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WATER UPTAKE AND DIFFUSION IN CO-GROUND STARCH-FILLED POLY (VINYL ACETATE) COMPOSITES

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Abstract: The article presents results on the incorporation of starch in a poly (vinyl acetate) matrix by co-grinding. This treatment permits a good dispersion of the filler in the matrix and favors agglomeration phenomena which limit segregation and enhance interactions between the two materials. The composite materials offer interesting water resistance properties. Water absorption phenomena were studied and it was shown that water penetration in the materials is controlled by diffusion. The diffusion coefficients of water were determined for the matrix, the filler and the mixture and they are respectively equal to $3.3 \cdot 10^{-11}$, $1.1 \cdot 10^{-10}$ and $5.5 \cdot 10^{-11}$ m²/s.

Keywords: Co-grinding, composite materials, degradable filler, water uptake, diffusion.

1. INTRODUCTION

Starch-filled composite materials have received considerable interest over the recent years due to the biodegradability, renewability and low cost of the filler. Among the different processes used to produce polymeric composite materials, co-grinding is the most recently developed. It allows a good homogeneity of the composite and good interactions between the two materials (Zapata-Massot and Le Bolay 2007), permitting to offer interesting properties. In a previous study (Seyni *et al.*, 2008), it was shown that co-grinding makes it possible to enhance the mechanical properties of starch-filled poly (vinyl acetate) composites compared to blending.

Water uptake is generally the first step of biodegradation. It is strongly linked to the polymer hydrophilic behavior (Verdu 2000). This one is influenced by the chemical structure. Indeed, it is low for carbonaceous or fluorinated groups, medium for moderately polar groups (like esters or ethers) and high for groups which are hydrogen bonds donors (acid, alcohol or amide). When a hydrophilic polymer is immersed in water, the liquid molecules diffuse in the polymer, leading to a material swelling occurring more or less rapidly, depending on the polymeric chains relaxation. Above the glass transition temperature, the chains relaxation is rapid and water diffusion can occur into the polymer network, following the Fick's laws. Below the glass transition temperature, chains relaxation can be slow and one can observe deviations from Fickian behavior. Alfrey *et al.* (1966) proposed three models to describe the transport phenomena into glassy polymers:

- Diffusion is Fickian if the water diffusion rate is lower than the relaxation rate. The mechanism is controlled by diffusion.
- Water diffusion rate is higher than relaxation rate. The mechanism is controlled by relaxation.
- The two rates are comparable.

Friesch (1980) has expressed the water diffusion mechanism according to the following equation:

$$\frac{m_t - m_i}{m_\infty - m_i} = k.t^n \quad (1)$$

where m_i is the initial mass of the polymeric sample, m_t , its mass at immersion time t , m_∞ , its mass at equilibrium, n , the diffusional exponent and k , the system constant.

This equation is considered to be valid for $(m_t - m_i)/(m_\infty - m_i) < 0,6$.

The value of n depends on the diffusion mechanism. It is equal to 0.5 for Fickian diffusion, to 1 for a relaxation mechanism, and between 0.5 and 1 for the third case described above.

Simplifying the second Fick's law, Crank (1975) has expressed equation (1) as follows:

$$\frac{m_t - m_i}{m_\infty - m_i} = \frac{4}{e} \left(\sqrt{\frac{D}{\pi}} \right) \sqrt{t} \quad (2)$$

where e is the polymer sample thickness and D the diffusion coefficient.

Several authors (Peppas and Sinclair 1983, Russo *et al.*, 2007, Yu *et al.*, 2008, Tang *et al.*, 2008) studied water diffusion in hydrophilic polymers, using this equation to determine the diffusion coefficient in their materials.

In this paper, we present results on the influence of co-grinding poly (vinyl acetate) and starch on the behavior of the mixtures in water. Co-grinding was realised in a laboratory tumbling ball mill. We will first comment the size variation to explain how the composite materials are produced. Then, we will present the evolution of the water uptake of co-ground samples. From these results, we will study the influence of co-grinding on the water diffusion mechanism and coefficient.

II. APPARATUS, METHODS AND MATERIALS

The products were ground in a 5-liter ceramic tumbling ball mill containing ceramic balls (5.5, 9.5 and 12.5 mm). The balls occupied 20 vol. % of the chamber and the powder 10 vol. % of the void space between the balls. The rotating speed of the chamber was fixed at 75 % of the critical speed, i.e. 100 rpm.

The matrix was poly (vinyl acetate) (PVAc). The initial particles were sieved between 80 and 100 μm . As it can be observed in Figure 1.a, the particles, produced by emulsion polymerization followed by drying, are spheroids. They are composed of small grains. The PVAc density is 1783 kg.m^{-3} . The filler was waxy maize starch (Figure 1.b) with a particles size between 4 and 30 μm . Individual particles and agglomerates compose the initial powder. The starch density is 1330 kg.m^{-3} . The PVAc – starch mixtures contained 25 wt. % starch. Indeed, it has been shown in a previous study that this filler rate permits to improve significantly the mechanical properties of the composite (Zapata *et al.*, 2004).

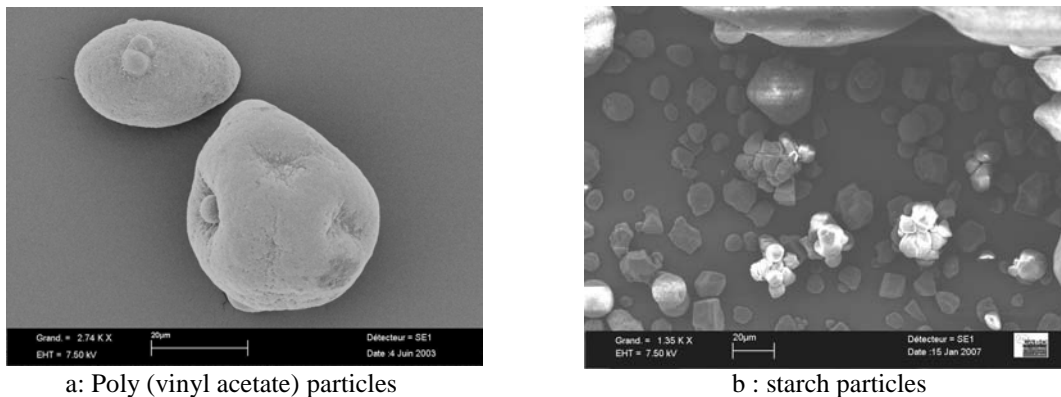


Fig. 1. SEM micrographs of poly (vinyl acetate) and starch particles

Small powder samples were taken at various grinding times in different parts of the mill and analysed by means of a laser diffraction granulometer Malvern Mastersizer 2000 to determine their size distribution. The average size, d_{50} , corresponding to a cumulated volume fraction of 50 %, was then calculated. Some particles were analysed by scanning electron microscopy (Leo 435 VP). Powder discs, with a mass around $0.6 \text{ g} \pm 10^{-4} \text{ g}$, were formed by pressing the particles in a Carver press. The mould diameter was 8 mm and the applied force was 30 kN. The discs were introduced in distilled water contained in a flask and weighted at different times after being removed from water and rapidly dried on a blotting paper. Three discs were used for each series of experiments. The water uptake, WU, was calculated from the equation:

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

III. RESULTS AND DISCUSSION

3.1 Size and morphology evolution

The analysis of the size and morphology evolution permits to understand the behavior of the products during grinding and to study the fragmentation and agglomeration phenomena occurring during the treatment. Results have been presented in details in a previous article (Seyni *et al.*, 2008), and only the main results on this point are reported here, since they are useful to understand water uptake phenomena. PVAc and starch particles were ground separately first and together then. Figure 2 presents the variation of the mean sizes during grinding.

The mean size of PVAc particles decreases first due to a fragmentation of the particles, and after a limit size of 58 μm is reached, a competition between fragmentation and agglomeration occurs. The mean size of starch particles evolves differently, since it increases from the treatment beginning due to agglomeration, to oscillate then around 30 μm . These results are in agreement with those presented by Schönert (1988) and may be

explained by the fact that the limit size that can be reached when grinding polymer particles, which are macromolecules, is several tens of μm . Consequently, since the initial mean size of PVAc is about $86 \mu\text{m}$, a little fragmentation may occur before agglomeration phenomena appear. On the contrary, initial starch particles are small ($13 \mu\text{m}$ approximately, i.e. lower than the limit grinding size). So, the mean size increases due to immediate agglomeration.

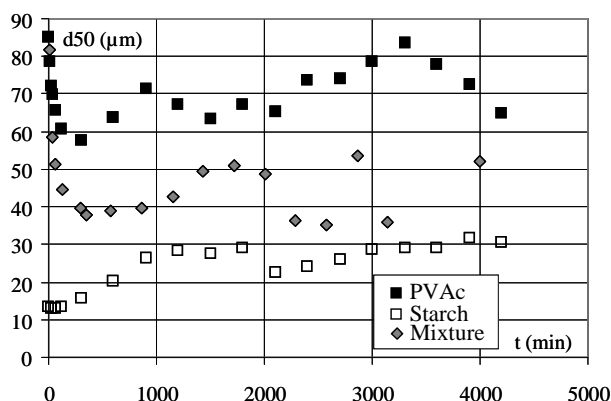


Fig. 2. Variation of the mean size of the two products and the mixture with the grinding and co-grinding time

As for the co-ground mixtures containing 25 wt. % of starch, their size distributions are gathered in Figure 3. Before grinding, two peaks are observable, the right-hand side one corresponding to PVAc and the other to starch. The peak of PVAc shifts towards the left during the first 300 minutes, due to particle fragmentation already observed when grinding this polymer alone. During this period, the starch peak does not evolve significantly, but at 900 minutes, one can observe that it tends to disappear. Moreover, a peak appears around $350 \mu\text{m}$. Finally, for longer co-grinding times, the main peak shifts to the right, while the proportion of the peak at $350 \mu\text{m}$ increases.

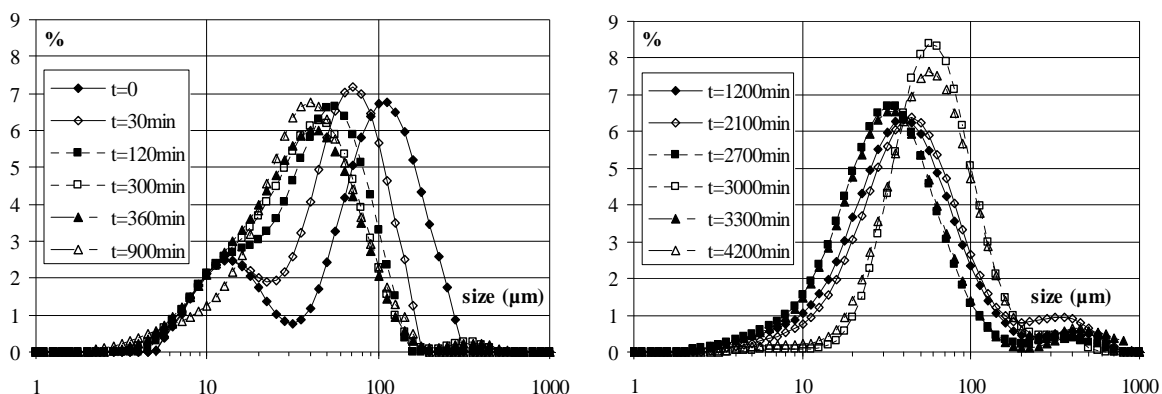


Fig. 3. Evolution of the size distributions of the co-ground mixtures

The disappearance of the starch peak and the presence of the peak at $350 \mu\text{m}$ may be explained by agglomeration phenomena that are illustrated by the SEM micrographs of Figure 4.

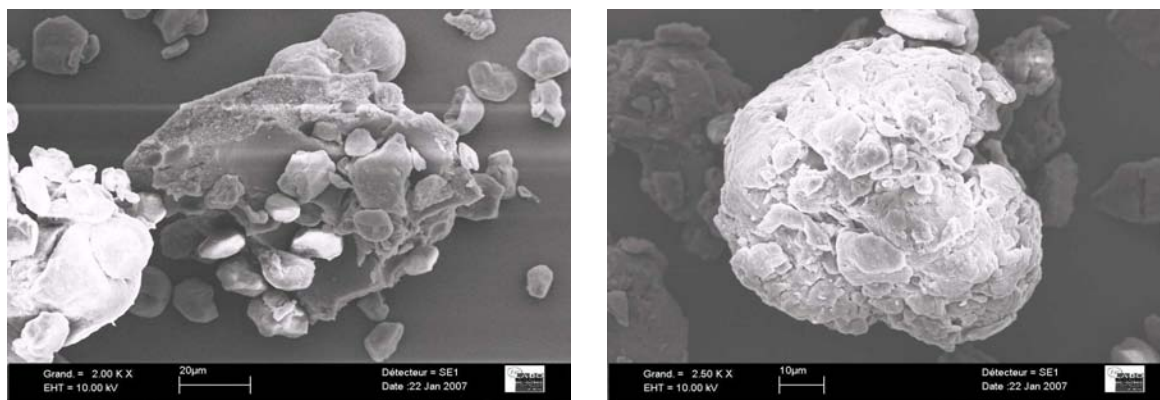


Fig. 4. Micrographs of PVAc – starch agglomerates

Indeed, after PVAc particles are fragmented, small starch particles stick on the matrix fragments (left micrograph of Figure 4). Since filler particles are no more free in the mixture, they can not be detected by the granulometer. Furthermore, agglomeration continues as the processing time is prolonged, and some large agglomerates made up of the two materials are formed (right micrograph of Figure 4): PVAc-starch agglomerates tend to agglomerate between them. Thus, the filler is well dispersed in the matrix and no segregation may occur during handling.

The consequence of this is that the mean size of the mixture drawn in Figure 2 decreases strongly up to 300 minutes resulting from PVAc fragmentation, increases slightly up to 900 minutes because of an agglomeration of starch on PVAc, and increases significantly then due to an agglomeration of PVAc – starch agglomerates. Finally a compaction of these big agglomerates, combined with a competition between fragmentation and agglomeration lead to oscillations of the mean size.

3.2 Behavior of the materials in water

PVAc discs produced by pressing particles ground different times (between 0 and 4200 minutes) have been immersed in water. Figure 5 shows how the water uptake evolves with the immersion time.

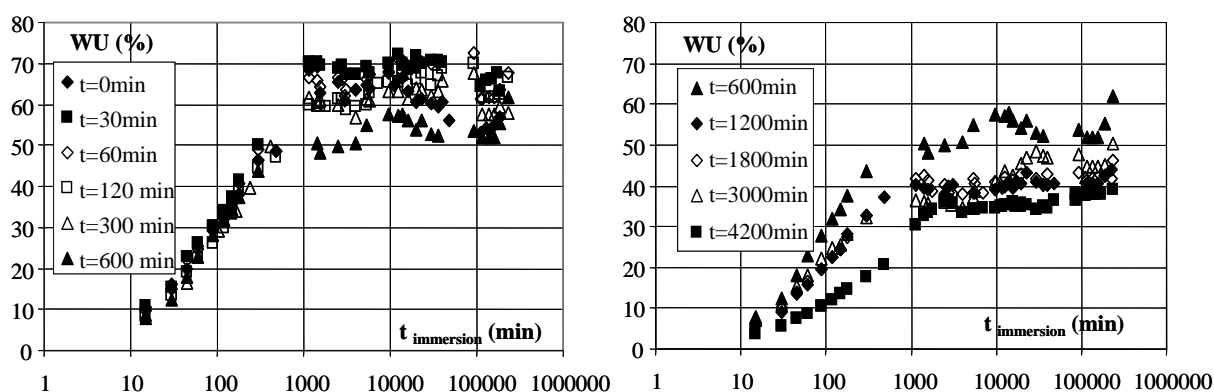


Fig. 5. Influence of the immersion time and the grinding time on PVAc water uptake

The water uptake increases with the immersion time for values of this one lower than 1140 minutes (19 hours). The affinity of the polymer with water may be attributed to the presence of acetate groups. Water is absorbed by the polymer. In this range of the immersion time, an increase of the grinding time leads to a decrease of WU, in particular for high grinding times. This may be the result of an amorphisation of the polymer or a degradation of the molecular chains. Between 1140 and 100 000 minutes (70 days), WU does not evolve significantly and equilibrium in the water uptake is reached. The influence of the grinding time on the values of WU at equilibrium is similar to that on the absorption rate in the first part of the curves. Above 70 days of immersion, a swelling of the discs and a degradation of their surface is observed. Consequently, WU increases again.

Starch discs were submitted to the same treatment. For grinding times lower than 60 minutes, the discs disaggregate rapidly. This is due to the good affinity between starch and water, resulting from the presence of all the $-OH$ groups of the glucose molecules constituting starch. For grinding times between 120 and 300 minutes, similar curves as those with PVAc were obtained for immersion times lower than 1140 minutes, probably because of a modification of the molecular chains. However, when the maximum water uptake is reached, WU does not level off as for PVAc, but it decreases, certainly because of a partial starch release in water. For grinding times higher than 600 minutes, one notes a degradation of the starch discs, all the more fast as starch was ground a long time. This behavior can result from a too important degradation of the molecular chains under the action of the balls.

Finally, the same experiments were realized with discs of co-ground mixtures (Figure 6). The water uptake increases as for the matrix ground alone in the first zone of the curves (immersion times < 1140 minutes) and levels off then when an equilibrium is reached. It can be seen that WU is slightly higher for the mixture than for the matrix, because of the strong hydrophilic behavior of the filler that permits to enhance water absorption. For co-grinding times lower than 600 minutes, the absorption rate increases with the treatment time, on the contrary of PVAc. This may be related to the size and SEM observations presented in the previous paragraph. Indeed, as co-grinding occurs, the dispersion of the filler in the matrix and its adhesion on PVAc fragments (limiting segregation) are favored. For co-grinding times between 600 and 1800 minutes, the water uptake is strongly

reduced, as for the matrix alone, probably for the same reasons, but it does not evolve for longer co-grinding times, since an equilibrium in the composite formation and thus in the water absorption kinetics may be reached. It has to be noted that the water uptake equilibrium period is shorter for the mixture than for the matrix because of a starch release in water after 12 000 minutes immersion, and WU decreases. The starch release is low for long co-grinding time, because starch is protected by the matrix. Finally a disc swelling is observed after 70 days of immersion, in particular for the shorter co-grinding times.

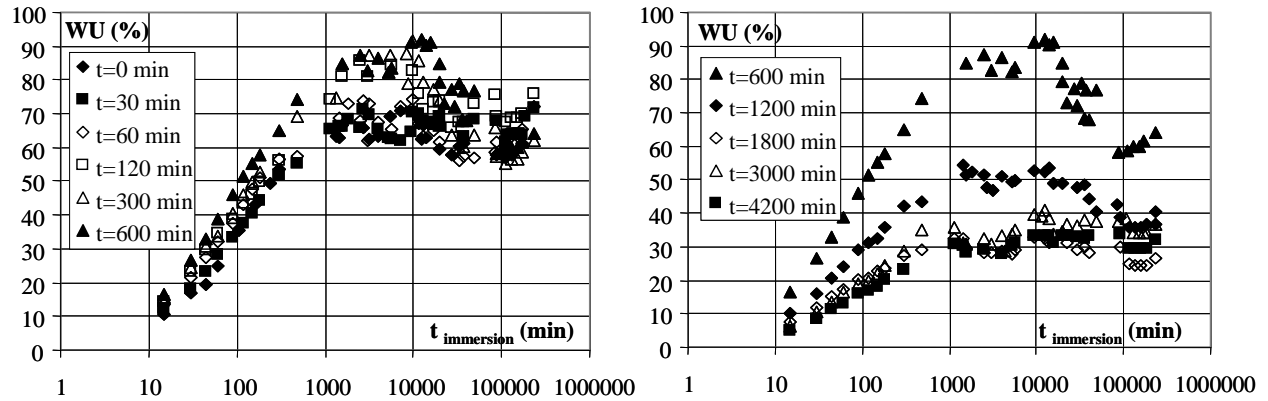


Fig. 6. Influence of the immersion time and the grinding time on mixtures water uptake

These results are interesting since they mean that, when co-grinding the mixtures during an adapted time, it is possible to partially replace the synthetic matrix by a degradable and cheap filler, and to have a good resistance of the composite to water.

3.3 Analysis of water diffusion in the materials.

As shown in Figures 5 and 6, water uptake increases with the immersion time because of a diffusion of water in the materials. Equation (1) has been used to characterize the diffusion mechanism. In this way, we have plotted in Figure 7 the variation of $\ln [(m_t - m_i)/(m_\infty - m_i)]$ versus $\ln (t_{\text{immersion}})$ for the matrix and the mixture. The points plotted on the figures represent all the results obtained for all grinding and co-grinding times.

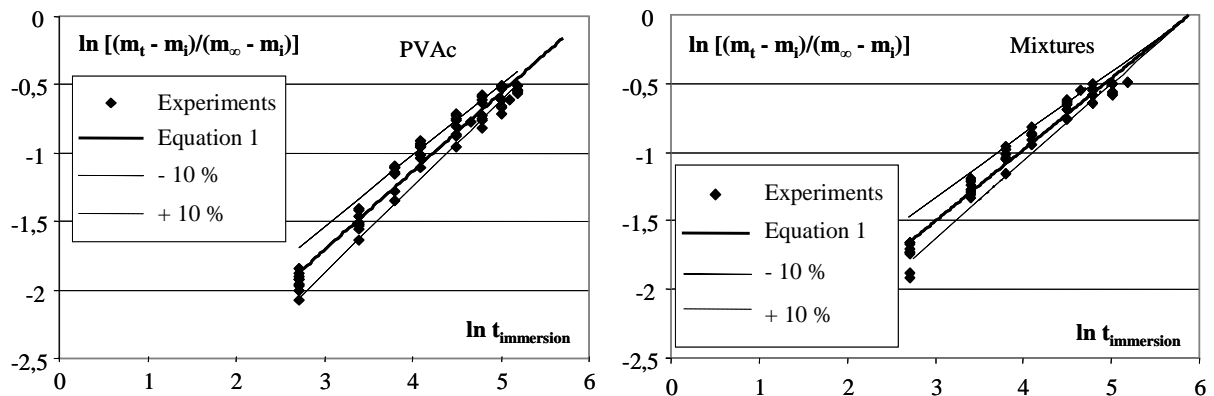


Fig. 7. Variation of $\ln [(m_t - m_i)/(m_\infty - m_i)]$ versus $\ln (t_{\text{immersion}})$ for the matrix and the mixture

These points are well distributed around a single line, whatever the processing time of the powder in the mill. The exponent n , defined by the slope, is equal to 0,57 for the polymer alone and 0,52 for the mixture. These two exponents are close to 0,5, indicating that the mechanism of penetration of water within the discs is controlled by diffusion. Thus, using equation (2), the diffusion coefficients of water in PVAc and in the composite have been determined. They are respectively equal to $3.3 \cdot 10^{-11} \text{ m}^2/\text{s}$ for PVAc and $5.5 \cdot 10^{-11} \text{ m}^2/\text{s}$ for the mixtures, and they are independent of the grinding or co-grinding time. The diffusion coefficient is higher for the mixture because of the presence of starch. It was not possible to realise the same work with the filler data for all the grinding times because of the disintegration of most of the discs when immersed in water. However, we have teated the data obtained for 300 minutes of grinding and we have determined a diffusion coefficient equal to $1.1 \cdot 10^{-10} \text{ m}^2/\text{s}$, which is similar to the value obtained by Russo *et al.* (2007). The diffusion coefficient of the mixture logically lies between those of the two materials.

In order to go further, we were interested in the variation of the discs mass at equilibrium (Figure 8). It is constant for PVAc and increases for the mixture during the first grinding times, and then it decreases to stabilize for long grinding times. To continue the analysis, we plotted in Figure 9 the variation of m_∞ with $1/d50$.

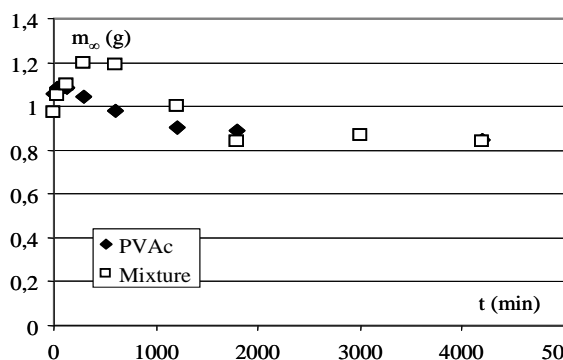


Fig. 8. Variation of m_∞ with the grinding time

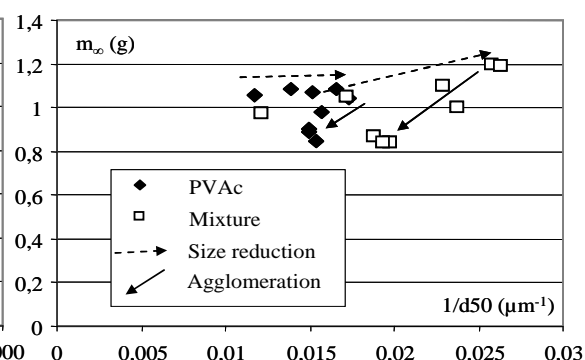


Fig. 9. Variation of m_∞ with $1/d50$

One can observe two phases, the first one for ascending values of $1/d50$ (i.e. for the size reduction) and the second one for decreasing values of $1/d50$ (i.e. for the agglomeration of the particles). In the first phase, the mass at equilibrium is constant in the case of PVAc, which could be expected since this parameter depends on the material which is only the polymer. On the other hand, the mass increases slightly in the case of the mixture. This can be due to a modification of the disc structure, resulting of a modification, with co-grinding, of the dispersion of the filler in the matrix. In the second phase, the mass at equilibrium decreases in both cases, due to an amorphisation of the polymers or a chain degradation.

IV. CONCLUSION

A study on co-grinding of poly (vinyl acetate) and starch was implemented in order to show the possibility to replace partially the synthetic polymeric matrix by a vegetable, degradable and largely available filler. A size and morphology study has permitted to explain how the composite particles are formed. Then, a study of the behavior of the materials in water has led to the conclusion that introducing starch in PVAc increases the water absorption and the starch release, but these phenomena can be reduced by applying an adapted co-grinding treatment that may avoid the use of a compatibiliser to favor interactions between the matrix and the filler. It was shown that the water uptake is controlled by diffusion and the diffusion coefficients were calculated. That of the mixture is higher than that of the matrix because of the presence of starch which is strongly hydrophilic.

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