case of the PN757 sample. Since this stage was

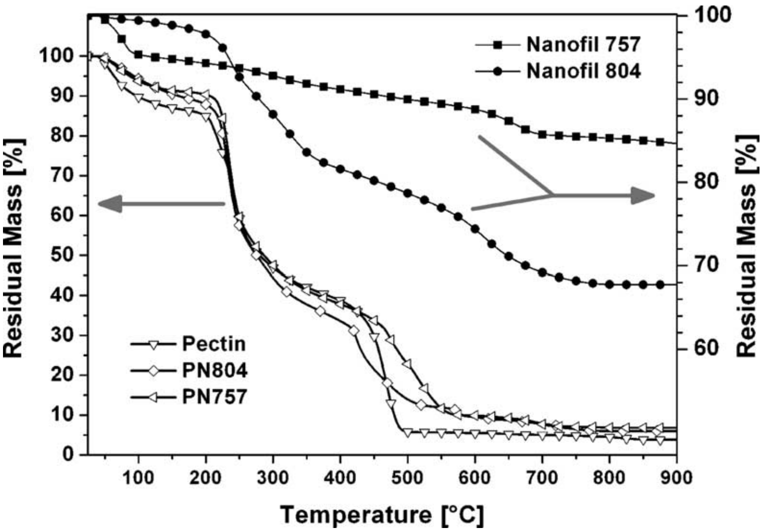

Fig. 4. Thermogravimetric analysis of the samples in flowing air atmosphere.

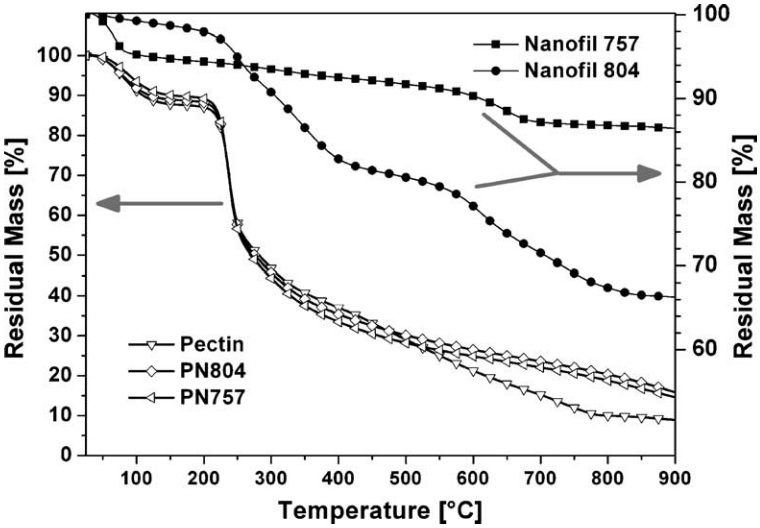

Fig. 5. Thermogravimetric analysis of the samples in flowing nitrogen atmosphere.

attributed to oxidative reactions, this is a first indication of a lower content of oxygen in the composite samples, as we will show later.

The thermal decomposition of pectin samples in nitrogen atmosphere does not show the third step due to the oxidation process (Fig. 5). After the second step, the weight of the three pectin samples continuously decreases with a constant rate, different for each sample. In particular, the milled pectin sample presents the higher weight loss rate. Probably the presence of clay into the polymer matrix (PN757 and PN804 samples) enhances thermal stability by acting as mass transport barrier to the thermo oxidation products coming out of the sample. Generally, the influence of clay on the thermal degradation is not limited to the labyrinth effect of the silicate layers but also by the changes in the crystal morphology. In our case, however, as show by the X-ray analysis, the clay does not seems to influence the final morphology of the samples (Fig. 3), and therefore the effect is to be due to the diffusion decrease of the gases.

4.3. Mechanical properties

The elastic modulus of the milled pectin, and the pectin-clay composites are compared in Fig. 6. 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 clay into the pectin matrix. In any case, one can expect a stronger effect of the grinding procedure on PN757 sample with respect to PN804, due to the presence in this sample of the barrier effect produced by the organic modifier in the clay. As a matter of fact we observe that the addition of the Nanofil 757 greatly improves the elastic modulus of the sample, whereas milling the pectin with Nanofil 804 does not generate a significant improvement in the elastic modulus. Probably, for the pectin nanocomposites, the extent of the improvement of the modulus does not depend only upon the average aspect ratio of the dispersed clay particles. The results seem indicate that the interaction between pectin and clay is a relevant parameter for the stiffness improvement. Indeed the excellent modulus in the case of PN757 can be attributed to the strong interactions between pectin matrix and silicate layers via formation of hydrogen bonds. The organic pendants of the Nanofil 804 probably create an interface between clay sheets and pectin molecules hindering or reducing the formation of hydrogen bonds between them.

4.4. Water vapour diffusion

Composites and nanocomposites are multiphase systems in which the coexistence of phases with different permeabilities can cause complex transport phenomena (Peterlin, 1975). When only one phase is permeable to the penetrant, or shows a much higher permeability than the other phases, one can

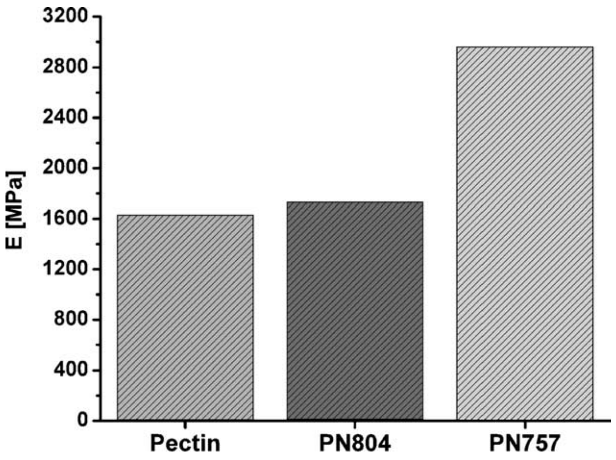

Fig. 6. Tensile modulus of the pectin samples and its nanocomposites counterpart.

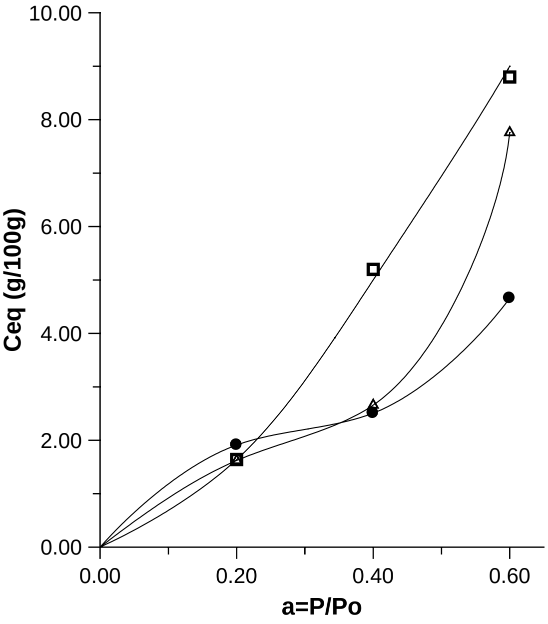

Fig. 7. Sorption isotherm of water vapor for samples: pectin (●), PN804 (▲), PN757(□).

assume that transport only occurs in the permeable phase. This phase is presumed to have the same specific sorption capability, irrespective of the extent of the impermeable phases.

Morphology and microstructure of these multi-phase systems are expected to play a very important role in determining the transport phenomena (Peterlin, 1975; Vieth, & Amini, 1974). On the other hand, the presence of highly dispersed clay platelets ought to increase to a large extent the tortuosity of the system, leading to an expected large decrease in the value of the diffusion coefficient. In some cases, however, the presence of the montmorillonite layers can introduce specific sites in which hydrophilic molecules can be adsorbed and immobilized (Vieth & Amini, 1974).

Fig. 7 shows the equilibrium concentration, C_{eq}(g/100 g), of water vapour as a function of the activity, $a = P/Po$, for the pure pectin (sample Pectin), the nanocomposite with the unmodified clay (sample PN757) and the nanocomposite with the organically modified clay (sample PN804).

The sorption curve of the pure pectin follows classical dual-sorption behaviour (Crank, 1956): at low activity (up to $a=0.2$), a rapid increase of vapour concentration followed by a plateau 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 immobilized. It is assumed that these specific sites on the matrix have a finite capacity. When the preferential sites are occupied the isotherm becomes linear due to the normal vapour dissolution. At higher activities the presence of vapour molecules determines the plasticization of the polymeric matrix and we observe a transition in the curve followed by an exponential increase of vapour concentration.

The isotherm of both nanocomposites follows the same trend of sample Pectin, showing a higher water uptake at activity above to 0.4. The plasticization effect of the water, above activity 0.4, is stronger in the nanocomposites that follow the Flory-–Huggins behaviour (Vieth & Amini, 1974). This behaviour represents a preference for the formation of penetrant-penetrant pairs, so that the solubility coefficient continuously increases with the activity. The first molecules sorbed tend to locally loosen the polymer structure and make it easier for 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.

From the first part of the isotherms, when the sorption can be assumed ideal and following the Henry's law, we derived a sorption parameter (S):

$$S = \frac{dC_{eq}}{dp} \tag{1}$$

where p is the partial pressure of the water vapour.

The numerical values of S are reported in Table 1. Both the nanocomposites show lower sorption respect to the pure pectin sample, at low water activity. Such a result suggests that the polar group of the pectin are less available to the sorption of the water molecules because they are shielded and/or weakly bonded with the clay. However, at high water activity, the structure is more easily opened and plasticized by the entering molecules, and we observe a higher sorption.

For all the composite systems the diffusion coefficient, at different vapour activities, was obtained from a plot of the reduced sorption:

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

where d (cm) is the thickness of the sample, C_t is the water concentration at time t, and C_{eq} is the water concentration at the equilibrium value.

In the case of Fickian behaviour, the reduced sorption curve presents an initial linear behaviour followed by a plateau indicating the equilibrium sorption; from the first linear part the mean diffusion coefficient, D (cm^2/s), for each vapour activity, is obtained.

For polymer-solvent systems, the diffusion parameter is usually not constant, but depends on the vapour concentration, according to the empirical equation:

$$D = D_0 \exp(\gamma C_{eq}). \tag{3}$$

where D_0(cm^2/s) is the zero concentration diffusion coefficient (related to the fractional free volume and to the microstructure

Table 1
Water vapour transport parameters for pectin samples

Sample	S^a (g/100 g mmHg)	$D_0 \times 10^9$ (cm^2/s)
Pectin	9.55	1.08
PN804	8.20	0.967
PN757	8.20	0.482

[a] Evaluated as the slope of the straight line at $a \leq 0.2$ in the C_{eq} versus p (in mmHg) curve.

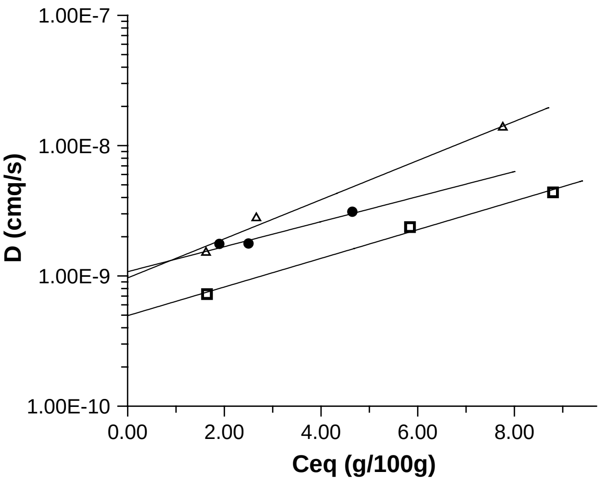

Fig. 8. Diffusion coefficients, D (cm^2/s),as function of C_{eq} (g/100 g) of water vapor for pectin (●), PN804(▲), PN757(□).

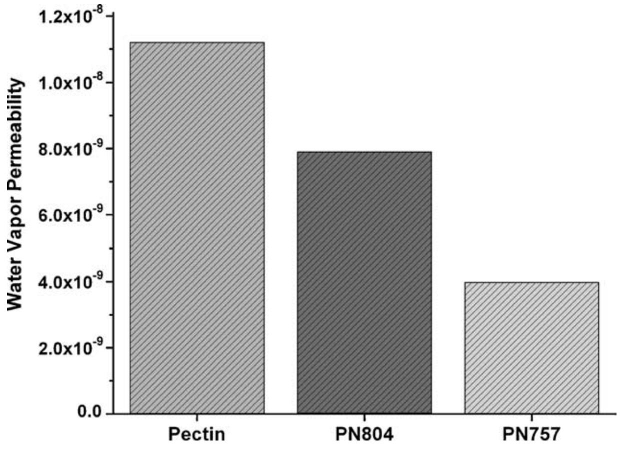

Fig. 9. Permeability to water vapour for the analysed samples.

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.

Fig. 8 shows the diffusion parameter, D (cm^2/s), as a function of the concentration of sorbed water, C_{eq}(g/100 g), for the investigated samples. All the samples show a linear behaviour, following Eq. (3). Therefore the values of D_0 were obtained by extrapolation to zero vapour concentration. The obtained values are reported in Table 1. The extrapolated diffusion parameters of the nanocomposite samples are lower than the pure pectin. The lowest D_0 is shown by the nanocomposite filled with the natural clay (sample PN757). Such a result suggests that the unmodified clay is better dispersed into the continuous matrix than organically modified one, showing more interactions. Thus it constitutes a better barrier to the transport of water molecules in the matrix.

The permeability of the samples to the vapours is calculated as the product of sorption and diffusion:

$$P = D_0 S \tag{4}$$

It represents the thermodynamic P parameter, considering that we use the zero-concentration diffusion coefficient and the derivative of the equilibrium concentration vs. pressure at low vapour pressures. Although it is not a technological parameter, that can be only determined in the use conditions of the material, it is of fundamental importance with the purpose to correlate the physical properties to the structure of the samples.

Fig. 9 shows the permeabilities of the analysed samples. As expected, from the discussed sorption and diffusion results, the permeability of the nanocomposites is lower than the pure pectin, and the sample with improved barrier properties to water vapour is the one filled with the unmodified clay.

4.5. Oxygen gas diffusion

Fig. 10 presents a comparison of oxygen diffusion coefficients determined from kinetic gravimetric sorption in pectin samples at 25 °C. The diffusion coefficients increase with increasing penetrant pressure or concentration, which is in qualitative agreement with the concentration dependence of diffusion coefficients of gas in rubbery polymers. In fact, when the pressure is increased two opposite effects may occur: (i) pressure increase leads to an increase of the polymer density, via polymer compaction, thereby reducing the segmental motions inside the polymer; (ii) concurrently the pressure increase corresponds to an increase of the penetrant concentration in the polymer film. The diffusing molecules can plasticize the macromolecular chains and tend to enhance the diffusion process by increasing the segmental motions.

(Naito, Bourbon, Terada, and Kamiya (1991,1993)) have proposed to describe simultaneously both opposite effects related to pressure, at a given temperature, by the following expression:

$$D(C,p) = D_0 \exp(\beta p + \alpha C) \tag{5}$$

where:

- D_0 is the diffusion coefficient at $C=0$ and $p=0$;
- the term exp (βp) represents the hydrostatic pressure effect, β being a negative term because it expresses the drop of D;

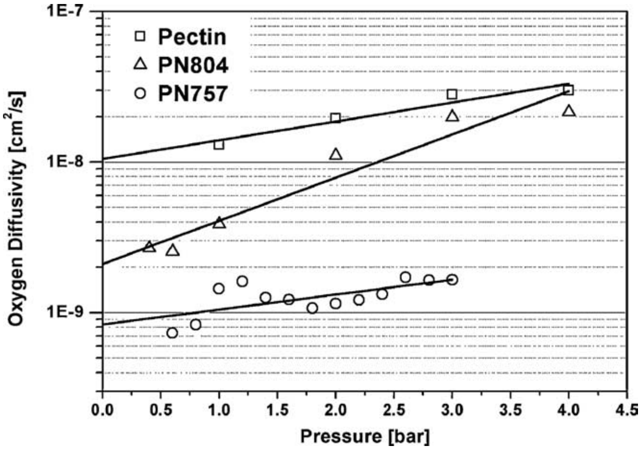

Fig. 10. Diffusion coefficients of oxygen in Pectin samples at 25 °C from kinetic gravimetric sorption experiments.

– the term exp (αC) characterises the increase of dissolved molecules in the polymer resulting from the plasticization, and hence, the more important available free volume.

Extrapolation to zero pressure of the diffusion coefficients reported in Fig. 10 indicates a decrease in oxygen diffusion from 1.05×10^{-8} to 8.34×10^{-10} cm^2/s due to the clay addition. The diffusion coefficients of the samples PN757 and PN804 are systematically lower than that obtained in the pure pectin samples. The pressure effect on the diffusion coefficients, however, shows dissimilar behaviour for the two nanocomposites samples. Sample PN804 presents higher value in the sorption with respect to both the sample PN757 and the pure Pectin sample. Probably, Nanofil 804 layers introduce specific sites in which oxygen molecules can be immobilized, enhancing its plasticization ability on the pectin molecules.

5. Concluding remarks

We have prepared two composites of pectin with 3% of both a natural and an organically modified clay (Montmorillonite), using a new alternative method, that relies on solid-state mixing at room temperature. This technique (High Energy Ball Milling) involves an efficient mixing of the organic and inorganic components by mechanical milling. The mixed powders were cast by water as films and characterized. The absence of the peak corresponding to the basal spacing of the clay in the X-ray diffractograms of the composite samples allowed us to suggest the exfoliation of the clay, due to the procedure of milling. It was found that the physical properties were improved in the nanocomposites, in particular in the sample containing the natural sodium montmorillonite. Indeed the elastic modulus increased from 1630 to 2962 MPa, the oxidation was delayed of 30 °C and the diffusion of water vapour and oxygen was found lower than the pure pectin.

Acknowledgements

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References

Alexandre, M., & Dubois, P. (2000). Polymer-layered silicate nanocomposites preparation, properties and uses of a new class of materials. *Materials Science and Engineering R-Reports*, *28*, 1–11.

Benjamin, J. S. (1970). Dispersion strengthened superalloys by mechanical alloying. *Metallurgical Transactions*, *1*(10), 2943–2951.

Coffin, D. R., & Fishman, M. L. (1994). Physical and mechanical properties of highly plasticized pectin/starch films. *Journal of Applied Polymer Science*, *54*, 1311–1320.

Crank, J. (1956). *The mathematics of diffusion*. London: Oxford University Press.

Fishman, M. L., Coffin, D. R., Konstance, R. P., & Onwulata, C. I. (2000). Extrusion of pectin/starch blends plasticized with glycerol. *Carbohydrate Polymers*, *41*(4), 317–325.

Fishman, M. L., Coffin, D. R., Onwulata, C. I., & Konstance, R. P. (2004). Extrusion of pectin and glycerol with various combinations of orange albedo and starch. *Carbohydrate Polymers*, *57*(4), 401–413.

Giannelis, E. P. (1996). Polymer layered silicate nanocomposites. *Advanced Materials*, *8*(1), 29–35.

Le Baron, P. C., Wang, Z., & Pinnavaia, T. (1999). Polymer layered silicate nanocomposites: An overview. *Applied Clay Science*, *15*, 11–29.

Magini, M., Burgio, N., Iasonna, A., Martelli, S., Padella, F., & Paradiso, E. (1993). Analysis of energy transfer in the mechanical alloying process in the collision regime. *Journal of Materials Synthesis and Processing*, *1*(3), 135–144.

Mitchell, J. R., Hill, S. E., & Ledward, D. A. (1998). *Functional properties of food marcomolecules* (2nd ed.).

Naito, Y., Bourbon, D., Terada, K., & Kamiya, Y. (1993). Permeation of high-pressure gases in poly(ethylene-*co*-vinyl acetate). *Journal of Polymer Science, Part B: Polymer Physics*, *31*(6), 693–697.

Naito, Y., Mizoguchi, K., Terada, K., & Kamiya, Y. (1991). The effect of pressure on gas permeation through semicrystalline polymers above the glass transition temperature. *Journal of Polymer Science, Part B: Polymer Physics*, *29*(4), 457–462.

Padella, F., Incocciati, E., Nannetti, C. A., Colella, C., Casadio, S., & Magini, M. (1998). Mechanically activated low-temperature synthesis of Sr-doped lanthanum manganite. *Materials Science Forum*, *105*, 269–272.

Peterlin, A. (1975). Dependence of diffusive transport on the morphology of crystalline polymers. *Journal of Macromolecular Science-Physics*, *B11*(1), 57–87.

Shim, H-S. , Hajaligol, M. R., & Baliga, V. L. (2004). Oxidation behaviour of biomass chars: Pectin and populus deltoides. *Fuel*, *83*(11–12), 1495–1503.

Sorrentino, A., Gorrasi, G., Tortora, M., Vittoria, V., Costantino, U., Marmottini, F., et al. (2005). Incorporation of Mg–Al hydrotalcite into a biodegradable poly(ε-caprolactone) by high energy ball milling. *Polymer*, *46*, 1601–1608.

Suvorova, A. I., Tyukova, I. S., Smirnova, E. A., & Peshekhonova, A. L. (2003). Viscosity of blends of pectins of various origins with ethylene–vinyl acetate copolymers. *Macromolecular Chemistry and Polymeric Materials*, *76*, 2038–2042.

Vieth, W. R., & Amini, M. A. (1974). In H. B. Hopfenberg (Ed.), *Permeability of plastic films and coatings*. London: Plenum Press.

Waymack, B. E., Belobe, J. L., Baliga, V. L., & Hajaligol, M. R. (2004). Effects of metal salts on char oxidation in pectins/uronic acids and other acid derivative carbohydrates. *Fuel*, *83*(11–12), 1505–1518.