Calcium Carbonate in Blown HDPE Film

New Developments to Increase Productivity and Profitability

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Many interesting developments have taken place in the film industry over the past few years due to new improved resins and the increased capability of extrusion lines. Technical progress must however be subject to the cost factor and the use of mineral modifiers, especially calcium carbonate can play an important role. Most polymers are ductile but may become brittle under certain circumstances.

Introduction

It is now well established that the introduction of both elastomeric and hard mineral particles can increase the impact toughness of semi-crystalline polymers.

W and P.Bartczak showed that the critical inter-particle distance, which is a fundamental property of the matrix material, is affected by the presence and characteristics of the particles dispersed in the matrix. Compared to elastomeric particles, $CaCO_3$ increases the stiffness but does not affect the Tg of the final compound.

A.S. Argon from the MIT claimed that by introducing hard fillers ($CaCO_3$), interfaces around those inclusions will be generated. Interfaces consist of preferentially oriented crystalline lamellae, having a lower plastic shear resistance in the crystal planes parallel to the filler particle surface. If $CaCO_3$ particles are well enough dispersed in the matrix, the oriented lamellae form bridges between particles lowering the shear resistance throughout the structure and so enhance the toughness of the matrix .

In this investigation, the impact toughness of HDPE modified with fine particles of $CaCO_3$ was determined to study the influence on the processing and productivity of polyethylene film manufacturing.

Materials and Methods

The calcium carbonate used in this work was surface-coated and had a top cut (d98%) of 7 and a mean particle size (d50%) of 1.7 microns (µm).
This fine $CaCO_3$ was first compounded in LLDPE (MFI = 1g/10', under 2.16 kg at 190°C) to give a 65% master batch
The reference film had the following composition:

HDPE GM 9450F (MFI = 0.2g/10' under 5 kg at 190°C) from Basell	80%
LLDPE from Sabic (MFI = 1 under 2.16 kg at 190°C)	15%
White master batch	5%

The test extruder was an HDPE Kieffel line with a 25 L/D 80 mm screw. The extruder was equipped with a 200 mm IBC die and the AERO-COOL system.

The initial parameters for the production of the reference sample were :-

- Lay flat width : 1440 mm
- Thickness : 14 µm
- Weight per metre : 39.13 g/m
- Blow-up ratio : 4.584
- Constant line speed: 111 m/min
- Constant output: 261 kg/hr
- Screw speed: 102 rpm
- Specific screw output : 2.56 kg/rpm/hr

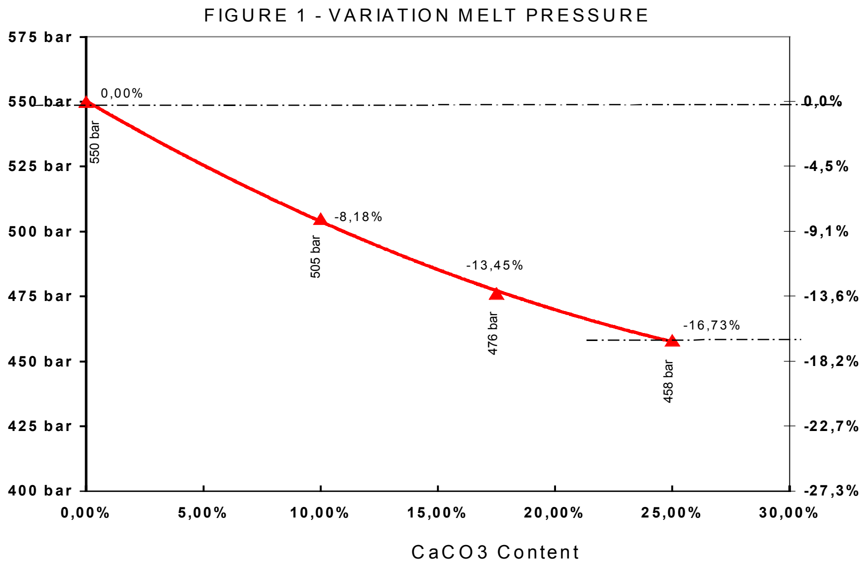
Different mineral loadings (10, 17.5 and 25 %) by weight in the film were studied. During the different trials, the film thickness was down-gauged to ensure a constant weight per running metre.

Results

A Productivity Improvement

Output Extrusion Line Increase

By introducing the 65 % concentrate in a ratio of 15.3, 26.8 and 38.3 % corresponding to a $CaCO_3$ content in the film of 10, 17.5 and 25 %, the melt pressure decreased by 16.73 % or from 550 down to 458 bar. This reduction of pressure is shown in figure 1.



This beneficial behaviour could be explained thanks to the following 5 factors :

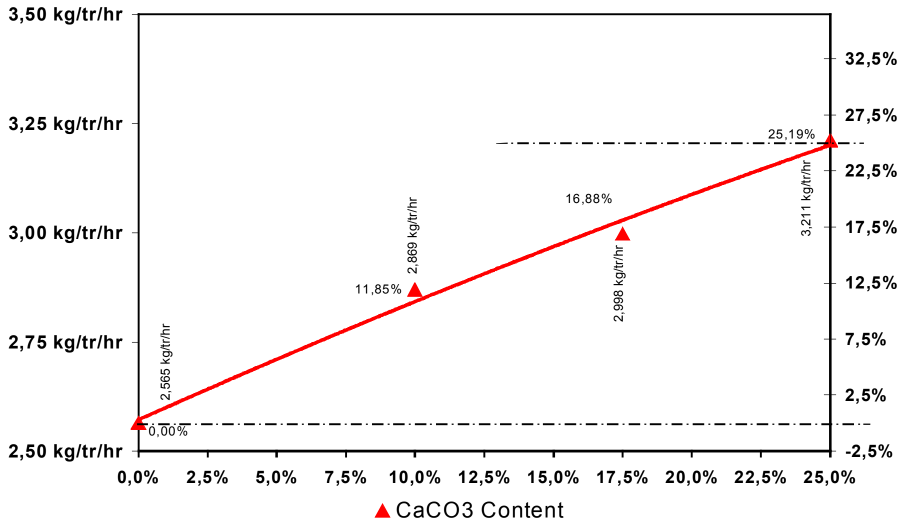
1. The internal volume of the screw will be reduced due to the non-dilation (expansion) of $CaCO_3$ particles replacing polymers.
2. The viscosity of the blend will be reduced compared to that of the reference blend. The increased internal friction from $CaCO_3$ particles in the polymer mix raises the shear, reducing the melt viscosity .
3. Due to the good thermal conductivity of the $CaCO_3$ particles, exchange of heat is improved providing a higher melt homogeneity.
4. Increase of the blend density HD + LL + White + $CaCO_3$
5. The efficiency of the grooved feed section of the extruder is improved by the compound pellets.

Due to this fall of pressure, the increase of the specific screw output and the faster cooling of the bubble, the output of the blown film line can be increased.

During the trials, we achieved without any problem, an output of 310 kg/hr at 132 m/min line speed means an increase of 18.8% with a blend containing 20 % $CaCO_3$ compound (or 13.05 % $CaCO_3$).

As a general rule, the use of 1% $CaCO_3$ will increase the output by at least 1%. Depending upon the machine specification, the production programme and the polymer blend composition of the film, this output increase could reach up to 1.5 % for each percent of $CaCO_3$.

FIGURE 2 - VARIATION SPECIFIC OUTPUT

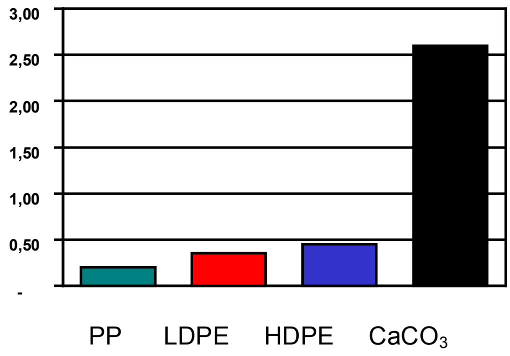


Bubble stability

Besides this tremendous increase of productivity, $CaCO_3$ will also improve the quality of the polyethylene bubble by increasing its stability. This is again due to the excellent heat conductivity which is 5 times higher than the polymers'. The better melt strength and the excellent cooling give the bubble a remarkable stability even at higher outputs and line speeds.

The neck height of the HDPE bubble can now be increased from the usual 8 x die diameter to 12 x die diameter.

FIGURE 3 – THERMAL CONDUCTIVITY (W/ M°K)



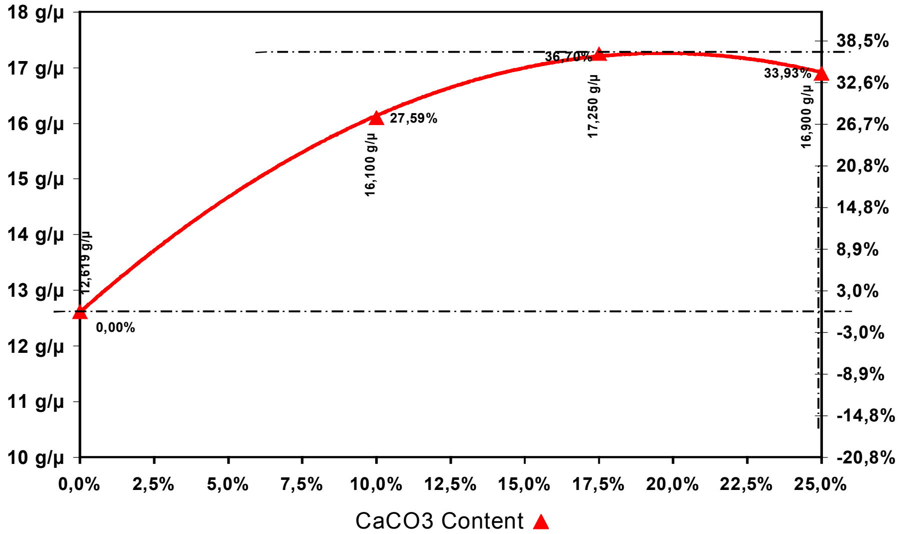
This higher stability improves the process, resulting in a better film quality with :

(a) Closer thickness tolerances (less deviation)
(b) Excellent micro and macro film flatness, thus good film appearance
(c) A slight decrease of width variation and pleats in the film
(d) An increased output thanks to higher neck.

Dart Drop Increase

By achieving an extremely good dispersion of the very fine $CaCO_3$ particles in the PO matrix and by reaching the critical and necessary ratio to create the appropriate network as described in the different studies mentioned in the introduction, the toughness will be dramatically increased. In figure 4 we give the evolution of this value. The maximum of 17.25 g/µ or + 36.7 % of the original dart value is achieved with a 20 % $CaCO_3$ content.

FIGURE 4 - VARIATION DART DROP TEST

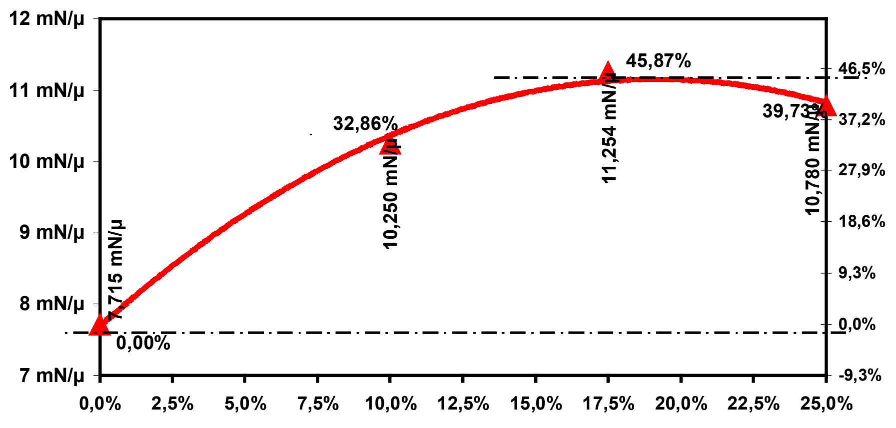


The dart impact is of great interest in some applications, specially for all types of bags. Thus, if the final requirements for some applications only specify the dart value, the film thickness can be reduced whilst still attaining the value of the original reference film.

Elmendorf Tear Resistance

Here again, $CaCO_3$ dispersed in the film improved the tear resistance. Figure 5 shows an increase up to 11.254 mN/µ or + 45.87 % of this value in the machine direction.

FIGURE 5 - VARIATION ELMENDORF MD

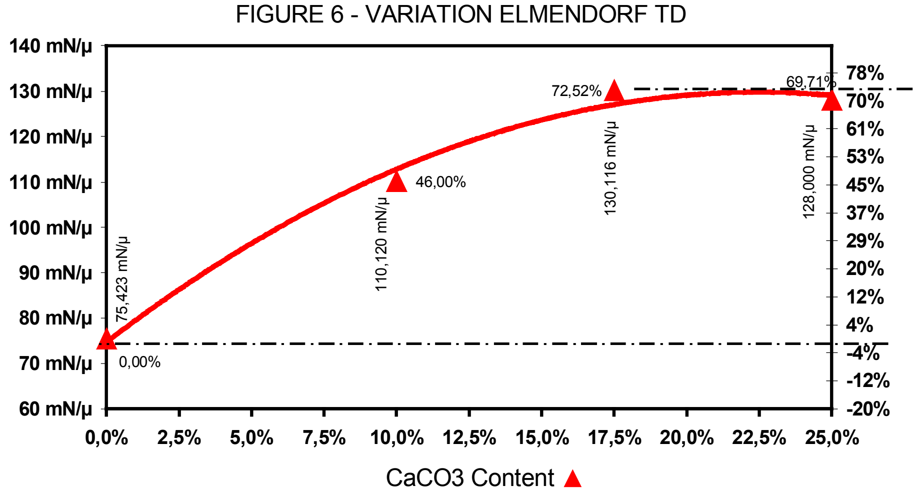


These results are impressive and are the result of the creation of a stable 3-dimensional polymer matrix.

Thus the same benefits are to be found when the tear resistance is measured in the TD. However, these values are much higher and so are not so critical to the properties of the final film.

Figure 6 shows an increase up to 130,116 mN/µ or nearly 70 %.

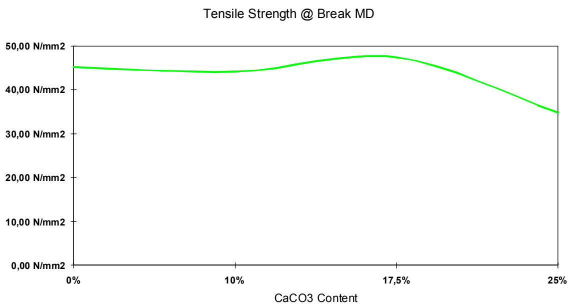
FIGURE 6 - VARIATION ELMENDORF TD

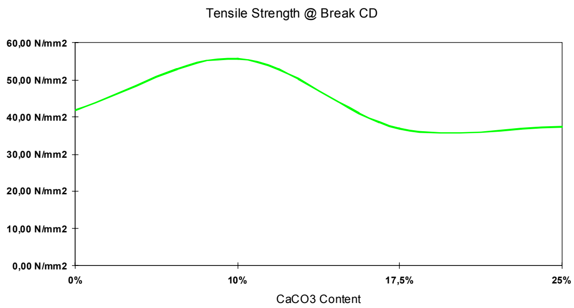


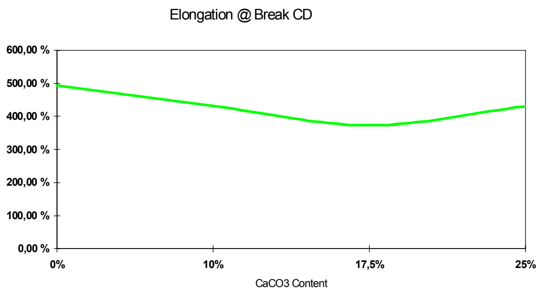
The improvement of these mechanical properties results from the better and controlled orientation of the polymer chains. Calcium carbonate is both binding the polymer chains and inhibiting their orientation in the film.

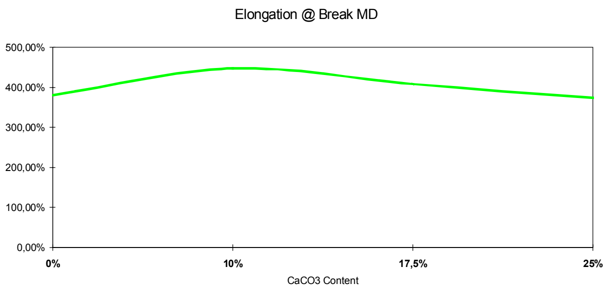
Tensile Strength/Elongation at Break

By using resins with low MFIs, corresponding to those of the polymers used to blow the film, the expected decrease of the tensile strength is minimised and reduced to a maximal loss of 10 % at a mineral loading of 25 %. Moreover this slight loss could be assigned to the reduction of thickness when $CaCO_3$ is introduced.









Orientation / Isotropy

The optimum mechanical properties of high molecular weight HDPE films are obtained if the molecular chains are orientated equally in the MD and TD directions. In this case the film has a good isotropy. This is all the time achieved with optimum adjustments of the processing parameters. With the use of $CaCO_3$ compounds, the balance of the orientations and the film isotropy are improved.

The MD and TD orientations depends from the "actual draw down" or from following ratio :

ACTUAL DRAW DOWN = LINE SPEED / MELT SPEED AT BUBBLE NECK-IN POSITION

The best mechanical film properties are obtained when the value of this actual draw-down is between 1.5 and 2, or when the polymer speed at the bubble neck-in position is high and the neck height is very high.

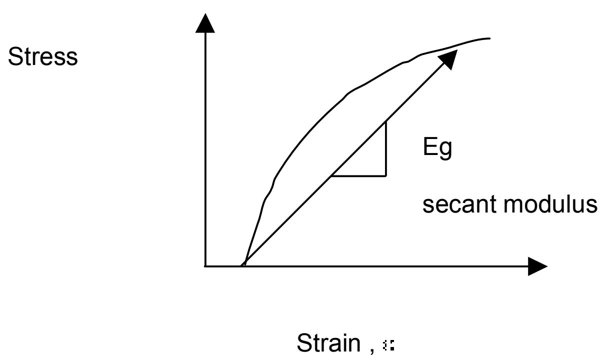
With 15 to 35 % compound, the increased bubble stability allows much higher neck heights - up to 12 x die diameter. The bubble neck-in melt speed is then over 50 % of the line speed and the optimum film orientation can now be achieved. The dart and Elmendorf values are maximised and the TD/MD ratio is low.

C Improvement during Converting

Secant Modulus

Eg (secant modulus) is determined by the shape of the line connecting the origin and a given point on the strain-stress curve.

This characteristic is particularly important during the film converting operations, for example during the stacking of the bags at the end of the bag maker. By increasing the secant modulus, the converting machines are able to run at much higher speeds without any disruption during the bag stacking. The scrap rate of the converting machines is reduced.



Printability

It is generally agreed that the presence of $CaCO_3$ in polyolefines enhances printability.
This assumption has been once again verified during bag production.
$CaCO_3$ creates micro-roughness of the surface, allowing better adhesion of the ink to the substrate.
But due to the permanent presence of $CaCO_3$, the corona treatment is enhanced and the effect will be prolonged. Due to higher treatment level, the printing speed can be increased and the scrap rate due to poor ink adhesion is reduced.

Improved Heat Sealing

Heat sealing is improved. The main reason is the high thermal conductivity of $CaCO_3$. The sealing bar temperature can be reduced and less polymer degradation occurs. Once again the processability and productivity of the bag maker are significantly improved.

C Better Profitability

Higher Throughput & Lower Extrusion Costs

Depending on the parameters of each production unit, the costs incurred in the production of HDPE films could be different. In the table below, we have taken into consideration the costs obtaining on the trials dates (fixed costs, variable costs, polymer costs).
It was shown that due to lower melt pressure and the excellent cooling, productivity could be increased depending on the mineral loading, together with down-gauging to compensate for the extra weight of the $CaCO_{3.}$ By improving the mechanical properties, we came to the firm conclusion that substantial cost savings could be achieved in this trial.

TiO_2 Reduction

It is well known that $CaCO_3$ particles help to disperse fine particle pigments such as TiO_2 or carbon black, increasing their efficacy. When $CaCO_3$ particles are added into the film they will contribute to the light diffraction and so increase the opacity. These 2 effects allow the reduction of the TiO2 content by 20 to 30 %, depending on final opacity required.

The use of $CaCO_3$ in waste bags, could also bring comparative advantages by reducing pigment content in colour master batches.

Down-Gauging / Raw Material Savings

It has been demonstrated that the mechanical properties are improved by the addition of $CaCO_3$. Depending upon the final requirements, the thickness of the film could be adjusted to fulfil the specifications of end users. In this experiment, the dart drop increased by up to 37 % and the Elmendorf tear strength by up to 46 % in the machine direction.

The optimum $CaCO_3$ concentration always depends on the production programme, on the polymers used and on the extrusion line. As results are related directly to the real thickness of the film, which is decreased with $CaCO_3$ loading, we do recommend choosing the final content of $CaCO_3$ in the film in accordance with the optimum mechanical characteristics. For this trial, the optimum $CaCO_3$ loading is 15 % corresponding to 23 % of compound.

Film producers, and specially bag~~s~~ manufacturers, where dart drop and tear strength are of major importance, could then decide to produce thinner films with equal mechanical properties or the same thickness with much improved mechanical properties. $CaCO_3$ could then help to upgrade standard resins, allowing them to compete with higher performance resins.

Consequently down-gauging will lead to raw material savings. Less energy is then required. The ecological aspects are without any doubt in favour of $CaCO_3$. Moreover $CaCO_3$ is a sustainable raw material.

Higher Throughput and Lower Extrusion Costs

Depending on the parameters of the extrusion line, the production costs of HDPE films could be different. Figure 7 shows the calculation of the extrusion costs with and without $CaCO_3$.
We take in consideration , the following costs:

- FIXED COSTS for depreciation of building and machinery and the interest for the capital.
- VARIABLE COSTS for labour, scrap production, spare parts and electrical power. The production with $CaCO_3$ needs slightly more spare parts, but the scrap rate is reduced from 2.5 to 1.25 %.
- OVERHEAD COSTS are evaluated at 50 000 €.

Figure 7 – Table with Cost Structures

	0 % $CaCO_3$	10% $CaCO_3$	17.5 % $CaCO_3$	25 % $CaCO_3$
Production (mT/Year)	**2.660**	**2.926**	**3.126**	**3.325**
Total Fixed Costs	**236.875 €**	**236.875 €**	**236.875 €**	**236.875 €**
Variable Costs	**228.359 €**	**234.147 €**	**237.660 €**	**240.878 €**
Polymer Costs	**2.056.111 €**	**2.246.466 €**	**2.361.295 €**	**2.471.805 €**
Total Costs	**2.521.345 €**	**2.717.488 €**	**2.835.830 €**	**2.949.558 €**
Price/Kg of Good Film	**0,95 €**	**0,93 €**	**0,91 €**	**0,89 €**
Total Saving Money	**0,00%**	**- 3,88%**	**- 5,71%**	**- 7,51%**
	0 €	**- 91.472 €**	**- 165.130 €**	**- 242.442 €**

With the polymer prices listed in figure 8 and a compound price of 750 €/kg, the costs of the polymers are 1.79 €cent/kg less and the extrusion costs are lowered by 4.91 €cent/kg. The total saving is 6.7 €cent/kg or 5.9 % of total costs. Over the year, when 20 % $CaCO_3$ master batch is used, this Kiefel line will produce 395 tons more film and the total saving is 150 000 €. (see annexe 1)