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Effect of the Mineral Filler on the Surface Properties of Co-Ground Polymeric Composites

Céline Zapata-Massot, Nadine Le Bolay*

Abstract

This study presents results on the influence of the nature of the filler on the surface properties of polymeric composites produced by co-grinding in a tumbling ball mill. The polymer used in the study was poly(vinyl acetate) which is a model material, while two mineral fillers were tested, i.e., calcium carbonate and silica. The variations of the surface properties of the separately ground and co-ground materials were studied for different grinding times, using the sessile drop method, and the properties

were compared to those of matrix-filler blends. The different components of the surface energy were determined by Van Oss decomposition. Grinding generates a large change of the particle surface and especially of the Lewis acid-base energy. These changes depend on the filler nature. In addition, particle agglomeration may be due to an electronic deficit at the particle surface, which is immediately replaced by another particle also possessing an electronic deficit.

Keywords: co-grinding, composite materials, surface properties, tumbling ball mill

1 Introduction

Several processes are used to produce polymeric composite materials. Most of them have limitations which may be of thermal order, in the case of extrusion for example, of chemical order, in the case of chemical synthesis, or of homogeneity of the mixture, in the case of powder mixing. Among the different processes, co-grinding is the most recently developed.

Mineral fillers such as calcium carbonate and silica are often used and permit the decrease of the material costs and also an increase in the physico-chemical properties and the applications of the polymers. An enhancement of the properties is not only due to a good dispersion of the filler in the matrix, but also to the adhesion between the two products, which must be of good quality. This phenomenon translates the intensity of the intermolecular forces exchanged at the interface between the materials. The parameters having an influence on the adhe-

sion are numerous, since they depend on the nature, the intensity and the number of interfacial bonds, the component structures or the interfacial cracks. They can be summarized into three groups: those depending on the filler (nature and composition, proportion in the mixture and size); those depending on the matrix (rheological properties and nature), and those depending on the interface (thickness and interfacial forces). Due to the diversity of parameters, several adhesion models have been proposed in the literature, and have been summarized by Schultz and Simon [1]. They can be divided into two groups: mechanical adhesion of the matrix in the filler pores and specific adhesion (electrostatic, interfacial diffusion, thermodynamic adsorption and chemical bonds).

The different research studies used to study interactions involved various particulate processes, but none of them have used co-grinding. This paper discusses the influence of co-grinding on the surface properties of matrix-filler systems during the production of polymeric particulate composites. The polymer used was poly(vinyl acetate), while two fillers were chosen, i.e., calcium carbonate and silica, in order to study the influence of the filler on the interfacial properties. The sessile drop

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method was used, and among the different adhesion models, that based on thermodynamic adsorption (characterizing solid wettability) was chosen.

This model, initially developed at the end of the 1960's, is based on the works of Zisman et al. [2–3] on the study of solids wettability. It proposed correlations between the wettability characteristics (contact angle and superficial or interfacial energies) and the composite performances, and was the starting point for the definition of interfacial phenomena.

Van Oss [4] proposed that interparticle phenomena result from the combination of two forces, i.e., Van der Waals (non dispersive) and Lewis acid-base (dispersive) forces. In contrast to the case for liquids, the lack of molecular and atomic mobility in solids does not permit the direct determination of the surface energy, and the use of an indirect method, such as the study of the interactions between the solid and a liquid, is required.

When a liquid drop is deposited on a solid surface, equilibrium is established between the solid, the liquid and the vapor, leading to a contact angle, θ , defining the wettability between the liquid and the solid. This angle corresponds to the minimum energy between the three phases at equilibrium.

Young and Dupre (according to Van Oss [4]) have expressed this equilibrium, using the interfacial energies as:

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

The measurement of the contact angles between the solids and several liquids having various surface tensions permits the determination of the dispersive and the non dispersive values of the system.

In this paper, these different components of the surface energy are determined, and their evolution during co-grinding is explained by analysis of the molecules present.

2 Experimental Procedures

Dry batch grinding experiments were performed in a 5 dm³ 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. The ball loading volume represented 20% of the whole volume of the chamber, while the powder filling rate was 10 vol.% of the void space between the balls.

The matrix used in this study was poly(vinyl acetate) (PVA). The particles are spherical agglomerates produced by emulsion polymerization or aggregates of



Fig. 1: SEM photos of the products.

these agglomerates. The particle mean size is 83 μm , and the polymer density is 1190 kg/m³. Two mineral fillers were used: calcium carbonate (calcite – mean size, $d_{50} = 16 \mu\text{m}$ and density = 2710 kg/m³) and silica (mean size $d_{50} = 96 \mu\text{m}$ and density = 2330 kg/m³). SEM photos of the products are presented in Figure 1.

The products were ground separately at first and then combined and ground together. The filler proportion in the mixtures was fixed at 15 vol.%. This percentage permits a major enhancement of the polymer mechanical properties [5].

The mill was filled with the balls and the powder, and then started. It was stopped at different times to take samples from various regions of the chamber, with quantities that were small enough to minimize the powder consumption in the mill.

The size distributions were measured by means of a dry laser diffraction granulometer (Malvern Mastersizer S). The data were treated according to the Mie theory which permits the limitation of artifacts at small sizes. The average size, d_{50} , was also calculated. The samples were also observed with a scanning electron microscope (Leo 435 P).

Surface energies were determined using the sessile drop method. The powders were compacted in a Carver press to form discs, and the contact angle between a liquid drop of known properties and the discs was measured. Three liquids were used. Their properties are presented in Table 1. 30 discs of $0.5 \cdot 10^{-5} \text{ m}^2$ (diameter = $8 \cdot 10^{-5} \text{ m}$) were formed for each sample and ca. 20 drops of each liquid was deposited on the discs.

3 Preliminary Study

Different authors have characterized solids wettability by various methods. Siebold et al. [6] and Orkoula et al. [7] were interested in the evolution of the contact angle for several mineral solids according to the analysis technique. Buckton and Newton [8] have studied the operating conditions influencing the measurement of the contact angle between a liquid drop and a solid surface. Two parameters seem to have an influence, i.e., the force used to form the discs and the drop size.

Table 1: Properties of the solvents at 20 °C.

	ρ ($\text{kg}\cdot\text{m}^{-3}$)	γ_L ($\text{mJ}\cdot\text{m}^{-2}$)	γ^{LW} ($\text{mJ}\cdot\text{m}^{-2}$)	γ^{AB} ($\text{mJ}\cdot\text{m}^{-2}$)	γ^+ ($\text{mJ}\cdot\text{m}^{-2}$)	γ^- ($\text{mJ}\cdot\text{m}^{-2}$)	μ ($\text{Pa}\cdot\text{s}$)
1-Bromonaphthaline (1-BR)	1484	44.4	44.4	0	0	0	$4.89\cdot 10^{-3}$
Formamide (FO)	1130	58	39	19	2.28	39.6	$4.55\cdot 10^{-3}$
Water	1000	72.8	21.8	51	25.5	25.5	$1\cdot 10^{-3}$

A preliminary study was realized to determine the best values of these parameters, which allowed reproducible measurement of the angles. In this study, discs of polymer and polymer- CaCO_3 blends were used. The force was varied between 5 and 20 kN, and drops of 0.5 to 5 μL were deposited.

It was observed that the force used has no significant effect on the contact angle. However, it influences the dispersion of the results, which is reduced for medium forces. In addition, for low forces, the compaction of the particles is not sufficient and the discs are porous. When high forces are applied to the surface, the structure of the discs is modified and their homogeneity is affected. Therefore, angle measurements are not reproducible. As a consequence, a force of 15 kN was chosen, and the variation in results was less than 5%.

The drop volume does not influence the angle value or the dispersion of the results. Thus, a fixed drop volume of 3 μL was chosen.

4 Evolution of the Particle Size during Grinding

The components were firstly ground separately to understand their behavior during the treatment and then together. In a previous study [9], the current authors presented detailed results on the size evolution and on the kinetics based on a laser sizer analysis and on a quantitative SEM analysis, permitting the explanation of the mechanism by which composite materials are produced by co-grinding. A summary of the data is presented here in order to link the variations of the size and the surface properties.

Figure 2 presents an example of the evolution of the size distributions (for PVA) during grinding. It should be noted that the size distributions of the other products evolve in a similar manner. Figure 3 shows the variations with time of the mean size of the different products ground separately and of the PVA- CaCO_3 and PVA-silica mixtures.

The size distributions shift rapidly to the left during the first part of the experiment, leading to a rapid decrease of the mean size. Following this, the evolution is lower, since it results from a combination of fragmentation and

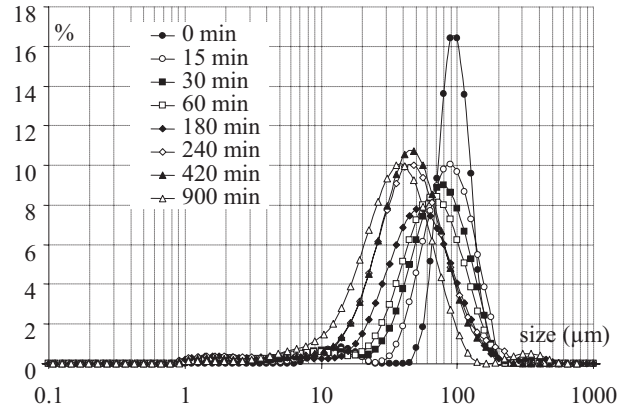


Fig. 2: Variations of the size distribution of the polymer.

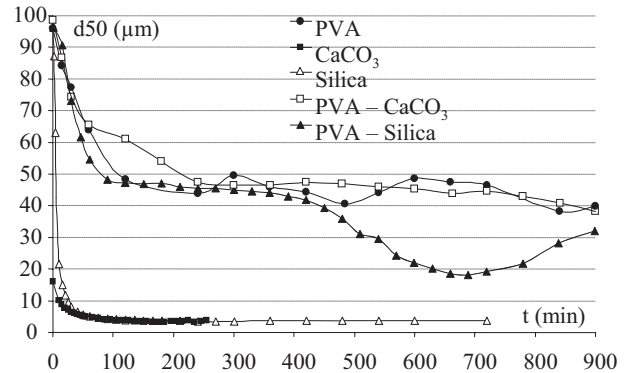


Fig. 3: Variations of the mean sizes of the products and of the mixtures.

agglomeration phenomena. A limiting mean size is then reached. As for the products ground alone, the polymer behavior is different from that of the other two. In addition, the fragmentation rate is faster and the limiting size is lower for the minerals than for PVA. Concerning the mixtures, the polymer and the mineral particles firstly break individually, which leads to a size decrease. When mineral fragments reach a small size (few μm), they rapidly stick on polymer particles. SEM photos in Figures 4a and 4b show polymer particles coated by calcium carbonate and silica, respectively, after co-grinding for 10 min. As a consequence, there are no free mineral fragments remaining. As the treatment is extended,

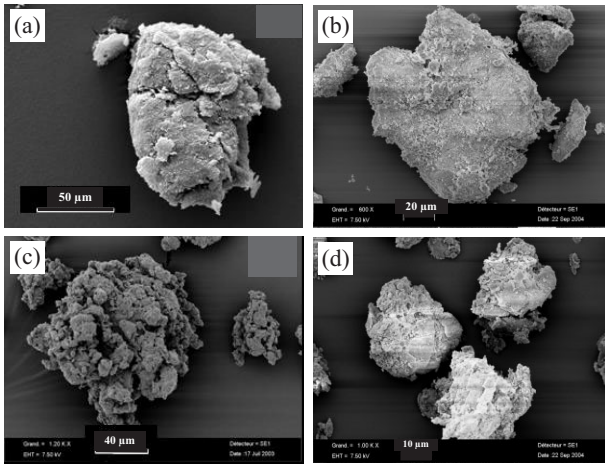


Fig. 4: SEM photos of (a) PVA coated with CaCO_3 , (b) PVA coated with silica, (c) agglomerated particles of type a, (d) agglomerated particles of type b.

coated polymeric particles are broken. Moreover, the mineral fragments which are stuck in the polymer also break under the effect of the balls. Broken mineral fragments then stick onto fresh polymer surfaces. Thus, although the limiting size that can be reached by the mineral particles when ground alone is not lower than 3 μm, it does not exceed 600 nm for co-grinding. The filler dispersion in the matrix is better in co-ground mixtures than in blends. Finally, coated polymer particles agglomerate to form a composite material, which are shown in Figures 4c and 4d. Competition occurs between agglomeration and fragmentation, leading to oscillations in the size.

5 Characterization of the Surface Properties

In order to study adhesion at the interface between the matrix and the fillers, experiments were undertaken to characterize the evolution of the wettability of the products and the mixtures with different grinding times.

5.1 Surface Energies of the Products

With regard to the fillers, it was not possible to press the products in order to form discs having sufficient mechanical resistance. Thus, their surface properties could not be determined experimentally. Nevertheless, data from the literature were used. Wu et al. [10] have shown for calcium carbonate that the global energy is important initially ($\gamma_s = 57 \text{ mJ/m}^2$) and decreases progressively during grinding to reach 37 mJ/m^2 at the end of the experiment. This reduction is due to the fact that the Lewis acid-base component, γ^{AB} , and especially the electron

donor parameter, γ^- , decreases. In addition, carbonate presents a dissymmetry of the electronic charges, with a preponderance of negative charges due to the oxygen atoms. During grinding, particles are broken, and the γ^- characteristic decreases. As a consequence, calcium carbonate particles agglomerate, and the charge dissymmetry decreases due to polar bonds between the particles. Since the asymmetry of the electronic charges of silica is of less importance, the initial energy is lower (50 mJ/m^2). As for the polymer, Figure 5 presents the evolution with time of the contact angles measured for the three solvents. Two types of behavior are observed, the first with water and formamide (which possesses a dispersive component) and the second with 1-bromonaphthalene (which does not possess a dispersive component). In the first case, the angle increases during the first 240 min. The affinity between the solvents and the polymer is progressively reduced, since the polymer tends to become hydrophobic. After 240 min, grinding has no additional effect, since a thermodynamic equilibrium is reached. In the second case, the opposite behavior is observed, since the affinity between the polymer and 1-bromonaphthalene is enhanced by grinding. The variations of the global energy, γ_s , as well as its two components (γ^{AB} and γ^{LW}) deduced from the contact angles are shown in Figure 6, while Figure 7 presents the

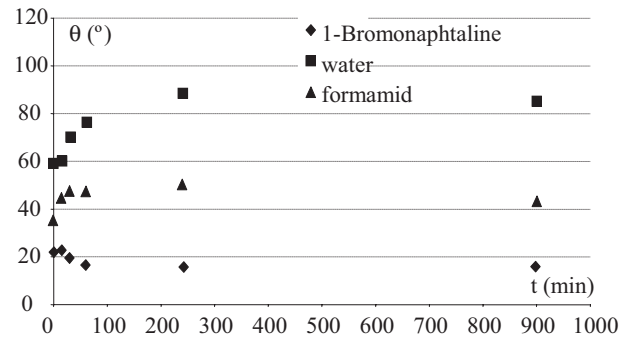


Fig. 5: Evolution of the contact angles with time measured for the three solvents.

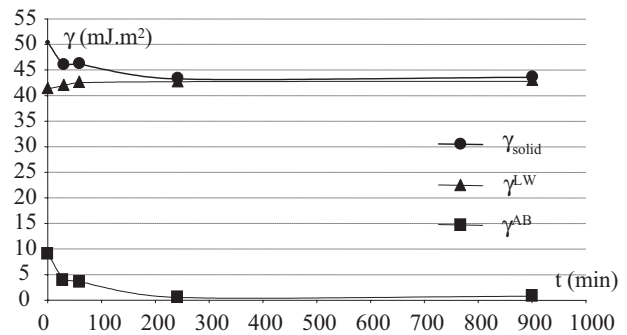


Fig. 6: Evolution of the global energy of the polymer and its components during grinding.

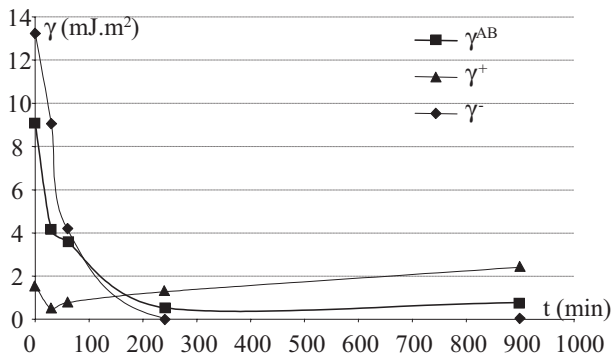


Fig. 7: Evolution of the Lewis acid-base component and its parameters.

evolution of the Lewis acid-base component and the electron acceptor (γ^+) and electron donor (γ^-) parameters.

The nondispersive component, γ^{LW} , does not evolve significantly. Thus, the global energy varies, due to an evolution of the dispersive component, γ^{AB} . Indeed, these two parameters decrease rapidly at first and then level off. Such a decrease expresses the fact that the polarity of the solid becomes less important. It can be seen that the variation of γ^{AB} is mainly the result of a significant change in the γ^- parameter. The electron acceptor parameter, γ^+ , does not evolve significantly. This may be attributed to the fact that before grinding, the presence of the acetate group in the polymer provokes a dissymmetry of the electronic charges. During grinding, an amorphization of the polymer occurs, and in parallel, the molecular chains may be cut. This may lead to disorganization in the distribution of the surface energies, which decreases the dissymmetry of the electronic charges in the polymer. Thus, the initial value of γ^- is equal to 13 mJ/m² and γ^{AB} is initially equal to 9 mJ.m⁻². These two values tend to zero after 240 min.

5.2 Surface Energies of Co-ground Mixtures

Figure 8 shows the evolution with time of the global energy, γ_s , and of the γ^{AB} and γ^{LW} components for the two co-ground mixtures (PVA-calcite and PVA-silica). The results for PVA are included in Figure 8 to make the analysis easier. As was observed for the polymer, the nondispersive component, γ^{LW} , is mostly constant, and its value is similar for all cases, regardless of the filler used. However, the evolutions of the energies are different for the PVA-silica system than for the polymer alone or for the PVA-calcite system. The global energy and the dispersive component increase during the first 240 min of grinding and then decrease when a silica filler is used, while they decrease rapidly at first and level

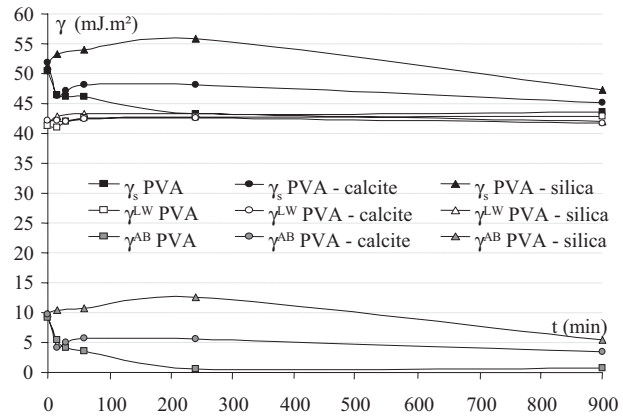


Fig. 8: Variation of the global energy and its components during grinding.

off with the calcite filled composite, as was observed for the polymer alone.

A Van Oss decomposition was applied and the results are summarized in Figure 9.

When adding calcium carbonate, the levels of the different energetic components of the blends (before grinding) are similar to those of the polymer. As co-grinding occurs, the curves can be divided in three parts:

- Between 0 and 15 min, all the components evolve similarly for the polymer and for the calcite filled mixture, since they all decrease. The polymer and the calcite are both fragmented separately. Consequently, the explanations given previously can be applied here. However, the values of γ^{AB} are slightly higher for the mixture. This is due to the fact that γ^- is two times higher for the mixture than for the polymer during this grinding period. This may be attributed to the presence of calcium carbonate in the mixture. Indeed, this product has a high dissymmetry of its electronic charges which is transferred to the polymers. The decrease of γ^- at the beginning of co-

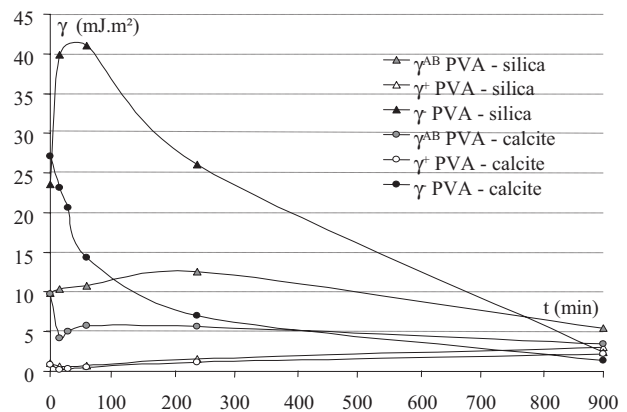


Fig. 9: Variation of the dispersive components of the surface energy during grinding.

grinding may be explained by a loss of crystallinity of the polymer, as indicated above, and also by the generation of bonds between the negative sites of calcite (oxygen atoms) and the positive sites of the polymer (carbon and hydrogen atoms), contributing to an equilibrium in the electronic charges distribution. These bonds lead to a faster decrease of γ^- in the case of the mixture than for the polymer.

- Between 15 and 240 min, γ_S and γ^{AB} still decrease in the case of the polymer, while they increase before they eventually level off for the mixture. Calcium carbonate fragments stick on the polymer particles and coat them progressively during this period. Thus, the surfaces of the discs are mainly constituted of calcium carbonate, the energetic level of which is higher than that of the polymer. The dispersive component of the mixture decreases less than it does for the polymer.
- At the end of the experiment, the energetic values are not modified significantly since the nature of the particle surface does not evolve any further.

The results obtained with the mixtures containing silica corroborate this interpretation. This filler initially possesses a more homogeneous distribution of the electronic charges than calcite. The particles are fragmented and the bonds are cut as grinding begins. Thus, a higher dissymmetry of the electronic charges occurs in the silica molecules, and γ^- increases. Simultaneously, as the polymer is ground, the value of γ^- decreases and the phenomenon appearing with silica is preponderant. Thus, the energy parameters increase. After 60 min of grinding, all silica particles are fragmented and the dissymmetry of the electronic charges is at a maximum. Bonds are created between the polymer and the silica, following the same mechanisms as those proposed for PVA-calcite co-grinding. Then, at longer grinding times, agglomeration softens the phenomena. Nevertheless the energetic level of the mixture containing silica remains high. In addition, the nature of the filler and the evolution of the molecular bonds influence the energetic components. Consequently, the surface properties of co-ground composite materials are different from those of the blends.

6 Conclusions

Grinding leads to major changes of the surface of particles, and especially of Lewis acid-base energies. Thus, particle agglomeration may be attributed to an electronic defect at the particle surface. This defect may be replaced by another particle also possessing an electronic defect. The interface between the matrix and the filler, in the case of blends, may be limited to the proximity of the particles. On the other hand, in the case of co-grinding, the modification of the particle surface creates a

bond formation between the filler and the matrix. This modification depends on the nature of the filler since the evolution of the electronic charges greatly influences the surface properties.

7 Nomenclature

d_{50}	mean diameter of particles (m)
μ	viscosity (Pa·s)
ρ	density (kg/m ³)
γ_L	liquid surface tension (mJ·m ⁻²)
γ_S	solid surface tension (mJ·m ⁻²):
	γ^{AB} = Lewis acid-base (dispersive) component;
	γ^{LW} = Lifshitz Van der Waals (nondispersive) component;
	γ^+ = electron acceptor parameter;
	γ^- = electron donor parameter (mJ·m ⁻²)

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