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On the interest of using degradable fillers in co-ground composite materials

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A B S T R A C T

The article presents the results of a study whose objective is to show the interest of using vegetable and biodegradable fillers in composite materials. The incorporation of fillers made up of starch in the synthetic polymeric matrix was carried out by co-grinding, a process supporting the dispersion of one component in another one and thus supporting the homogeneity of the composite properties. The follow-up of the particle size and morphology has permitted to identify how the composite is formed. We could note that co-grinding makes it possible to improve the mechanical properties of the composite material, not only through a better dispersion of the filler in the matrix, but also thanks to a modification of the interface properties. Finally a study on the material degradation in water has shown that the incorporation of a vegetable, degradable and cheap filler in the synthetic matrix and the application of co-grinding during an adapted time offer interesting water-resistant properties.

Keywords:

Co-grinding
Composite materials
Synthetic polymer
Starch
Surface and mechanical properties
Degradability

1. Introduction

Starch has a great number of non-food uses (paper, textile, chemistry). Its incorporation in plastics has for a long time been a subject of study for various reasons. On the one hand, plastics represent a source of very polluting materials because of their chemical, physical and biological resistance. On the other hand, certain applications of plastics have constraints (fragmentability) where starch comes in as a technical solution.

In 1987, a formulation containing starch was developed, enabling it to be transformed like a conventional thermoplastic polymer [1]. Its mechanical behaviour rests on the presence of water in starch. Indeed, water, due to its plasticizer effect, permits to lower the glass transition and the fusion temperatures of starch and thus to work below its decomposition temperature. Then, the material can be transformed by injection moulding. This product is considered to be completely biodegradable.

Other studies were undertaken in a different direction: the addition of native starch granules in polymer films allows to modify the mechanical properties of the films which become breakable, which may increase their degradation rate. The simplest approach consists in mixing starch at the native state with molten polymer [2]. However starch thus added reduces the mechanical properties of the material before degradation. These properties must be equivalent to those of a non-filled product. The maximum rate of starch to be introduced is therefore limited. It is interesting to enhance the

interfacial properties between starch and the matrix, which are responsible for these weak mechanical properties. In that way, one of the solutions is to add a compatibiliser in the synthetic polymer-starch blend. Depending on the polymer's nature, this compound can be esterified starch [3,4], starch grafted by a polymer [5,6] or a maleated polymer [7].

The last solution could be to work on the size reduction of starch and on the improvement of its dispersion within the matrix. In this study, we propose to work in this way by using co-grinding to process starch-filled synthetic polymer composites. This process was used in the generation of composite materials with mineral fillers [8], and it was shown that co-grinding makes it possible to clearly improve the mechanical properties of composite materials, compared with a simple blending [9]. This work was completed with a model polymer (poly (vinyl acetate)), that we will preserve for the study presented in this paper. The objective is to show the feasibility of incorporating degradable fillers by co-grinding. Indeed, the incorporation of such a filler is a challenge, since if the minerals are rapidly ground, thus permitting to easily disperse in the matrix a filler with a size lower than the micrometer [10], the same does not apply to starch which is a macromolecule, and as far as we know there is no data in the literature on this point.

We present the mechanisms at the origin of the generation of such a composite material. In this way, the evolutions of the size and the morphology of the particles during co-grinding were followed. Moreover, for a better understanding of the phenomena appearing during processing, the surface properties of the materials were characterised. Finally, modifications induced by co-grinding on certain use properties (mechanical properties and degradability) were analysed.

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2. Experimental procedure

Dry batch co-grinding was performed in a 5-litre ceramic tumbling ball mill containing ceramic balls with a size between 5 and 12.5 mm. The rotating speed of the chamber was fixed at 100 rpm, i.e. at 75% of the critical speed, while the ball loading volume represented 20% of the whole volume of the chamber. The powder filling rate was fixed at 10 vol.% of the total void space of the balls.

Poly (vinyl acetate) (PVAc) was provided by the company Elotex – Switzerland. It consists of agglomerates produced by polymerization in emulsion followed by drying. Its density is of 1783 kg/m³. The initial size distribution of the polymer being very broad, the particles were sieved, and those whose size is between 80 and 100 µm were retained for this study. With regard to starch, it comes from waxy maize (Waxyls – Roquette Frères). The average initial size of the particles is 13 µm and the density is 1330 kg/m³. The starch powder consists of individual particles, as well as a few agglomerates (Fig. 1). Fig. 2 shows a SEM micrograph of the two products. The small particles are mostly starch but also small PVAc particles while the big ones are PVAc. Starch particles are more angular than PVAc ones.

The products were first ground separately in order to characterize their respective behaviours during the treatment. They were then co-ground during various times. The mixtures contained 75 wt.% of PVAc and 25 wt.% of starch. In a former study carried out with calcium carbonate as filler [9], it was shown that these proportions permit to improve significantly the mechanical properties.

Small powder samples were taken in various zones of the chamber in order to be analysed. The size distribution of the particles was measured by means of a laser diffraction granulometer Malvern Mastersizer 2000. The data was treated according to the Mie theory which permits to limit artefacts at small sizes of the distribution. The average size, d_{50} , corresponding to a cumulated volume fraction of 50%, was calculated from the size distributions. Selected samples were observed with a scanning electron microscope (LEO 435 VP).

Surface energies were measured using the sessile drop method (Digidrop GBX). The powders were compacted in a Carver press to form cylindrical discs with a diameter of 8 mm. Different forces were applied on the surface of the discs and it was verified that a force of 30 kN allows to have a better reproducibility in the angle measurements (variation of less than 1% between the angles). Three solvents, whose properties are gathered in Table 1, were used.

The mechanical properties of the composites were determined on films of dimensions 10 mm × 5 mm × 0.3 mm. The films were obtained by pressing the powder in a brass mould in a Carver Laboratory Press, at a temperature of 150 °C (i.e. above the melting temperature of the components) and at a pressure of 34 bar. The heating time was set at

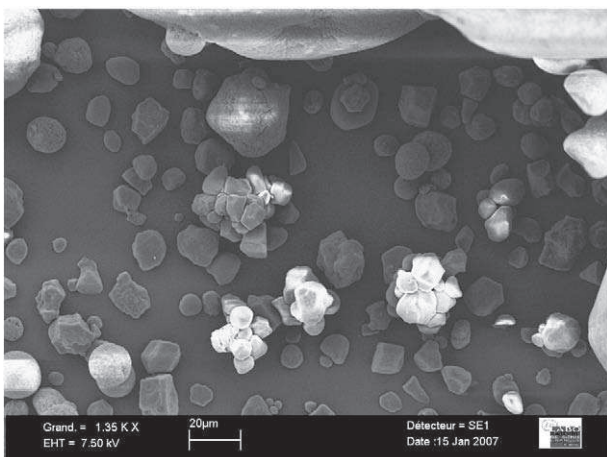


Fig. 1. Micrograph of starch particles.

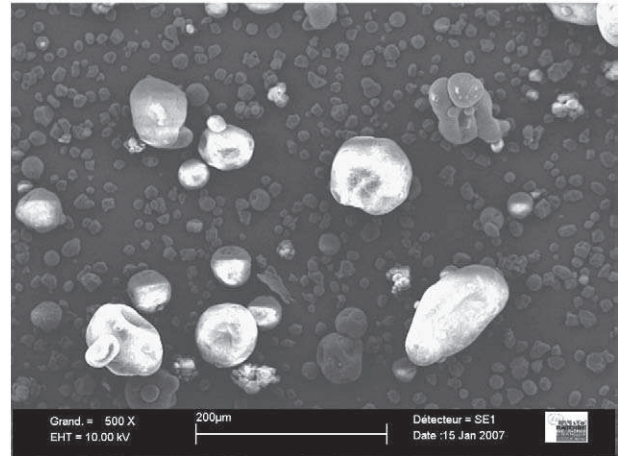


Fig. 2. Micrograph of the mixture.

5 min. The films were then rapidly cooled in liquid nitrogen. Two series of experiments were made:

- In a first series of experiments, the nonlinear mechanical behaviour of starch-filled composites was analysed using an Instron 4301 testing machine working in tensile mode. The initial gap between pneumatic jaws was adjusted to 10 mm. Force (F)–elongation ($L-L_0$) curves were obtained for each sample at a temperature of 20 °C and with a cross-head speed of 10 mm min⁻¹. 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 S_0 is the initial cross section.

Five films were tested for each powder sample.

- In the second series of experiments, dynamic mechanical tests were carried out with a spectrometer RSA2, using the tensile mode. The frequency was 1 Hz and the temperature varied between 0 and 200 °C, with an increment of 1 °C and 5 s of stabilization between measurements. The operating conditions were chosen in such a way that observed behaviour strictly obeys the laws of linear viscoelasticity. The storage component E' was measured. Finally, degradability tests were performed by introducing in water the same discs as those produced for surface properties characterisation. The discs, after being weighted, were placed in a hermetic flask containing 20 g of water at room temperature. Their initial weight was close to 0.6 g and measured with a precision of 10⁻⁴ g. At different times, they were removed from water, their surface was rapidly dried on a blotting paper, and they were then weighted. The water uptake, WU, of the discs was calculated from the relation:

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

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

Three discs were used for each series of experiments.

3. Study of grinding and co-grinding mechanisms

The study of the production mechanisms of the composite particles was based on the one hand on size and morphology analysis, and on the other hand on surface properties.

Table 1
Properties of the liquids at 20 °C

	ρ (kg m ⁻³)	γ_L (mJ m ⁻²)	γ^{LV} (mJ m ⁻²)	γ^{AB} (mJ m ⁻²)	γ^+ (mJ m ⁻²)	γ^- (mJ m ⁻²)	μ (Pa s)
1-Bromonaphtalene (1-BR)	1484	44.4	44.4	0	0	0	4.89×10^{-3}
Formamid (FO)	1130	58	39	19	2.28	39.6	4.55×10^{-3}
Water	1000	72.8	21.8	51	25.5	25.5	1×10^{-3}

3.1. Mechanisms based on size and morphology analysis

3.1.1. Properties of separately ground products

The two products were first ground separately. Fig. 3 shows the evolution versus time of their mean sizes. Concerning PVAc, this parameter decreases during the first 5 h due to a fragmentation of the particles (Fig. 4). A limit size at about 58 μm is then reached. This value is in agreement with those obtained by Schönert [11] for polymers. After that time, agglomeration phenomena are important (Fig. 5) and the mean size increases progressively. Finally, after 15 h of grinding, a competition between fragmentation and agglomeration leads to an oscillation in the size curve.

As for starch, its behaviour is different since the initial mean size is close to 13 μm , i.e. lower than the limit grinding size defined by Schönert for the macromolecules. Thus, one notes that before 2 h, the size does not evolve significantly. Indeed, the initial particles are made up of a mixture of individual grains and small agglomerates of grains, as indicated in Section 2. At the beginning of grinding, the agglomerates dissociate under the effect of the balls and the smallest individual grains agglomerate. This is carried out without substantial variation of the mean size. Thereafter, agglomeration becomes preponderant (Fig. 6) and the mean size increases to reach 30 μm . After 30 h of grinding, some agglomerates are compacted under the effect of the balls (Fig. 7), while others are fragmented. Thus, the mean

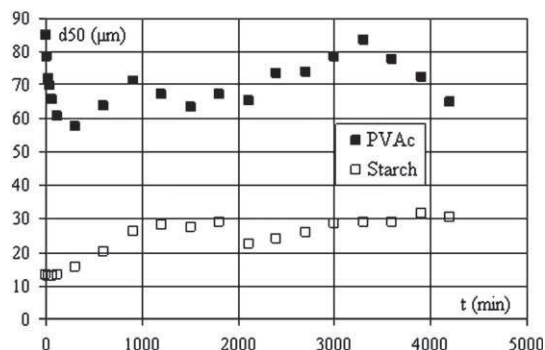


Fig. 3. Variation of the mean size of the two products.

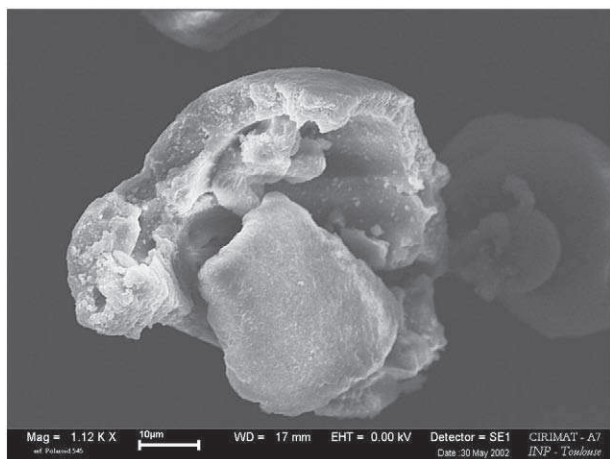


Fig. 4. Micrograph of a PVAc fragment.

size decreases to reach 22 μm . Finally, a competition between fragmentation and agglomeration also occurs.

3.1.2. Properties of co-ground PVAc–starch particles

The mixture used in the study consists of the two materials presented previously, namely of the large particles of poly (vinyl acetate) which constitute the matrix and of the small particles of starch which constitute the filler, which is present at a rate of 25 wt.%. The size distribution before co-grinding thus consists of two peaks (Fig. 8). The right-hand side one corresponds to the PVAc particles, whereas the left-hand side one corresponds to the starch particles, which are smaller.

In the first hours of co-grinding, the peak of the filler is not changed, in accordance with what was observed when it was ground alone, and this because of the small size of the particles. On the other hand, the main peak, corresponding to the matrix, shifts towards the small sizes, which means that the particles are fragmented. Moreover, the fragmentation rate of PVAc particles is similar if the particles are ground alone or in the presence of the filler, since the maximum of the peak is at 44.8 μm after 300 min of co-grinding, and at 45.5 μm when the matrix is ground alone during the same time. After 300 min, the size distributions do not shift any more towards the small sizes, which seems to imply that the fragmentation of the matrix is completed. On the contrary, one notices a peak around 350 μm , resulting from the agglomeration of starch and small polymer fragments on the large polymer fragments (Fig. 9).

This leads first to a strong reduction of the mixture mean size up to 300 min (Fig. 10). Thereafter, and up to 900 min, this one levels off because of a moderate agglomeration. Moreover, the size distributions between these two times are very similar. But after 900 min, the average size increases significantly, resulting from an important agglomeration and a disappearance of the small particles (as shown on the size distribution measured at 2100 min and the SEM photo of Fig. 11, on which agglomerates can be seen, whereas the small free starch particles are no longer visible).

Then, successions of fragmentation of the agglomerates and agglomeration generate an oscillation of the mean size resulting from a more or less important presence of large or smaller agglomerates. The starch is thus progressively integrated within the agglomerates and is well dispersed in the matrix.

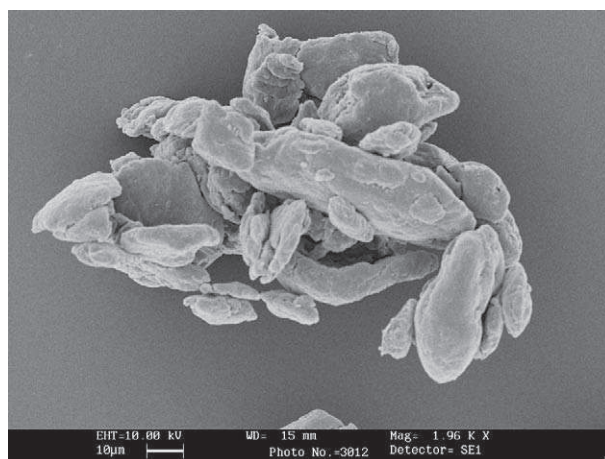


Fig. 5. Micrograph of a PVAc agglomerate.

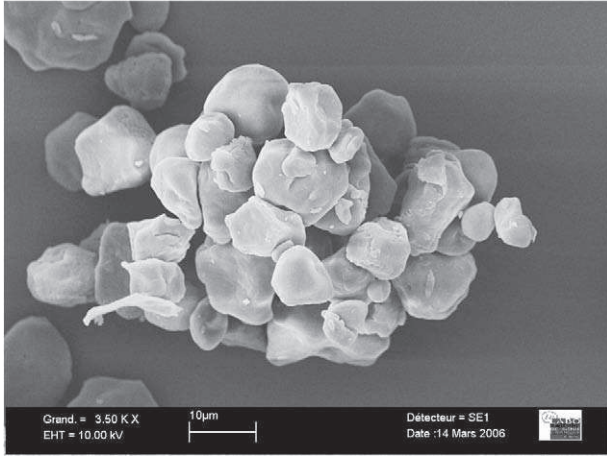


Fig. 6. Micrograph of a starch agglomerate.

3.2. Analysis of surface properties

For a better understanding of the phenomena leading to the production of composite particles, we have determined the surface properties of polymer, starch and mixture during their grinding and co-grinding. Indeed, the use properties of a composite material are strongly influenced by the interactions between its components, which are defined by the intermolecular forces.

According to Van Oss [12], interparticle phenomena result from the combination of two forces: Van der Waals and Lewis acid-base, the latter being decomposed into electron acceptor and electron donor parameters. Since it is not possible to determine directly the surface energy of a solid, as it is for a liquid, because of a lack of molecular and atomic mobility, an indirect method is needed, such as the study of the interactions between liquids and the solid. When a liquid drop is deposited on a solid surface, equilibrium is established between the solid, the liquid and the vapour, leading to a contact angle, θ , between the drop and the solid surface, corresponding to the minimum energy between the three phases. Good and Van Oss [13] have expressed this equilibrium according to the following equation:

$$\frac{1 + \cos \theta}{2} \gamma_L = \sqrt{\gamma_s^{LW} \gamma_L^{LW}} + \sqrt{\gamma_s^+ \gamma_L^-} + \sqrt{\gamma_s^- \gamma_L^+} \quad (4)$$

By measuring the contact angle with the solid of a non-polar solvent like 1-Bromonaphtalene, whose components γ_L^+ and γ_L^- are null, one can determine the Van der Waals force of the solid, γ_s^{LW} .

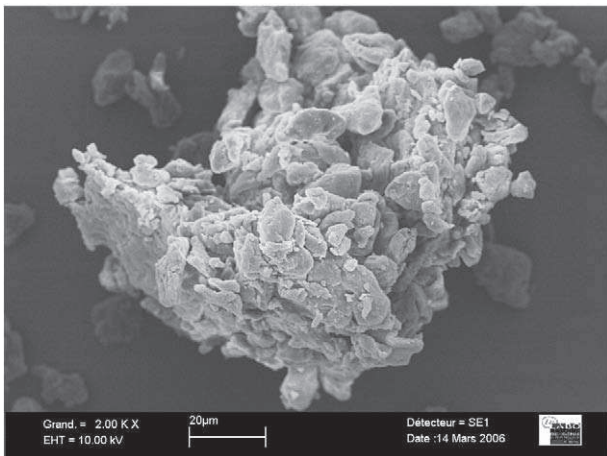


Fig. 7. Micrograph of a compacted starch agglomerate.

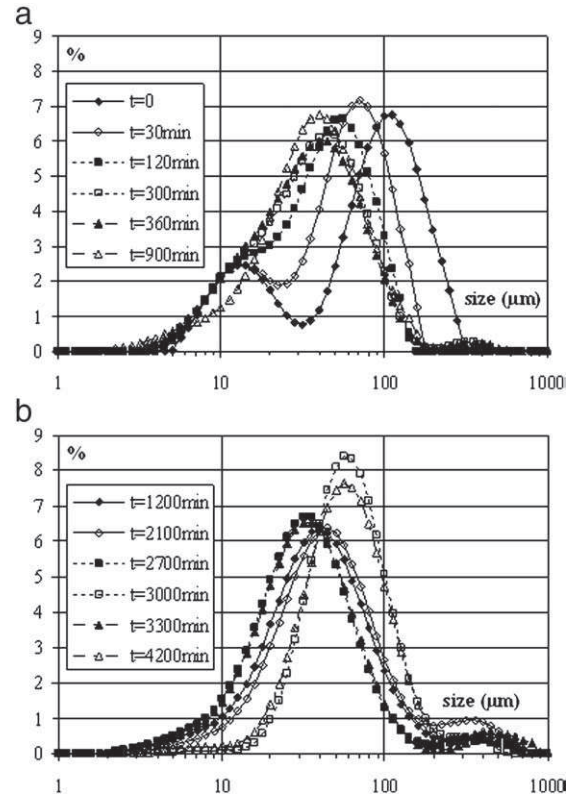


Fig. 8. Evolution of the size distribution of the mixture during co-grinding. a: times between 0 and 900 min. b: Times between 1200 and 4200 min.

Then, by using two polar solvents like water and formamide, one determines the two acid and base components, respectively γ_s^+ and γ_s^- . The global acid-base force, γ_s^{AB} , is equal to twice the square root of the two polar components' product.

3.2.1. Surface properties of PVAc and starch ground separately

In Fig. 12 are reported the γ_s^{AB} and γ_s^{LW} components, as well as the total energy of poly (vinyl acetate), which is equal to the sum of the two components. The total energy of PVAc decreases slightly during the first 360 min before stabilizing. This variation results from a reduction of the γ_s^{AB} component, whereas the γ_s^{LW} component remains relatively constant.

The decomposition of γ_s^{AB} into electron donor and acceptor parameters (Fig. 13) leads to note that it is the electron donor parameter, γ_s^- ,

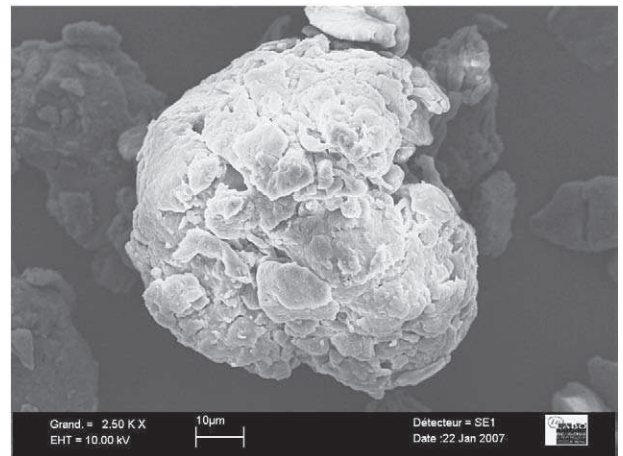


Fig. 9. Micrograph of a mixture agglomerate.

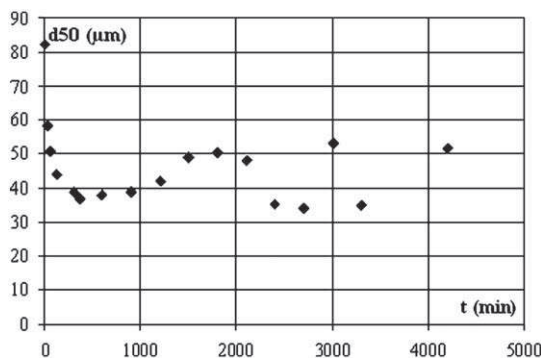


Fig. 10. Variation of the mean size of the mixture.

which strongly decreases, sign of a reduction in the basic character. These tendencies result from an amorphisation of an initially semicrystalline polymer, i.e. of a progressive destruction of crystallites. Molina-Boisseau and Le Bolay [14] showed that poly (vinyl acetate) ground in a vibrating bead mill loses 90% of its crystallinity after 600 min of grinding. Moreover, the electron donor parameter can be imputed to the presence of the acetate group which causes a dissymmetry of the electronic charges. During polymer grinding, not only are the particles fragmented, but the molecular chains may also be cut, as shown by Molina-Boisseau and Le Bolay [14] in a study on polystyrene grinding in a vibrating bead mill. This involves a disorganization of the distribution of surface energies, which reduces the dissymmetry of electronic charges within the polymer. The electron donor parameter decreases then strongly and tends even towards zero.

The same experiments were carried out with starch. It was observed that γ_s^{LW} remains constant, as for PVAc. On the other hand, contrary to the matrix, total energy increases slightly in the first moments of grinding, due to an increase in the polar component. To understand better these quite surprising evolutions, it is advisable to analyse in detail the variation of the electron donor and acceptor parameters (Fig. 14). Thus, γ_s^- is more than 5 times higher than for the matrix before grinding (54 mJ m^{-2}), and decreases to approximately 20 mJ m^{-2} ; this parameter is thus reduced by a factor 2.5 between the beginning and the end of starch grinding. As for γ_s^+ , it increases from 0.5 to 2.5 mJ m^{-2} ; this parameter is thus multiplied by a factor 5. Consequently, whereas it is the electron donor parameter which is largely preponderant, it is the electron acceptor parameter which defines the variation of the γ_s^{AB} force, which is a function of the two parameters' product. This shows that it is necessary to be very careful when global data is analysed, and in the case of starch, a decomposition of the acid–base force is necessary.

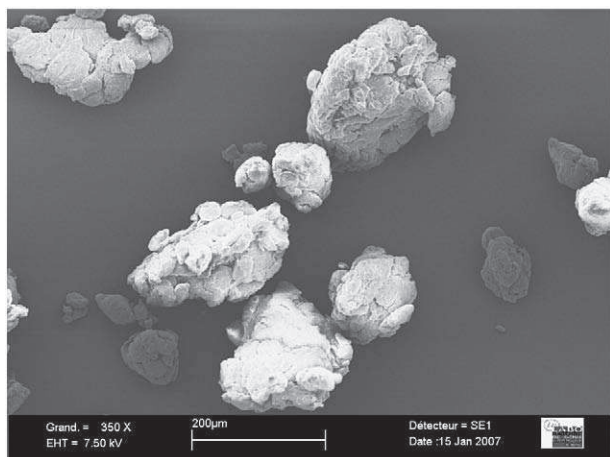


Fig. 11. Micrograph of large agglomerates.

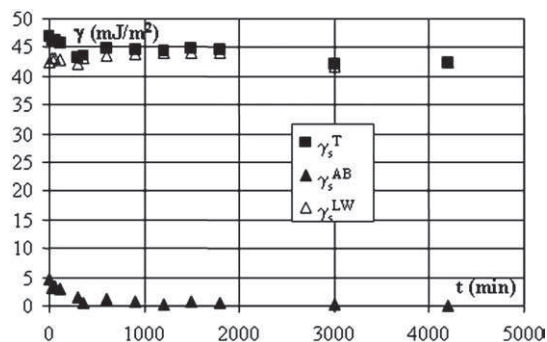


Fig. 12. Influence of the grinding time on the total, polar and non-polar energies of PVAc.

Starch consists of several tens of thousands of glucose units. The presence of the alcohol group causes a dissymmetry of the charges, generating a very strong initial value of γ_s^- . If grinding does not make it possible to break starch particles, of initial size lower than the limit value of fragmentation of this type of material, it affects indisputably the molecular chains, inducing the reduction in the electron donor parameter.

3.2.2. Characterisation of the composite's surface energies

When co-grinding PVAc and starch, the Van der Waals force does not evolve as for the two separate products. The variations of the Lewis acid–base force, as well as γ_s^+ and γ_s^- are presented in Fig. 15.

The difference in behaviour of non-filled PVAc and PVAc filled with starch comes from the electron donor parameter. We will therefore study the variation of this component. One can distinguish two steps:

- Up to 10 h of co-grinding, we noted, by observing the size distributions and SEM photos, that each material behaves independently, since agglomeration is not significantly observed. Starch being in minority proportion in the mixture, the surface of the discs used for the deposit of the solvent drops is mainly made up of polymer and, to a lesser extent, of starch. This phenomenon is accentuated during co-grinding because the polymer particles break, leading to an increase in their surface, contrary to starch whose surface is not increased because of the noted defect of fragmentation. The component γ_s^- of the mixture thus decreases to a value much lower than that of the starch, increasingly in minority in terms of surface.
- From 20 h of co-grinding, agglomeration between the two components is more significant, and the polymer fragments are gradually coated with starch. Since the starch electron donor parameter is higher than that of polymer, one could expect to see γ_s^- for the mixture tend towards the starch value if it totally coated PVAc. Nevertheless, one can observe that γ_s^- for the mixture increases only very slightly up to 3000 min. This increase remains

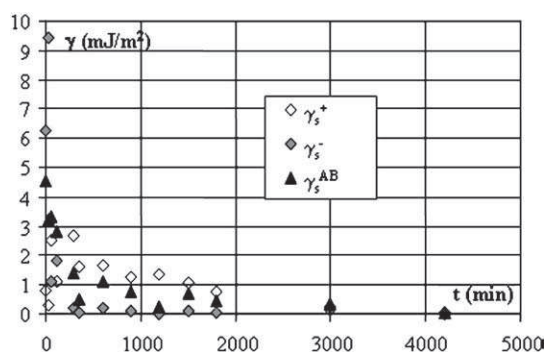


Fig. 13. Decomposition of the polar energy of PVAc.

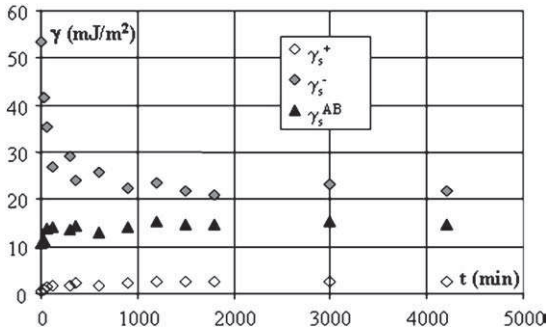


Fig. 14. Decomposition of the polar energy of starch.

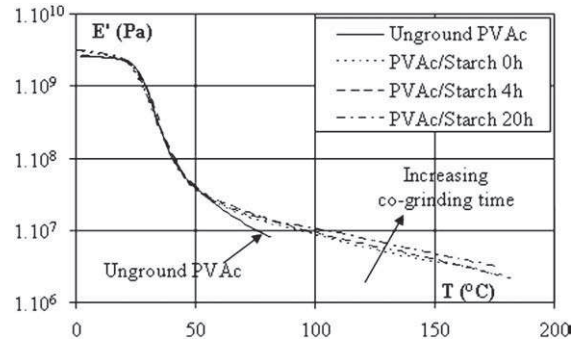


Fig. 16. Storage tensile modulus versus temperature.

weak compared to that of the starch alone, undoubtedly because of a fragmentation of the composite agglomerates which can give access to their heart, i.e. to their polymeric part. The surface of the discs can then comprise polymer zones, of considerable surface, so that the increase in γ_s^- remains moderate. Moreover, interactions between the atoms of hydrogen and oxygen of the acetate function of PVAc and alcohol function of starch can support a balance of the electronic charges, limiting the increase in γ_s^- .

The study of the energetic characteristics of the products on the one hand, and of the composite on the other hand made it possible to complete the size and morphology analysis. The characterisation of the surface properties of materials thus brings complementary elements to define the production mechanisms of composite materials.

4. Characterisation of the properties of composite materials

The incorporation of a filler in a polymer matrix can modify a significant number of its properties, according to the type of filler used. As regards the system selected here, we chose to study the effect of the addition of starch on the mechanical properties, which are the properties most usually influenced by the addition of a filler. Lastly, the objective being to support the degradability of synthetic material, we will characterise how the addition of starch and co-grinding can act on this property.

4.1. Study of mechanical properties

The mechanical properties of composite materials are the properties for which there are the greatest numbers of studies, with the objective of defining the best operating conditions for their improvement. Concerning those of composites with a matrix made up of poly (vinyl acetate), there is little information in the literature. Kovacevic et al. [15,16] studied the mechanical properties of composites made up of such a matrix filled with calcite, silica or kaolin, and produced

chemically. They noted that the presence of reinforcement had a favourable effect on the properties of formed films. However, they can become breakable when the filler concentration becomes too high, because of a risk of filler agglomeration supporting the formation of cracks. Zapata et al. [9] showed that by co-grinding particles of poly (vinyl acetate) and calcite, it was possible to improve the mechanical properties of the composites, on the one hand by strongly reducing the size of the filler, which makes it possible to enhance its dispersion within the matrix, and on the other hand by modifying the interactions between matrix and filler. Vargha and Truter [17] studied the mechanical behaviour of mixtures produced by partial transesterification of poly (vinyl acetate) and starch. These authors could not measure the mechanical properties of samples of such composites which were very breakable contrary to the polymer alone. It was thus necessary to plasticize the matrix to avoid this problem. Nevertheless they noted that the presence of starch generates a strong reduction of the Young modulus, and also of the stress and strain at break, compared to the plasticized matrix alone. Moreover, an increase in the proportion of starch has a negative effect on these parameters.

Co-grinding allowing a better dispersion of the filler in the matrix than a simple blending, it is appropriate to study its influence on the mechanical properties of co-ground composite materials. For this purpose, two series of experiments were carried out: one by dynamic mechanical analysis (small deformations with a progressive temperature rise) and the other by non-linear mechanical tests also called traction tests (high deformations at ambient temperature).

4.1.1. Results of dynamic mechanical tests

The dynamic mechanical analysis permits to characterise the viscoelastic behaviour of the material. For this purpose, the storage tensile modulus of unground PVAc and mixtures of PVAc and starch co-ground various times is plotted versus the temperature in Fig. 16.

The presence of starch allows to slightly increase the storage tensile modulus in the glassy plateau (temperature lower than 20 °C). This expresses a small reinforcing effect of the filler. One also notes a difference between the curves in the rubbery plateau (temperature

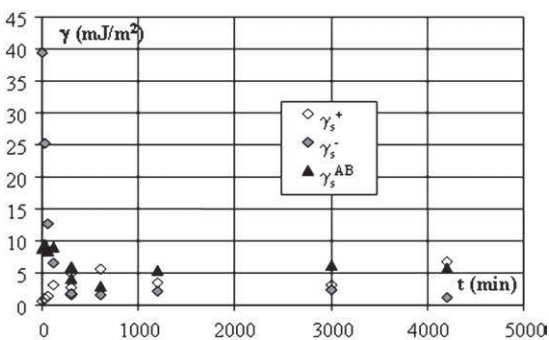


Fig. 15. Decomposition of the polar energy of the mixture.

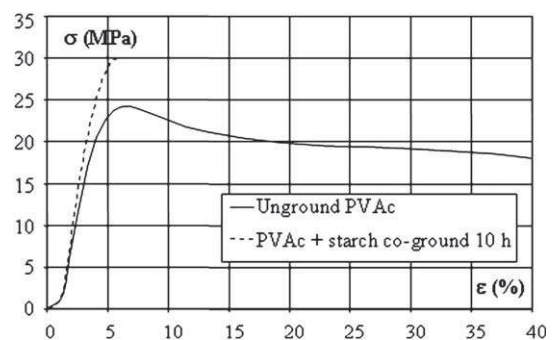


Fig. 17. Variation of stress versus strain.

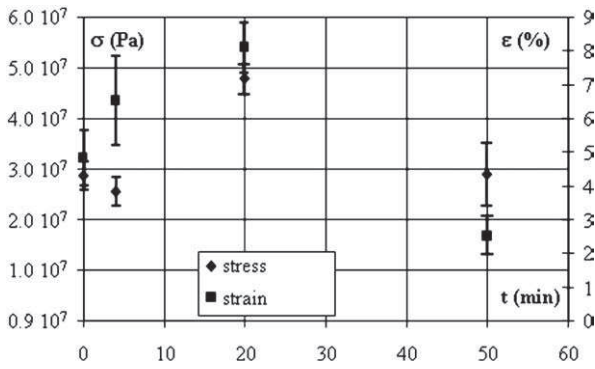


Fig. 18. Influence of the grinding time on stress and strain at break.

higher than 50 °C), in the absence or in the presence of starch, since the storage tensile modulus is a little higher with starch. Finally, it is also observed that the elastic modulus increases slightly with the co-grinding time. One can thus conclude that starch acts as a reinforcing agent for PVAc. However, the effect of this filler is less marked than what Zapata et al. [9] obtained by using calcite, because it is difficult to fragment starch particles. The dispersion of the filler in the matrix is less efficient than with calcite.

4.1.2. Results of non-linear mechanical tests

The stress-strain curves of unground PVAc and of a mixture co-ground during 10 h are presented in Fig. 17. The unfilled PVAc presents a linear elastic behaviour until it reaches a maximum considered as the plastic flow followed by a plateau extending on important strains before break. This curve is traditional for thermoplastic polymers. As for the filled composite, it does not present a plastic flow anymore but behaves like a fragile material. In comparison to unfilled PVAc, an increase in the stress at break, and a reduction of the strain at break can be observed for the composite.

The same kinds of measurements were made for other co-grinding times. From this data, we determined the stress and strains at break (Fig. 18).

If short co-grinding times do not allow to improve these parameters, it is different for longer times. Thus, after 4 h of co-grinding, the stress at break is of the same kind of order as the values measured for the blend. Stress and strain at break are improved by longer co-grinding (20 h), which confirms the better dispersion of the starch filler. On the other hand, a too long co-grinding time has an unfavourable effect, undoubtedly because of a degradation of the molecular chains of PVAc. Thus, there is an optimum co-grinding time permitting a good dispersion of the filler in the matrix.

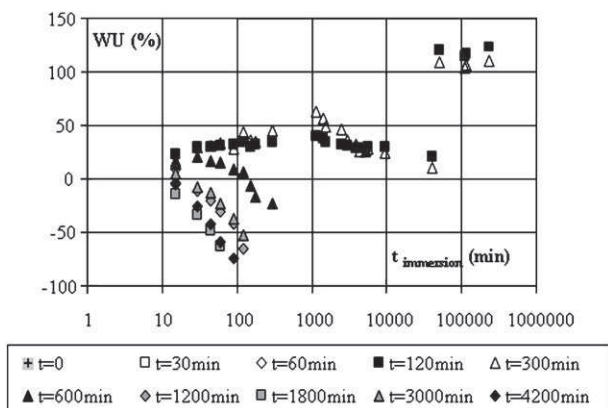


Fig. 19. Influence of the immersion time on the starch water uptake for different grinding times.

If the effect of starch is not strongly marked, it is advisable however to be positive in the analysis, since one adds a vegetable degradable filler which is less expensive than the matrix and makes it possible to lower the price of the composite material. Moreover, the action of co-grinding led to a light improvement of the mechanical properties by supporting filler dispersion and adhesion between the matrix and the filler. Moreover, an optimum co-grinding time is observed.

4.2. Degradation behaviour

The interest of incorporating starch in a synthetic polymer is not only to make the material less expensive, but also to confer a partial or total degradability to the composite. However, the composite material must not degrade too quickly in order to offer at least the same use properties as synthetic polymer alone. In particular, it is common to exploit this type of material in everyday life by putting it in contact with aqueous media. It is then appropriate if the presence of starch does not reduce the composite material's water resistance. The water swelling and degradation behaviour of discs of PVAc, starch or mixtures ground various times were thus studied during more than 5 months.

4.2.1. Swelling of the two materials ground alone

Fig. 19 shows the influence of the immersion time on water uptake of starch for different grinding times. The scale of immersion time is logarithmic in order to better analyse the phenomena proceeding in the first hours of experiments lasting several months. For grinding times ranging between 0 and 60 min, the discs are rapidly disaggregated (a few minutes) and no curve is observable. This phenomenon is due to the good affinity between the two components, which led to a high value of the electron donor parameter (Fig. 14). For 120 and 300 min of grinding, the discs behaviour is better, probably because of a modification of the molecular chains. One notes a

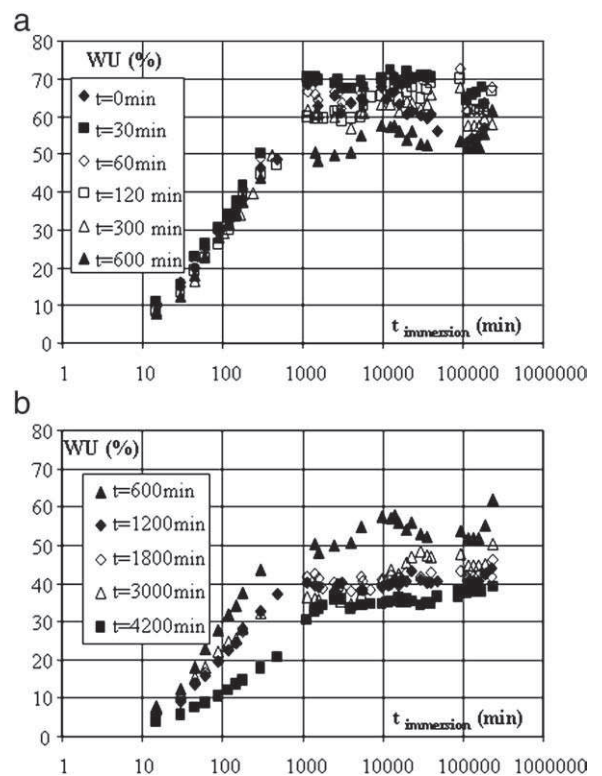


Fig. 20. Influence of the immersion time on the PVAc water uptake for different grinding times. a: grinding times between 0 and 600 min. b: Grinding times between 600 and 4200 min.

progressive absorption of water, which leads to an increase of WU up to 1140 min (19 h). Beyond this immersion time, WU decreases. Angellier et al. [18] as well as Vargha and Truter [17] attributed this decrease to a partial release of starch in water. Finally, after approximately 45000 min of immersion (roughly 30 days), WU increases rapidly. The consistency of the discs is modified: they swell and their colour changes, passing from white to brown. For grinding times higher than 600 min, a progressive degradation of the starch discs occurs, all the faster as this one was crushed a long time. This behaviour can result from an excessive degradation of the molecular chains under the action of the balls.

Concerning poly (vinyl acetate), the results of the influence of the immersion time on the water uptake are gathered in Fig. 20 for several grinding times. All the curves can be divided into three parts:

- during the first one, for immersion times lower than 1140 min (19 h), the water uptake increases with the immersion time. The rate of water absorption depends on the grinding time. Thus, it increases very slightly between 0 and 30 min of grinding, and then decreases also slightly up to 600 min of grinding. It decreases further, but in a more substantial way, between 600 and 1200 min, and stagnates up to 3000 min before decreasing again. This may be due to an amorphisation of the polymer or a degradation of the molecular chains.
- in the second part of the curves, between 19 h and 70 days of immersion (approximately 100000 min), WU does not evolve practically any more and it corresponds to an equilibrium in water absorption. One can note light fluctuations on the plateau which are certainly due to the fact that the water remaining on the surface of the discs, when they are withdrawn from the flasks, is not removed exactly in the same way from one weight measurement to another. This may have an incidence of a few percentage points on the determination of the water uptake, because of the relatively low initial mass of the discs. The water uptake at equilibrium varies similarly to the absorption rate with the grinding time, namely a light increase for short grinding times, and then a more or less fast reduction.
- beyond 70 days, one observes a new increase in WU, essentially for the shortest grinding times. Like in the case of starch, we have noted that the discs processed with polymer particles ground during a short time are swelled and their surface is degraded. On the other hand their aspect is unchanged when the polymer is ground for a long time.

4.2.2. Swelling of the co-ground mixture

The same experiments were carried out with discs of mixtures co-ground various times. The results are gathered in Fig. 21. Four zones are observed on the curves in this case:

- in the first zone, always defined for immersion times lower than 1140 min (19 h), the water uptake increases with the immersion time just like for PVAc alone. By comparing the data at $t=0$ (that is to say unground PVAc and PVAc-starch blend), one notes that WU is slightly higher for the mixture. The presence of starch thus supports the absorption of water because of its hydrophilic property. The grinding time influences differently the absorption rate. Indeed, it increases gradually between 0 and 600 min of co-grinding, whereas it has an opposite effect (although little marked) for PVAc ground alone. So it can be said that the presence of starch enhances the kinetics of water absorption. Beyond 600 min of co-grinding, the absorption rate strongly decreases up to 1800 min, but has no significant evolution for longer co-grinding times. It is necessary to insist on the fact that the values of WU for discs made with the mixture co-ground more than 1800 min are comparable with those of the discs of PVAc ground alone during 4200 min.
- the second zone lies between 1140 min and approximately 12000 min of immersion (8 to 9 days). One observes a plateau on the curves, and the influence of the co-grinding time on the values of WU is identical

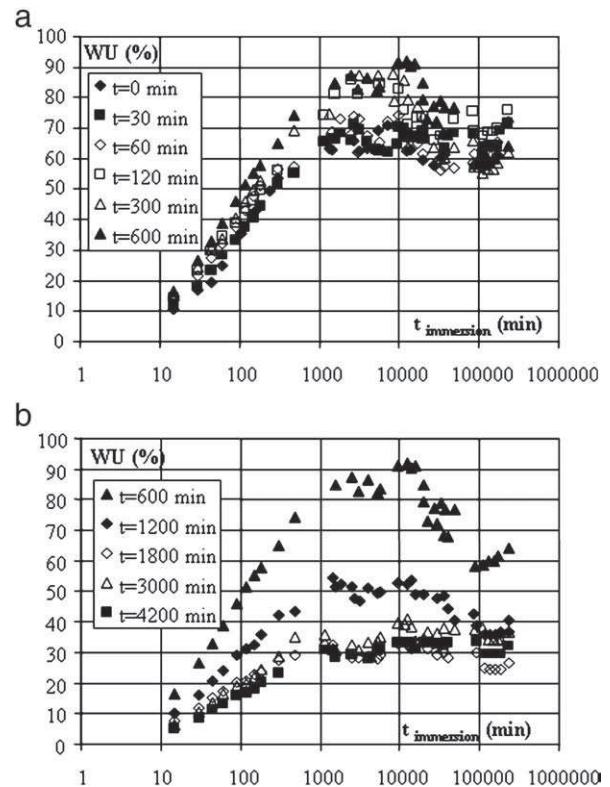


Fig. 21. Influence of the immersion time on the composite water uptake for different co-grinding times. a: Co-grinding times between 0 and 600 min. b: Co-grinding times between 600 and 4200 min.

to that on the absorption rate in the first zone of the curves. It should be noted that the maximum value of WU reaches nearly 90% for the co-ground mixture against 70% for the matrix ground alone. The hydrophilic property of starch may be the reason of this difference.

- the third zone is defined between 12.000 minutes and 100.000 minutes of immersion (approximately 70 days). During this period, the water uptake decreases, as it was noticed for the discs made with starch ground during 120 and 300 minutes. Angellier et al. [18] and Vargha and Truter [17] observed the same phenomenon, due to a release of starch. The weight loss is all the higher as the water uptake is important. It should be noted that one does not observe a decrease of WU for the three highest co-grinding times.
- finally, in the fourth zone, beyond 70 days, WU increases again for co-grinding times lower than 600 min, and one then witnesses a swelling of the discs and a degradation of their surface all the more marked since the co-grinding time is short. On the other hand WU and the aspect of the discs remain unchanged for higher co-grinding times.

The results obtained for long co-grinding times are particularly interesting because they mean that by incorporating a vegetable, degradable and cheap filler in a synthetic and more expensive matrix, and by co-grinding the mixture during an adapted time, one observes the same water-resistant behaviour as synthetic polymer alone.

5. Conclusions

Co-grinding was implemented to incorporate a starch filler in a polymer (poly (vinyl acetate)). The production mechanism of the composite material was explained while being based on the one hand on particle size and morphology analysis, and on the other hand on the study of surface properties. Polymer particles are initially fragmented, while those of starch remain intact. The energetic level of the mixture decreases, and more particularly the electron donor parameter. This decrease may be attributed to a loss of the polymer

crystallinity and a cut of the molecular chains of the materials. Hereafter, starch coats the polymer fragments and thus confers gradually to the whole its energetic level, which is higher than that of the polymer, while the average size of the particles increases. After a long treatment, the agglomerates break, and the energetic level of the composite decreases, undoubtedly because the polymer located in the middle of the agglomerates becomes accessible again.

The addition of starch to the matrix permits to increase the stress at break of the composite, but strongly reduces its strain at break. Co-grinding favours the dispersion of starch in the matrix and the adhesion between the two components, allowing a low increase of the mechanical properties compared to blends. However, a long grinding time has a negative effect since starch chains may be cut. As for water resistance, the presence of starch favours the kinetics of water absorption and starch release, especially for co-grinding times lower than 600 min. On the contrary long co-grinding times reduce the water absorption kinetics, as well as starch release and composite degradation.

Therefore, in the range of co-grinding times tested in this study (0 to 70 h), an intermediate value around 20–30 h offers interesting mechanical and degradation properties.

Nomenclature

d_{50}	mean diameter of particles (m)
E'	storage tensile modulus (Pa)
F	force (N)
L	film length (m)
L_0	initial film length (m)
m_i	initial weight of the disc (kg)
m_t	weight of the disc at time t (kg)
S_0	film section (m)
t	time (min)
$t_{\text{immersion}}$	immersion time of the disc (min)
T	temperature ($^{\circ}\text{C}$)
WU	water uptake (%)
ε	nominal strain (%)
γ_L	liquid surface tension (mJ m^{-2})
γ_s	solid surface tension (mJ m^{-2}): γ^T = total solid surface tension; γ^{AB} = Lewis acid–base (dispersive) component; γ^{LW} = Lifshitz Van der Waals (non-dispersive) component; γ^+ = electron acceptor parameter; γ^- = electron donor parameter (mJ m^{-2})
μ	viscosity (Pa s)
ρ	density (kg/m^3)
σ	nominal stress (Pa)
θ	angle between the liquid and the disc ($^{\circ}$)

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