



# MINERALS ADDING VALUE TO POLYETHYLENE FILM EXTRUSION:

## Process Optimisation and Economics

### Abstract

Minerals have, historically, been added as extenders and low-cost fillers for polyolefins, PVC and others polymers. Recent studies have shown that minerals, specifically ground calcium carbonates, alter processing cycle times and improve physical properties of polyolefins<sup>1,2</sup>. To verify these findings we studied the thermal characteristics for blown LLDPE film with mineral additives. Masterbatches were prepared with various calcium carbonate grades, and surface-modified calcined clays. Laboratory-scale films were produced, and processing temperatures monitored. Improved thermal properties of the resultant films gave processing benefits, including output-rate and bubble stability. Laboratory findings were verified at a waste bag production facility. Using a full-scale line, film output speeds were increased by 20 % with the addition of 20 wt.% calcium carbonate. Bag conversion was also enhanced.

The physical properties of the laboratory films were measured. With the addition of surface-modified calcium carbonate improvements were seen in impact strength, tear strength and coefficient of friction. The use of water-based inks was assessed by water contact angle measurement. Addition

of minerals increased contact angle (cosq) proportional to concentration.

IMERYS' carbonate additives were found to give a number of cost benefits: processing rates could be increased; films could be downgauged; expensive antiblocks could be excluded; and surface treatment time before printing could be reduced.

### Introduction

In any multiphase system, each component has an influence on the processing and performance of the product. Blown polyolefin films are affected by changes in processing equipment, polymer type and additives. By including functional mineral additives to the polymer melt, significant changes can be made to these systems. Heating and cooling of blown film are influenced by the fundamental properties of components within the melt. By studying the thermal processing of each component and equating these to processing changes, the effect on processing can be understood. Previous data have shown that minerals require specific particle size distributions, a maximum particle size, and surface-modification to compatibilize the mineral and polymer<sup>3,4,5</sup>.



TABLE 1: Legend and physical data for mineral fillers.

Code	Mineral type	Mean psd	Aspect Ratio (µm) by Sedigraph
C1	Marble	0.5	1
C2	Marble	1.2	1
C3	Marble	2	1
C4	Marble	3	1
K1	Calcined clay	2	8
K2	Silane-coated calcined clay	1.5	5



Ruiz found that hexene, octene and butene LLDPE blown films had increased strength with the addition of up to 20 wt.% surface-modified GCC (ground calcium carbonate). Extrusion outputs increased by 22 %, 39 % and 47 % respectively with 20 wt.% gcc. Cooling rates were improved due to the greater thermal conductivity of the mineral compared with that of the bulk polymer. There may also be changes in extensional viscosity with certain minerals. The difficulties of processing linear resins compared with LDPE are well documented, and it is here that the benefits of mineral addition are most significant.

Organic coated calcium carbonates of fine particle size are already in use commercially to improve the processing of polyethylenes, and to aid bubble stability. The study described here encompasses particle size, loading and shape effects of minerals in LLDPE blown film. During processing, film temperatures were monitored and equated to the thermal properties of the matrices.

Physical properties of thin-gauge (40  $\mu\text{m}$ ) films were measured to assess end-use viability. Surface properties were characterised by dyne solutions. These properties were correlated with flexographic testing of print properties and surface tension measurements of corona-treated films. Surface roughness was also measured.

### Materials and Preparation

Coated calcium carbonates are often favoured in polyethylene films because processing can be improved whilst maintaining a good balance of mechanical properties. Indeed some properties, such as film toughness, are significantly enhanced. For this study, other minerals are included to provide additional, comparative data. They are not, as far as we are aware, currently in commercial use at these concentrations.

All minerals were IMERYS materials, and were either commercial or experimental grades. Details are given in [Table 1](#). The polymer was Exxon Escorene LL3001.32, a hexene copolymer LLDPE film grade, MFI 1.0 g 10 min<sup>-1</sup>.

### Laboratory Trials

Masterbatches of coated calcium carbonate

(60 wt.%) and other minerals (40 wt.%) in LLDPE were prepared on an APV Baker Perkins 2030 twin screw compounder. Die temperature was 200°C, and extrusions were run at a constant torque of 50%. Each mineral was let down in virgin resin on a Killion KN150 38 mm laboratory blown film line to produce 20 wt.% mineral-filled films. Film gauge was 0.025 mm and 250 mm layflat. Films K1 and K2 contained the unmodified and silane-treated calcined kaolins respectively and C1 to C4 contained surface-treated gccs. Additionally, films with 0 (U), 10 (C2/10), 30 (C2/30), 40 (C2/40) and 50 wt.% (C2/50) gcc were prepared.

### Plant Trials

C2 masterbatch (C2) was prepared at 60 wt.% on a Werner and Pfleiderer ZSK-40 twin screw compounder. Die temperature was 200°C, and extrusions were run at a constant torque of 85-90%, with an output of 100 kg/hr. The masterbatch was let down in virgin resin on a Battenfeld line (250 mm die), with a BUR of 2.4:1. The line had in-line conversion to produce dustbin liners (trash bag). Film gauge was 25  $\mu\text{m}$ . Bags containing 0, 5, 10 and 20 wt.% C2 were prepared.

### Experimental

#### Film Processing 1, Laboratory Trials

Extrusion experiments were conducted on a Betol BK 32 laboratory-scale film line (80 mm diameter, 0.80 mm die gap, 450 mm max. layflat, 32 mm single screw extruder), to produce a 40  $\mu\text{m}$  gauge film. The extruder and die temperatures were consistent throughout the experiment, as were the extrusion rate and line speed. Die temperature was set at 245 °C, extrusion rate was 5 kg hr<sup>-1</sup> and line speed was 10 m min<sup>-1</sup>.

Film temperature was measured with a Minolta Land Cyclops 343 portable infrared (IR) thermometer. This measured the emitted IR radiation at 3.43  $\mu\text{m}$  (3430 nm) wavelength, giving a true value for the surface temperature of the polymer. Emissivity differences were compensated for as necessary.

External air cooling was maintained by setting the air ring configuration and flow rate. The temperature of the film was recorded at various points along the bubble.

As each filler was added, so the temperature changes at the points along the bubble were noted. A mean reading was displayed, collected over a ten second period. Three such readings were taken. The mean is quoted in the data.

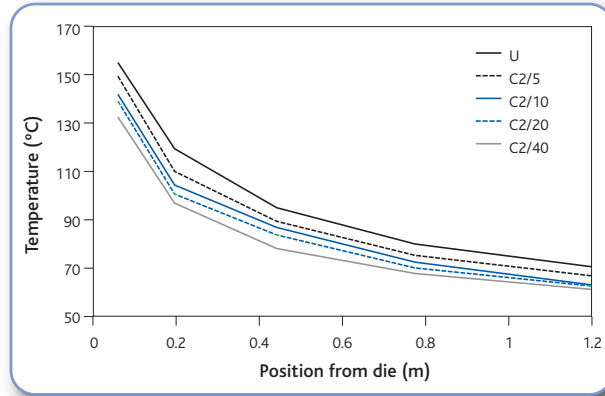
**Film Processing 2, Plant Trials**

The integrated film/conversion line was optimised for maximum throughput under standard processing conditions, with the hexene LLDPE. Extrusion conditions were noted, and outputs from the film line, and bag converter measured. The C2 masterbatch was then added, to give final concentrations of 5, 10 and 20 wt.%. Conditions and throughputs were again measured. Each bag was weighed and compensations made for this in the conversion data.

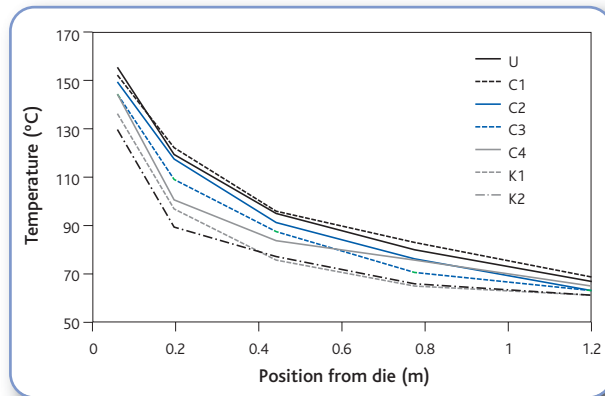
**Physical Testing of Films**

Drop dart impact strength for each film was measured with a Kayness D2085AB impact tester according to ASTM method D1709-91<sup>6</sup>. Tear strength, by ASTM method D922-24a, was measured with a Thwing-Albert Elmendorf tear tester. Tensile strength was measured in the machine and transverse directions with a Flexsys T2000 tensometer using ASTM method D882. Blocking was assessed with a Kayness 9046 blocking force

**FIGURE 1:** The effect of mineral addition on the thermal profile of the bubble.



**FIGURE 2:** The effect of mineralogy on the thermal profile of the bubble



**TABLE 2:** Processing data from plant trials.

C2 concentration (wt.%)	Output per screw RPM (%)	Die pressure (Bar)
0	100	307
5	99.5	301
10	101	292
20	105	294

**TABLE 3:** Physical properties of blown films.

	Elmendorf Tear Strength (ASTM D1922-24A)		IFIW Impact Strength (ASTM D3763-93)
	MD tear strength (g)	TD tear strength (g)	Peak Energy (J/mm)
U	368 ± 31	512 ± 53	0.49 ± 0.4
C2	429 ± 22	720 ± 34	0.83 ± 0.11
K1	465 ± 64	839 ± 46	0.31 ± 0.02
K2	477 ± 39	741 ± 35	0.31 ± 0.0

tester, according to ASTM D3354B. A Kayness sliding sled CoF tester was used to measure static and kinetic coefficients of friction, as specified in ASTM D1894-93.

**Water wettability and surface tension measurements**

Industrial dyne solutions were used to estimate the critical surface tension. The unfilled film and C2/10 to C2/50 were corona-treated. The treatment levels were adjusted to obtain surface tensions of  $42 \pm 2$  dynes  $\text{cm}^{-1}$  for the unfilled film to conform with recognised levels for flexographic printing. Surface tensions of these were measured with an FTA200 dynamic instrument using the water contact angle method.

**Flexographic printing**

Print quality of each film was assessed by flexographic printing with water-based inks on an IGT F1 tester, with an antilox force of 50 N, printing force of 100 N and a print speed of  $0.5 \text{ ms}^{-1}$ . Print density was measured with a Gretag D186 densitometer.

**Surface Topographies**

Surface profiles of an area (1 mm x 1 mm) of each film were mapped with a Talystep profilometer. From these, surface roughness was calculated by Walsh analysis of the data.

**Results and Discussion**

**Film Processing 1, Laboratory Trials**

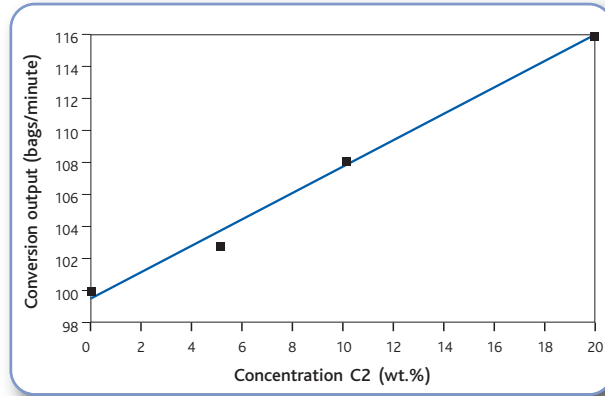
Figure 1 illustrates the effect of filler loading on the thermal profile of the bubble, with C2 as the single mineral source. As addition levels increased, so the temperature at a specific point along the bubble decreased. This led to a stepped lowering of the freeze-line. Changes in temperature profile with different particle size and mineralogy are shown in Figure 2.

**Physical Properties**

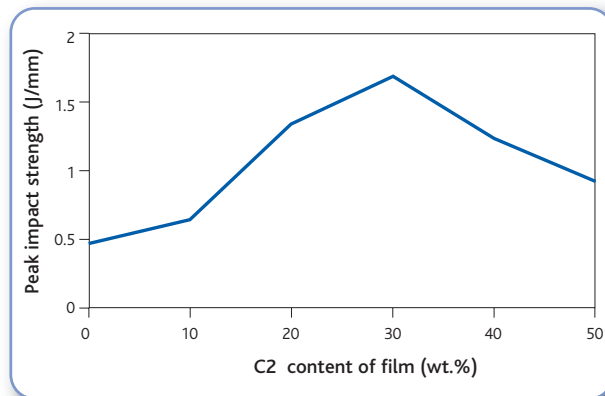
Physical property data of the films (Table 3) show increases tear strength and drop dart impact in C2, compared with U. K1 and K2 both have higher tear strength, but a reduction in impact strength.

The impact strength of the films increased with the addition of C2, up to 30 wt.% (Figure 4), illustrating the extent of mineral reinforcement.

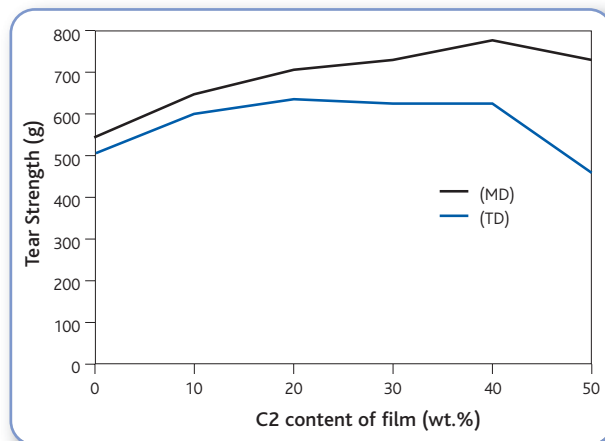
**FIGURE 3. Concentration of C2 versus bag conversion rate.**



**FIGURE 4. Impact strength of films containing C2.**



**FIGURE 5. Tear strength of films containing C2.**



**Film Processing 2, Plant Trials**

The addition of high levels of C2 resulted in higher Elmendorf tear resistance. In the machine direction, additions of up to 40 wt.% increased tear strength. A maximum at 20 wt.% C2 was seen in the transverse direction.

As the mineral content of the film increased, so blocking decreased (Figure 6).

**Surface properties**

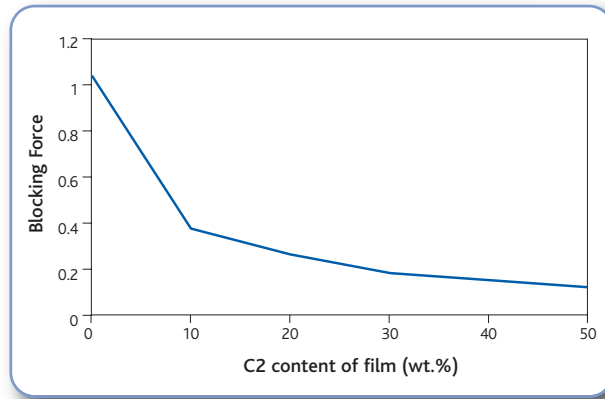
C2/10 to C2/50 showed a trend of increasing surface tension with mineral concentration (Figure 7). These differences were also observed in print quality. Printing results for C2/10 to C2/50 revealed a trend of increased print density with mineral addition (Figure 8). K1 and K2 gave densities similar to those for C2/40 and C2/30 respectively.

The roughness of surface profiles was quantified by Walsh analysis, given in Table 4. The mineral-free film was very smooth with little surface variation at any span length. K1 and K2 both had highly irregular surfaces, indicated by the high  $\mu_2$  values. C2/10 to C2/50 showed an increase in roughness with concentration.

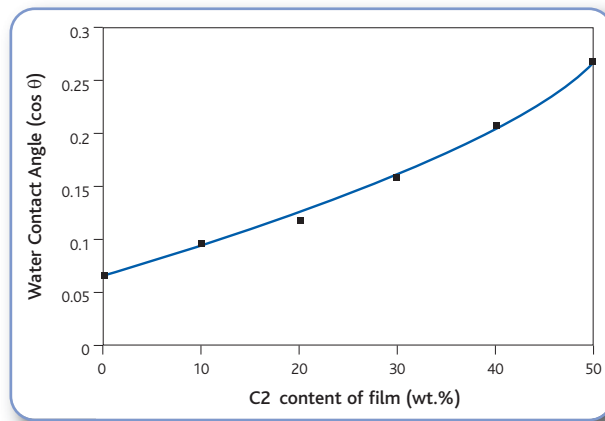
**Discussion**

Several factors are known to affect the thermal properties of blown films<sup>7</sup>. The most significant are the orientation and crystallinity of the polymer itself and the presence of additives. The former have not

**FIGURE 6:** Blocking properties of films containing C2



**FIGURE 7:** Surface tension of films containing C2, measured by water contact angle (after corona treatment).



**TABLE 4:** Walsh analyses of surface roughness.

Span Length (µm)	Walsh $\mu_2$ values ( $\times 10^{-2}$ )					
	8	16	32	64	128	256
U	0.2	0.5	0.8	1.2	1.3	1.0
C1	0.2	0.3	0.5	1.3	3.4	6.8
C2	0.2	1.0	4.2	16.5	37.2	68.5
C3	0.6	4.0	15.2	32.9	42.5	48.5
C4	0.7	3.2	12.9	37.3	65.2	101.5
C5	1.7	10.0	31.8	73.3	128.1	151.7
K1	1.2	6.4	24.0	63.6	112.3	102.8
K2	0.7	3.3	18.2	68.2	170.4	654.7

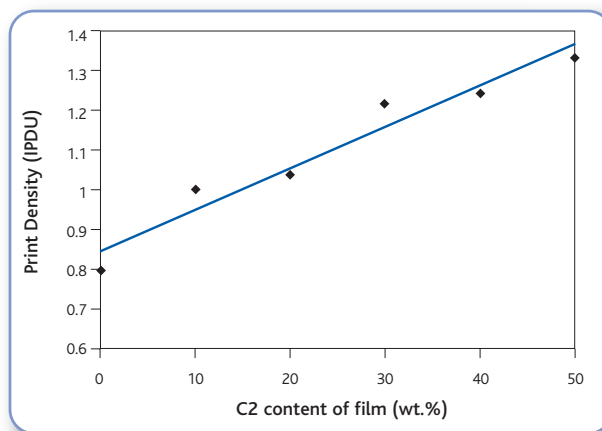
been considered in this paper, as the processing conditions of all the blown films were comparable. The latter was considered to be most influential in the current study. Due to the greater thermal conductivity of the added minerals, we can predict that the higher the loading of this phase, the greater will be the bulk heating or cooling effects. This was confirmed by the data in Figure 1, where the addition of increasing levels of C2 served to successively lower the temperature of the melt at the die, and thus throughout the profile. The freeze-line dropped correspondingly.

The effect of particle size and shape on bubble cooling is shown in Figure 2. The addition of calcium carbonate led to lowering of the film temperature at any specific point. As the mean particle size increased, so the cooling effects became more apparent. The higher aspect ratio mineral, K1, behaved similarly to the mineral-free polymer. We concluded that particle shape influenced the rate of cooling.

A study of the electron micrographs of film cross-sections (C2 and K1) can be used to explain this effect. Orientation of K1 was seen in the machine direction of polymer. Parallel alignment lowers particle-particle contact and increases the thermal conduction path through the polymer phase. As the polymer is known to be less thermally conductive than the mineral any such orientation will reduce its bulk cooling, when compared with an equivalent low aspect ratio mineral such as ground calcium carbonate. Voids or air pockets in the film can also have a marked influence on cooling. No voidage was seen in the C1 to C4 films. In K1, occasional debonding between polymer and mineral appeared as small voids. Entrained air leads to a lowering of the bulk conductivity, and hence reduces the rate of cooling. For 10 wt.% additions of minerals, the voidage was considered of secondary importance. If higher levels are included in the film, typically over 20 wt.%, they can become the dominant feature.

Laboratory observations were supported by plant trial data. Addition of C2 masterbatch led to increased extruder throughput at equivalent screw speeds. Additionally the bubble cooled quicker, and the line could be

**FIGURE 8: Water-based ink printing results for all films.**



run faster with a consequential rise in bag production from 100 to 116 bags per minute (with 20 wt.% addition).

Physical properties of the films (given in Table 3 and Figures 4 and 5) correlate with interfacial characteristics between the mineral and polymer. Surface-modified gcc, having a similar surface energy to polyethylene, will be compatible in the matrix. Impact resistance is therefore high. Where the two systems are less compatible, as in K1 and K2, residual stresses may concentrate around the particles. Impact strength may thus be lower. Tear strength is believed to be dependent on reducing tear propagation. Mineral addition improved tear resistance in all systems. The fine particles prevented tear propagation by acting as a physical barrier to the rupture of the oriented polymer chains<sup>9</sup>. Marginally higher tear strength for K1 and K2 is explained in terms of interfacial debonding of mineral particles dissipating tear energy and physically preventing tear propagation.

Blocking force of the films decreased with increasing concentration from U to C2/50. Levels of 5 wt.% are sufficient to act as a suitable anti-blocking additive, although this could be considered as an additional benefit, rather than a significant functional change.

Print properties of the films are related to both surface energetics and surface roughness. As contact angle measurements will be influenced by surface topography, absolute conclusions cannot be drawn.



Clearly, increased addition of a compatible, well-dispersed mineral, such as a surface-modified gcc (as in C2/10 to C2/50) improves water-based ink adhesion. This can be enhanced further by corona treatment. The disproportionately high surface topographies for K1 and K2 are considered to be due to poor interfacial adhesion of the mineral in the polymer matrix. Thus addition of less compatible minerals will also increase printability, but may do so by increasing surface roughness.

The use of high loadings of calcium carbonate is beneficial both in terms of physical property improvements and print adhesion. Calcined kaolins are seldom used at concentrations of 20 wt.% in polyethylene film, and a comparison of physical properties with carbonate additives is inadvisable. Calcined kaolin is used widely in agricultural polyethylene films (at concentrations up to 10 wt.%) as an infra-red blocking agent, or at ppm levels as an antiblock<sup>10</sup>. By selection of mineral additives and concentrations, polyethylene films can be modified to the demands of the end user.

### Summary

We have demonstrated that some physical and mechanical properties of linear low-density polyethylene (LLDPE) extruded and blown films are improved by the addition of surface-modified calcium carbonate. Thus by adding C2 processing output may be increased by up to 50 %. Drop dart impact strength and tear resistance is increased significantly, giving the ability to down-gauge. Anti-blocking additives are not required, at recommended addition levels.

These findings were supported by plant trials using a standard film extruder with in-line bag conversion. Increased productivity and energy savings were observed.

If film clarity is not required, using a functional, tailor-made additive, such as IMERYS' C2 calcium carbonate will result in a product that is easier and faster to process, and may be printed with little, or no additional treatment.

### Acknowledgments

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