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Size reduction of polystyrene in a shaker bead mill—kinetic aspects

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Abstract

This paper reports an experimental study of polystyrene grinding in a shaker bead mill. The objective is to characterize the influence of the operating conditions on the evolution of the particle size. The effects of temperature, vibration frequency, and bead and polymer loads have been examined. Grinding kinetics have been predicted by combinations of four log-normal laws. The number of sub-populations used for the prediction has been defined after SEM observations. The kinetic parameters (mean size, standard deviation and proportionality coefficient) of the different laws have been determined and their evolution during grinding has been analysed.

Keywords: Grinding; Vibrated mill; Polystyrene; Size reduction; Kinetics

1. Introduction

Particle fineness is increasingly required for a wide range of applications. Fine grinding is one of the processes used for the production of powders possessing low sizes. Many studies have been performed on the fine grinding of minerals [1,2]. Nevertheless, several kinds of materials do not behave as minerals. In particular, polymer milling is often carried out according to empirical procedures that do not permit a scale up of the process. The development of models for the prediction of mill behaviour depends on the knowledge of the influence of operating conditions on the evolution of polymer properties and goes through the characterization of the grinding kinetics.

Several studies have been performed on polymer fine grinding, but most of them are concerned with the determination of various properties of the polymers after fragmentation [3–5], and results on the particle size are rare. Vivatpanachart et al. [6] have studied the influence of the grinding time on the size distribution of polystyrene and polyethylene particles. The curves evolve similarly for both products. Thus, the fraction of the largest particles as well as the distribution width decreases with time. Polystyrene grinding is easier than polyethylene grinding, therefore the size of the polystyrene particles is more homogeneous and decreases quicker. Pan and Shaw [7] have studied the size evolution of polyamide and polyethylene particles. These authors have obtained fragments of 3–5 μm, constituted of agglomerates of very small grains. In both cases, grinding has been carried out in small vibrated mills using cryogenic temperatures, however the authors have not studied the influence of working parameters on the size evolution.

This paper deals with polystyrene grinding. A preliminary study is presented on pregrinding of polystyrene beads in a laboratory blade mill. The effect of different operating conditions on the particle size in a vibrated bead mill is then characterized. Finally, kinetic laws are proposed.

2. Experimental procedure

Batch runs have been performed in the experimental apparatus presented in Fig. 1. A shaker bead mill consisting of a 1-litre polytetrafluoroethylene cylindrical vessel (152 mm high, 100 mm internal diameter, 3 mm wall thickness) is used. It contains the grinding medium and the polystyrene particles, and it is closed by a screwed cover. The vessel is fixed to a plate moving vertically. The vertical vibration is provoked by an eccentric effect. The eccentricity is induced by a rod–handle system driven by an electric motor. The vessel is immersed in a liquid bath (water at room temperature or liquid nitrogen) in order to control the temperature.

The grinding medium is composed of spherical glass beads having a diameter of 1.2–1.4 mm, while the polystyrene particles introduced in the shaker mill have a mean size of about 100 μm. Thus, the initial ratio between bead and polymer diameters is chosen at an optimum value

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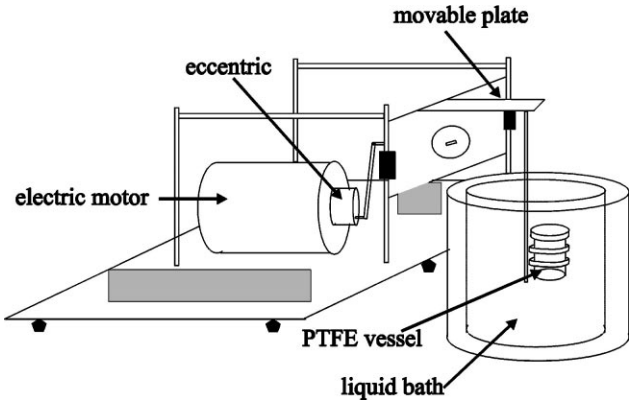

Fig. 1. Experimental set-up.

determined by a study presented elsewhere [8]. Moreover, the bead load is varied from 0 to 50 vol.% (0–738 g), the polymer load is fixed between 12.5 and 100 vol.% (10.8–86.4 g) of the interstitial voidage of the beads. Finally, the rotation speed is 386 or 586 rpm and the amplitude is fixed at 2 cm.

The polymer particles are obtained after a pregrinding of polystyrene beads (1 mm diameter, Elf Atochem) in a laboratory blade mill (Janke and Kunkel). A pregrinding temperature of 18°C is fixed by water circulating in a double jacket surrounding the mill chamber.

Concerning the procedure for the vibrated mill, the glass beads and polymer, after being weighed are introduced in the vessel. The vessel is then closed, placed in the liquid bath and fixed to the plate. The mill is then started and stopped at various times to obtain polystyrene samples. The particle quantity taken for each sample is very small compared to the initial polymer mass, so as not to modify this parameter significantly during the run.

The size distributions are measured by the means of a Malvern mastersizer S based on laser diffraction. The liquid used for the analysis is water containing a surfactant. The mean size, d50(t), corresponding to a cumulative frequency of 50% at time t is calculated from the granulometer results. Scanning electron microscopy (Jeol T33A) images of the particles are used to confirm the fragmentation mechanism.

3. Pregrinding of polystyrene beads

Polystyrene is initially available in the form of spherical beads having a diameter of about 1 mm (Fig. 2a). However,

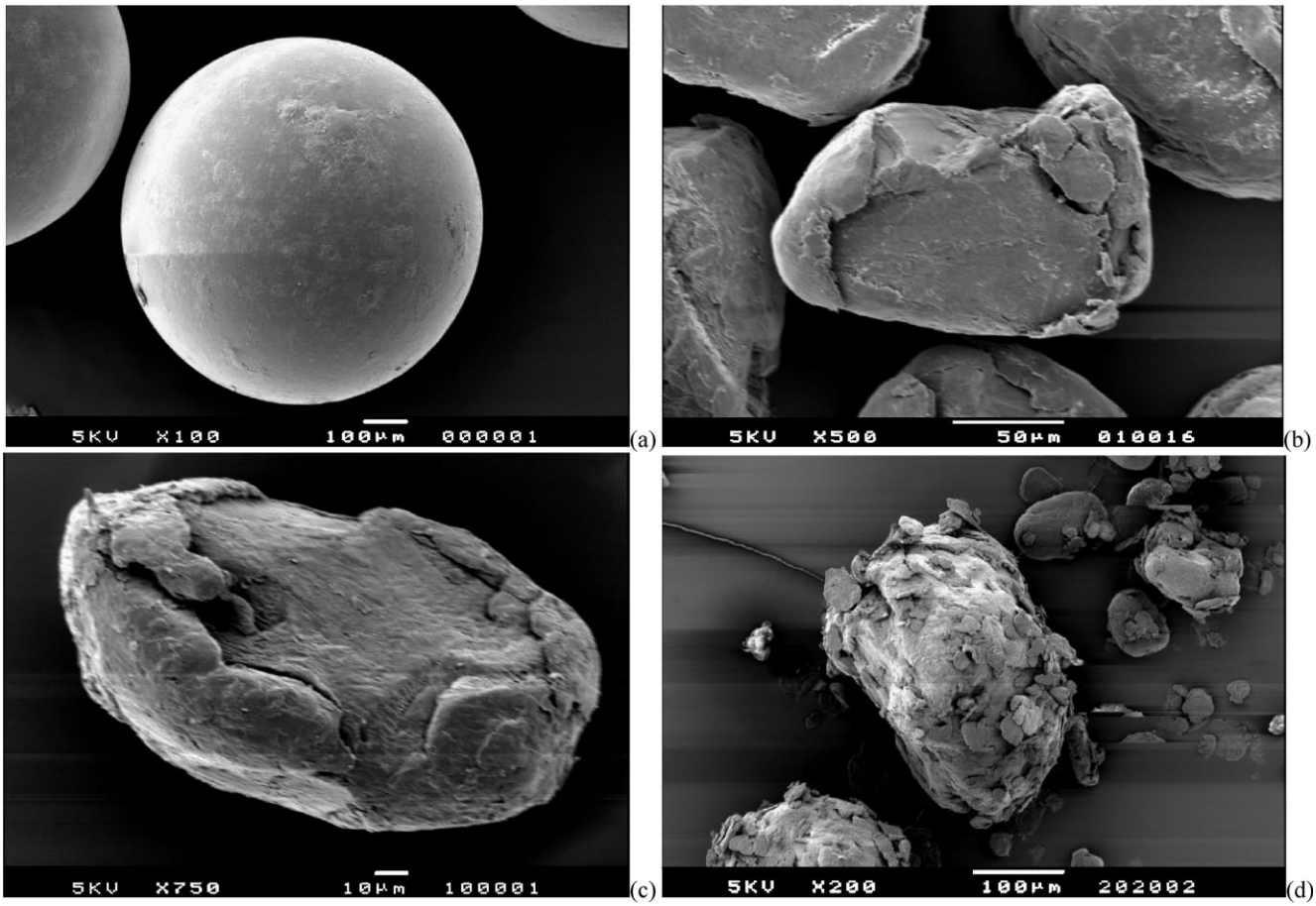

Fig. 2. SEM pictures of polystyrene: (a) initial; (b) after 1 min of pregrinding; (c) after 10 min of pregrinding; (d) after 40 min of pregrinding.

a preliminary study [9] has shown that grinding in the shaker mill is efficient if the particles diameter is not greater than 100–150 μm. This is the reason for which the polymer beads are preground in the blade mill and fragments in the range 80–100 μm are recovered after sieving.

Several pregrinding runs have been realized for different times in order to characterize the effect of this treatment on the fragments. These times have been varied from 1 to 40 min. Fig. 2 presents SEM pictures of particles for various pregrinding times. Already at the first minute, the particles lose their sphericity and present a rough surface as the mill blades cut particle layers, which may then be folded and welded under the effect of local heating near the blades. This operation proceeds with time, as the particle roughness increases (Fig. 2d).

It could be supposed that this morphology evolution may have an influence on the polymer behaviour in the vibrated bead mill. We have, therefore, performed two additional experiments in this mill with polystyrene which has been preground for 10 and 40 min. The operating conditions chosen for the runs in the shaker mill are as follows: temperature: −196°C; frequency: 586 rpm; amplitude: 2 cm; bead load: 20%; polymer load: 60%.

The evolution of the mean size with time is shown in Fig. 3. Grinding in the shaker mill is enhanced in the case when the particles have spent a longer time in the blade mill. Indeed, after a 10 min pregrinding period, the particle surface is made up of welded layers which may be removed under the stress of the beads in the shaker mill. As shown in Fig. 3, the mean size decreases rapidly from 100 to 80 μm. However, the particle centre remains compact, and thus, may not be broken as the shaker mill is not efficient enough.

As for the 40 min pre-treatment run, even the particle centre is composed of superimposed layers. Grinding in the shaker mill is then easier and the size reduction is greater. The blade mill does not permit to reduce the polymer particle size to very low values however, it is useful for the production of brittle particles.

The study on polystyrene grinding in the vibrated bead mill has been undertaken using polymer particles produced after a 40 min pre-treatment period in the blade mill, which leads to a significant size reduction that allows for the characterization of the influence of operating conditions on the grinding kinetics.

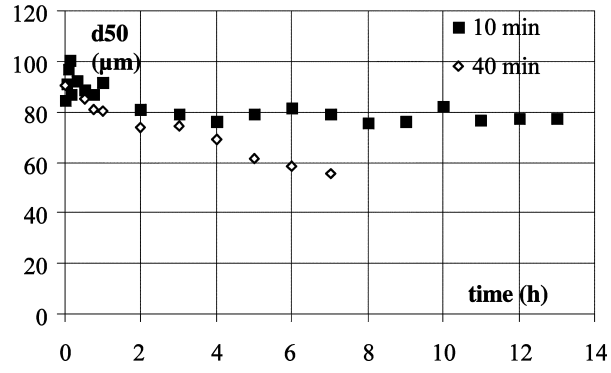

Fig. 3. Influence of the pregrinding time on the size reduction of polystyrene in the vibrated mill.

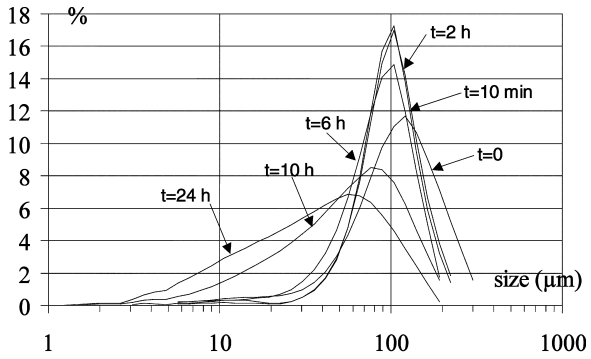

Fig. 4. Example of the evolution of the size distribution of polystyrene during grinding (temperature: 18°C, bead load: 20%, powder load: 100%, frequency: 586 rpm).

4. Polystyrene grinding in the vibrated mill

4.1. General size distribution and evolution of mean size

Fig. 4 presents an evolution of the size distribution of polystyrene during grinding. The same evolution has been observed for most of the runs. The initial load distribution is monomodal, with a mode around 100 μm. From the first moments, small fragments having a size smaller than 10 μm are produced. This phenomenon happens during the first 10 min, leading to a change in the distribution. Afterwards, the curve does not evolve significantly for several hours. Thus, the distribution after 6 h of grinding is not very different from that at 10 min. However, for longer times (more than 8 h), the distribution peak is displaced from the larger towards the lower sizes.

Fig. 5 shows the evolution of the mean size with time (same conditions as in Fig. 4). Different fragmentation steps

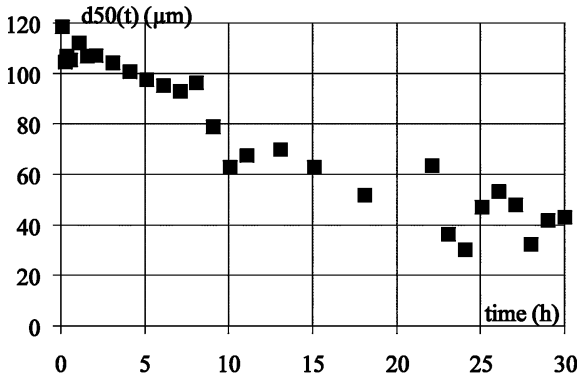

Fig. 5. Evolution of the mean size with time.

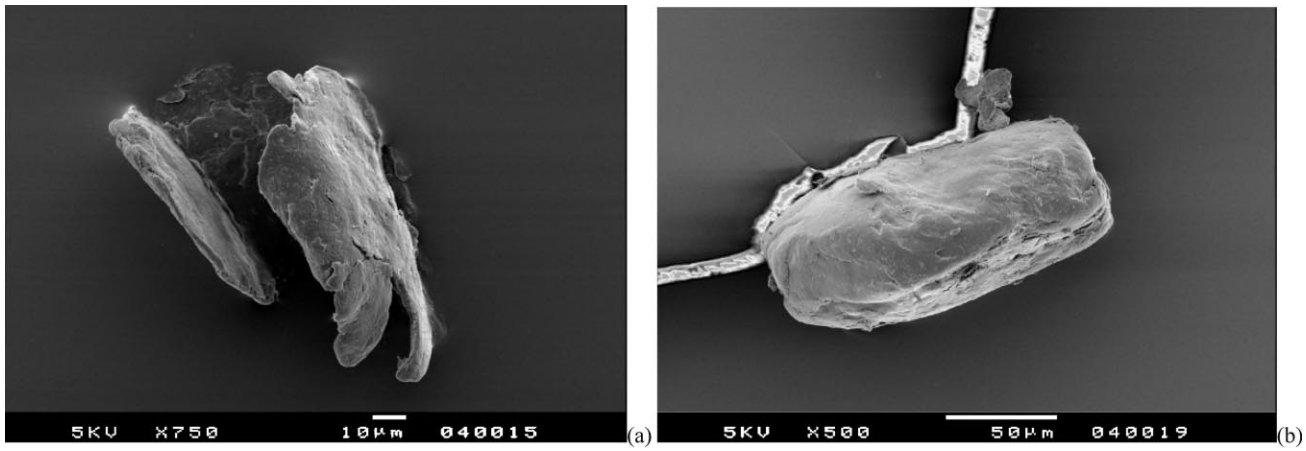

Fig. 6. SEM pictures of particles after grinding: (a) chip; (b) core of the particle after chipping.

may be seen. Indeed, a small reduction (about 12%) of the mean size occurs in the first few minutes. The size then levels off during the next 2 h and decreases again, more slowly (8% from 2 to 8 h). A third reduction period rather rapid and more important (27%) may then be observed. After 10 h, a slight increase of the size is observed, followed by a new decrease. Finally, there is a competition between size enlargement and reduction after 24 h, i.e. when a limit size of 30 μm is reached. The values of the times and of the reduction percentages are specific to the run presented in this figure and vary with the experimental conditions.

As previously specified, preground particles consist of chips superimposed in layers. Under the action of the beads in the shaker mill, the surface chips, which are not well welded to the particles are rapidly eliminated (Fig. 6a), leaving the core uncovered (Fig. 6b). This core is also made up of chips which are first unstuck from the particles. This unsticking is gradual, and leads to a plateau on the curve. The chips are then broken, thereby developing the phenomenon of size reduction. The repeated unsticking–breaking process goes on until elementary chips are obtained. Finally, welding and fragmentation of the chips occur.

4.2. Influence of the temperature on the evolution of the particle size

The glass transition temperature of polystyrene being at +80°C, two experiments have been performed where the liquid bath surrounding the mill vessel is water at room temperature or liquid nitrogen at a cryogenic temperature. The variation of the reduced mean size with time is reported in Fig. 7 for the two temperatures. Grinding with cryogenic conditions is faster. The plateaus are therefore observed at the same sizes for both temperatures, but they are shorter for the cryogenic temperature. This may be explained by the nature of the polystyrene, which is not a brittle material at room temperature. A decrease of this parameter will weaken the polymer making it easier to grind. Furthermore, when water is used as the regulation medium, local heating may happen under the stress of the beads. Thus, there may be an increase of the temperature which may even become higher than the glass temperature at different points of the mill. A ductile fragmentation is therefore conceivable. Lecoq [10] has studied the grindability of different materials in an impact test. He has shown that some polymers (polystyrene, polycarbonate) may have a brittle or a ductile behaviour, while others, such as polyamide, may melt under the effect of impact. In the case of poly(methyl methacrylate), the author has observed a brittle–ductile transition. When working at cryogenic conditions, which are far from the glass temperature, local heating may be minimized.

In spite of this advantage, cryogenic grinding is complicated and expensive to implement and should be limited to the materials which cannot be ground at ambient temperature, such as polyethylene [11].

Following this discussion, it does not seem necessary to grind polystyrene at a cryogenic temperature even though the fragmentation rate is higher. Consequently, the influence of the other parameters has been studied at ambient temperature.

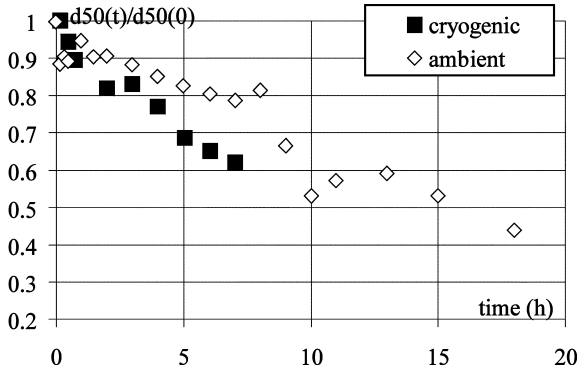

Fig. 7. Influence of the grinding temperature on the reduced mean size (bead load: 20%, powder load: 100%, frequency: 586 rpm).

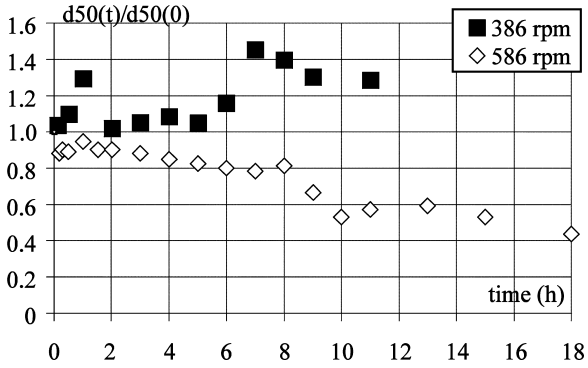

Fig. 8. Influence of the frequency on the evolution of the reduced mean size (bead load: 20%, powder load: 100%).

4.3. Influence of the frequency

Fig. 8 presents the evolution of the reduced size for two frequencies (386 and 586 rpm). The evolution of the curve at 586 rpm has been commented on previously. As for the lowest frequency, there is no size reduction. On the contrary, the mean size increases. Indeed, due to the morphology of the preground particles, the surface chips may be unstuck under the beads stress but the energy transmitted by the beads at this low frequency is not sufficient to pull the chips out. The measurement technique used by the laser granulometer is such that the unsticking leads to an increase of the sizes given by the apparatus. Moreover, this increase may also be due to small particles sticking on larger ones. These suppositions have been verified by SEM analysis.

4.4. Influence of the bead load

The influence of the bead load has been characterized for values of this parameter between 0 and 50%. The results are gathered in Fig. 9. When comparing the curves of the two highest loads, one can note that the minimum size that can be obtained is higher with a bead load of 50%, a condition which does not favour the movement of the components in the vessel and therefore reduces the strength of the collisions [12]. Nevertheless, this high load does not have a negative effect on grinding during the first few hours (Fig. 9b). Indeed, the first size reduction is more important when the load is increased. The number of collisions is enhanced even if their strength is reduced. Besides, bad mixing observed in the system [12] leads to an increase of polymer–polymer contact. Moreover, the amount of particles in the vessel, and consequently, the number of surface chips are increased. The probability that the chips hook together is thus greater. An increase in the number of collisions and of the hooking number may lead to a greater reduction of the size at the beginning of the experiments. To confirm this explanation, a run has been made without any grinding medium, and as shown in Fig. 9b, a small decrease of the mean size occurs in the first few minutes.

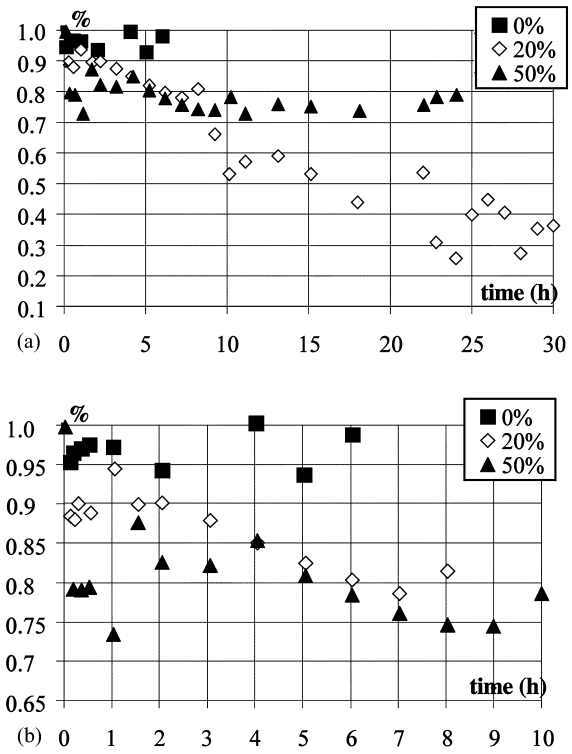

Fig. 9. Influence of the bead load on the evolution of the reduced mean size: (a) during the entire experiment; (b) during the first 10 h (powder load: 100%).

With a bead load of 50%, the second reduction happens, however the third one is not observed as the shocks are not efficient enough to cause a breakage of the chips of the layer concerned.

4.5. Influence of the polymer load

The polymer load has been varied from 12.5 to 100% of the interstitial voidage of the beads. As shown in Fig. 10, the grinding limit of polystyrene, which is at a reduced size of approximately 0.25, is reached in all cases, but quicker when the polymer load is low. Furthermore, an increase of the size is observed after this limit is reached.

The analysis of the curves at the beginning of the experiments (Fig. 10b) permits to conclude that the size reduction does not follow the same mechanism when polystyrene load is high or low. Thus, if the results obtained for a load of 100% are comparable to those described in the previous sections, those of the lowest loads (12.5 and 30%) are different. The initial size reduction is missing, the size even increases since its reduced value is higher than unity. In addition, the size increase is more important at 30% than at 12.5%. The particle size stabilizes rapidly, the plateau length increasing with polymer charge. Finally, the size diminishes quicker when the polymer load is low, and the curves at 12.5 and 30% do not present the successive plateaus observed with high powder load.

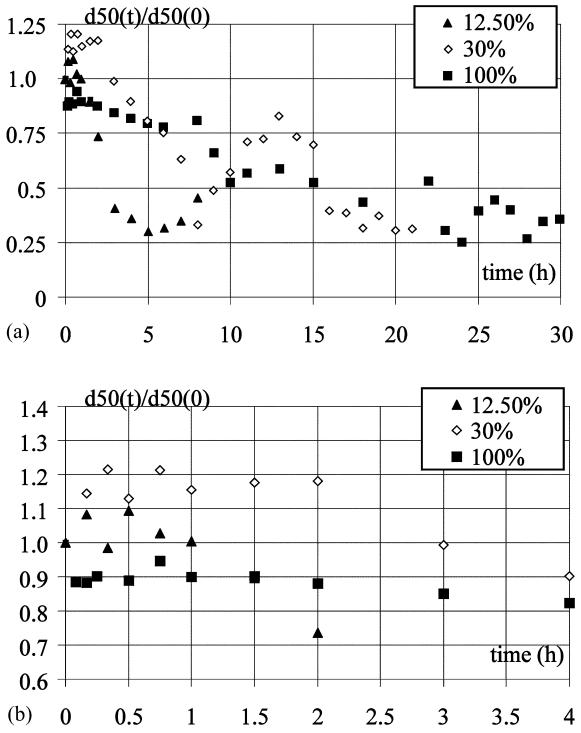

Fig. 10. Influence of the polymer load on the evolution of the reduced mean size: (a) during the entire experiment; (b) during the first 4 h (bead load: 20%).

The absence of the first decrease of the size at low polystyrene loads is certainly due to a low probability of particle–particle contact, limiting therefore the possibility of chip hooking. On the other hand, a decrease of the powder charge improves the collision strength imposed by the glass beads. If this strength is high enough, it may weaken the welding between the chips directly through the whole particle. This explains why the plateau is shorter and the fragmentation rate is higher when the load is 12.5%. In this case, the increase of the energy transmitted to each particle is important enough so that the fragmentation does not occur according to the same mechanism. The size distribution (Fig. 11) evolves differently, presenting bimodal curves after 3 h.

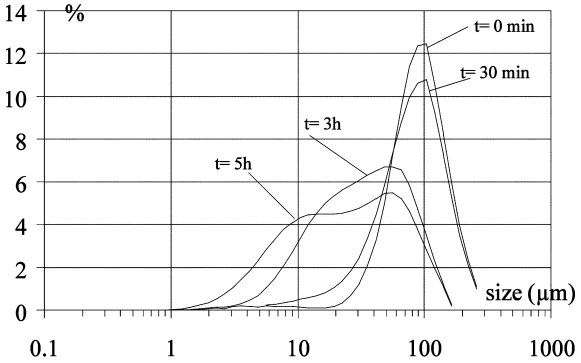

Fig. 11. Evolution of the size distribution of polystyrene for a powder load of 12.5%.

5. Determination of the kinetic laws

The objective of the characterization of the kinetics is to predict the evolution of the size distribution of polystyrene with time for various operating conditions. Batch grinding kinetics have already been described by classical equations [13], by an approximate solution proposed by Kapur and Agrawal [14] or by statistical laws with two or three parameters. This last methodology has been chosen to correlate the results of this paper. Three statistical laws are often used [15]: the normal, the log-normal and the Rosin–Rammler laws. Lyczko et al. [16] have tried to apply these laws to the results obtained on polystyrene grinding in different bead mills. They have shown that the log-normal law was the best to predict the size distributions. Nevertheless, these distributions were not well fitted by a single law, which may be explained by the presence of more than one particle population in the mill (mother particles initially; daughter particles, chips and broken chips then).

Consequently, we have tried to predict the experimental size distributions by different combinations of normal, log-normal and/or Rosin–Rammler laws. On the basis of morphological observations, we have considered that the distributions should be predicted by a combination of four laws at the most, corresponding to the four sub-populations under consideration.

After different tries, a combination of log-normal laws has allowed for the best fitting of the results. For a sub-population i, this type of law is written as

$$\mathrm{LN}_i(x) = \frac{\mathrm{d}W}{\mathrm{d}\ln x} = \frac{1}{\ln \sigma_{gi}(2\pi)^{1/2}} \times \exp\left[\frac{-(\ln x - \ln x_{gi})^2}{2\ln \sigma_{gi}^2}\right] \quad (1)$$

where x_{gi} is defined as

$$\log_{gi} = \frac{\sum \log x \, \mathrm{d}w}{\sum \mathrm{d}w} \quad (2)$$

and σ_{gi} is equal to

$$\log_{gi} = \left[\frac{\sum (\log x - \log x_{gi})^2 \mathrm{d}w}{\sum \mathrm{d}w}\right]^{1/2} \quad (3)$$

Mother particles seem to be a single population which can be predicted by one log-normal law. Progressively, as grinding proceeds, different sub-populations appear, which can also be predicted by log-normal laws. Finally, the sub-population of coarser particles disappears.

Thus, the size distributions, $F(x)$, can be expressed by a combination of four log-normal laws:

$$F(x) = f_1 \mathrm{LN}_1(x) + f_2 \mathrm{LN}_2(x) + f_3 \mathrm{LN}_3(x) + f_4 \mathrm{LN}_4(x) \quad (4)$$

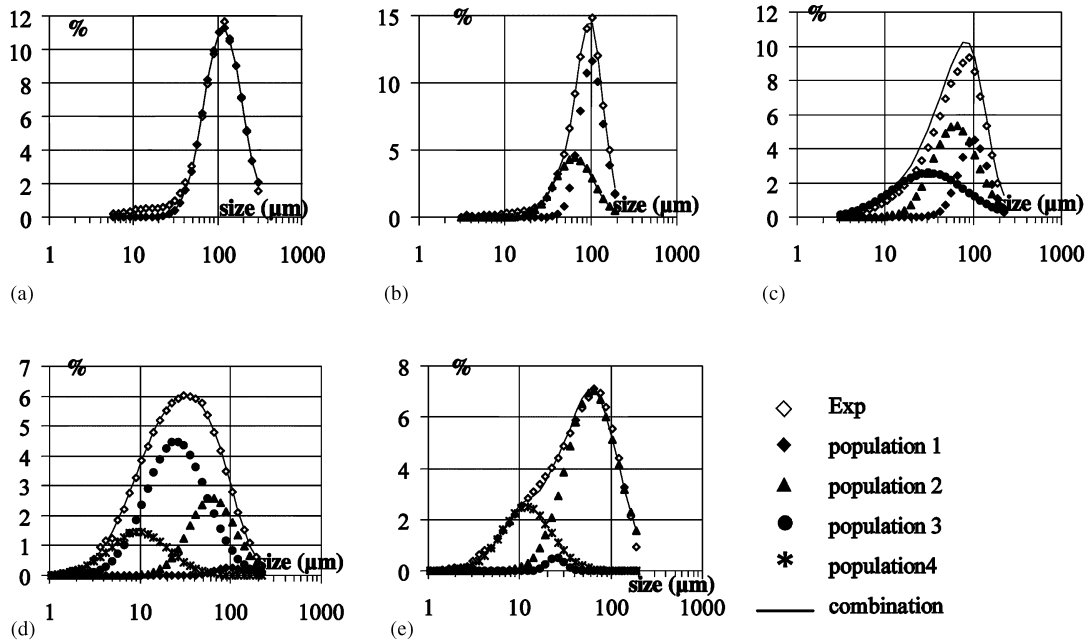

Fig. 12. Comparison of experimental and calculated distributions (bead load: 20%, powder load: 100%, frequency: 586 rpm): (a) initial; (b) 6 h; (c) 11 h; (d) 17 h; (e) 20 h.

where index 1 corresponds to the sub-population of coarser particles; index 2, to the sub-population of daughter particles; index 3, to the sub-population of chips; index 4, to the sub-population of broken chips; and f_i a proportionality coefficient for the law i.

For each time of all the runs, the parameters of the different laws are determined by the nonlinear least-squares method. The distributions are then calculated by Eq. (4). An example of the comparison between experimental and calculated distributions is presented in Fig. 12. The comparisons for other operating conditions are presented elsewhere [8]. The evolution of the size distribution is well predicted by the combination proposed above.

The evolution of the mean sizes and of the standard deviations of the four laws is depicted in Fig. 13 for the run with operating conditions specified in the figure. Initially, the mean size of the coarser particles, i.e. mother particles is about 115 μm and diminishes rapidly to reach approximately 100 μm. This corresponds to the first reduction of d50(t), with a removal of small surface chips. However, these small fragments are not numerous enough to be taken into account as a sub-population in the model. Thus, only one sub-population is considered and remains alone during the three first hours, i.e. at the first plateau of the d50(t) curve. Between 3 and 8 h, parallel to the second reduction and the second plateau of d50(t), a second population appears, corresponding to particle cores after chipping. Here again, small fragments are not detectable because of their low proportions. After 8 h, this third population of small particles, which had been seen earlier in SEM pictures is recognized by the model. Thus, three populations at about 100, 62 and 25 μm are present in the mill. Progressively, chips are broken, leading to a fourth sub-population having a size of around 10 μm. Finally, the coarser particles disappear at the end of the run indicating that all the particles have undergone at least one chipping.

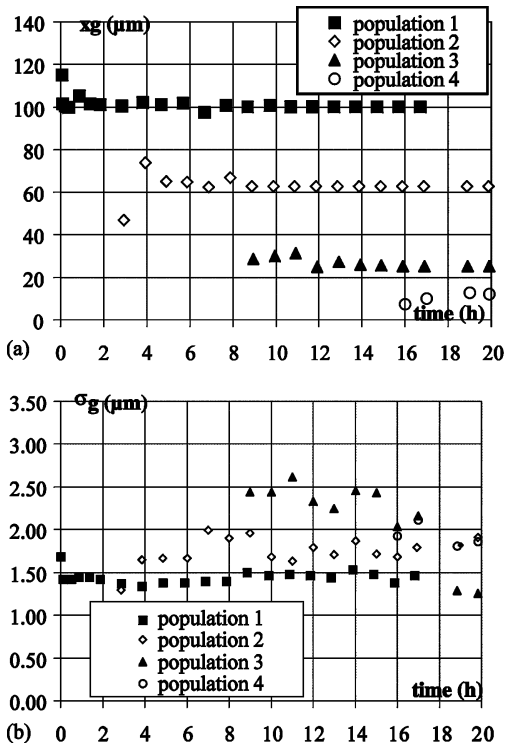

Fig. 13. Variation of (a) the mean sizes and (b) the standard deviations of the four log-normal laws (bead load: 20%, powder load: 100%, frequency: 586 rpm).

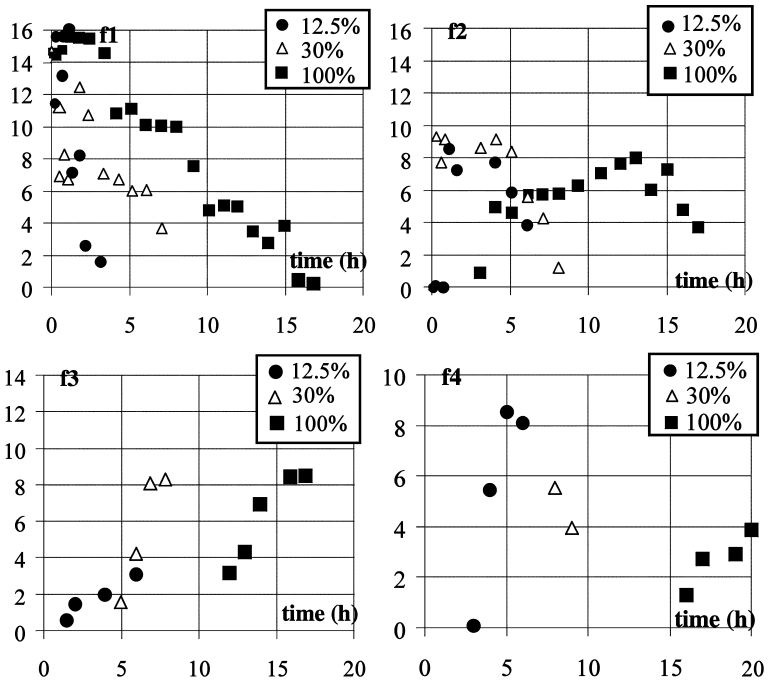

Fig. 14. Influence of the polymer load on the proportionality coefficients.

As for the standard deviations (Fig. 13b), they do not evolve significantly during grinding and are quite comparable for all the sub-populations. The values of the sub-populations sizes and standard deviations estimated by the model are quite identical, irrespective of the operating conditions used. Nevertheless, these sub-populations appear or disappear more or less rapidly, depending on the operating conditions, having therefore an influence on the evolution of the proportionality coefficients.

Concerning these coefficients, Fig. 14 shows their variations with time for the three polymer loads used in this study. The first coefficient decreases with time, indicating that the sub-population of coarser particles disappears to the detriment of the others. The decrease is faster when the load is low and occurs by steps for the highest load, in relation with the d50(t) reduction. The second coefficient goes through a maximum. Indeed, firstly the second sub-population is supplied by the coarser particles, and then daughter particles are broken to produce the third population. Consequently, the second coefficient diminishes, while the third one increases at the same time. Finally, the proportion of fine particles produced belatedly, tends to increase with time.

The same kind of evolution of the coefficients has been observed for the experiment carried out at a cryogenic temperature but the coefficients have varied more quickly than at room temperature, in relation with the rate of the size reduction. As for the run with the high bead load, only two sub-populations have been identified by the model due to the moderate size decrease for this condition. Moreover, there is no significant effect of this parameter on the variation of the coefficients.

In this model, four sub-populations have been taken into account, i.e. daughter particles have always been considered as a single population. We may have considered dividing this family into several sub-populations corresponding to the various chipping steps, however, the identification of too many kinetic parameters has no real sense.

The grinding kinetics of such materials is very complex. Consequently, a classical approach does have limitations. The method chosen in this study permits to take into account the evolution of the particle morphology, i.e. all the sub-populations which appear or disappear during the size reduction. Its use for the scaling of a mill impose to express the kinetic parameters as functions of the operating conditions. Nevertheless, the complexity of polystyrene grinding needs the acquisition of more data on the size evolution for each fragmentation step.

6. Conclusions

A study has been carried out in order to characterize the kinetics of polystyrene grinding in a shaker bead mill. Preliminary work on polymer pregrinding in a blade mill has shown that the material has to spend a minimum time in this apparatus to become brittle and to be able to break under the beads stress in the shaker mill. Particles are then made up of superimposed layers of chips. Polystyrene can be ground at room temperature due to its high glass temperature.

The influence of operating conditions in the vibrated bead mill on the size reduction has been examined. Thus, grinding

can only occur if the frequency is high enough. Moreover, the bead load has to be low in order to allow for a satisfactory movement of beads and polymer in the mill and to favour therefore size reduction. The grinding rate is enhanced by a decrease of the polymer charge. Furthermore, this parameter influences the fragmentation mechanism of the particles. Indeed, a high polymer load leads to particle–particle contact which generates hooking between surface chips. On the contrary, chips of the centre of the particles are removed with more difficulty due to a reduction of collision strength.

The size distributions have been fitted by a combination of four log-normal laws corresponding to the four sub-populations obtained after grinding. The parameters of the laws (mean sizes, standard deviations and proportionality coefficients) have been determined. The first two parameters are constant during grinding and are not influenced by the operating conditions. On the contrary, the proportionality coefficients evolve with time and under the effect of the operating conditions.

7. Nomenclature

d50	size for a cumulated fraction of particles of 0.5 (μm)
d50(0)	d50 at initial time (μm)
d50(t)	d50 at time t (μm)
f_i	proportionality coefficient (dimensionless)
$F(x)$	calculated fraction of particles of size x (dimensionless)
LN(x)	fraction in volume for log-normal law (dimensionless)
w	fraction of particles of size x (dimensionless)
W	cumulated fraction of particles with a size lower than x (dimensionless)
x	size (μm)
x_{gi}	mean size of the log-normal law for the sub-population i (μm)
σ_{gi}	standard deviation of log-normal law for the sub-population i (μm)

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