MECHANICAL BEHAVIOUR OF POLYPROPYLENE COMPOSITES CONTAINING ULTRAFINE PARTICLES. CORRELATIONS WITH GRANULOMETRY AND MICROSTRUCTURE

P. Mareri [1], S.Bastide [1], N. Binda [1], and A. Crespy [1]

[1] *Laboratoire Matériaux Matrices Minérales et Organiques, Ecole des Mines d'Alès, 30319 Alès Cedex*

SUMMARY : It is now well-known that the introduction of a mineral filler in a thermoplastic matrix increases Young modulus but dicreases impact strength. The use of ultrafine mineral particles is one of the solutions for avoiding this decrease providing that the particles size remains small.

In this study, we used three kaolins with differents particle size as fillers in a polypropylene matrix.
Image analysis was used to characterize the particle size in situ.
The results we obtained show that :
- The initial particle size can be noticeably modified. Indeed, particles of small tend to agglomerate.
- The microstructure of the matrix is modified, but not enough to explain the mechanical properties variations.
- The mechanical properties depend widely of the presence of aggregates.To confirm this point, a surface treatment was used to scatter the particles. We noticed an increase of the impact strength, due to the vanishing of the aggregates.

KEYWORDS: mineral filler, particle size, polypropylene, polymer matrix, particle-reinforced composites, image analysis, mechanical properties, impact strength.

INTRODUCTION

When ultrafine particles are incorporated in a polymer matrix, parameters, such as size, shape, volume ratio, filler dispersion and surface properties, have considerable influence on the mechanical properties of the composite material, in a direct or indirect way, by modifying the cristallinity.
The use of ultrafine particles is a recent solution for improving the impact strength [1,2,3], but the in situ granulometry may be damaged by the phenomenon of agglomeration [4,5]. To test the influence of this parameter , we studied mechanical properties of polypropylene matrix composites filled with 3 kaolins. The granulometry differed from one to another.

First, we measured in situ granulometry of these composites. Related to this measurement, we determined the microstructure change of the matrix and their mechanical characteristics.
Then, reffering to the same method, we used a surface treatment to improve the particles scattering of the initially finest kaolin.

MATERIALS

Polypropylene

The polypropylene, homopolymer isotactic, used is refered to as 3400 MA1 and was supplied by APPRYL
Its characteristics are as follows :
melt flow index: 40g/10mn (230°/2,16Kg)
density 950 kg/m^3
melt temperature 163°C
Glass temperature 10°C
Mw 220537 g/mole

Kaolins

The fillers are kaolins distributed by Kaolins d'Arvor. They are referred to as : K88, Kcent and K20C. Their respective median diameter (d50) are : 0.2 to 0.5 µm, 0.5 to 1 µm and 1 to 2 µm. From a chemical point of view, they are similar.

Composites

The incorporation weight rates of kaolin are 10, 20, 30 and 40%. When used, the surface agent rates are 0.25, 0.5, 1 and 2.5 wt%. This surface agent is a quaternary amonium, supplied by CECA and referred to as Noramium M2C. Composites are obtained by compounding, and the samples are injection molded.

EXPERIMENTAL TECHNIQUES

Mechanical characterization

The conditions of the uniaxial tensile tests are defined by the ISO 527 standard. We determine Young's modulus, yield stress and strain, break stress and strain.
The conditions of the impact test are defined by the ISO 179 standard. The tests were carried out on both notched and unnotched samples. The notch is V shaped and 2mm deep.

Microstructural characterization

Microstructural characteristics were determined using DSC testing. Temperature setting is shown below :

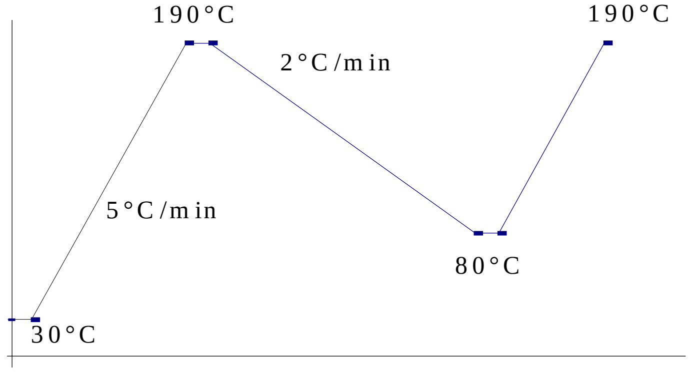

Figure 1 : Temperature setting for DSC tests

3 samples per materials were tested. The following values were determined : DH_c and DH_f, cristallinity and fusion enthalpie, T_f fusion temperature, T_0 and T_c, onset and cristallization temperatures.

Granulometry characterization
Image analysis was used to measure –in situ- the surface average, the spreading and the size distribution. These measurements were carried out from SEM photos of polished sections of composites after filtering and thresholding. The photos were performed in a Jeol JSM 35 CF microscope. Samples were taken in a quarter of the cross section of the tensile samples. We suppose a double symmetry.
Surface average is a value indicating the average granulometry inside the composite.
Spreading characterizes size homogeneity and discloses the presence of aggregates.
Consequent to preliminary tests, we decided to enlarge photo size 500 times and to substract the background noise each time because of impurities.

RESULTS AND DISCUSSION

Granulometry
Surface average and spreading are shown on figures 2 and 3. K88, initially the finest, has , in situ, the coarsest particle size, because of a high agglomeration tendancy.

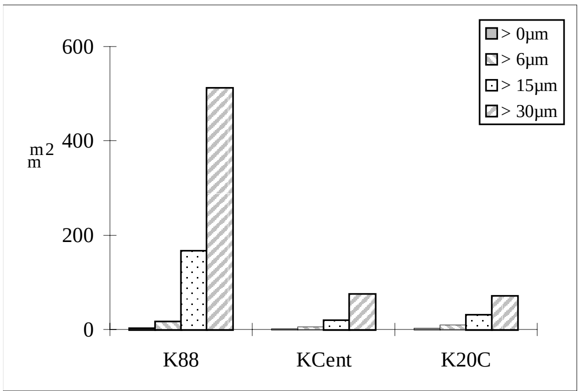

Figure 2 : Surface average inside the composite

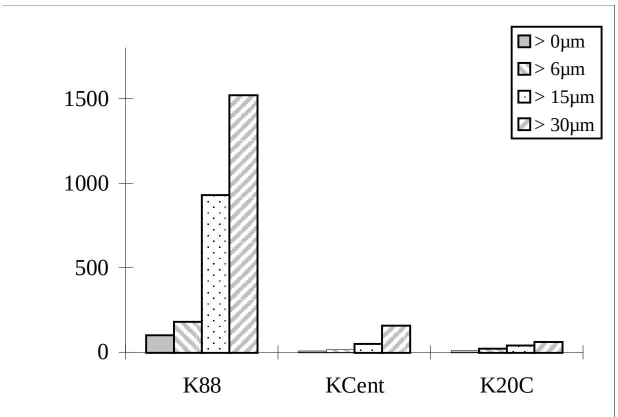

Figure 3 : Spreading inside the composite

Spreading confirms the simultaneous presence of ultrafine particles and of large aggregates, even in a small number. Even though, a large number of big aggregates has been detected in situ, the K20C particles size remained greater than that of the Kcent.

We can suppose a threshold granulometry below which non treated kaolin will have a coarser and more heterogeneous in situ granulometry.

Microstructure

Figures 4, 5, 6 and 7 lead to the following conclusions :

PP/K88 : temperatures and enthalpies evolutions show that this composite has the highest cristallinity rate and we can suppose the existence of large radial lamellae.

PP/Kcent : cristallinity phase seems to be reduced and made of fine radial lamellae.

PP/K20C : Two types of cristallinity structures appear, depending on filler rate.

According to kaolin used, the observed differences remain small, especially when weight rates are low. However, we can conclude that nucleation is more depending on particle surface than particle size or the presence of aggregates. Cristallinity rate depends on dispersion as it is affected by the distance between particles.

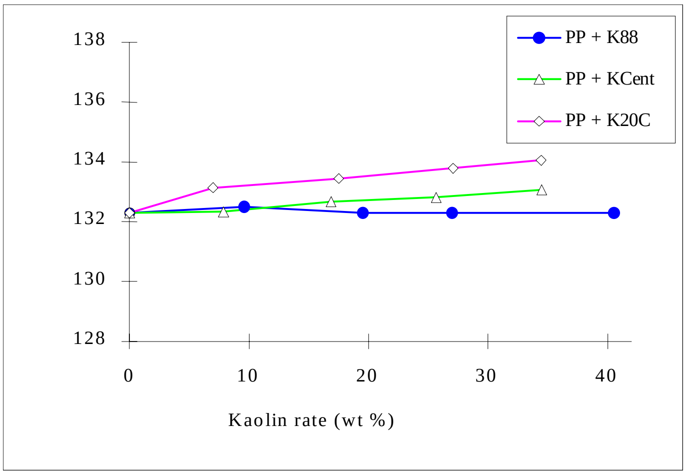

Figure 4 : Onset temperature

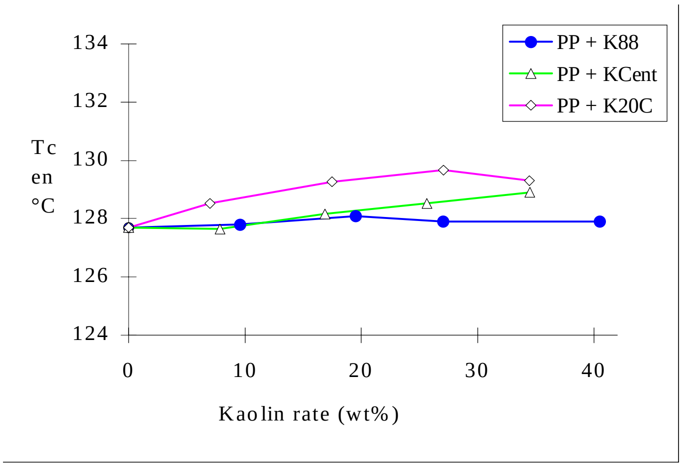

Figure 5 : Cristallization temperature

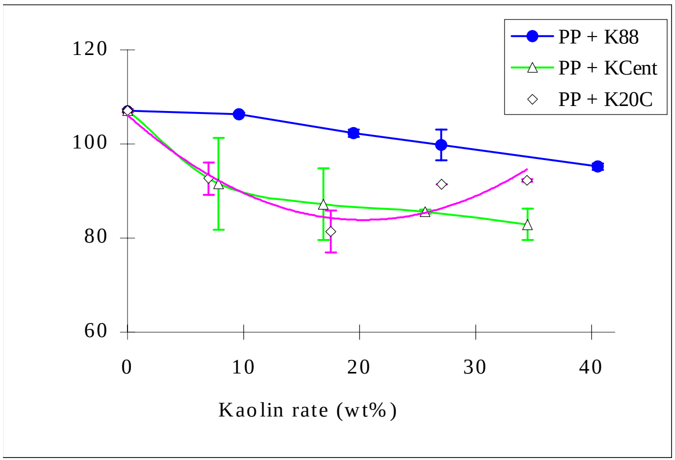

Figure 6 : Cristallization enthalpy

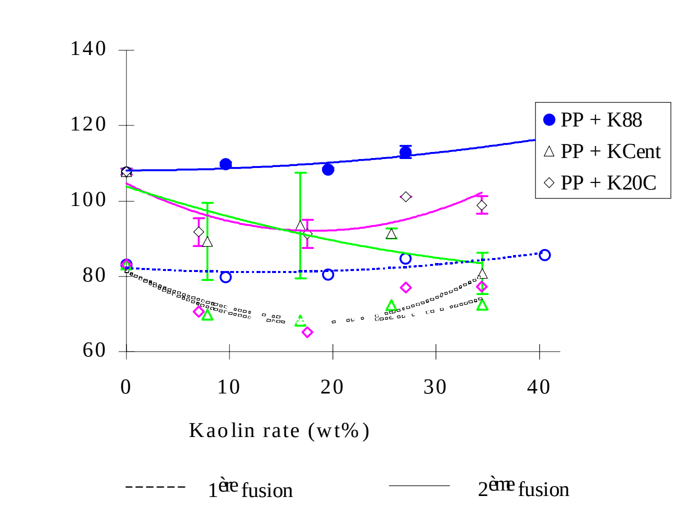

Figure 7 : Fusion enthalpy

Mechanical behaviour

The influence of incorporating kaolins on tensile behaviour, as well as on impact strength, is shown in figures 8 and 9 :

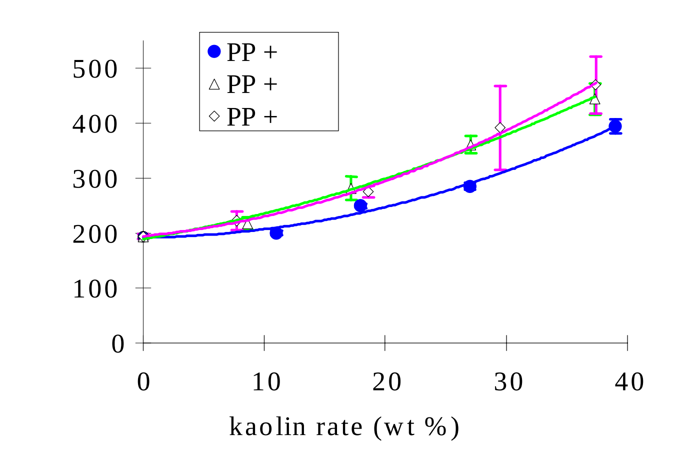

Figure 8 : Young modulus of composites

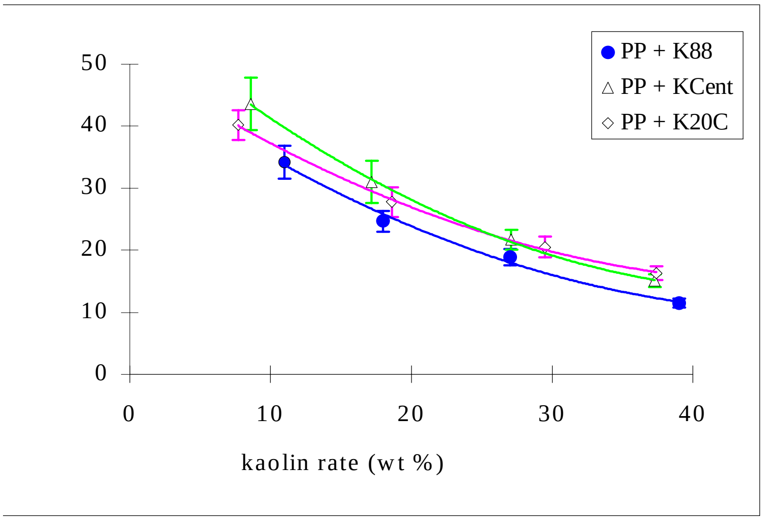

Figure 9 : Unnotched impact strength

These results show that, rates being equal, K88 filled composite is the least stiff and has the lowest impact strength. Such results are obtained considering notched impact test items. Kcent and K20C filled composites have very similar tensile behaviour. Relating these results to the poor microstructure evolution and in situ granulometry measurements, we can conclude that tensile behaviour is highly dependent on filler size and is greatly damaged by poor dispersion.
Concerning the impact test, we show that Kcent and K20C filled composites have similar strength. We can note that their particle sizes are very close. K88 filled composite has the lowest strength.

As in the case of tensile properties, we can not connect microstructure variation and impact strength evolution. Therefore, the in situ granulometry is the prime parameter.
Even in a small number, we can conclude that large aggregates are responsible for the mechanical properties decrease.
To confirm this hypothesis, kaolin K88, initially the finest, was treated to improve the dispersion. Figures 10 and 11 show the efficiency of the treatment. Indeed, we observe that the granulometry is finer and more homogeneous.

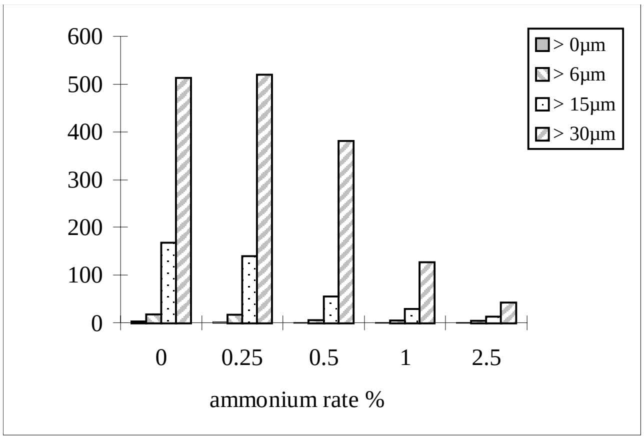

Figure 10 : Influence of treatment on the surface average

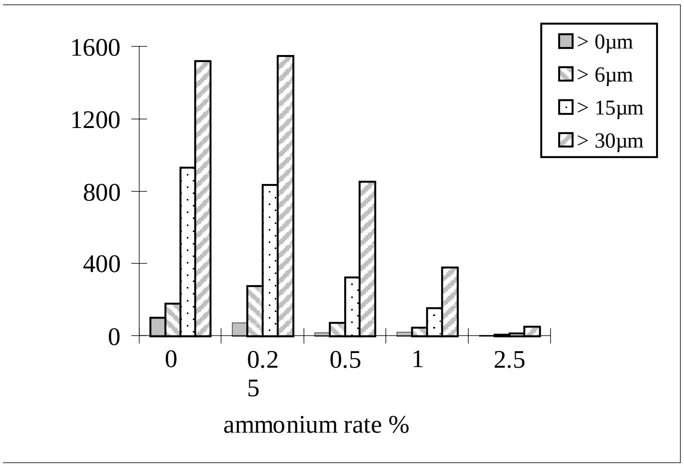

Figure 11 : Influence of the treatment spreading

The study of the composites microstructure has confirmed the previous conclusions : nucleation does not change because of the aggreagtes, and the cristallinity rate is gouverned by the distance between particles. Concerning the tensile properties, we noticed a stiffening and an increase of the ultimate values. Test were carried out on PP/noramium blends and they show a plastifying effect. This could explain higher ultimates values. Concerning impact tests, as well as for notched and unnotched -figure 12- samples, a significant improvement is found.

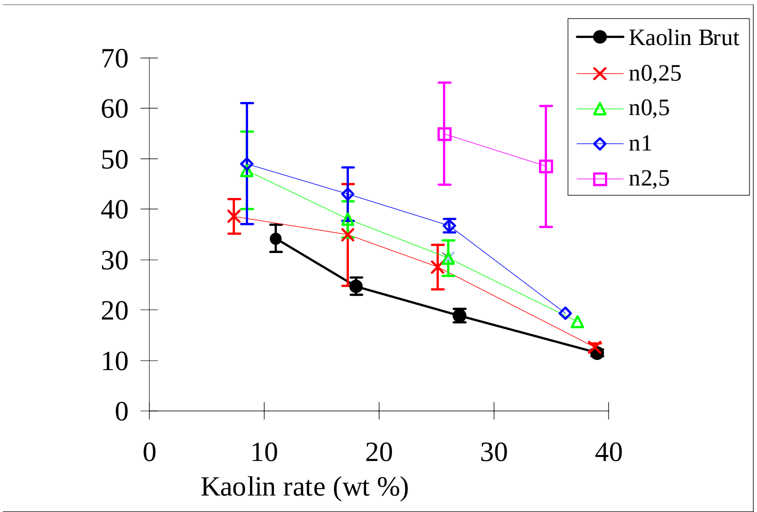

Figure 12 : Unnotched impact strength vs treatment rate

Connecting these results and the dispersion improvement, we can conclude that the vanishing of the aggregates lead to a significant increase of mechanical properties.
Test carried out [6] on PP/noramium blends and the study of their microstucture showed that improvements could not be attributed to matrix modifications.

CONCLUSION

The work presented here concerned the study of the influence of particle size and dispersion on mechanical properties of 3 PP/Kaolin composites. Each of the 3 kaolin used had a different particle size.

In situ measurement of granulometry clearly showed that the initially finest particles have a high tendancy to agglomerate. Microstructure variations in terms of particles size are low. On the other hand, agglomerates, even if their number is small, has a negative effect on mechanical properties.

Therefore, we choose to use a surface treatment to scatter particles. The good dispersion was verified by the in situ granulometry analysis. Microstructure study has confirmed the low influence of granulometry, but mechanical properties of kaolin filled composites, with the kaolin being well scattered, are clearly higher.

REFERENCES

1 Svehlova V. , Poloucek E. « Note on notch and unotch toughness of PP-CaCo3 composites : influence of particle size and dispersion degree » Die angewandte makromolekulare chemie 174, 1990, pp. 205-212.

2 Svehlova V. , Poloucek E. « Mechanical properties of talc-filled PP. Influence of filler content, filler particle size and quality of dispersion. » Die angewandte makromolekulare chemie 214, 1994, pp. 91-99.

3 Sumita M., Ookuma T., Miyasaka K., Ishikawa K. « Effect of ultrafine particles on the elastic properties of oriented polypropylene composites » Journal of materials science, 17, 1982, pp. 2869-2877.

4 Herzig R., Baker W.E. « Correlations between image-analysed morphology and mechanical properties of calcium carbonate-filled PP » Journal of materials science, 28, 1993, pp. 6531-6539.

5 Ess J.W., Hornsby P. R., Lin S.Y., Bevis M.J. « Characterization of dispersion in mineral-filled thermoplastic compounds », Plastics and rubber applications, 4, 1984, pp.7-14.

6 Mareri P. « Etude de la dispersion de fines particules de kaolin au sein d'une matrice polypropylène. Influence sur les propriétés mécaniques du polymère chargé. », Thèse, Université de Montpellier, 1998.