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Production of PVAc–starch composite materials by co-grinding — Influence of the amylopectin to amylose ratio on the properties

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ABSTRACT

Mixtures of polyvinyl acetate (PVAc) filled with two starch types containing different amylopectin to amylose ratios were co-ground in a laboratory tumbling ball mill. The influence of the starch nature and of the co-grinding treatment on the production mechanism and on the composite properties was studied. The thermal and mechanical properties were characterized, as well as the behavior in water.

The presence of starch in the mixture reduces agglomeration phenomena between matrix particles, as well as the mobility of polymeric chains. While a simple mixing of the constituents generates starch concentration points in the matrix, co-grinding favors filler dispersion and PVAc–starch interactions enabling an increase of the mixture properties without adding any chemical agent. The amylopectin to amylose ratio does not affect significantly mechanical properties while a high amylopectin rate promotes water uptake.

1. Introduction

Millions of tons of petrochemical polymer materials are produced each year for life usage. Most of them are used during a short period and become rapidly wastes. These materials are always more expensive. That is why starch filled composite materials were subjects of great interest during these last decades due to the biodegradability and the low price of starch.

A lot of studies are reported in literatures on composites combining starch and various polymers such as polystyrene [1,2], polyethylene [3,4], polyvinyl acetate [5–9], polyvinyl alcohol [10–13], and polylactic acid [14–17]. Different processes are used to produce these materials: blending, chemical synthesis, and extrusion. In most cases, there are no interactions between starch and matrix, leading to low mechanical properties of materials. Indeed starch is hydrophilic while most polymers are hydrophobic or less hydrophilic than starch. To avoid this problem, authors proposed to use compatibilizers, starch modification, grafting, crosslinking, and plasma treatment. Kovacs and Tabi [18], when producing polylactic acid–starch blends by injection molding, found that by using adequate drying conditions, it is possible to develop strong adhesion between starch granules and polylactic acid matrix, without any coupling agent.

Co-grinding is a simple process favoring dispersion of small filler particles in a matrix and interactions between both constituents. This process allows improving the use properties of the materials with regard to a simple mixture, without using any treatment by a chemical agent [19]. It was applied to fill non-degradable or biodegradable matrices with minerals [20], non-degradable polymers [21] or starch [22,23].

Starches contain a mixture of amylose, which has a linear structure, and amylopectin, which has a branched structure, in various proportions depending on the sources [24]. In most studies reported in literatures, authors used only one starch, and few studies were performed on the influence of the amylose to amylopectin ratio on properties. Zhang and Thomas [25] produced blends of polyhydroxybutyrate filled with two starches containing 30 and 72% amylopectin. They concluded that the presence of starch improves thermal, rheological and mechanical properties due to intermolecular hydrogen bonding, and the improvement is more significant with the starch containing the higher amylose rate. Taghvaei-Ganjali et al. [26] studied the effect of amylose to amylopectin ratio on physico-chemical properties of rubber compounds filled by three types of starches with different amylopectin contents. They showed that the filler rubberization is enhanced with high amylopectin contents because of a higher branched structure, what influences the mechanical properties of the mixtures. Zou et al. [27] prepared starch-based superabsorbent polymers using four starches. They studied the effect of the amylose to amylopectin ratio on the grafting reactions and the performance of the mixtures. They noted that the high molecular weight and branched structure of amylopectin reduces the polymer chain mobility and increases the viscosity, resulting in a lower grafting efficiency.

In a previous paper [28], composites of polyvinyl acetate filled with a waxy starch, almost essentially made of amylopectin, were produced by co-grinding. The work was mainly concentrated on the identification of grinding and co-grinding mechanisms, based on the one hand on

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granulometric and morphological analyses and on the other hand on the characterization of surface properties.

In the present study, two starches with different amylose to amylopectin ratios were used as fillers of a polyvinyl acetate matrix and the mixtures were co-ground in a tumbling ball mill during different times. Thermal and mechanical properties, as well as the behavior in water were analyzed.

2. Products, apparatus and experimental procedure

Two types of starch were used in this study. The first one is from waxy maize (Waxilys — Roquette Frères). It is a starch of crystalline type A, containing more than 99% of amylopectin. Grains are of polyhedral shape (Fig. 1a) and the average particle size is 13 μm. The second starch is a Eurylon also issued from corn (Roquettes Frères), but of crystalline type B, containing 70% of amylose and 30% of amylopectin. Grains are rounder than those of Waxilys starch, and they are individualized or form agglomerates, some of them being rather big (Fig. 1b). The average size of the particles is 8.7 μm.

Polyvinyl acetate (PVAc) was gracefully supplied by the society Elotex — Switzerland. It is constituted by particles with a spheroidal shape, which are the result of the agglomeration of small grains produced by emulsion polymerization followed by drying. These spheroid particles can be single or agglomerated between them (Fig. 2, big particles). The average size of the PVAc particles is 120 μm.

In order to understand their own behavior, the three materials were dry milled alone in a 5 L ceramic laboratory tumbling ball mill (Prolabo) containing 20 vol.% ceramic balls with sizes between 5 and 12.5 mm. This range permits to always have an adapted ball to particle size ratio during grinding. The powder proportion in the mill was fixed at 20 vol.% of the interstitial void space between the balls. The rotation speed of the mill chamber was fixed at 100 rpm, corresponding to 75% of its critical rotation speed. Different experiments were performed during various times, and the whole powder was recovered after each experiment to be submitted to different analyses.

Then the same runs were realized with PVAc–Waxilys and PVAc–Eurylon mixtures containing 25 wt.% of starch. This rate was fixed in agreement with previous results [19,22] which indicated that it permits to have better use properties.

3. Characterizations

3.1. Powder analyses

Some analyses were done on powders directly picked up in the mill chamber. Indeed, the particle size distribution, expressed in volume, and the median size, d50, were obtained on dry particles, using a laser diffraction granulometer Mastersizer 2000. The data were treated with the Mie theory. Three measurements were done on each sample and a maximum difference of 0.5 μm was observed between the values of the median size of a sample. Particles were also observed with a scanning electron microscope LEO 435 VP after metallization.

Other particles of the samples were analyzed by differential scanning calorimetry (DSC) using TA instruments Q2000 in nitrogen atmosphere. The temperature was increased between 0 and 200 °C at a rate of 10 °C·min^{-1}. Two cycles were carried out and the thermograms shown refer to the second heating, while the first cycle was used to eliminate any thermal history and moisture content in the samples [29]. The glass transition temperature, Tg, of the matrix was determined from the thermograms. Some analyses were repeated 3 times and the difference between the Tg values was lower than 0.5 °C.

3.2. Analyses on films

For other analyses, films of a thickness around 0.5 mm were molded in a brass mold using a Carver Laboratory Press. Powder was introduced in the mold and heated during 10 min at 150 °C, i.e. above the melting temperature of the matrix. Then a pressure of 69 bars was applied during 30 s. Finally the films were cooled in cold water in order to avoid any crystallization of the matrix.

Test specimens of 25 mm × 5 mm were cut in the films in order to characterize their mechanical properties in traction by means of an apparatus Instron 4301, at ambient temperature and with a cross-head speed of 5 mm·min^{-1}. The initial gap between jaws was adjusted at 10 mm. The force (F) versus elongation was obtained for each sample. The nominal stress (σ) and the nominal strain (ε) were respectively calculated by equations:

$$\sigma = \frac{F}{S_0} \tag{1}$$

$$\varepsilon = \frac{L - L_0}{L_0} * 100 \tag{2}$$

where S_0 is the initial crosssection of the film, L is the sample length and L_0 its initial length. The Young modulus, E, was determined from the tangent slope of the low strain region. The strength (σ_b) and the maximum strain (ε_b) were reported for each sample. Mechanical tensile data were averaged over at least five specimens. The maximum error observed on each parameter was lower than 5%.

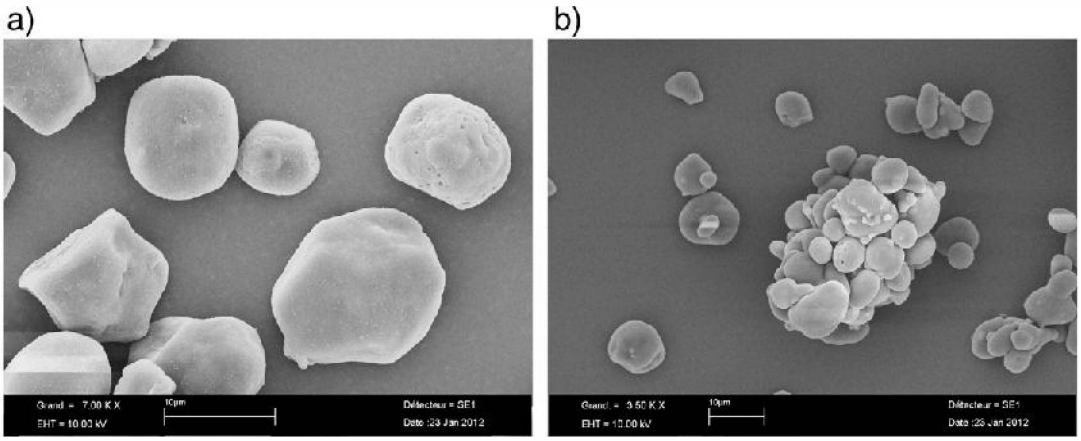

Fig. 1. SEM micrographs of starch particles. a. Waxilys. b. Eurylon.

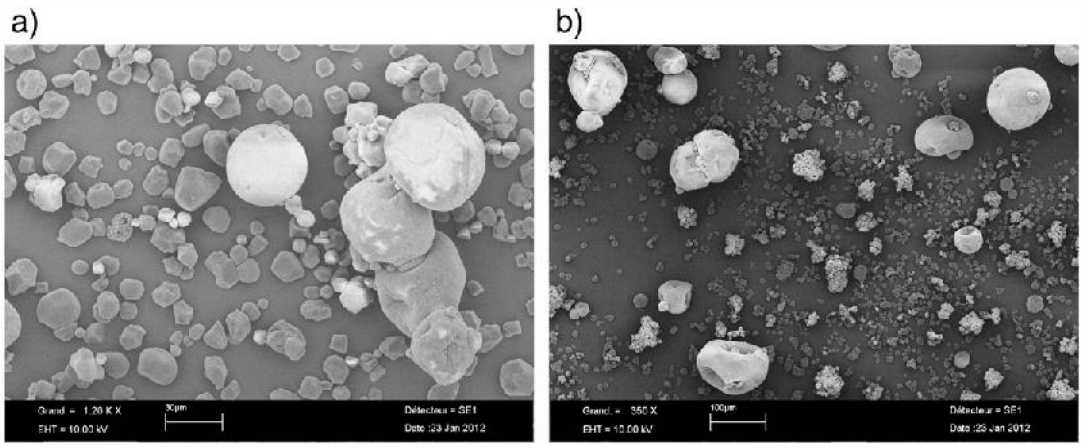

Fig. 2. SEM micrographs of PVAc–starch mixtures before grinding. a. PVAc–Waxilys mixture. b. PVAc–Eurylon mixture.

Films were also cooled in liquid nitrogen and then broken. Their sections were observed with a scanning electron microscope JMS 6100 JEOL after metallization.

Finally, circular pellets with a diameter of 15 mm were cut in films and placed during several months in closed flasks containing distilled water at 22 °C, in order to study their behavior in the liquid. The water was regularly changed and the pellets weighted after removal of water from their surface with an absorbent paper sheet. The water uptake was calculated by equation:

$$WU = \frac{m_t - m_i}{m_i} * 100 \quad (3)$$

where m_i is the initial pellet mass before immersion in water, and m_t the pellet mass after an immersion time t_{imm}. The reproducibility on water uptake was determined on three pellets of some samples for various immersion times and experiments were started at different periods of the year. A difference in WU of less than 2% was observed between the results.

Since error values are indicated in this section for each analysis and are very low, we decided not to report error bars on figures in order to present clearly the results.

4. Experimental results and discussion

4.1. Results of powder analyses

4.1.1. Particle size and morphology

Since these results were developed in details in a previous paper [28] for the PVAc–waxy maize starch mixture, we only synthesize here those necessary for understanding the study presented in this article, and we add data on PVAc–Eurylon mixture.

During their individual grinding, Waxilys particles are not fragmented because their initial size (given in Section 2) is lower than the limit size being able to be reached during macromolecule grinding (few tens of μm) [30]. On the contrary, they even agglomerate and the median size tends to increase slightly to reach 30 μm. As for Eurylon, big agglomerates break during the first minutes. Then one observes the same agglomeration behavior as with the Waxilys starch.

Fig. 3 shows the variation of the median size of PVAc particles ground alone and of the co-ground mixtures.

Concerning the matrix, big agglomerates observed in Fig. 2 are first fragmented at the level of the particle joints to individualize the particles constituting them. Then, the individual particles are fragmented progressively, leading to a decrease of their median size down to 40 μm. When this minimum size is reached, fragment agglomeration occurs and the median size increases. Finally, this one oscillates due to a competition between agglomerate fragmentation and re-agglomeration.

Both PVAc–starch mixtures have the same behavior during co-grinding, but their median size evolves differently from the matrix alone. Indeed, in the mixtures, matrix particle are first broken and those of starch stick on PVAc fragments. This is confirmed by the SEM micrograph of Fig. 4a taken after one hour co-grinding: one can observe big PVAc fragments on which small starch grains are stuck. The median size decreases. Starch coats gradually the PVAc fragments, the fragmentation of which continues. The whole is then compacted under the effect of balls (Fig. 4b and c). However, contrary to what was noted during the grinding of the matrix alone, we observe few re-agglomeration phenomena with mixtures. The median size stabilizes then towards 25 μm. One can say that, in a mixture, agglomeration of starch grains on matrix fragments is favored compared to matrix–matrix fragment agglomeration.

4.1.2. Thermal properties

DSC analyses were done on powders of the two starches, the matrix and the mixtures unground and co-ground at different times, and we focused on the second heating scan.

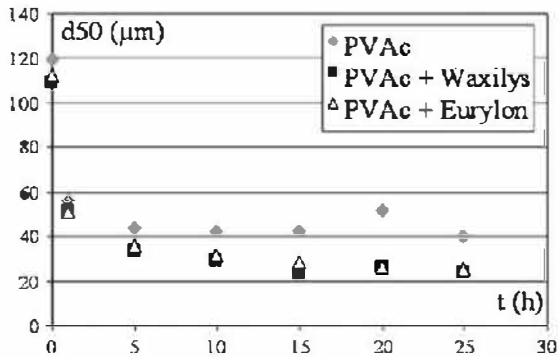

Fig. 3. Variation of the median size of the samples with and without starch during grinding.

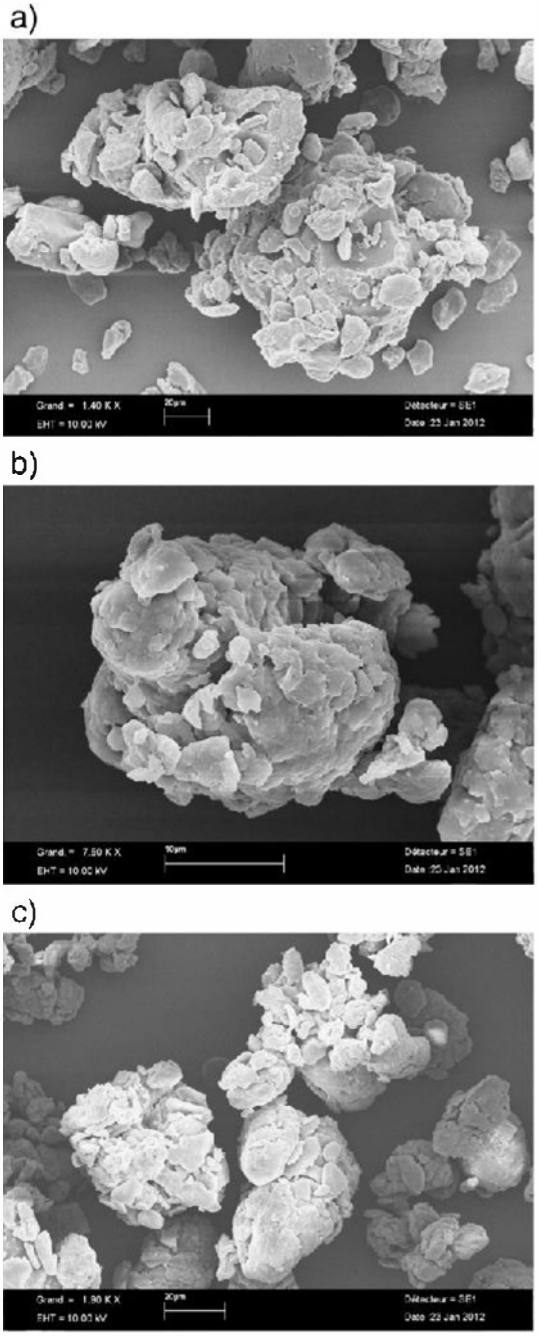

Fig. 4. SEM micrographs of co-ground mixture particles. a. PVAc–Waxilys (t = 1 h); scale = 20 μm. b. PVAc–Waxilys (t = 15 h); scale = 10 μm. c. PVAc–Eurylon (t = 25 h); scale = 20 μm.

As Sreekumar et al. [12] and Othman et al. [29] have already observed previously, the thermograms of both starches are flat.

Fig. 5a gathers PVAc thermograms for three grinding times, while Fig. 5b and c present those of the mixtures for the same times. The samples taken at other times were also analyzed but their thermograms are not presented in these figures to have them clear enough.

One can note on these figures an inflection of the curves at a temperature lower than 50 °C. This corresponds to the PVAc glass transition temperature which was determined from all the thermograms. The values are gathered in Fig. 6.

As for polyvinyl acetate, it was noticed that the glass transition temperature, initially at 40 °C, decreases when grinding is operated.

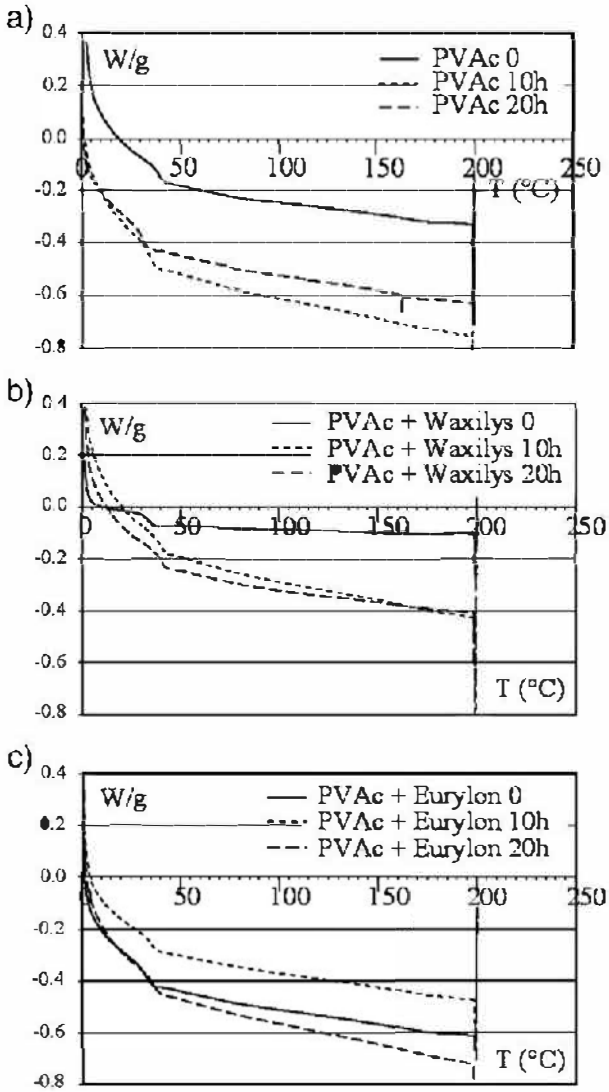

Fig. 5. Thermograms of the matrix and the mixtures for some grinding times. a. PVAc thermograms. b. Thermograms of PVAc + Waxilys. c. Thermograms of PVAc + Eurylon.

This treatment can lead to a scission of the molecular chains of the polymer [31], leading to a reduction of its molecular weight, and as a consequence, of its glass transition temperature. The grinding time does not have a significant effect on Tg.

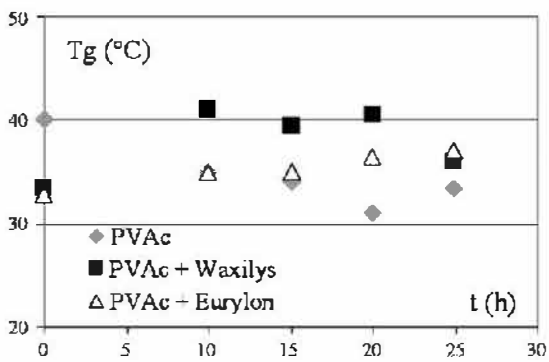

Fig. 6. Glass transition temperature (Tg) of the samples as a function of the grinding time.

When mixing starch to PVAc (t = 0), the matrix glass transition temperature is decreased because of hydrogen bonding between matrix and filler. Othman et al. [29] determined the melting and the crystallization temperatures of polyvinyl alcohol and corn starch blends. They observed the same decrease in these temperatures. Moreover the value of Tg, at t = 0 in Fig. 6, is very slightly lower in the presence of the starch with the higher amylose rate. Indeed, the linear structure of amylose favors hydrogen bonding compared to the crosslinked structure of amylopectin. Zhang and Thomas [25] produced blends of polyhydroxybutyrate and starches with various amylose to amylopectin ratios and they also noticed a lower value of Tg with blends containing the higher amylose rate.

Nevertheless, co-grinding increases the glass transition temperature. This can be due to a better dispersion of the filler in the matrix (that will be confirmed in the next section), leading to a more stable system in which the mobility of the molecular chains is reduced. With co-grinding, the difference between the values of Tg for the two mixtures is more important in favor of the mixture containing the starch with the higher amylopectin rate.

4.2. Properties determined on films

4.2.1. SEM observation of film section

Fig. 7 presents micrographs of the sections of composite films filled with Waxilys, respectively by simple mixture, and after 10 and 20 h of co-grinding. The same type of micrographs was obtained with the mixture PVAc–Eurylon.

On micrographs a and b, the starch grains are clearly recognizable. Moreover, adhesion between starch grains and the matrix is weak, what is highlighted by the absence of any physical contact between both components. The starch grains seem extracted from the matrix during the cutting of the composite film. Finally, we note zones of filler concentration, while other zones are exempt from it.

When matrix and filler are co-ground before molding, the film sections are very different. Indeed, some starch grains are still observable after 10 h, but they seem stuck in the matrix (micrograph c). After 20 h, no grain is observable (micrograph d).

These observations allow validating the interest of co-grinding to improve the dispersion of the filler in the polyvinyl acetate matrix.

4.2.2. Mechanical properties

The evolutions of the tensile modulus, strength and maximum strain versus co-grinding time are shown in Fig. 8 for the three materials (PVAc films, mixture PVAc–Eurylon, mixture PVAc–Waxilys).

The unfilled matrix displays a viscoelastic behavior with a high tensile modulus (around 250 MPa), a high strength (around 15 MPa) and a low strain (around 6). The grinding time does not have a significant effect on the mechanical properties of PVAc films what is consistent with the results obtained on the evolution of the glass transition temperature of the powder samples.

For low grinding times, adding starch particles results in an increase of the tensile modulus and in a decrease of both the strength and maximum strain. The PVAc materials filled by starch particles became brittle. This result is therefore an indication of the lack of intimate adhesion between both components of the composite structure. This is confirmed by the observation of the SEM micrographs of the film sections (Fig. 7a and b).

Vargha and Truter [5] studied the mechanical behavior of mixtures produced by partial trans-esterification of polyvinyl acetate and starch. They could not measure the mechanical properties of samples of such composites which were very brittle contrary to polymer alone.

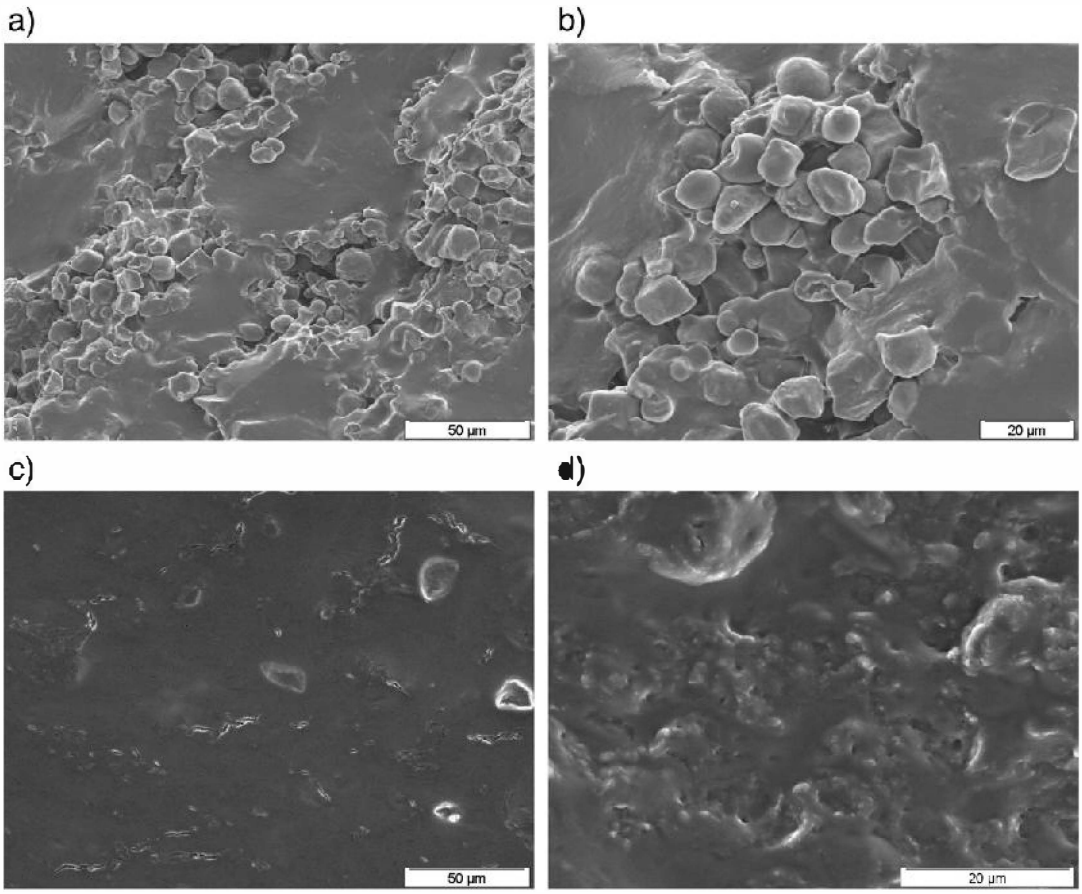

Fig. 7. SEM micrographs of PVAc–Waxilys film sections. a. Without co-grinding. b. Without co-grinding — detailed view. c. 10 hour co-grinding. d. 20 hour co-grinding.

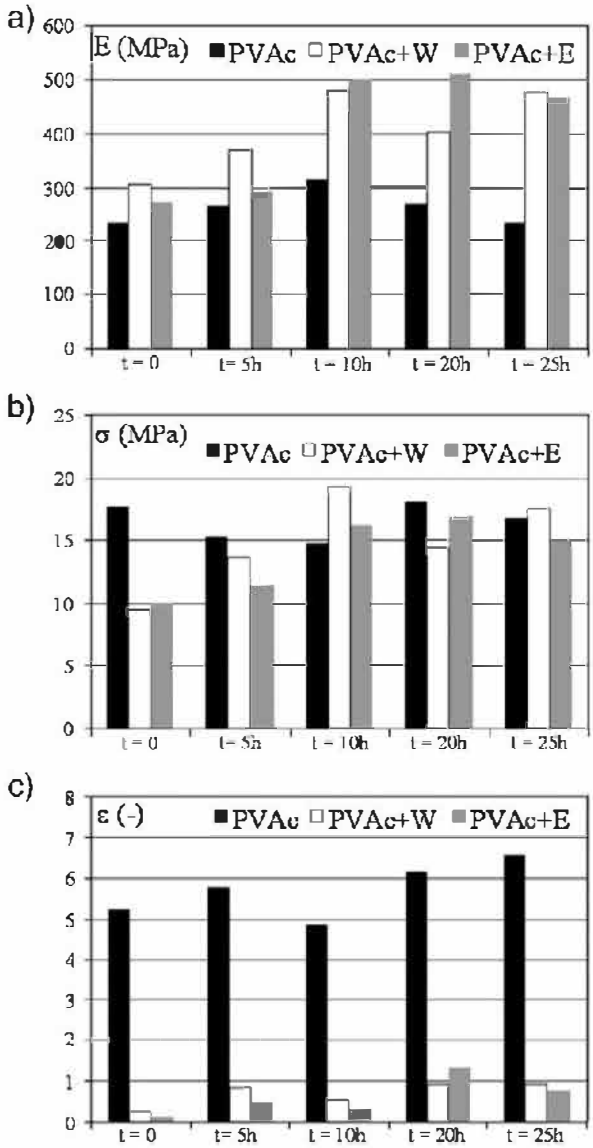

Fig. 8. Mechanical properties of the matrix and the mixtures. a. Tensile modulus. b. Strength. c. Maximum strain.

After 10 h of co-grinding, the filled films display a higher relative reinforcing effect. For instance, the Young modulus of a film reinforced with 25 wt.% of starch increased by a factor of 1.5 and the strength was of the same order as that for the unfilled materials. These results confirm that the co-grinding process allows a better cohesion between the filler and the matrix. Nevertheless, the composite materials remain brittle with a low strain.

Concerning the influence of the starch type on the mechanical properties, we cannot conclude because the tendency varied with the operating conditions.

4.2.3. Behavior in water and characterization of diffusional phenomena

Fig. 9 presents the variation of the water uptake of the matrix pellets immersed during different times, parameterized by the grinding time. The time scale is logarithmic to better analyze the phenomena taking place within the first immersion hours.

WU increases first with the immersion time, as water diffuses in pellets, to level off after 1000 min at a maximum value between 50 and 55%, corresponding to equilibrium in water uptake. This progressive increase may be attributed to a hydrophilic behavior of PVAc which is moderate given the maximum values of WU. We observe a small influence of the grinding time on the maximum value reached, due to a modification of the molecular chains as expressed previously. Finally, the water uptake decreases progressively during the few months of the experiment.

As for mixtures (Fig. 10), similar evolutions are observed when the matrix is filled with starch having a high amylose rate. Eurylon seems to have the same hydrophilic behavior in water than PVAc.

On the contrary, Waxilys is a highly hydrophilic starch due to the fact that amylopectin structure is more open and consequently can absorb more water than amylose. Kibar et al. [32] also noted that water uptake of mixtures filled with starch increases as the amylose rate decreases. Mani and Bhattacharya [33] evoked an increase of the gelatinization and a degradation of the ramified structure of amylopectin that make the mixture more sensitive to water. Without co-grinding ($t = 0$), the maximum water uptake is a little bit lower than for the two other systems, but this difference must be taken with care because of the dispersion irregularity of starch in matrix when unground. Indeed, in order

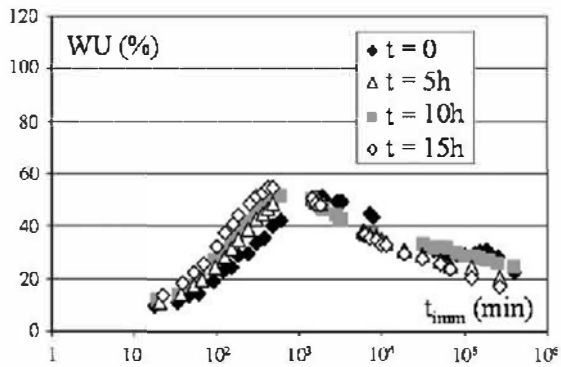

Fig. 9. Influence of immersion and grinding times on PVAc water uptake.

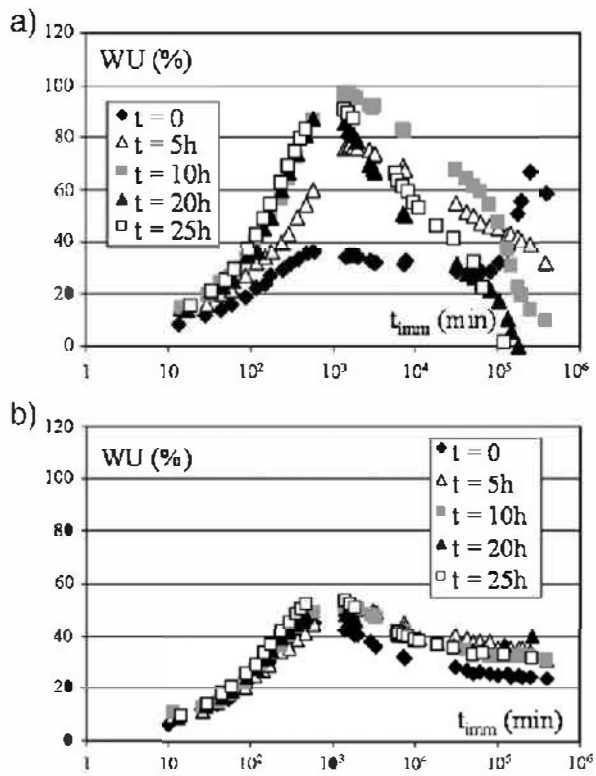

Fig. 10. Influence of immersion and co-grinding times on mixture water uptake. a. PVAc–Waxilys mixtures. b. PVAc–Eurylon mixtures.

the filler plays its real role, it needs to be well dispersed within the matrix to create a network. Bridges generated by the contact between starch grains will favor the water absorption in the whole pellet. However, as can be seen on the micrographs of Fig. 7b, pellets contain aggregates of starch grains surrounded with unfilled matrix. A simple mixture of the constituents does not thus generate this network. However, once water has saturated matrix, it can reach concentrated starch zones and water absorption by the very hydrophilic starch can proceed. This is translated by the peak in the WU curve after 100 000 min of immersion. Water uptake kinetics and maximum value are greatly influenced by the co-grinding time, WU at equilibrium being close to 100% in some cases. Co-grinding favors the progressive dispersion of starch grains and the formation of a network through the pellets. Once this network established (after 10 h co-grinding) a longer co-grinding treatment has no significant effect on the first part of the curves and on water uptake equilibrium. As for the WU decrease (last part of the curves), it is more pronounced than for the two other systems. This may be attributed to starch release, as already suggested by Vargha and Truter [5] and by Angellier et al. [34].

Above the polymer glass transition temperature, chain relaxation is rapid and water diffusion within the polymer network may happen according to Fick laws. Below the glass transition temperature, chain relaxation is slower. According to Alfrey et al. [35], transport phenomena into glassy polymers may be described by three models:

- The water diffusion rate is lower than the relaxation rate of polymeric chains. The mechanism is controlled by diffusion which is Fickian;
- The relaxation rate is lower than the water diffusion rate. The mechanism is thus controlled by chain relaxation;
- Both rates are comparable.

Frisch [36] expressed the mechanism of water diffusion by the following equation, valid for values of the left member of the equation lower than 0.6:

$$\frac{m_t - m_i}{m_\infty - m_i} = k \cdot t_{imi}^n \quad (4)$$

where m_∞ is the pellet mass at equilibrium, t_{imm} the immersion time, k the system constant and n the diffusional exponent depending on the diffusion mechanism. The exponent n is equal to 0.5 if the diffusion is Fickian.

This equation was applied to the results presented in Figs. 9 and 10, by expressing the logarithm of the left member of the equation versus the logarithm of the immersion time. Exponents n, equal to the slope, were determined for the various operating conditions and are gathered in Fig. 11. They are close to 0.5, indicating that the mechanism of water penetration into the pellets is controlled by Fickian diffusion. The intercept points of the straight lines were also determined.

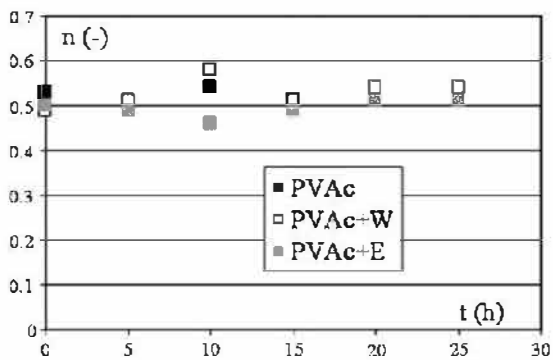

Fig. 11. Diffusional exponent versus co-grinding time.

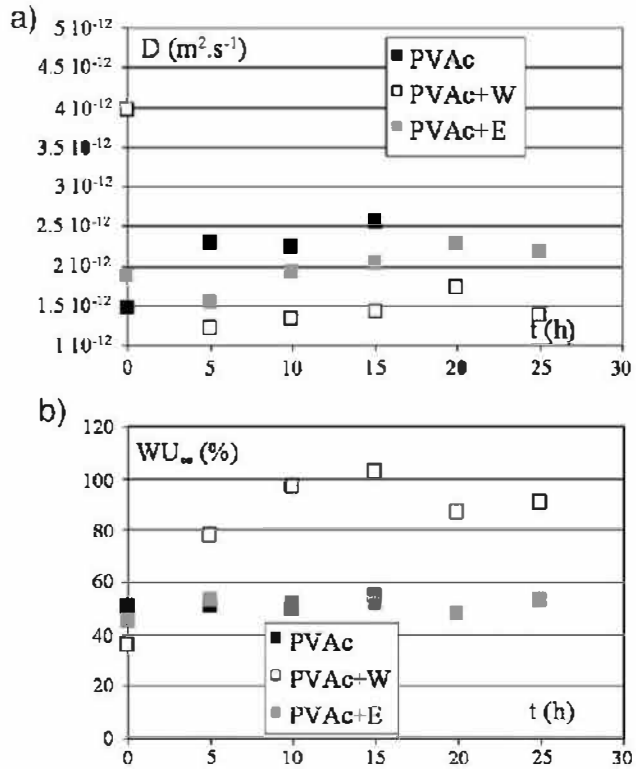

Fig. 12. Diffusion exponent and water uptake at equilibrium versus co-grinding time. a. Diffusion exponent. b. Water uptake at equilibrium.

In that case, Crank [37] precised that the constant k is equal to $(4 / e) \cdot (D / \pi)^{0.5}$, where e is the pellet thickness and D the diffusion coefficient. D was thus calculated from the intercept points of the lines and the values are shown in Fig. 12, as well as the water uptake at equilibrium.

For the reason previously evoked of a bad dispersion of the filler in the matrix, data obtained for unground materials will not be discussed. When grinding is performed, one can notice that the diffusion coefficient is lower for mixtures than for the matrix alone. Moreover, the higher the amylopectin rate, the lower the diffusion coefficient. Finally the diffusion coefficient increases slightly with an increase of the co-grinding time up to 20 h. This may be attributed to higher inter- and intra-molecular interactions in the presence of starch, which reduce chain mobility. These interactions slow down water diffusion. This is particularly the case for waxy starch with its ramified structure. These results are in accordance with the evolution of the glass transition temperature previously discussed, which is the highest in the presence of waxy starch and the lowest for the matrix alone. When the grinding time increases, the chain length decreases leading to a small enhancement of the diffusion coefficient.

Concerning the values of WU_∞, they are similar and constant for the matrix and the mixture filled with starch containing the high amylose rate, whatever the grinding time, while those of mixtures containing starch with a high amylopectin rate are higher, in accordance with explanations given for Figs. 9 and 10 on the variation of the water uptake.

5. Conclusions

A study on co-grinding polyvinyl acetate filled with starch was performed in order to show the opportunity of partially replacing the synthetic matrix by a vegetable, degradable and available filler. Two starches having different amylopectin to amylose ratios were used.

Granulometric and morphological analyses have permitted to define the mechanism by which the composite material is formed. Co-grinding

permits a better dispersion of the filler in the matrix than a simple mixing, thus favoring PVAc–starch interactions. Mechanical properties of materials in traction are thus improved.

The glass transition temperature of polyvinyl acetate was determined by DSC analysis. The filler presence leads to an increase of Tg due to a limitation of the polymeric chains mobility. Consequently, the higher the ramified amylopectin rate, the higher the glass transition temperature.

Moreover, the presence of starch with a high amylopectin rate favors the composite water uptake if starch is well dispersed in the matrix under the effect of an optimized co-grinding treatment. Starch nature, linked to its botanical origin, influences the properties of composites produced by co-grinding.

Nomenclature

D	diffusion coefficient m^2/s
d50	particle median size μm
e	pellet thickness m
E	Young modulus Pa
F	force N
L	sample length m
L_0	sample initial length m
m_i	initial pellet mass kg
m_t	pellet mass at time t kg
m_∞	pellet mass at equilibrium kg
n	diffusional exponent
S_0	initial crosssection of the film m^2
t	grinding time s
T	temperature °C
Tg	glass transition temperature °C
t_{imm}	immersion time s
WU	water uptake %
WU_∞	water uptake at equilibrium %
ε	nominal strain %
ε_b	maximum strain %
σ	nominal stress Pa
σ_b	strength Pa

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