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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:

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

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

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%.

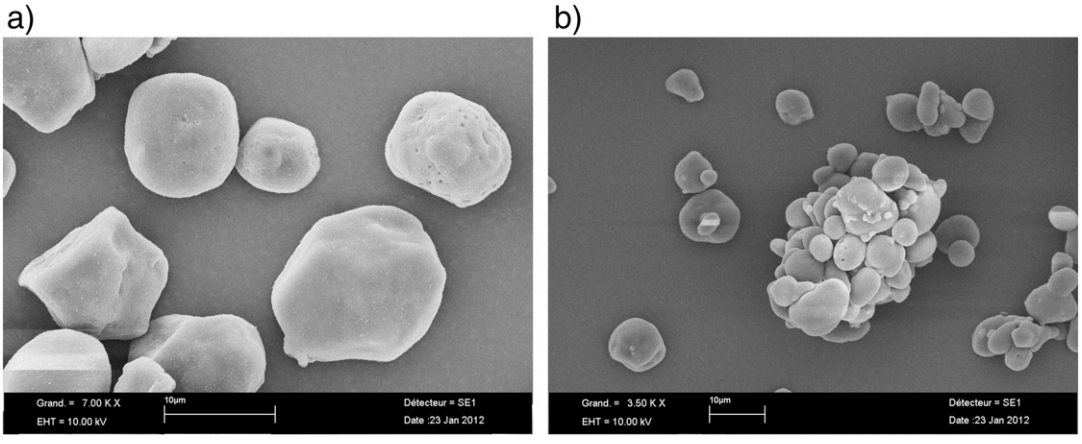

Fig. 1. SEM micrographs of starch particles. a. Waxilys. b. Eurylon.