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How to combine a hydrophobic matrix and a hydrophilic filler without adding a compatibilizer – Co-grinding enhances use properties of Renewable PLA–starch composites

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ABSTRACT

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Composites
Properties

In order to avoid the use of compatibilizers or plasticizers, co-grinding was performed to produce PLA–starch composite materials. Fragmentation and agglomeration phenomena were analysed to propose a production mechanism. Co-grinding enhances dispersion of the filler in the matrix and interactions between the materials. Consequently while blending the two materials has a negative effect on mechanical properties, co-grinding permits to improve them if optimized operating conditions are applied. Water uptake and diffusion are also controlled by co-grinding conditions. This treatment allows the production of composite materials offering good use properties without any use of a compatibilizer or a plasticizer.

1. Introduction

Eco-design of polymers and composites is based on an important issue that faced society over the last two decades: what to do with tons of non-degradable wastes issued from petrochemical polymers which have already caused serious environment damage? For several years, the use of biodegradable polymers is favoured, in particular in short-life applications for which petroleum polymers are particularly not interesting. One of the ways to propose biodegradable polymers is the development of synthetic polymers using monomers from natural resources. A promising polymer in this regard is poly(lactic acid) (PLA), because it is made from agricultural products and is biodegradable. PLA is easily hydrolysed in the presence of moisture, and its hydrolysed products are non-toxic. It offers many excellent properties such as good biocompatibility and manufacturing. However, synthetic biodegradable polymers are often more expensive than petrochemical polymers and mechanical properties (stress and elongation) must be adapted to their application (drug delivery, scaffold, packaging, etc.).

Like many polymers from petroleum, polymers from renewable resources are rarely used alone, and biodegradable fillers are often added. Among them, starch is widely used since it is completely biodegradable, renewable, cheap (what permits to reduce the composite cost) and enhances the composite biodegradability rate.

Unfortunately, PLA and starch are thermodynamically immiscible since PLA is hydrophobic and starch is hydrophilic. This leads to poor adhesion between the two components, and consequently poor and irreproducible performances. Zhang and Sun [1] have determined the tensile strength and the elongation of PLA alone and of a PLA–starch blend and they have observed that both properties of the blend are divided by two compared to those of PLA.

Since interfacial adhesion plays a vital role in properties of polymeric composites, various compatibilizers were investigated by different authors to improve the interactions between the components constituting the blends. Yu et al. [2], Acioli-Moura and Sun [3] and Wang et al. [4] used methylenediphenyl diisocyanate, what permitted to improve the interface between the matrix and the filler. PLA–starch mixtures had mechanical properties close to those of PLA. However, methylenediphenyl diisocyanate is not a good candidate for environment and is unsuitable for food packaging. Zhang and Sun [1] used maleic anhydride and added an initiator to improve compatibility between PLA, starch and maleic anhydride. Mechanical properties were improved compared to virgin PLA/starch but they were lower than those of PLA alone. However, compatibilizers are undesirable for full-biodegradation.

Other authors added plasticizers to improve the interface between PLA and starch. The products often used as plasticizers

are small molecular agents such as citric acid ester, glycerol, formamide, polyethylene glycol or water [5–7]. The use of plasticizers leads to additional production cost.

Co-grinding is an alternative to improve the interface between the matrix and the filler without adding any agent. This process was used to produce composites made of petrochemical polymers filled with a mineral [8], non-degradable polymers [9] or starch [10,11], and it was shown that the use properties of composite material could be significantly improved in comparison to blends due to better interactions between the components.

In this work, starch-filled PLA composite materials were produced by co-grinding in a tumbling ball mill. Fragmentation and agglomeration phenomena were studied to understand how the composite materials are formed. In this way, the size distribution and mean size of the particles were measured and the particles were observed by scanning electron microscopy in order to propose a mechanism by which the composite material is produced. Then a study of the surface properties of the materials ground alone and co-ground was performed to understand the evolution of the interactions between matrix and filler during grinding. These different properties have an influence on the use properties; that is why it is very important to understand how they evolve during co-grinding. Finally, the evolution of use properties (mechanical properties, water uptake and diffusion) during co-grinding was characterized, the objective being to study if co-grinding permits to enhance these properties compared to those of blends and to define the best co-grinding conditions.

2. Materials and methods

L,D-Polylactic acid (PLA) PABRL-68 (Galactic, Belgium) containing approximately 12% of D-lactic acid was used as the matrix. Its molecular weight, Mn, given by the supplier, is equal to 68 kDa, while the polymolecular index Mw/Mn is 2.78. Since PLA was supplied in the form of granules of approximately 3 mm, these ones were previously ground during 3 min in a thermostatically controlled laboratory knife mill. The powder was then sieved and the particles below 400 μm were kept for the experiments performed in the present work. A SEM picture of pre-ground particles is presented in Fig. 1a. The PLA special gravity is 1250 kg m^{-3} and its glass transition temperature, determined experimentally by differential scanning calorimetry (DSC Netzsch Phenix 204), is 58 °C. A similar value of Tg was proposed by Lu and Chen [12]. The mechanical properties of the matrix were determined experimentally. They are the following: Young modulus = 3.6 GPa; stress at break = 13.7 MPa; elongation at break = 8.7%. These values are in the order of magnitude of the data given by the supplier.

The filler was a waxy maize starch (Waxilys – Roquette, France). It is mainly composed of amylopectine (99%). The particles size ranges from 4 to 32 μm. As shown in Fig. 1b, the initial sample contains individual particles and some agglomerates. The filler special density is 1330 kg m^{-3} and its glass transition temperature, determined experimentally by differential scanning calorimetry, is 90 °C.

The products were dry ground in a laboratory ceramic tumbling ball mill (Prolabo, France) having a capacity of 5 L and rotating around its horizontal axis. The mill chamber contained ceramic balls having three diameters (5.5, 9.3 and 17.5 mm) with a proportion of ¼, ¼ and ½ respectively. The interest of using different ball sizes is to have always a ball size adapted to the decreasing particle diameter. The ball filling rate was fixed at 20% of the chamber volume. Each material was first ground alone to understand its own behaviour during the treatment and then the two products were ground together to produce the composite. During each experiment the powder filling rate, corresponding to the percentage of the free
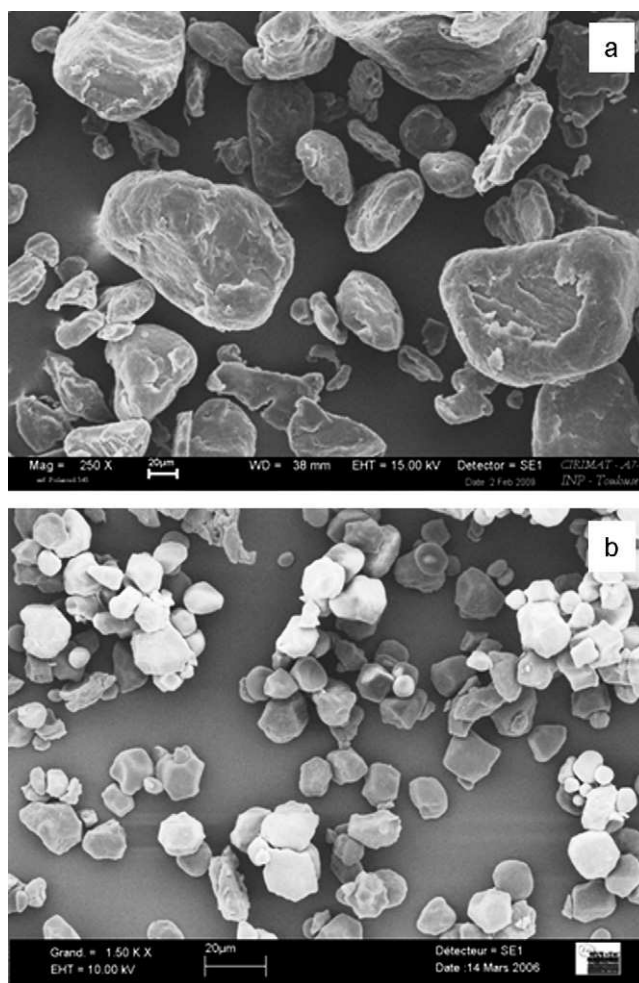

Fig. 1. SEM micrograph of (a) preground PLA particles and (b) starch particles.

volume between the balls occupied by the powder, was fixed at 10 vol.%. The ball and the powder rates were low compared to values usually used in industrial tumbling ball mills to minimize the powder consumption. The rotation speed of the mill was fixed at 100 rpm which corresponds to 75% of the critical speed. The starch percentage in the mixtures was equal to 20 wt.%, since it was shown in previous studies that a filler rate of 20–30% permits to have the best use properties of co-ground composites containing minerals or starch as fillers [13–15].

Powder samples were taken at different grinding times in various zones of the mill to be sure that they were representative of the whole particles. The sample quantities were small enough not to significantly modify the powder volume in the chamber. For some analyses (granulometry, morphology) the powder was used as sampled, while for others (surface characterization, mechanical properties and water uptake) pellets were needed. In this last case, the powder was introduced in a cylindrical mould and compacted at 60 °C in a Carver press. A pressure of 150 bars was applied during 15 min. These conditions permit to have the best reproducibility of the analyses. The pellets diameter was 12 mm and their mass was around 500 mg for water uptake and 200 mg for surface and mechanical properties.

The size distributions of the powders, expressing the volume percentage of particles in different size classes, were measured by means of a dry laser diffraction granulometer Malvern Mastersizer 2000. The data were treated according to the Mie theory which permits to limit artefacts at small sizes of the size distributions. The mean size, d50, corresponding to a cumulative frequency of 50%,

	ρ (kg m^{-3})	μ (Pa s)	γ_L (mJ m^{-2})	γ_d (mJ m^{-2})	γ_p (mJ m^{-2})
Diiodomethane	3320	2.8×10^{-3}	50.8	50.8	0
Formamide	1130	4.55×10^{-3}	58	39	19
Water	1000	1×10^{-3}	72.8	21.8	51

was calculated. The reproduction in the size measurements was verified and the difference between the mean sizes was less than 1%. Selected powder samples and pellets surfaces were observed using a scanning electron microscope Leo 435 VP.

Matrix–filler interactions were characterized by analysing surface properties. In that way, a sessile drop method was adopted, using a Digidrop Contact Angle Meter from GBX Scientific Instruments. Drops (3 μL) of different liquids were deposited on the pellets surface and the static contact angle (θ) was measured by means of a high resolution camera and software, calculating the slope of the tangent to the drop at the liquid–solid interface. Five measurements were done with each liquid on different locations of the pellets and the difference between the angles was less than 1°. Two polar liquids (water and formamide) and a non-polar liquid (diiodomethane) were used, whose properties are presented in Table 1. The energy components of the two products and of the composites were determined from the angles and the influence of grinding and co-grinding on these parameters was studied.

Mechanical properties of pellets were determined at room temperature (21 °C) using diametral compression tests called Brazilian disc tests [16]. Pellets were placed vertically between two plates and an increasing compression force (F) was applied until the rupture of the pellets. The applied force and the space between the plates were measured. The related tensile stress (σ) can be calculated from the force according to the following equation:

$$\sigma = \frac{2F}{\pi . D_p . H} \qquad (1)$$

where D_p and H are respectively the initial diameter and the thickness of the pellet.

The strain (ε) is the ratio between the diameter variation of the pellet and its initial diameter, expressed in percentage. The stress and strain at break and the Young modulus were calculated from the measured data. Three experiments were realized for each sample and it was checked that the reproducibility error was less than 5%.

To study the behaviour of the ground and co-ground materials in water, pellets were introduced in flasks containing distilled water and regularly removed from water, dried on a paper sheet and weighted. The experiments were performed during 16 months and the water uptake, WU, was calculated with the equation:

$$WU = \frac{m_t - m_i}{m_i} \times 100 \qquad (2)$$

where m_i is the initial pellet mass and m_t the pellet mass at immersion time t_{imm}.

3. Experimental results and discussions

3.1. Evolution of the size and morphology of the particles

The two products were first ground separately to study their fragmentation and agglomeration mechanisms. Concerning PLA grinding, the evolution of the size distribution is presented in Fig. 2. Initially, the size distribution is spread. Rapidly after grinding begins, a displacement of the size distribution towards the right is observed, which means that the smallest PLA particles are no more present in a free state in the mill chamber. This is due to an agglomeration phenomenon as it can be noticed on the SEM micrograph of
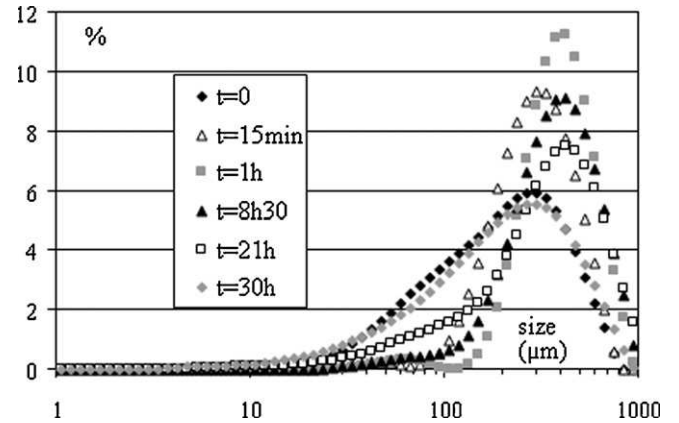

Fig. 2. Variation of the size distributions of ground PLA.

Fig. 3 taken after 15 min of grinding. Small PLA particles are stuck on big ones. This phenomenon has been noticed during the first 3 h of the experiment. After 8 h, the size distribution shifts towards the left, i.e. towards the small sizes because PLA particles begin to break. All these observations lead to the variation of the mean size plotted in Fig. 4. The PLA mean size, initially equal to 200 μm, increases rapidly during the first 3 h to reach 400 μm, and then levels off for 5 h, to finally decrease slowly.

As for starch (Fig. 4), its initial mean size is 13 μm, i.e. lower than the minimum size (several tens of μm) that can be reached when grinding macromolecules [17]. Consequently, it is not reduced during the treatment. It is constant during the first 2 h and increases then. It was controlled by SEM that during the first period a disaggregation of the starch agglomerates happens. Then, the size increase is the result of agglomeration of individual particles. Finally the size oscillates due to a competition between agglomeration of individual particles and fragmentation of agglomerates.

In a second time, PLA–starch mixtures were co-ground. The variation with co-grinding time of the size distribution is presented in Fig. 5. The initial size distribution is bimodal (PLA peak at large sizes
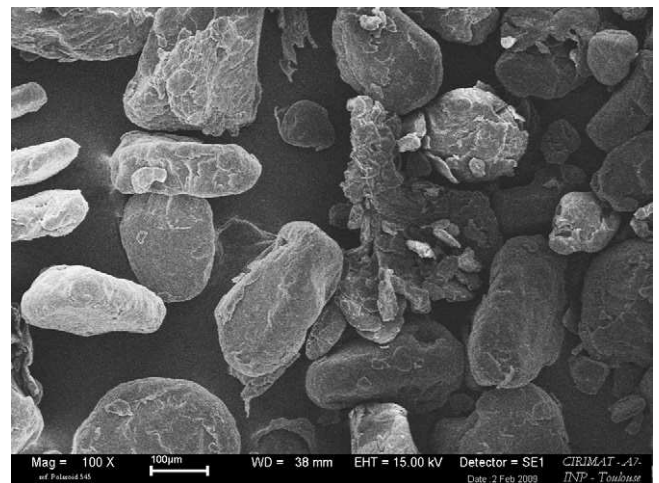

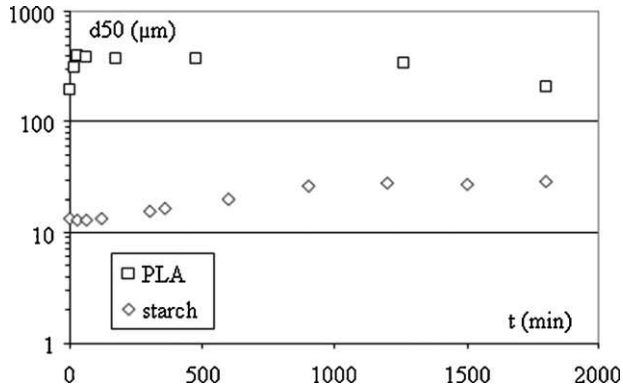**Fig. 3.** SEM micrograph of PLA particles after 15 min of co-grinding.

Fig. 4. Influence of the grinding time on PLA and starch mean sizes.

and starch peak at small sizes). Under the effect of co-grinding, the starch peak disappears during the first 3 h due to agglomeration of its small particles on PLA big ones (Fig. 6a). On this SEM micrograph, one can see that starch particles are individual, what means that the agglomerates observed in Fig. 1b have been dissociated. The mean size increases from 176 μm to 250 μm during this period. Afterwards the remaining peak (at high sizes) shifts towards the right. This may be attributed to the fact that small PLA particles stick on big ones, as it can be seen on the SEM micrograph of Fig. 6b taken after 8 h. Thus the mean size increases drastically to reach 392 μm at that time. Finally the peak at large sizes shifts towards the left, i.e. towards smaller sizes and the mean size decreases, strongly in a first time to reach 52 μm after 45 h and more slowly then up to 25 μm after 76 h. The SEM micrograph of Fig. 6c permits to explain this evolution by a breakage of the agglomerates. Composite particles are produced, in which starch is well dispersed in PLA and well stuck on the matrix. Moreover, the presence of starch permits to limit agglomeration between PLA particles themselves and favours the fragmentation phenomenon since after 30 h the mean size is equal to 209 μm for PLA alone and to 151 μm for the mixture.

3.2. Characterization of the surface properties of the products ground alone and co-ground

The characterization of the surface properties of the matrix, the filler and the mixture permits a better understanding of the intermolecular interactions between the materials constituting the composite and of the effect of co-grinding on these interactions. These ones influence the use properties of the composite. While it is possible to determine directly the surface energy of liquids, in the case of solids the lack of molecules and atoms mobility imposes to
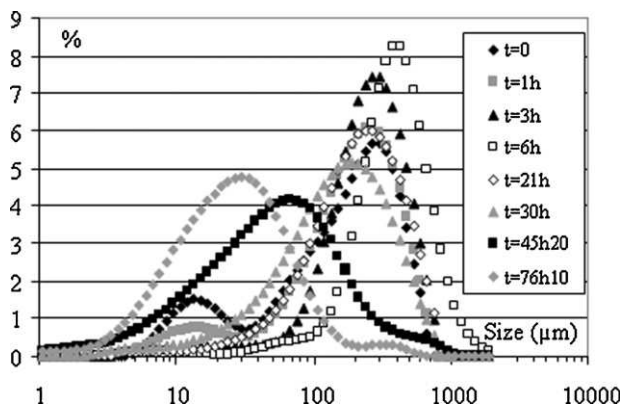

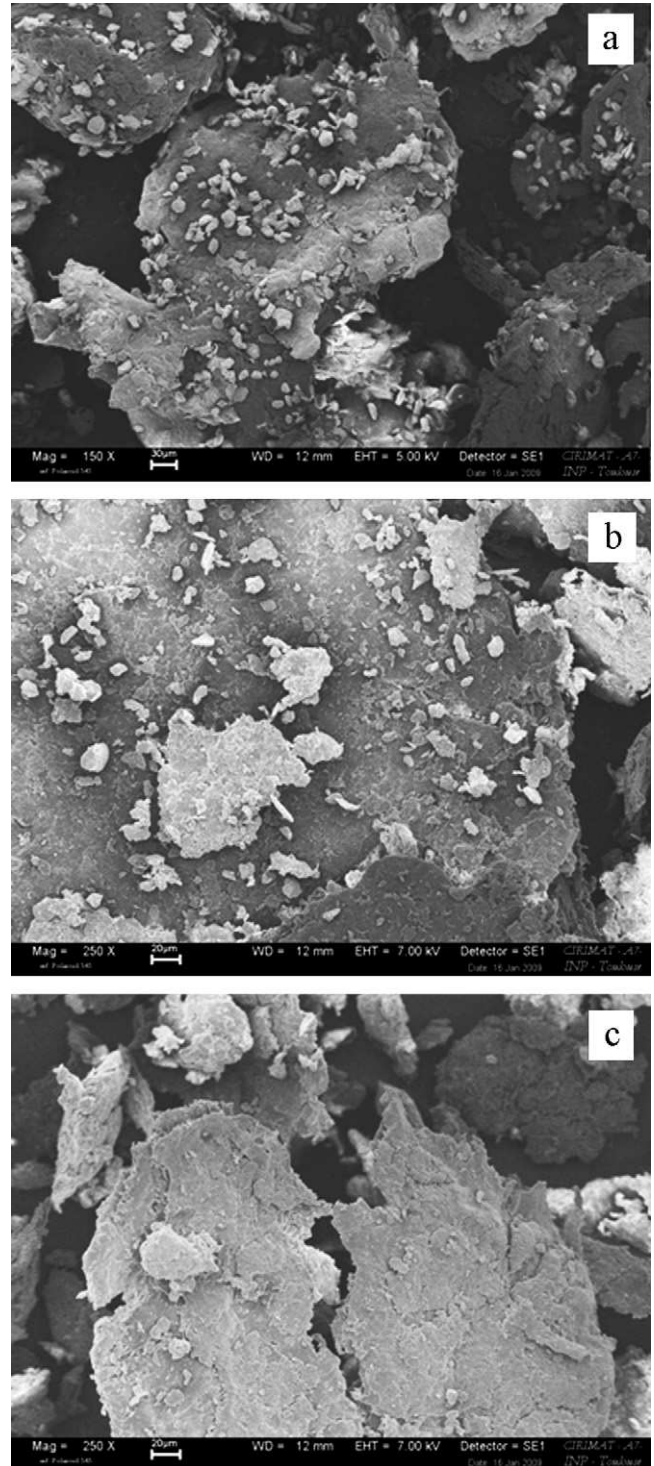**Fig. 5.** Variation of the size distributions of the co-ground mixtures.

Fig. 6. SEM micrographs of mixture particles at a co-grinding time of (a) 1 h; (b) 9 h; and (c) 30 h.

use indirect methods such as the study of the interactions between the solid and a liquid.

When a liquid drop is deposited on a solid surface, equilibrium between the solid, the liquid and the vapour is established, leading to a contact angle, θ, defining the wettability between the liquid and the solid. This angle corresponds to the minimum energy between the three phases at equilibrium. Different models have been proposed in the literature to establish a relationship between the contact angle and the surface energies of the solid. Among

them, two models are often used in the literature and were already applied to composites produced by co-grinding and made of synthetic polymeric matrix (poly(vinyl acetate) and polystyrene) and a filler consisting of a mineral (calcium carbonate and silica) or starch [8,10,11]. Since they have been developed in details in these references, only a short description will be given, necessary for the study presented here.

In their model, Owens and Wendt [18] considered that a total surface tension can be expressed as the sum of dispersive (γ^d) and non-dispersive or polar (γ^p) components, the last one resulting from hydrogen bonding and dipole–dipole interactions. The relation permitting to determine the energy components from the contact angle is:

$$\frac{1 + \cos\theta}{2}\gamma_L = \sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p} \tag{3}$$

where indexes S and L correspond to solid and liquid respectively.

Van Oss et al. [19] proposed the so-called Lifshitz–van der Waals approach in which the total surface tension is divided in Lifshitz–van der Waals (γ^{LW}) and acid–base (γ^{AB}) components. The last one is decomposed in acid (γ^+) and basic (γ^-) components. The expression used in this model is thus:

$$\frac{1 + \cos\theta}{2}\gamma_L = \sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+} \tag{4}$$

In previous studies [8,10,11], it was shown that the dispersive component for the first model and the Lifshitz–van der Waals component for the second one do not evolve significantly during grinding or co-grinding. The acid component of the Lifshitz–van der Waals model was very low in all cases, indicating that the polymers and the composites are electron donors. Moreover the polar component of the first model and the basic component of the second one evolve in the same way during grinding or co-grinding. Finally, considering the Lifshitz–van der Waals model, the study of the influence of grinding or co-grinding on surface properties should not be based on the analysis of the global acid–base component because it is a combination of two phenomena (acid and basic) that can evolve in an opposite manner.

Due to all these considerations, it was decided to apply only the model of Owens and Wendt to the results of this study. The evolution of the contact angles measured with the two materials ground separately is not presented here. Only the data on the water angles are discussed. Indeed, initially they are equal to 16° for starch and 72° for PLA, indicating that starch is very hydrophilic while PLA is hydrophobic. As grinding proceeds the angle between water and PLA pellets does not evolve significantly. On the contrary, as detailed in a previous study [11], for starch it increases during the first 6 h of grinding due to the fact that the material becomes progressively more hydrophobic. The contact angle levels off then since thermodynamic equilibrium is reached.

The energy values (dispersive, polar and total) of the Owens and Wendt model are gathered in Fig. 7 for the two materials ground alone. The dispersive components do not evolve significantly. Concerning the polar energy, the initial value of starch is high ($33\,mJ/m^2$) due to the presence of numerous hydrophilic hydroxyl ($-OH^-$) groups in glucose units while that of PLA is lower, resulting from a balance between polar carboxyl ($-C=O$) groups and non-polar methyl ($-CH_3$) groups. During grinding, the starch polar energy decreases, probably due to conformation modifications of starch molecules, while PLA polar energy remains quite constant. The total energies evolve as the polar ones.

The same kind of study was done while co-grinding the mixture (Fig. 8). As already indicated previously for the two materials ground alone, the variation of the dispersive energy is not significant when co-grinding them. The initial polar energy of the simple mixture is equal to $25\,mJ/m^2$ (i.e. between the values of both initial
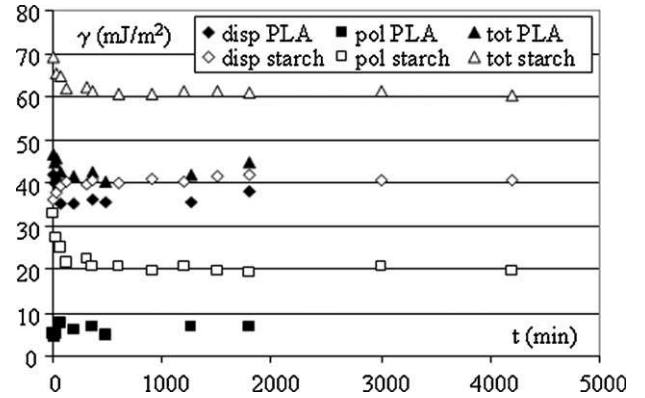

Fig. 7. Influence of grinding on the surface energies of PLA and starch.

materials), indicating their simultaneous presence at the pellets surface (see Fig. 9a where starch can be seen among PLA). Co-grinding leads to a drastic decrease of this parameter during the first 8 h. This can be explained by the observations made on size distributions. Indeed small PLA particles stick progressively on PLA–starch agglomerates, thus covering starch particles (see Fig. 9b where the pellet surface is more homogeneous than the surface observed in Fig. 9a). Consequently, the pellets surface becomes more constituted of PLA whose polar energy is lower. For longer times, since agglomerates are broken, starch may be more present on the pellet surface. This, combined to intermolecular interactions between the two materials generates a progressive increase of the polar energy. Finally, it remains constant at a value comprised between those of the two separately ground materials.

3.3. Characterization of the mechanical properties of the materials

Two series of experiments were carried out: one with PLA alone and one with the composite mixture. Examples of stress–strain curves (of PLA and mixtures ground or co-ground during 1 h and 30 h) are presented in Fig. 10. It can be seen that the PLA behaviour is brittle while the composite behaviour varies from brittle to ductile when the co-grinding time is increased. Moreover, after a treatment of 1 h, the limit stress and strain are lower for the composite mixture than for PLA, while it is the opposite after 30 h. From these first data, one can already say that adapted co-grinding has a positive effect on the mechanical properties of the mixture.

To enrich this first analysis, the evolution of the Young modulus versus the treatment time is plotted in Fig. 11 as well as the stress and strain at break in Fig. 12. The three parameters do not evolve significantly for PLA. On the contrary, adding starch to PLA
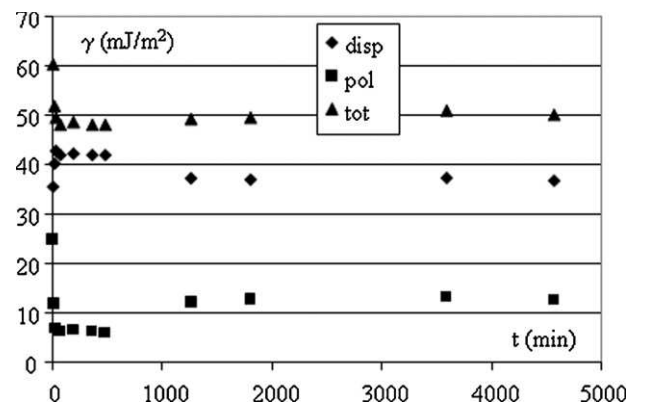
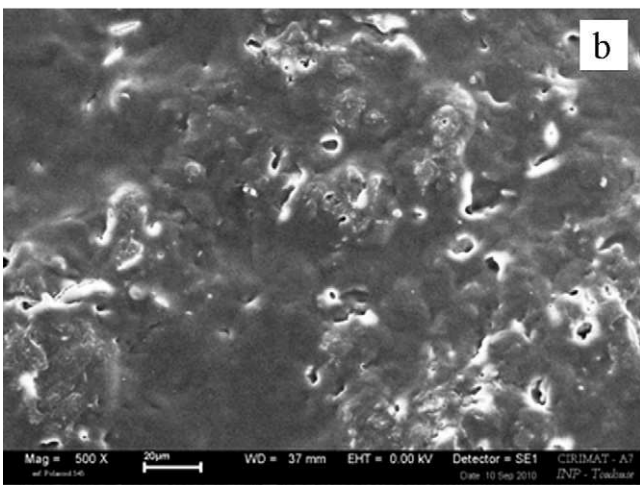

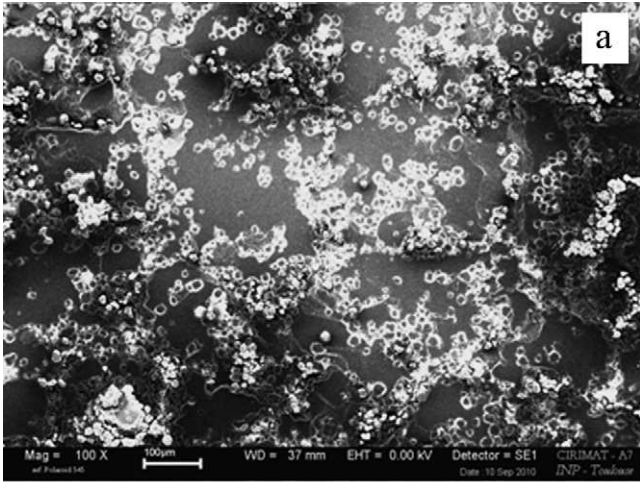**Fig. 8.** Variation of the mixture surface energies.

Fig. 9. SEM photo of a pellet surface ((a) co-grinding time = 0 and (b) co-grinding time = 6 h).

and mixing them (without grinding) has a very negative effect on the parameters since adhesion of the filler on the matrix is bad and starch has lower mechanical properties than PLA. This kind of reduction of the mechanical properties when adding starch to PLA was already observed by Zhang and Sun [1] who added a compatibilizer to enhance the mechanical properties.

The three parameters increase when co-grinding is proceeded. The values after 30 h of co-grinding are 2.2 times (for ε), 3.5 times (for σ) and 4.9 times (for E) higher than with a simple mixing and
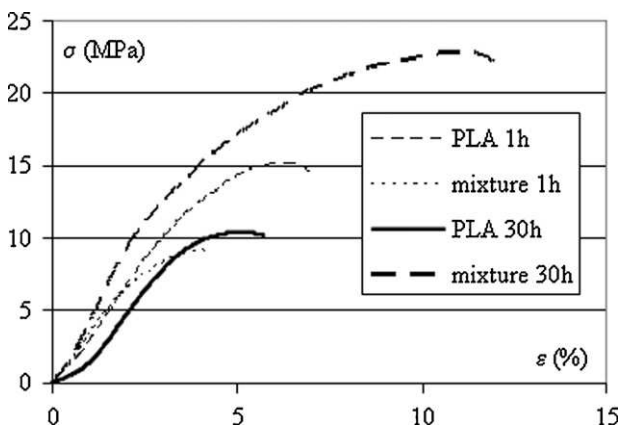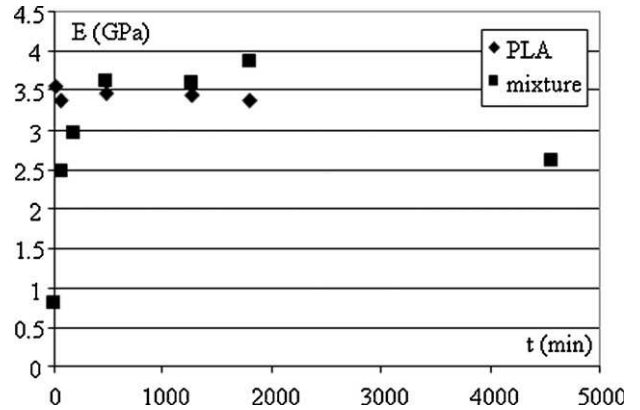

Fig. 11. Variation of the Young modulus of PLA and mixtures.

even higher than the values measured for PLA alone. The filler is well dispersed in the matrix and interactions between the materials are favoured by co-grinding. The enhancement of the different parameters is more important that what was observed in a previous study on co-ground composites made up of polystyrene and starch (mechanical parameters multiplied by a factor of 1.5–2) [20] since PLA possesses carboxyl groups whose interactions with hydroxyl groups of starch, favoured by co-grinding, certainly have a more positive effect on the properties compared to polystyrene–starch interactions. However, a too long treatment leads to a decrease of the three parameters, probably because of a degradation of the molecular chains. Co-grinding the mixture during an optimum time permits to have better mechanical properties than for the matrix alone, without using a chemical agent, what is interesting for environment.

3.4. Study of the materials behaviour in water

Using degradable materials for packaging presents a great interest for environment, but it is important that the material is not too rapidly degraded. It was shown in a previous study [11] that adding starch to polystyrene has a negative effect on the resistance to water of blends when they are only mixed and a minimum co-grinding time, the value of which increases with the filler rate, is necessary to enhance the resistance of the composites to water without any compatibilizer. In this work, it is shown how the incorporation of starch in PLA and the implementation of co-grinding may have an influence on the water uptake and diffusion in the materials used in a pellet form. Results on the materials ground alone will be presented before those obtained with the mixtures.
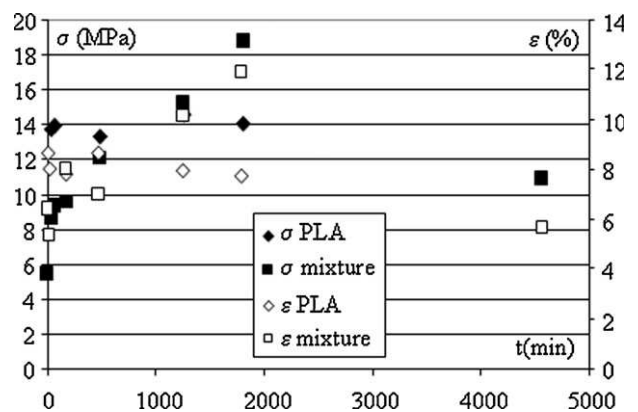

Fig. 10. Examples of stress-strain curves for PLA and mixtures.

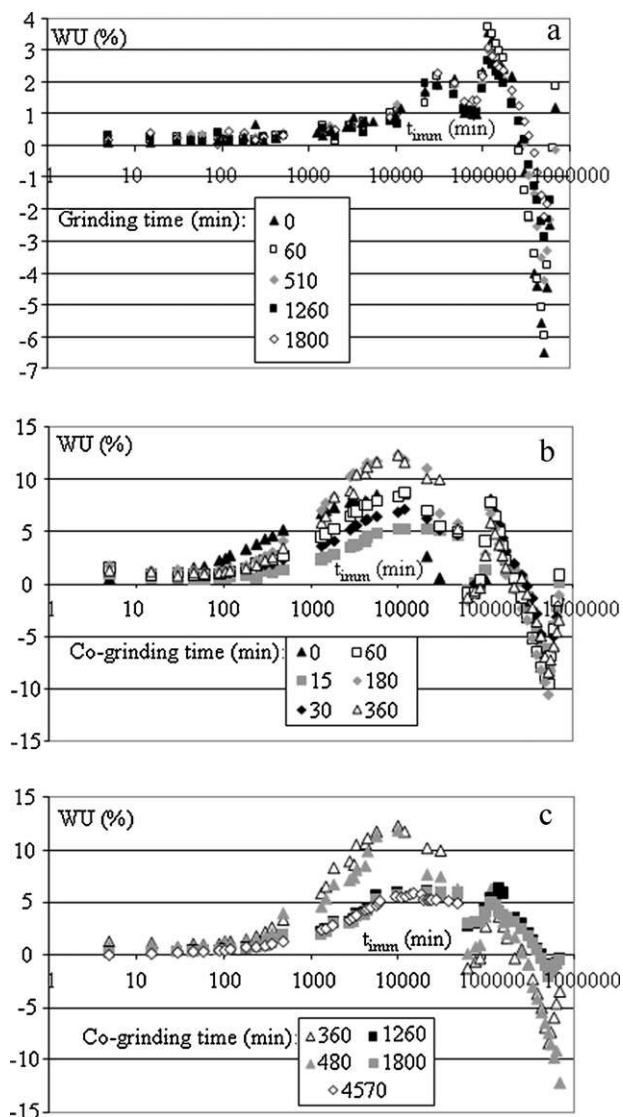Fig. 12. Variation of the stress and strain at break of PLA and mixtures.

Fig. 13. Influence of grinding on the water uptake of (a) PLA; (b and c) mixtures.

Concerning starch, data obtained for 5 months were described and commented in details in a previous article [10]. In summary, it was shown that a minimum grinding time of 2 h was needed to avoid quasi-instantaneous disaggregation of the pellets in water. The reason of this is the very good affinity of starch with water, as already indicated in the section on the surface properties, resulting of the presence of the hydroxyl groups of glucose. For grinding times between 2 and 5 h, the pellets resistance to water was good, probably due to a modification of the molecular chains of starch, and consequently a progressive increase of the pellets mass, i.e. of the water uptake, was noted during immersion in water. The water uptake raised up to 60% after 1000 min of immersion. After one month of immersion, the pellet consistency changed due to a progressive degradation of starch. Finally, a too long grinding time, generating an excessive degradation of the molecular chains by the mill balls, induced a rapid disaggregation of the pellets.

Results obtained with PLA in this study are presented in Fig. 13a. The immersion time is in a logarithmic form to be able to analyse easily the period of WU increase during the first days of immersion. Three parts can be observed in the curves. In the first one, before 60 min of immersion, WU does not evolve significantly. In the second part (before 30,000 min of immersion, i.e. about 21 days), WU increases due to progressive water absorption. However, since the

water uptake never exceeds 2%, one can say that PLA has little affinity with water. This corroborates the high contact angles between water and PLA measured when studying the surface properties of the matrix. Due to the low values of WU observed, it is difficult to analyse any influence of the grinding time. In the third part of the curves (after 30,000 min), phases of WU decrease and phases of WU increase are observed. This is due to the progressive degradation of PLA. The water uptake is even negative, when the pellets mass is lower than the initial mass, but the values are less negative when the grinding time is long (6.6% for $t = 0$ and 2.2% for 1800 min).

Finally, the mixtures data are shown in Fig. 13b and c. As for PLA alone, one observes three zones in the curves: the first one before 60 min of immersion where WU does not increase except when the two materials are just mixed, the second one between 60 and 10,000 min of immersion (around 7 days) where the water uptake increases, and the third one after 10,000 min of immersion where the water uptake fluctuates strongly. The immersion time at which the first water uptake fluctuation appears is lower for the mixture than for PLA alone.

As indicated above, the water uptake does not increase during the first 60 min of immersion when the two materials are co-ground. This means that water does not diffuse in the pellets as soon as they are introduced in water. When the two materials are just mixed (co-grinding time = 0), the starch agglomerates observed on the SEM photo of Fig. 9a favour immediate absorption of water.

In the second zone, the water uptake increases progressively with the immersion time, and since starch is very hydrophilic, adding 20% of filler permits to increase significantly the water uptake compared to the hydrophobic matrix alone. The water uptake kinetics depends on the co-grinding time. Indeed, when the two materials are just mixed (co-grinding time = 0), WU is the highest when the pellet is immersed less than 1000 min, what is not the case after 1000 min. This may be attributed to the bad homogeneity of the mixture already noticed previously on the SEM micrograph of Fig. 9a, but also to bad interactions between the matrix and the filler already evoked, that may favour absorption of water by starch in the first immersion times. When co-grinding the two materials 15 min, the filler is well dispersed in the pellet and its proportion on the pellet surface is less than for the unground mixture and is certainly more representative of the proportion in the whole sample. The water uptake is lower than for co-grinding time = 0. An increase of the co-grinding time (between 15 and 180 min) has a positive effect on the water uptake. This may be due to the disagglomeration of starch agglomerates related previously that leads to the dispersion of smaller individual starch particles within the pellets volume and favours water absorption. After 360 min of co-grinding, the rate of water uptake decreases strongly first and then more slowly (for co-grinding times higher than 1000 min). This decrease of the rate may be attributed to agglomeration of small PLA particles on PLA–starch agglomerates that limits the presence of the filler on the pellets surface and creates a barrier to water, but also to an increase of the interactions between the matrix and the filler and a degradation of the molecular chains under the effect of a long action of balls. After 10,000 min of immersion, diffusion equilibrium is reached. The maximum value of WU (at equilibrium) is reached for a shorter immersion time than with PLA alone. This can be attributed to the presence of starch that is progressively and partially released in water as already suggested by Angellier et al. [21]. This release occurs before the degradation of the pellets and leads to a mass reduction, i.e. to the first WU decrease. The pellet mass measured at equilibrium will be named m_∞.

The third zone corresponds to degradation phenomena as for PLA alone. For the very first co-grinding times, WU is more negative for the mixture (−8.3%) than for PLA (−6.6%). This means that starch contributes to degradability. Then, mixture values become more negative when the co-grinding time increases up to 180 min
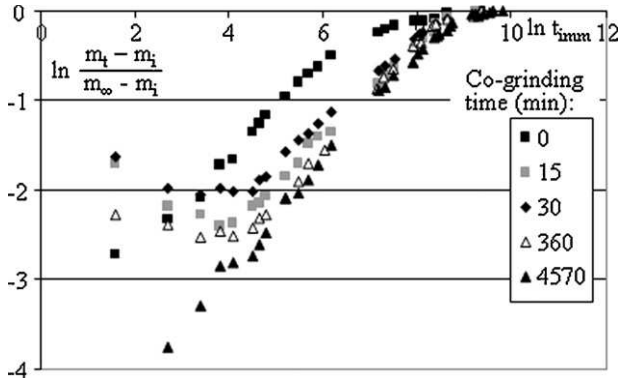
Fig. 14. Determination of the water diffusion mechanism for the composites.

(WU = −10.6%). It can be observed that the higher the water uptake during the water absorption phase (second part of the curves), the lower the negative value of WU.

For high co-grinding times (i.e. when the maximum water uptake is low in part 2 of the curves), WU is less negative to reach −2%. This may be a result of strong interactions between matrix and filler, but also probably a degradation of the molecules under a long effect of the mill balls.

To study the water diffusion observed in the second part of the water uptake curves, Frisch [22] has expressed the diffusion mechanism according to the following equation:

$$\frac{m_t - m_i}{m_\infty - m_i} = k \cdot t_{imm}^n \tag{5}$$

In this equation, n is the diffusional exponent which characterizes the diffusion mechanism. Indeed, when water diffuses in a polymer, this one swells and the swelling rate depends on the polymer chains relaxation. If the water diffusion rate is lower than the relaxation rate, the diffusion is fickian and n is equal to 0.5. When the opposite occurs, the mechanism is controlled by chain relaxation and n is equal to 1. This model has already been used to study water diffusion in starch [23,24] and in starch filled co-ground composites [11,25]. Moreover, in Eq. (5), k is a constant which can be expressed as follows when the diffusion is fickian [26]:

$$k = \frac{4}{H} \left(\sqrt{\frac{D}{\pi}} \right) \tag{6}$$

where D is the diffusion coefficient and H the pellet thickness.

It was tried to apply the model to the results of this study. Since PLA is hydrophobic, water diffusion is very low and no diffusional exponent and diffusion coefficient can be determined. As for starch, Seyni et al. [11] have shown that, when the grinding time permits to have a good resistance of the pellets to water, the diffusion is fickian and a diffusion coefficient equal to 1.1×10^{-10} m^2 s^{-1} was determined. Russo et al. [23] have found a similar value.

Concerning the mixtures, the variation of $\ln[(m_t - m_i)/(m_\infty - m_i)]$ has been plotted versus the logarithm of the immersion time (expressed in min) in Fig. 14 for some representative co-grinding times. When no co-grinding is applied, the points are gathered around a straight line for values of $\ln[(m_t - m_i)/(m_\infty - m_i)]$ lower than −0.5, i.e. for values of $(m_t - m_i)/(m_\infty - m_i)$ lower than 0.6 which is the validity limit of Eq. (5) [22]. For co-ground composites, when $\ln t_{imm}$ is lower than 4 (immersion time lower than 1 h) the model is not convenient since, as already indicated, no water uptake happens. Then the points are distributed around a line, the slope of which is the diffusional exponent. The lines equations have been determined by linear regression, and values of n are gathered in Table 2. Since the values are close to 0.5, one can say that the diffusion is fickian.

Table 2
Values of the diffusional exponents.

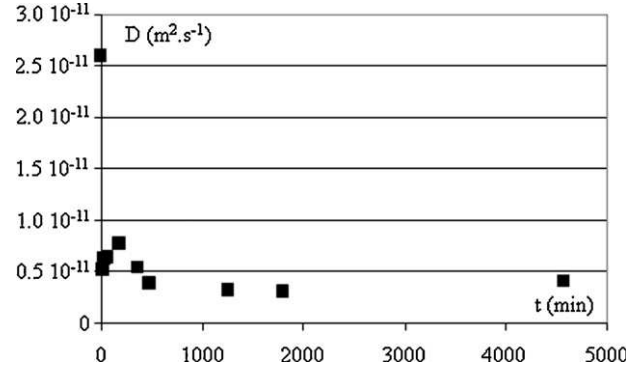|	Co-grinding time (min)									
	0	15	30	60	180	360	480	1260	1800	4570
n	0.54	0.51	0.46	0.51	0.55	0.55	0.54	0.52	0.54	0.55

Fig. 15. Influence of the co-grinding time on the diffusion coefficients of the composites.

The diffusion coefficients were then calculated for the different co-grinding times using Eq. (6). They are presented in Fig. 15. The mixture diffusion coefficients are lower than that of starch since the matrix is more hydrophobic than the filler. The variation of D with the co-grinding time logically follows the water uptake rate. D is the highest at $t = 0$ since the presence of starch agglomerates favours water diffusion. When co-grinding is implemented, diffusion coefficients are lower and, as for the water uptake rate and for the same reasons that will not be repeated here, D increases until the co-grinding time is equal to 180 min and decreases then to level off at long treatment times.

4. Conclusions

PLA–starch composite materials were produced by co-grinding. The two products were first ground alone and then co-ground, and size as well as SEM analyses have permitted to propose a mechanism of composite production.

The characterization of the surface properties of the products has allowed showing that PLA is a hydrophobic matrix and starch is a hydrophilic filler, due to the presence of numerous hydroxyl groups in glucose, but grinding reduced this hydrophilic behaviour and the starch polar energy component. Co-grinding the mixture enhances interactions between the two materials that have a great effect on the use properties of the composite. Indeed, a simple blend of hydrophobic PLA and hydrophilic starch leads to a reduction of the mechanical properties of the mixture by a factor 2.5 compared to those of the single matrix due to phase separation and bad adhesion. On the contrary, applying co-grinding permits to increase the mechanical properties, which are even higher than those of the single PLA matrix for optimized operating conditions. Finally interactions between matrix and filler influence also the composite behaviour in water. The water diffusion rate and the maximum water uptake of the composites vary, depending on the co-grinding time.

Co-grinding permits to produce composite materials offering good use properties without adding a compatibilizer or a plasticizer.

Acknowledgments

Appendix A. Nomenclature

d50	particle mean size (μm)
D	diffusion coefficient ($m^2\,s^{-1}$)
D_p	pellet diameter (mm)
E	Young modulus (GPa)
F	compression force (N)
H	pellet thickness (mm)
m_i	initial pellet mass (kg)
m_t	pellet mass at immersion time t_{imm} (kg)
n	diffusional exponent
t	grinding time (min)
t_{imm}	immersion time (min)
WU	water uptake (%)
ε	strain (%)
γ	surface energy ($mJ\,m^{-2}$)
σ	tensile stress (MPa)
θ	contact angle between a liquid drop and the pellet surface ($^\circ$)

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