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Mechanical properties and degradation of starch-filled polystyrene co-ground composites

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Abstract

A vegetable biodegradable filler was incorporated in a synthetic matrix to produce composite materials, using a co-grinding process. This process permits a better dispersion of the filler in the matrix and better interactions at the materials interface. The mechanical properties of the as-produced composite are slightly better than those of blends, and are not significantly enhanced compared to those of the matrix alone, but this process permits to reduce the consumption of synthetic polymers. Moreover, an adapted co-grinding time permits to offer good water-resistant properties to the composite compared to blends.

Keywords: co-grinding, composite materials, polystyrene, starch, mechanical and degradability properties

1. Introduction

For several years, and in the future, we are and we will be confronted with non degradable plastic wastes. Two ways are developed to control this problem: the recycling of synthetic polymers and the production of biodegradable products. Another way consists in combining synthetic polymers and biodegradable materials, these ones even permitting to enhance the properties of the first ones. In a context of biomass valorisation, one of the currently used biodegradable fillers is starch [1-4]. It is a biopolymer with immense potential, low price and abundant availability, not depending on fossil sources.

Several processes are used to produce polymeric composite materials. Among them, co-grinding is the most recently developed, and permits a good dispersion of the filler in the matrix, and a good interactions between the two materials [5]. Different studies were already realised using mineral fillers [6,7]. It was shown that co-grinding improves the mechanical properties of the composites compared to blending.

Recently, we have shown the feasibility of using starch in polymeric composites produced by co-grinding [8]. The matrix was poly (vinyl acetate) which was a model material. The mechanical properties and the resistance to water are improved compared to those of blends.

This paper presents results on the production of polystyrene-starch co-ground composites containing various proportions of starch. Co-grinding was realised in a laboratory tumbling ball mill. We present the mechanism by which the composite is produced. Moreover, we

analyse the influence of co-grinding on the use properties of the as-produced materials (mechanical properties and degradability).

2. Experimental procedure

Dry batch co-grinding experiments were realised using a 5-litre ceramic tumbling ball mill. The chamber was filled with ceramic balls with different diameters (5.5, 9.5 and 12.5 mm) and the products to be ground. Its rotating speed was fixed at 100 rpm, i.e. at 75 % of the critical speed. The ball filling rate was 20 % of the chamber volume while the powder filling rate was 10 % of the void volume between the balls.

The polystyrene used in this study was provided by Goodfellow. The initial particles have a size ranging between 20 and 630 μm , with an initial mean size of 255 μm . Their form and their surface are irregular (figure 1). The polymer properties are gathered in table 1.

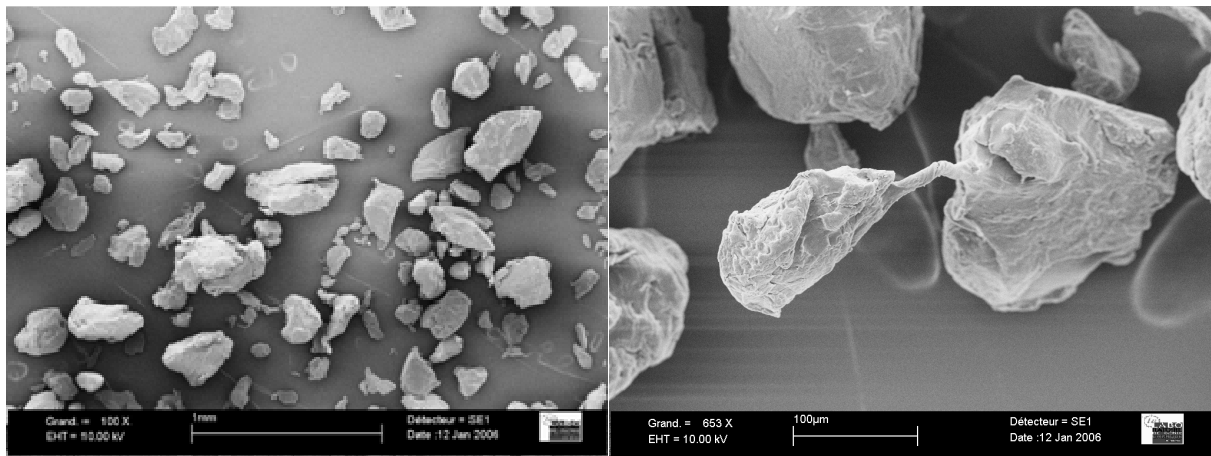


Figure 1: SEM micrographs of polystyrene

Density at 25 °C	1050 kg/m ³
Glass transition temperature	100 °C
Fusion temperature	270 °C
Degradation temperature	350 °C

Table1: Polystyrene properties

Waxy maize starch (Waxilys – Roquette Frères) was used as filler. It is mostly composed of amylopectin and is a semicrystalline polymer. The powder consists of individual particles, but also of some agglomerates (figure 2). The size of the particles varies between 4 and 32 μm and their initial mean size is approximately 13 μm . The density is 1330 kg/m³.

In a first series of experiments, the products were ground separately to study their behaviour to fragmentation and agglomeration. They were then co-ground. The mixtures contained various starch rates varying between 10 and 65 %. Very small powder samples were taken in different parts of the chamber and stocked in closed flasks to be analysed.

The size distribution was measured with a laser diffraction granulometer Malvern Mastersizer 2000. The mean size, d50, corresponding to a cumulated volume percentage of 50

% was determined. Different powder samples were observed by means of a scanning electron microscope (Leo 435 VP).

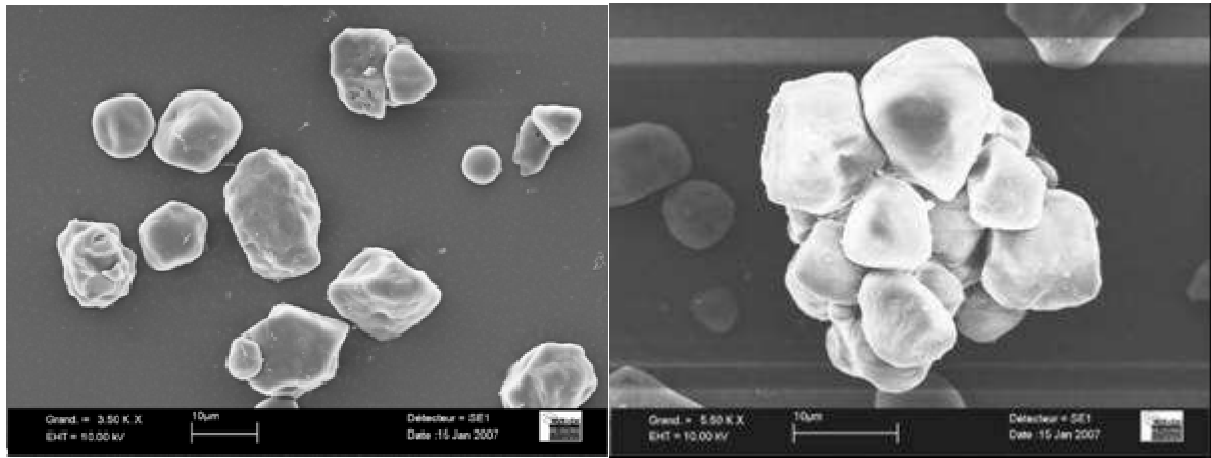


Figure 2: SEM micrographs of starch particles

Films with dimensions 10 mm x 5 mm x 0.3 mm were produced by pressing during 5 minutes the powder in a brass mould in a Carver Laboratory Press at 150 °C (above the melting temperature of the products) and at 34 bar. The films were then cooled in liquid nitrogen. The behaviour of the films was studied with an Instron 4301 testing machine working in tensile mode. The initial gap between the pneumatic jaws was fixed at 10 mm. Force (F) – elongation (L) curves were drawn at ambient temperature and with a cross-head speed of 1 mm/min. This low speed has been chosen because polystyrene is tough at room temperature. The nominal strain, ε , and the nominal stress, σ , were calculated by:

$$\varepsilon = \frac{L - L_0}{L_0} * 100 \quad (1)$$

$$\sigma = \frac{F}{S_0} \quad (2)$$

where L_0 is the initial length of the film and S_0 its initial cross section.

The nominal Young modulus and ultimate tensile properties, i.e. the strain at break and stress at break, were also characterised. Data were averaged over 5 specimens.

To study the degradability of the products, approximately 0.6 g of powders were compacted in a Carver press at 30 kN to form cylindrical discs with a diameter of 8 mm. Three discs per sample were realised. The discs, after being weighted, were introduced in hermetic flasks containing 20 g of distilled water at ambient temperature for several months. They were removed from water after different immersion times and their surface was dried on a filter paper to be weighted. The water uptake of the discs, WU, was determined by the equation:

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

where m_i is the initial weight of the disc and m_t its weight at time t.

3. Results and discussion

3.1. Size and morphology analysis

The two products were first ground separately. As for polystyrene, the variation of its size distributions and mean size is plotted in figure 3. The initial distribution is mostly monomodal, with a mode around 250 μm . For the first moments, the mode of this peak does not evolve significantly, even if the peak shifts very little towards the right, while a second peak appears around 35 μm .

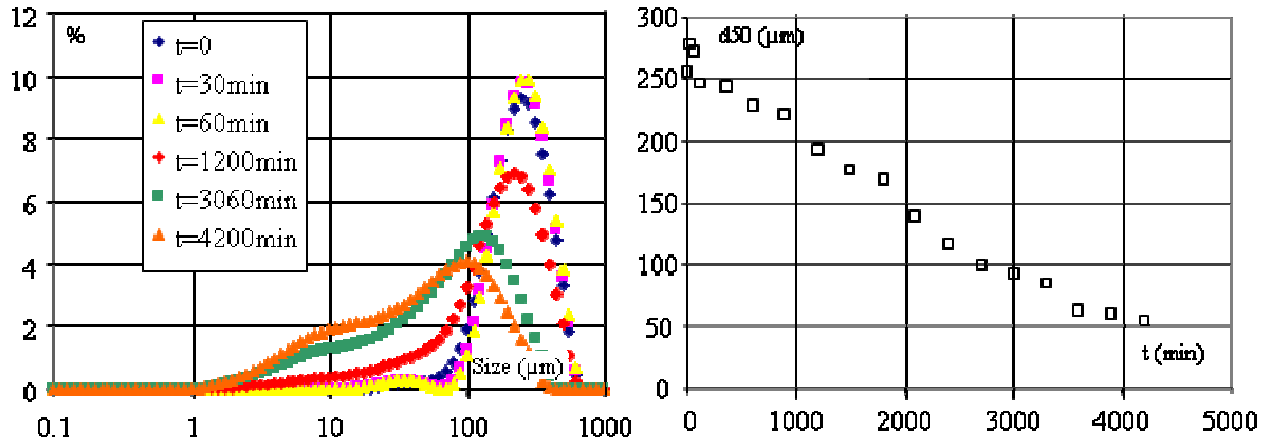


Figure 3: Variation of the size distribution and of the mean size of polystyrene

The second phenomenon may be due to the irregularity of the initial particles. Thus small excrescences can break away from mother particles and the surface of these ones become smoother (micrograph a of figure 4).

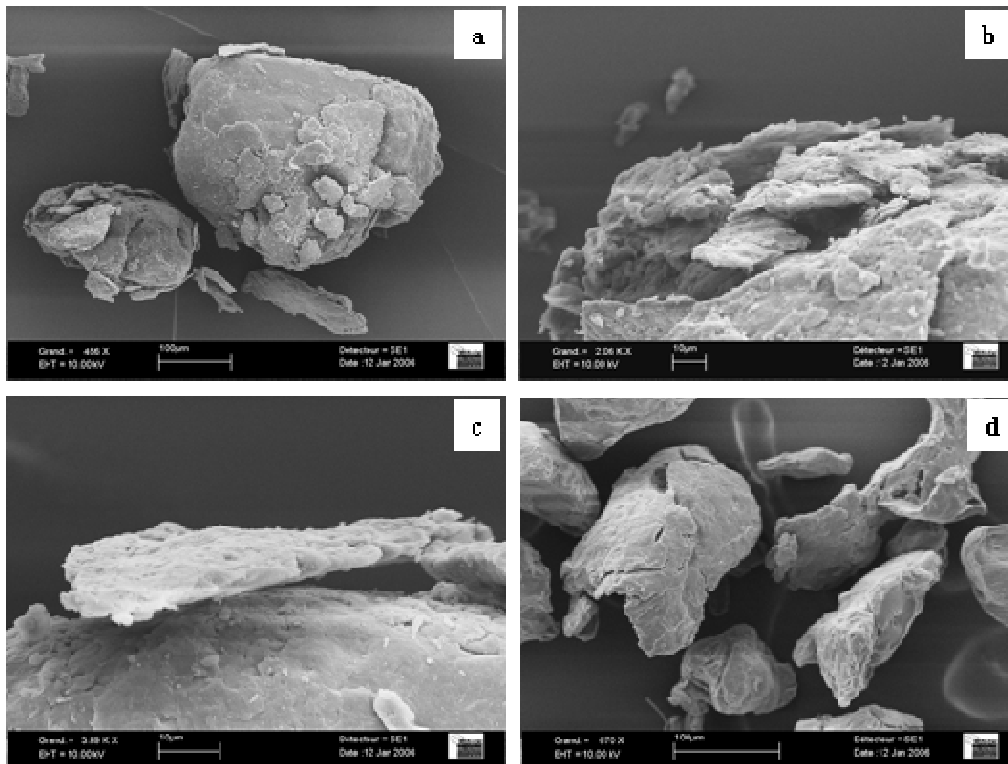


Figure 4: SEM micrographs of ground polystyrene particles

As for the first phenomenon, it may be attributed to the fact that polystyrene particles are very compact. The energy transmitted by the balls is not sufficient to reach the centre of the particles and provoke their fragmentation. Consequently this energy is mainly transmitted to the particles surface and provokes their chipping (micrographs b and c of figure 4). The progressive unsticking of the chips from mother particles leads to a small increase of their apparent size. Since the percentages are expressed in volume, the first phenomenon has more effect on the variation of the mean size than the second. Consequently, d_{50} increases from 255 to 278 μm during the first 30 minutes. After 60 minutes, d_{50} decreases because the chips are broken away (micrograph d of figure 4) from the particles and fragmented. The mean size levels off then between 120 and 360 minutes, when new chips are formed. Finally it decreases progressively to reach 50 μm , resulting from combined formation and break away of chips and fragmentation of the chips. Thus, the size distribution shifts towards the small sizes and a peak around 10 μm is observed.

Concerning starch (figure 5), the treatment does not permit to decrease the mean size because the initial size, which is near 13 μm , is lower than the limit grinding size defined by Schönert [9] for macromolecules, which is of several tens of μm as observed for polystyrene. On the contrary, particles agglomerate as shown on the micrograph of figure 5 and the size increases. Finally, a competition between fragmentation of the agglomerates and agglomeration occurs.

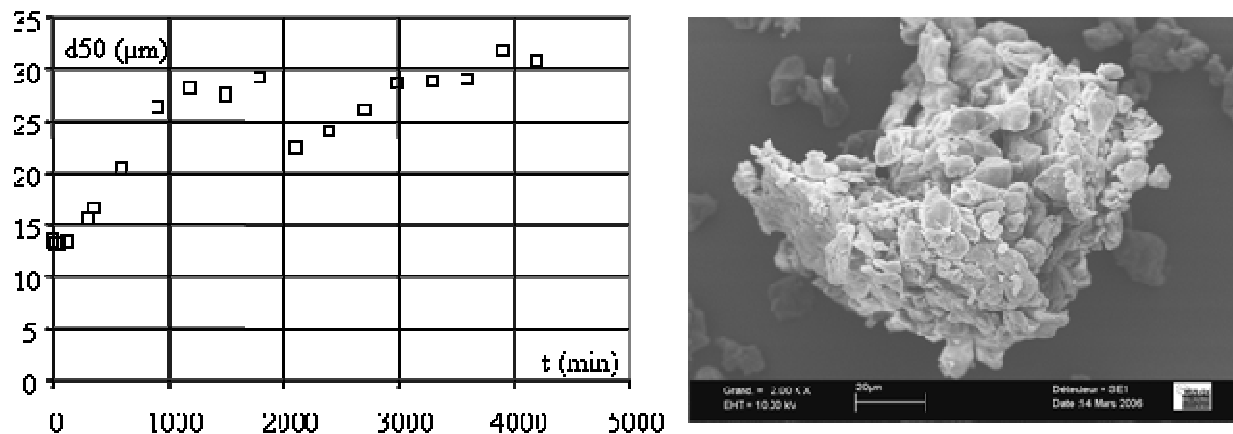


Figure 5: Variation of the starch mean size and SEM micrograph of an agglomerate

Mixtures of the two products containing various starch proportions (10 to 65 wt. %) were then co-ground. Examples of the variation of the size distribution are presented in figure 6 for mixtures containing 20 and 65 % of starch. Figure 6.a is representative of the mixtures containing 10 and 20 % of starch while figure 6.b is representative of the mixtures containing 35 to 65 % of starch. Moreover, in figure 7, the mean size is plotted versus the co-grinding time for all the tested starch rates.

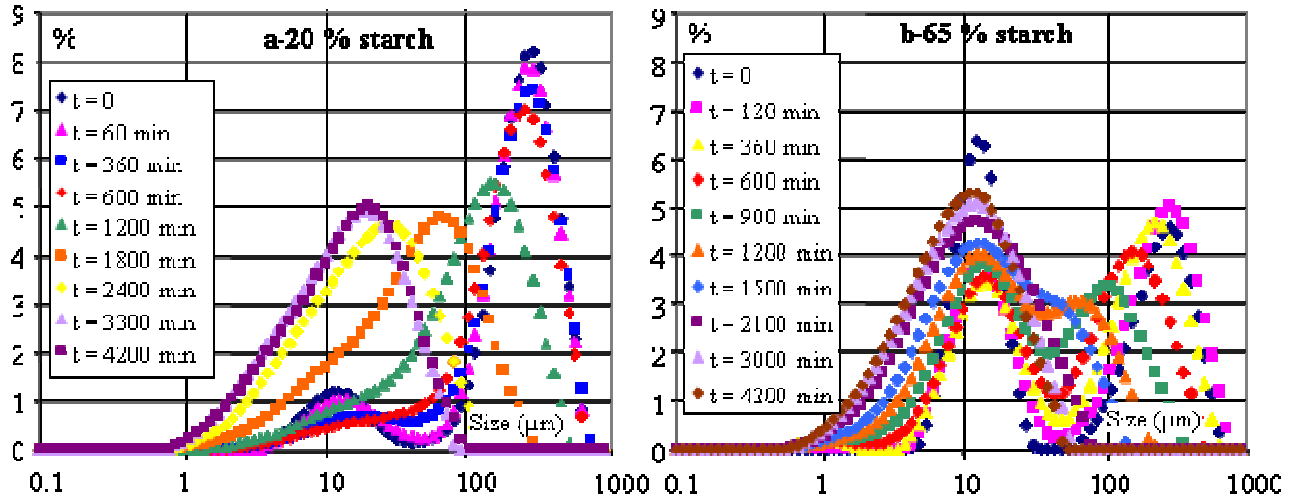


Figure 6: Variation of the size distribution of mixtures containing 20 % and 65 % of starch

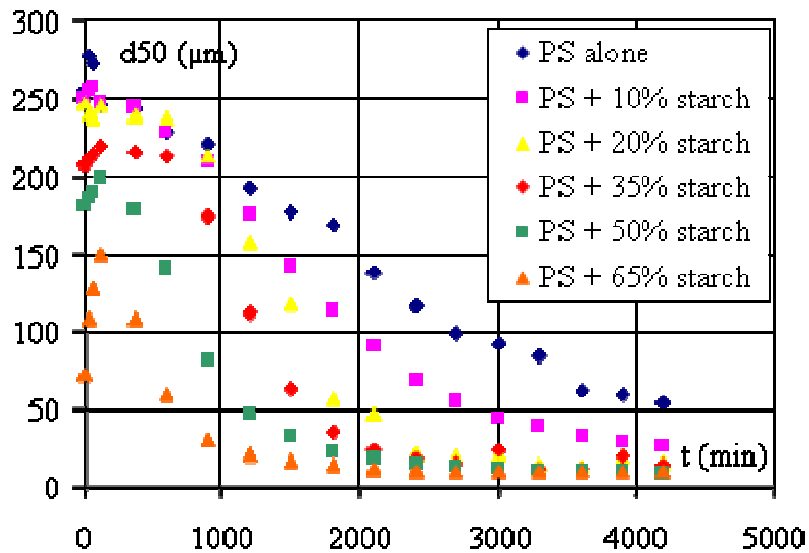


Figure 7: Influence of the starch rate on the variation of the mean size

From the observation of the size distributions, one can notice that the initial curves present two peaks. That of right-hand side corresponds to polystyrene while that of left corresponds to starch, the particles of which are smaller than those of polystyrene (figure 8.a).

Concerning the mixtures with a low starch rate (≤ 20 wt. %), as co-grinding proceeds, one can observe a difference in the curves before and after 600 minutes. Before that time, the mode of the polystyrene peak does not evolve significantly as when it is ground alone. The proportion of the starch peak decreases progressively, while a new particle population appears between the two initial ones. As it can be seen on figure 8.b, flat particles corresponding to polystyrene chips are produced and small starch particles are no more observable. Moreover, small polystyrene fragments, more irregular than starch particles, are present. One can thus think that starch particles stick rapidly on the polystyrene surface as it can be seen of the micrograph of figure 8.c taken after 60 minutes of grinding, while the matrix particles behave as when they are ground alone. Thus, the presence of the filler in small proportions seems not to have a significant effect on the grinding rate of the matrix during the first 600 minutes, and consequently the filler rate does not have any influence on the variation of the mean size as it can be observed on figure 7. After 600 minutes, the size distributions shift more rapidly

towards the left in the presence of starch than in its absence. This leads to a faster decrease of the mean size. This may be explained by the fact that when the polymer is ground alone, small fragments agglomerate on big particles for long co-grinding times. On the contrary, the presence of starch limits the agglomeration between polystyrene fragments and big particles. The filler acts as an agglomeration inhibitor as it was already observed with other composite systems [6,8]. It may be explained by the affinity between the components at their interface, as already shown by Seyni et al. [8] for starch filled poly (vinyl acetate) composites. Finally, composite particles, with a filler well dispersed in the matrix, are produced (micrograph 8.d).

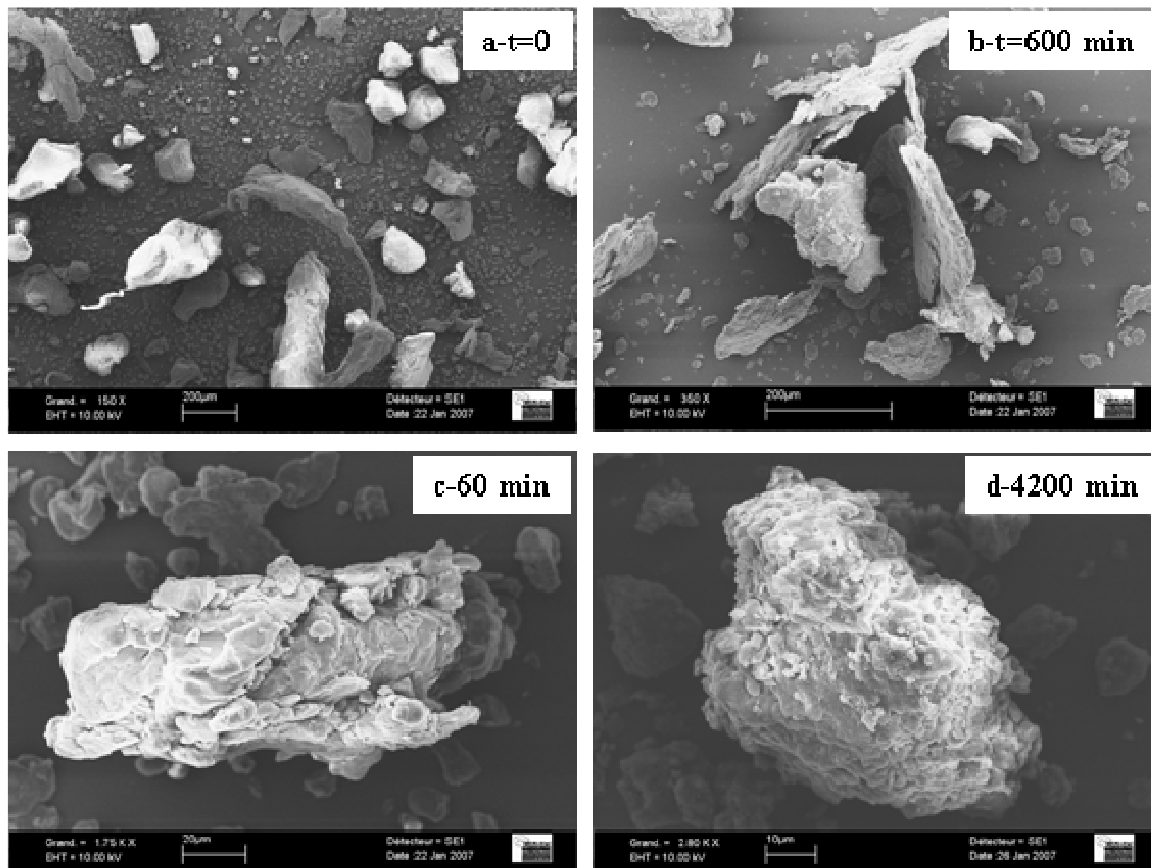


Figure 8: SEM micrographs of polystyrene–starch mixtures co-ground during different times

As for the mixtures with a high starch rate ($\geq 35\%$), polystyrene chipping also occurs, as well as agglomeration of starch on the matrix particles. However, since the starch rate is high, the agglomeration phenomenon is important. Thus, the proportion of the starch peak in the size distributions of figure 6.b decreases rapidly between 0 and 360 minutes, and the polystyrene peak is enlarged, on the left side due to the removal of chips and on the right side due to the agglomeration of starch particles. The consequence of this is a low value of the initial mean size when the starch rate is high (because of the low size of the filler particles) and a significant increase of the mean size during the first co-grinding times, even more so given that the filler rate is high. After this period, the inhibition effect of starch on the agglomeration between polystyrene particles is marked, since the peak at high sizes disappears rapidly. Starch may even act as a chipping accelerator. Indeed, if the starch proportion in the mixture is high, the polystyrene mass is then low because the solid load in the mill is constant for all the experiments. The starch particles are not fragmented, but contribute to the mixing of the whole, which facilitates the elimination of the chips from the matrix surface. The core of polystyrene particles is then more quickly subjected to a new chipping. The reduction of the mean size is thus accelerated, and it reaches more rapidly its

limit value when the starch rate is high. Furthermore, this limit value is lower for high starch rates than for low rates.

3.2. Mechanical properties of the composites

It is well known that the objective of introducing a filler in a matrix is to enhance the properties of this last. One of the properties often modified by the incorporation of a filler is the mechanical properties. We have studied the influence of the starch rate and of the co-grinding time on the Young modulus and on the stress and strain at break. It was not possible to test all the rates and times. Indeed, beyond 30 hours of co-grinding or 35 % of starch, the films had a tendency to break during their recovery after moulding.

The influence of the starch rate has been studied on mixtures co-ground during 10 hours (figure 9). With regard to the Young modulus, figure 9.a shows that this one tends to decrease slightly when starch is added. Nevertheless, once the filler added, the modulus does not vary significantly. The addition of starch, whatever its rate, has no significant effect on the stress at break, while the elongation is slightly increased for 20 % of starch and reduced for 35 %. However, the variation of these parameters is not very marked.

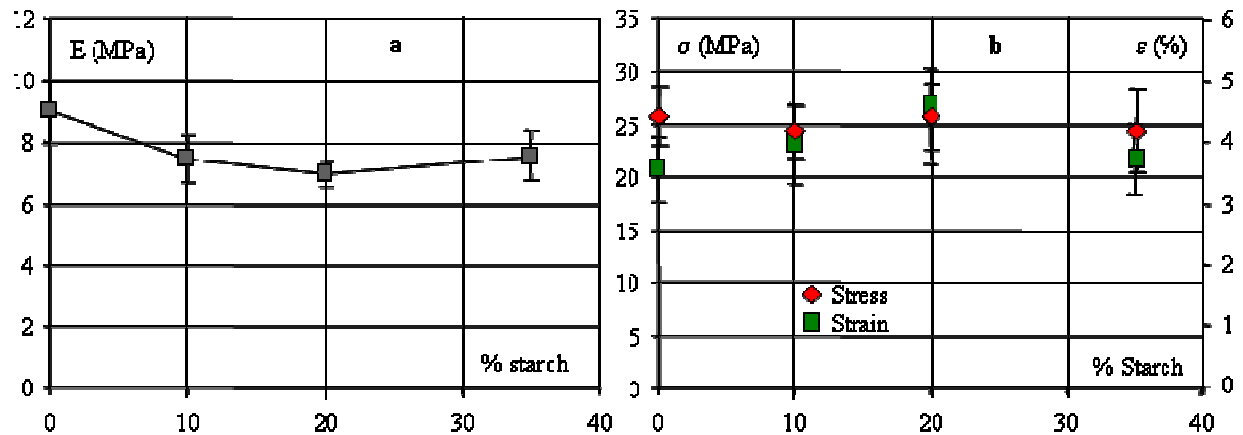


Figure 9: Influence of the starch rate on the Young modulus and the stress and strain at break

The influence of the grinding time has been studied for mixtures containing 10 % of starch (figure 10). Adding starch to polystyrene without co-grinding ($t = 0$) leads to a decrease of the Young modulus because polystyrene is more rigid than starch. Moreover, E increases with the co-grinding time until 20 hours and reaches a value higher than that calculated for polystyrene alone. A better dispersion of the filler in the matrix and the modification of the interactions between the materials have thus a positive effect on E . However, a long co-grinding time reduces the Young modulus, certainly due to molecular chains degradations. Concerning the stress at break, as for the E , an optimum value is obtained for 20 hours of co-grinding for the same reasons. Finally, the strain at break is also reduced by the presence of starch, but then it is not significantly affected as long as the grinding time does not exceed 20 hours. Beyond this value, a too important rate leads to a slight decrease of ϵ .

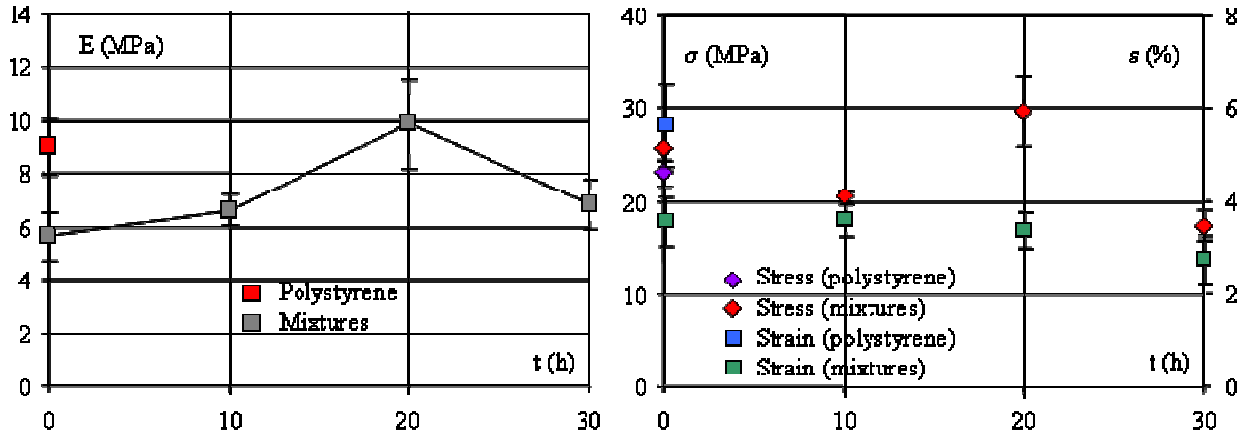


Figure 10: Influence of the co-grinding time on the Young modulus and the stress and strain at break

These different observations mean that the presence of starch has a slight negative effect on the mechanical properties of the composite compared to those of the matrix. Vargha and Truter [10] studied the mechanical properties of mixtures resulting from a partial transesterification of poly (vinyl acetate) and starch, and explained that it was not possible to characterize these properties without plasticizing the matrix. Moreover, they noted that the introduction of starch in the plasticized matrix generates a strong decrease of the Young modulus and of the stress and strain at break. These results corroborate ours. However, co-grinding permits to compensate this loss of properties without modifying the matrix.

3.3. Water uptake and degradability of the materials

The behaviour in water of the two products ground separately and co-ground for different times was characterised in order to study their resistance to water and degradability properties. Figure 11 shows the influence of the grinding and immersion times on the water uptake of the two products ground separately.

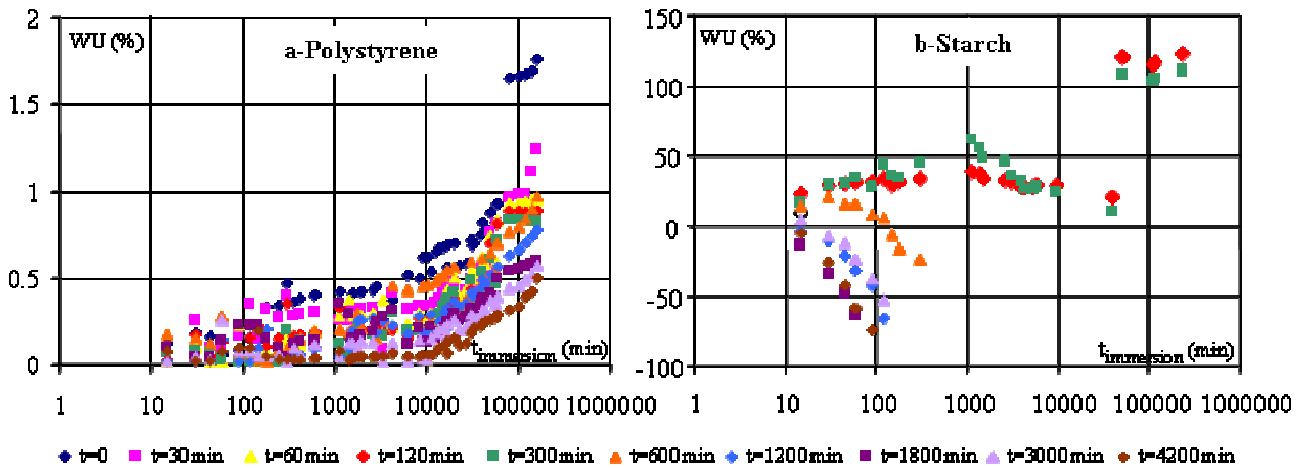


Figure 11: Influence of the immersion time on the water uptake of the two materials for various grinding times

The chemical structure of a polymer influences its hydrophilic behaviour and consequently its water uptake [11]. This one is low for carbonaceous or fluorinated groups, medium for moderately polar groups (like esters or ethers) and high for groups which are hydrogen bonds donor (acid, alcohol or amide). Consequently, one can concluded that

polystyrene absorbs very little water, as observed in figure 11.a. Indeed, WU is lower than 1 % for long immersion times. Moreover, long grinding times have a negative effect on the water uptake, probably because the molecular chains of the polymer are cut under the effect of a prolonged treatment, as noted by Molina-Boisseau and Le Bolay [12] when grinding polystyrene in a vibrated bead mill. As for starch, no result can be presented for grinding times lower than 60 minutes because the discs were rapidly disintegrated. The reason of this is the good affinity between starch and water, due to all the $-OH$ groups of starch. The resistance to water of the discs made up with starch ground for 120 and 300 minutes is better, probably because of a better cohesion of the discs, and WU reaches approximately 63 % after 1000 minutes of immersion in water. After this time, it decreases. Angellier et al. [13] explained this decrease of WU by a release of starch in water. After 45 000 minutes of immersion, the consistency of the discs is modified since they swell and become brown. Finally, a grinding time higher than 600 minutes has a negative effect on the water uptake of the discs which are progressively degraded. An excessive degradation of the molecular chains by the balls may be at the origin of the problem.

Mixtures discs were submitted to the same treatment. Two series of results are presented in figure 12. Figure a corresponds to a mixture containing 10 % of starch, while figure b corresponds to a mixture containing 35 % of starch. The same kind of results as those of figure b was obtained for 20, 50 and 65 % of starch.

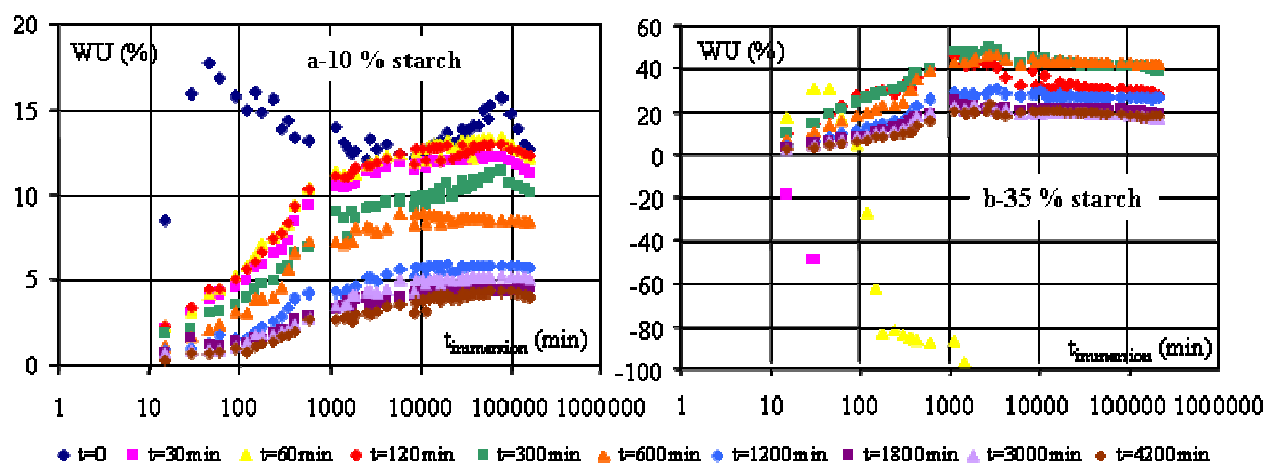


Figure 12: Influence of the immersion time on the water uptake of mixtures for various grinding times

An addition of 10 % of starch to the matrix leads to an increase of the water uptake compared to polystyrene alone because of the affinity of starch with water. Furthermore, for immersion times lower than 1000 minutes, WU increases with this parameter. A progressive diffusion of water in the discs occurs, and the diffusion rate is all the more low as the co-grinding time is high because of a degradation of the molecular chains. Between 1000 and 100 000 minutes, the water uptake levels off, since equilibrium in water absorption is reached. Finally, after 100 000 minutes, a release of starch in water generates a decrease of WU.

For higher starch rates, a minimum co-grinding time is needed to avoid a rapid disintegration of the discs. As it can be seen on figure 12.b, discs of blends produced by simple mixing of the two products ($t = 0$) disaggregate immediately, because starch is probably not sufficiently dispersed and protected by the matrix. Disaggregating is more progressive for 30 and 60 minutes of co-grinding. This has been observed for all the filler rates greater than 20 % and the higher this starch rate, the longer the co-grinding time needed

to avoid discs disintegration. If the co-grinding time is sufficient, the water uptake increases first with the immersion time and reaches then a plateau when the diffusion equilibrium is reached. The value of WU at the equilibrium decreases with an increase of the co-grinding time because of a progressive cutting of the molecular chains, and increases with the starch rate because of the affinity between the filler and water. Finally, a possible release of starch in water leads to a small decrease of WU for long co-grinding times.

One can thus conclude from these results that since polystyrene has little affinity with water, the phenomena observed in this study can be attributed to starch. Furthermore, a simple blending of polystyrene and starch particles does not permit a good resistance of the discs to water and a compatibilizer should be needed in this case. Co-grinding processed during a sufficient time make it possible to enhance the resistance of the composite to water without any compatibilizer.

Conclusions

A starch filler was introduced in a polystyrene matrix in order to modify its use properties. A co-grinding process was used in this objective. A study of the evolution of the size and the morphology of the particles has permitted to explain the mechanism by which the composite material is formed. The mechanical and degradability properties of the composite were characterized. It was shown that introducing starch in the matrix has a negative effect on the mechanical properties that co-grinding permits to compensate. However, a too long grinding time leads to a degradation of the molecular chains which affects the properties. Furthermore, a well chosen filler rate combined to an optimised co-grinding time permit to propose composites having a good resistance in water. The process permits to replace partially a synthetic polymer by a degradable polymer.

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