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New dispersion process for submicronic fillers in thermoplastics

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SUMMARY : The addition of sufficiently small-sized fillers in thermoplastics is supposed to allow an increase in stiffness while maintaining a good resilience. However, it is often difficult to obtain a good impact resistance because the dispersion of fine fillers is not perfect – even using a powerful tool like a corotating twin screw extruder. This implies that the material will inevitably contain agglomerates that will cause a drastic drop in the material's resistance, bringing it down to the level of that of a coarse-filler containing material.
CERDATO, jointly with APPRYL, has designed a patented process for the dispersion of fine fillers in an extruder that allows this problem to be solved. The originality of this process lies in the optimization of the deagglomeration of the filler before its feeding into the extruder. As an example, polypropylene/submicronic calcium carbonate compounds show a joint gain in stiffness and impact resistance, while a traditional incorporation process (fillers fed in the melt) leads to an important loss in impact resistance.

Introduction – Fillers and filled thermoplastics

Thermoplastics are commonly reinforced by the incorporation of relatively large amounts (up to 50% by volume) of rigid fillers like talc or calcium carbonate.

Fillers were originally introduced into thermoplastics to decrease the cost of the final material[1] and simultaneously increase its stiffness[2)]. Besides, fillers offer numerous other advantages as compared to non-filled materials [1-7)]: incorporated fillers reduce thermal dilation and shrinkage, increase the material strength at high temperatures, opacify it, and can bring a number of other specific properties like conductivity or flame retardancy to the material.

However it is also widely known that the main drawback of fillers is to generally decrease the impact resistance of the material due to a local stress concentration around the mineral particles[8)]. It is thus generally admitted that the addition of a rigid mineral filler to a thermoplastic such as polypropylene increases its stiffness (Figure 1) while decreasing its impact resistance [7-8] (Figure 2).

As a matter of fact, these observations are highly dependent on a number of factors like the type of polymer, filler content, filler size and shape, polymer/filler adhesion, dispersion state

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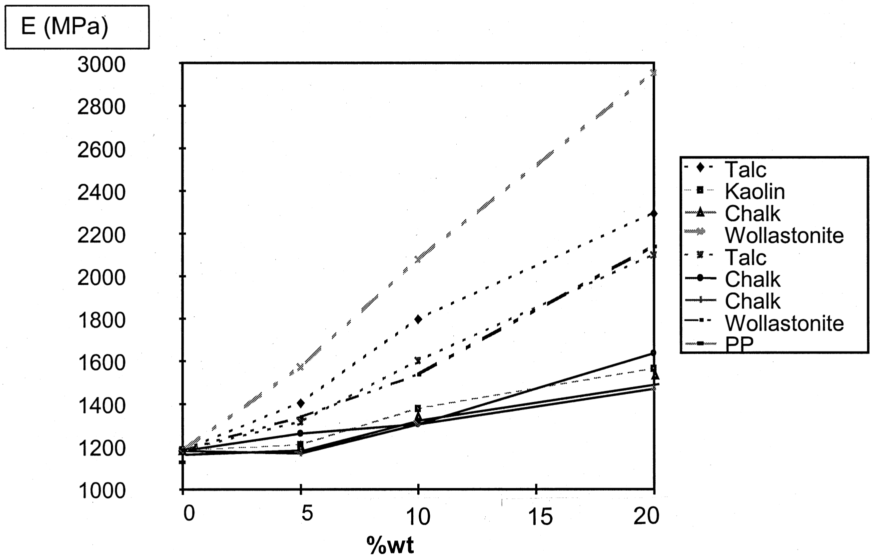

Fig.1 : Reinforcing effect of fillers in PP. The reinforcement is proportional to the filler content and generally to the filler aspect ratio (length/diameter).

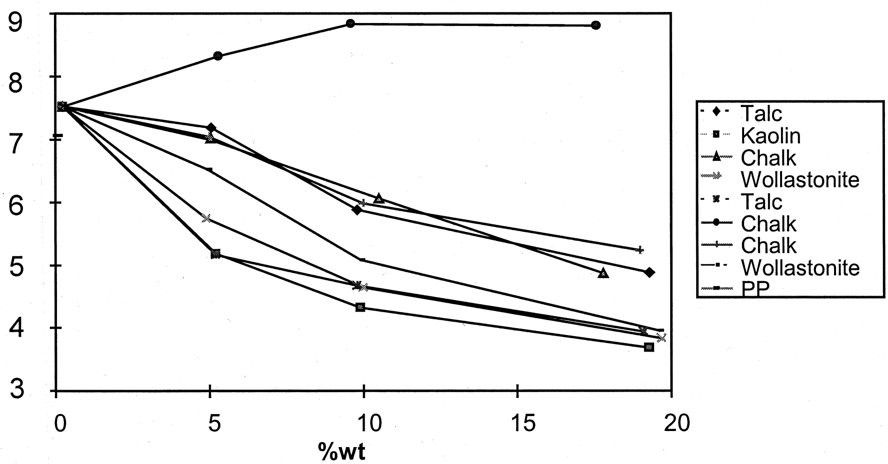

Fig.2 : Impact resistance of filled PP compounds (kJ/m^2). Only a treated calcium carbonate allowed an improvement in the impact resistance of the compound.

of the filler in the matrix, and even on the type of test [1,7]. For instance the presence of agglomerates of fillers in the matrix is very detrimental to the impact resistance [9,10] as these agglomerates act as weak points that easily initiate crazes. The use of coarse fillers also leads to a similar behaviour.

It is thus of interest to use ultrafine fillers, under the condition that they be thoroughly dispersed in the material. Nevertheless a perfect filler dispersion is all the more difficult to obtain as the filler is small-sized, even in a powerful mixing tool like a corotating twin screw extruder.

That is the reason why a new process was designed by CERDATO, jointly with APPRYL, for the dispersion of submicronic fillers in thermoplastics.

Slurry process versus classical compounding process : a comparison

In classical compounding methods, the filler is added to the polymer in the melt via a side feeder. This implies that the filler/polymer mixture only undergoes limited shear along the extruder, and that this shear is insufficient to break possible filler agglomerates (Figure 3).

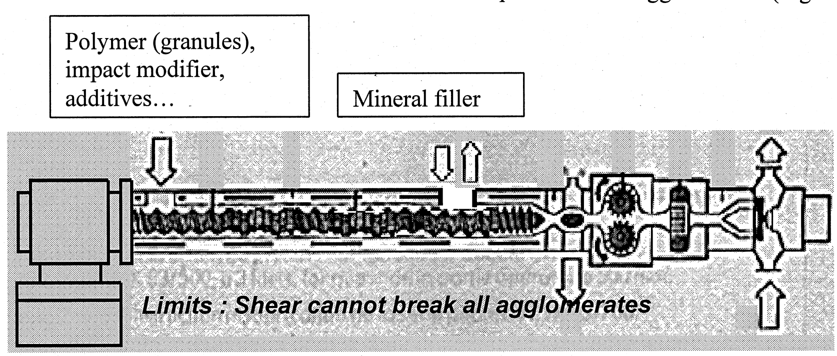

Fig 3 : Classical compounding

We have designed a new process called the « slurry process » in which a slurry of the filler is used instead of a dry form. The slurry is added via a pump at the entrance of the extruder to the polymer in a powdery form itself (Figure 4). This process shows a number of advantages : firstly, the filler is in a deagglomerated state in the slurry before use ; secondly, a premixing effect occurs between the powdery polymer and the filler at the entrance of the extruder ; and thirdly, the shear undergone by the filler/polymer mixture is higher that in the classical compounding process since the filler is directly added at the entrance of the extruder.

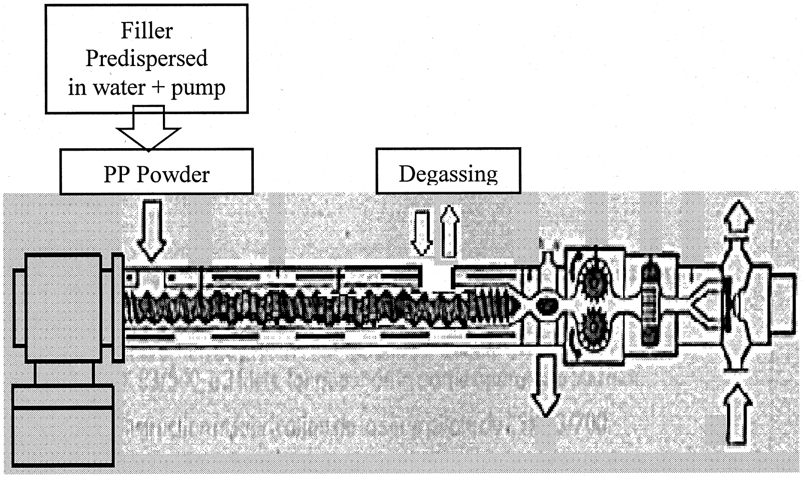

Table 1 shows a comparison of the two processes in the case of a polypropylene (block copolymer 3010 GN5 from APPRYL) filled with calcium carbonate (Setacarb OG from OMYA). Compounding was led on a Werner 40 corotating twin screw extruder.

Process		Reference (pure PP)	Classical	Slurry
Chalk	% wt	0.0	24.9	22.5
Flexural Modulus	MPa	992	1428	1379
Elongation at break	**%**	**639**	**125**	**594**
Unnotched Charpy Impact , 23°C	kJ/m^2	NB	140 100 % B	160 40% B 60% NB
Notched Charpy Impact, 23°C	kJ/m^2	13.7	10.3	50.0
Multiaxial Impact Total Energy, 3 mm, 4.3 m/s, 23°C	**J**	**80 (Ductile)**	**35 (Semi - Ductile)**	**74 (Ductile)**
MFI, 230°C, 5 kg	g/10min	10.5	4.0	4.5

Table 1. – Slurry process vs. Classical compounding process - a comparison.

While obtained moduli are similar for the two compounds, the impact resistance (Charpy, notched or unnotched, or multiaxial) is significantly higher in the case of the slurry process. The notched Charpy impact values show that calcium carbonate could even play a role as an impact modifier in this case.

These differences in impact resistance values can be explained by optical microscopy pictures which clearly show a great improvement in the dispersion of calcium carbonate owing to the slurry process.

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