The Use of Calcium Carbonate in Polyolefins Offers Significant Improvement in Productivity

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Abstract

The thermal conductivity, specific heat, and thermal expansion characteristics of calcium carbonate offer the ability to improve fabrication productivity and performance of physical properties. This paper will present case studies of plastics processing applications including blown films, extrusion coating, sheet extrusion / thermoforming, and extrusion blow molding. It is the attempt of these studies to show that the proper selection of calcium carbonate in conjunction with an optimized masterbatch carrier resin is required to achieve the desired productivity improvement. It is the unique selection of calcium carbonate and carrier resin that maintains or improves the physical properties for these respective applications.

Introduction

Physiochemical Aspects of Polyolefin – Calcium Carbonate Composite Blends

Many polyolefin applications have successfully demonstrated the use of calcium carbonate for productivity improvements and physical property enhancement.[1,2,3] One of the key properties of calcium carbonate that offers increased output when added to polyolefins is thermal conductivity. The thermal conductivity of calcium carbonate is 2.7 W/(m*K) as compared to less than 0.5 for neat polyolefin resins. This increased thermal conductivity of calcium carbonate loaded polyolefins provides the ability to melt resin - mineral composite blends faster during extrusion and provides for quicker cooling after a product has been extruded or formed. As summarized by Ruiz [2] and others, 1% addition of calcium carbonate by weight produces a 1% increase in volumetric output. This will vary either way depending on the specific fabrication process, equipment and other variables.

Another material property of calcium carbonate considerably different from that of polyolefins is specific heat. The specific heat of calcium carbonate is 0.9 KJ/(Kg*K) whereas polyolefins range from 1.8 to 2.4 KJ/(Kg*K) . The lower specific heat of calcium carbonate means less energy is needed to increase the temperature of resin - mineral composite blends. In radiant heat transfer processes, a resin – mineral composite blend will cool slower than that of the same neat resin. This is particularly important in extrusion coating processes which will be discussed in detail later in this paper.

It is also very important to understand the difference in specific gravity or density of calcium carbonate versus that of polyolefins. Calcium carbonate specific gravity is 2.7 g/cm^3 compared to a general range of 0.90 to 0.96 g/cm^3 for most polyolefins. This means 1 gram of calcium carbonate occupies approximately 1/3 the volume of 1 gram of polyolefin polymer. Outputs must be compared on a volume rather than weight basis. It also means that if product downgauging doesn't take place the increased weight must be recognized; therefore, items sold by weight should be relabeled accordingly. When polyolefins melt their density goes from 0.900-0.960 to 0.700 g/ cm^3 expanding significantly compared to calcium carbonate which increases in volume very slightly under polymer melt processing conditions.

Most polyolefin fabricators will use calcium carbonate via masterbatches in their processes. These are generally 70 to 80% by weight calcium carbonate in a polyolefin carrier resin. Loadings of up to 35% calcium carbonate in the finished product(s) have a significant effect on both processing and physical properties. For this reason, it is recommended to use the same carrier resin as the matrix polymer for the concentrate as is being used to fabricate the product. In cases of resins with a melt index (PE) or melt flow rate (PP) of less than 1.0 dg/min, it may not be practical to produce a masterbatch with the same resin, and a MI or MFR resin close to 1.0 should be selected.

Discussion

Blown Film Applications

Productivity. The most significant productivity improvement in polyolefin blown film applications shows up as increased volumetric output. Other benefits from the use of calcium carbonate are the ability to downgauge as a result of higher film physical properties, and longer run times between shutdowns for cleaning due to the mild scrubbing action of the calcium carbonate particles. For most blown film applications, Omyacarb® FT is recommended. This material, calcium carbonate (1), is calcite derived from marble. It is a fully beneficiated (meaning it has been processed to remove unwanted abrasive impurities), fine ground stearic acid treated calcium carbonate. It has a median diameter particle size of 1.4µ.

The ability to achieve increased volumetric outputs with the addition of calcium carbonate is a result of higher thermal conductivity and volumetric expansion with respect to temperature. Generally, as the level of calcium carbonate is increased in polyolefin blown film extrusion, a decrease in both drive amperage and head pressure is noted by the processor. Lower drive amps and head pressures allow the processor to increase the screw speed to previous amperage / pressure levels resulting in increased extruder throughput [4]. Improvements in resin – mineral composite thermal conductivity provides for faster melting and higher melt densities compared to that of the neat resin. This allows more product to move down the screw, hence higher volumetric output. As the film exits the die the higher resin – mineral composite thermal conductivity cools the film faster, which combined with the increase in volumetric, output allows processors to operate faster line speeds. As cited previously, typical output increases of 1% for each 1% of calcium carbonate can be expected; however, rate increases of greater than 100% with 25% calcium carbonate in LLDPE film and 21% with 15% calcium carbonate in HMW-HDPE film have been observed.

Physical property improvements have been noted in conjunction with the productivity increases mentioned. Key properties that are improved by the addition of calcium carbonate are impact strength, tear strength, stiffness, moisture vapor transmission rate (MVTR), and oxygen transmission rate (OTR).

Impact strength. This property results from a change in morphology of the polyolefin around the calcium carbonate particles [5]. Improved impact performance of resin – mineral composite systems provides higher dart impact at the same gauge, or equivalent performance at a reduced gauge. The impact strength performance was measured on films produced using Equistar Petrothene® GA 601-030 LLDPE as the matrix polymer. This material is a 1.0 dg/min melt index, 0.918 g/cm^3 ethylene - hexene copolymer referred to as resin (A). Calcium carbonate was introduced to the blown film extrusion process using a mineral – resin masterbatch. This masterbatch, (M1) was produced using resin (A) as the carrier resin with calcium carbonate (1). Please refer to Table 1 for the masterbatch compositions and weight fraction blends. Dart drop impact strength is shown in Figure 1 along with the respective improvements in productivity as tabulated.

Table 1. Masterbatch Compositions

Masterbatch	% Calcium Carbonate – Type	% Matrix Polymer – Type
M1	75% - (1)	25% - (A)
M2	60% - (1)	40% - (D)
M3	75% - (1)	25% - (E)

Impact performance of HMW-HDPE films were measured using Formosa E905 HMW-HDPE as the matrix polymer. This material, resin (B), is a 0.05 dg/min. melt index, 0.950 g/cm^3 ethylene – hexene copolymer. Calcium carbonate was again introduced via mineral – resin masterbatch (M1), and dart drop impact results are shown in Figure 2. HMW-HDPE films show a similar response with respect to impact performance as calcium carbonate was added. It is worthy to note that improvements increased significantly at higher calcium carbonate loading levels.

Figure 1. Dart Impact Strength ASTM D-1709, grams force 1MI Hexene LLDPE

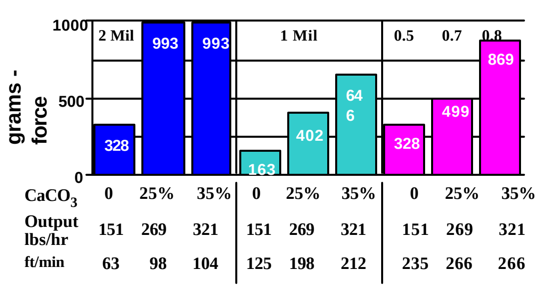
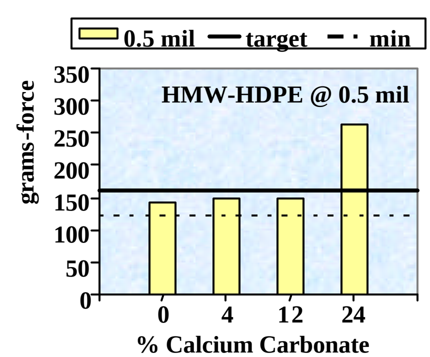


Figure 2. Dart Impact Strength ASTM D-1709, grams force HMW-HDPE Films Produced with Resin B and (M1) calcium carbonate masterbatch



Barrier properties. The addition of calcium carbonate to polyolefin films also improves barrier performance. Improved barrier allows processors the ability to downgauge and maintain barrier properties, or improve barrier characteristics at the same gauge. Figures 3, and 4, show water vapor transmission rate and oxygen transmission rate barrier properties respectively for resin (A) masterbatch (M1) composites. Figure 5, shows a similar improvement in results using resin (B) masterbatch (M1) composite when tested for water vapor transmission rate on 1 mil films. Oxygen transmission rate was not tested on the resin (B) films; however, carbon dioxide transmission testing was performed and a decrease in transmission rate was noted. These results in 1 mil films are shown in Figure 6.

Figure 3. WVTR Barrier Properties LLDPE Films

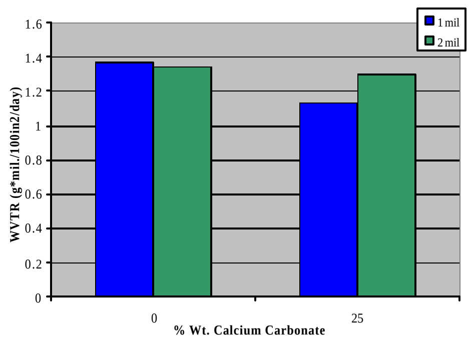


Figure 4. Oxygen Transmission Rate Barrier Properties LLDPE Films

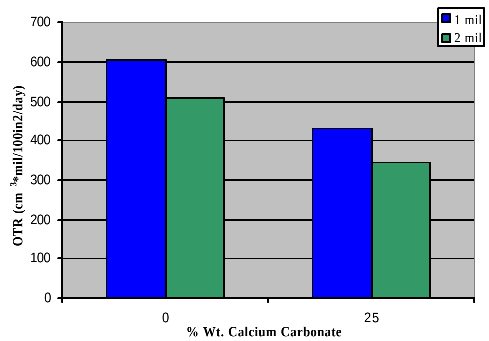


Figure 5. WVTR Properties of HMW-HDPE Films

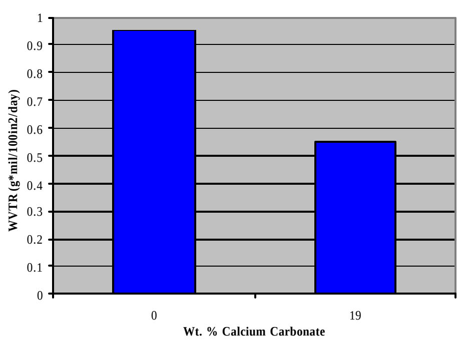
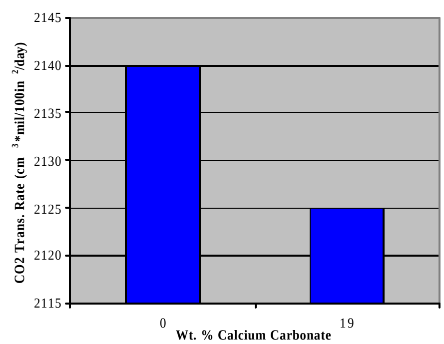


Figure 6. Carbon Dioxide Transmission Rate in HMW-HDPE Films



Extrusion Coating

Productivity. Polyolefin extrusion coating applications benefit from the addition of calcium carbonate showing significant gains in productivity.[1] As in the case for extruded blown film, increases in volumetric output are also seen in extrusion coating. Additionally, improvements in adhesion, heat seal and printability have been seen in extrusion coating. Typical high extrusion temperatures and low coating weights found in most extrusion coating applications necessitate the use of Omyacarb® 2SST. This material, calcium carbonate (2), has a 2.0µ median particle size, and is well coated with a stearic acid treatment.

Improved adhesion. Improved adhesion results from the specific heat difference between calcium carbonate and polyolefins. Heat losses between the die and the nip are predominately transferred via radiant heat mechanisms. Polymer extrudate temperature loss from the die to the nip has been found to be minimal when calcium carbonate is present in a resin – mineral composite blend. An extrusion coating trial with LDPE measured a melt temperature at the die of 305 ºC and 210 ºC at the nip using the neat LDPE. Using 33% by weight calcium carbonate (2), the temperature at the nip dropped to only 270 ºC, a 22% increase in melt temperature. In this case, additional oxidation and lower melt viscosity result in better adhesion. Improved adhesion can potentially afford faster line speeds, lower melt temperatures, and reduction or possibly the elimination of flame treatment.

Printability. The improvement in printability with the addition of calcium carbonate results from the rough microsurface that is produced. In Figures 7 and 8 show the surfaces at low and high magnification without and with calcium carbonate (2). The rougher surface improves the ink wet-out resulting in better defined printing.

Figure 7. No Calcium Carbonate

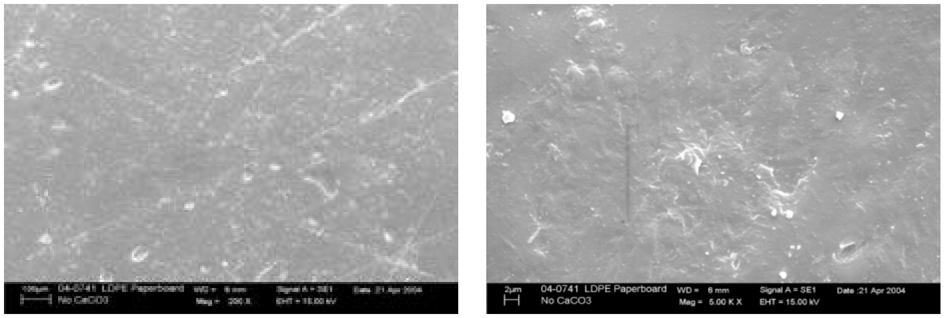
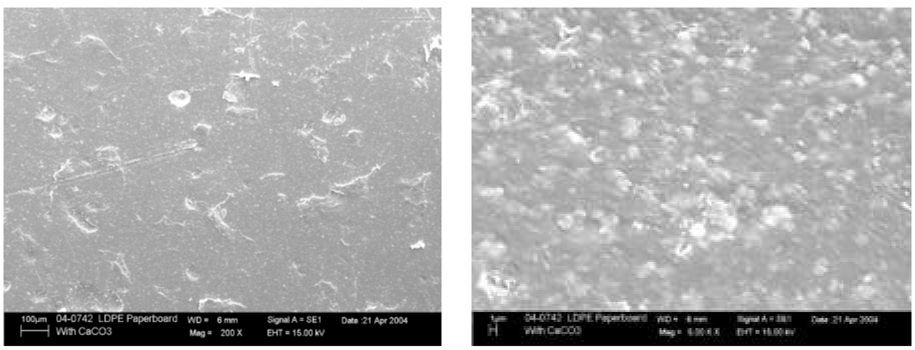


Figure 8. Calcium Carbonate



Heat Sealability. Improvements are the results of the higher thermal conductivity in the resin – mineral composite blends. Data specific to this performance attribute is unavailable at this time; however, suffice it to say, adjustment of temperature and dwell time of sealing equipment may be required for optimum sealing performance due to the rapid heat transfer facilitated by the calcium carbonate.

In most extrusion coating applications, converters process at constant coating weight. As calcium carbonate is added, thinner coatings result due to inherently higher specific gravity of the mineral vs. polyolefin polymers.

Polyolefin Sheet/Thermoforming

Similar opportunities to those already discussed exist for productivity and physical property performance in polyolefin – calcium carbonate mineral composites for sheet/thermoforming applications. Although commercial use in this application is somewhat limited, successful trials in both HDPE and PP have been conducted and demonstrate excellent performance.

Productivity. A case study on HDPE sheet was run on a commercial 114.3 mm (4.5"), 24:1 L/D Davis-Standard sheet extrusion line. The line was running 7.62 mm (0.300") thick sheet at 1.14 m/min (3.75 fpm). Upon the addition of 25% by weight calcium carbonate (1) via masterbatch (M1), the output was increased to 1.60 m/min (5.25 fpm), while reducing the gauge to 6.35 mm (0.250"). The sheets exhibited equivalent performance. Off-line thermoforming of the resin–mineral composite sheet showed a cycle time reduction from 6 minutes to 4.5 minutes. The heat deflection temperature and flexural modulus also showed modest increases with calcium carbonate added.

Another case study was run with both homopolymer and copolymer PP in 1.27 mm (0.050") and 0.69 mm (0.027") thicknesses. Increased output was observed as shown in Table 2. Thermoforming trials showed better nominal wall dimensional stability with respect to draw depth as calcium carbonate (1) was added. We have hypothesized that sheet produced with a resin - calcium carbonate mineral composite stays hotter as a result of its inherently lower specific heat.

In thermoforming, where the sheet is heated in a radiant oven and subsequently transferred to a forming stage in the process, radiant heat losses dominate. Using calcium carbonate, the zero shear viscosity of the composite system appears be reduced partially as a result of higher sheet temperatures that exist just prior to forming.

Table 2. Linear Output Polypropylene Sheet Extrusion Trial			
Calcium Carbonate (% Wt.)	0%	15%	25%
Homopolymer Output (m/Min.)	1.93	2.00	2.06
Copolymer Output (m/Min.)	2.02	2.02	2.16

Blowmolding

One gallon large handle narrow neck round containers were extrusion blowmolded on a Uniloy 2016 continuous extrusion reciprocating screw molder equipped with standard round tooling in a single head configuration. This machine operated with 63.5 mm (2.5") diameter screw, a 20:1 L/D, designed with a Maddox type mixing head to improve melt homogeneity. Resin (C), ChevronPhillps Marlex® HHM-5202 BN, a 0.35dg/min melt index, 0.951g/cm^3 ethylene – hexene copolymer was the base resin used throughout this course of study.

Calcium carbonate was introduced to the extrusion process via masterbatch.. Two masterbatches were studied both using calcium carbonate (1). Masterbatch (M2) was based upon Marlex® 9004 HDPE, a 5.4dg/min melt index, 0.954 ethylene-hexene copolymer, matrix resin (D). Masterbatch (M3) was based on CheveronPhillips Marflex® 7109 LLDPE, and is titled matrix resin (E). This material is a 0.9 dg/min melt index, 0.918 g/cm3 ethylene – hexene copolymer. Table 1. shown previously provides the masterbatch compositions. This experiment was designed to evaluate molded container performance in addition to measurements in productivity. Productivity improvements were measured on the (M2) composition only.

Productivity. The purpose of evaluating productivity on a volume equivalent basis is important to understand the true benefit of incorporating calcium carbonate. The addition of this mineral directly results in a natural downgauging effect when molding bottles at a constant weight. For this reason, measurements were made using constant wall thickness. Figures 9 and 10 show part temperatures upon exiting the mold. It was demonstrated that part exit temperatures can be reduced by 25%, or cycle time by as much as 30% under ideal conditions when molding an equivalent material volume.

Figure 9. Part Exit Temperature at Constant Wall Thickness & Constant Process Cycle Time

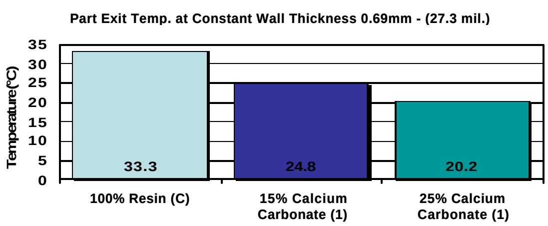
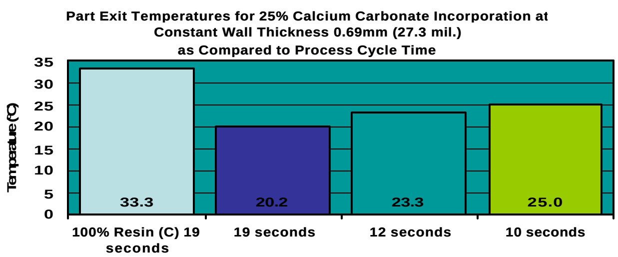
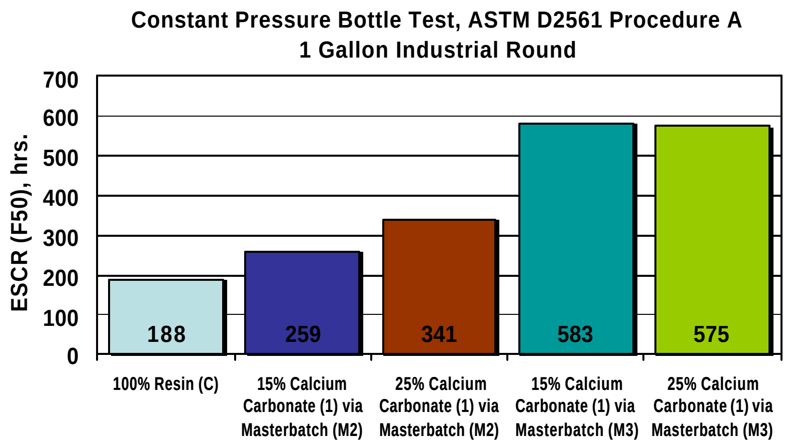


Figure 10. Part Exit Temperature at Constant Wall Thickness at Reduced Cycle Times



Molded container performance. Bottle ESCR was measured using ASTM D2561 Procedure A, constant pressure testing. When comparing against bottles made using neat resin, ESCR improved 67% with (M3) masterbatch to a total weight loading of 15% calcium carbonate. A 27% gain was realized using masterbatch (M2) under similar loading levels of calcium carbonate and molding conditions. Figure 11 shows the molded bottle ESCR data. Given this change in performance, we can postulate that a dramatic transformation in crystalline morphology has occurred, as a result from favorable thermodynamics in the resin – mineral composite material blend. This finding stresses the importance of selecting the optimal matrix polymer for the resin – mineral masterbatch. Container topload performance dropped slightly and drop impact results showed mixed results.

Figure 11. Constant Pressure Bottle ESCR



Conclusions

Calcium carbonate has been shown to improve manufacturing productivity and functional properties of extruded blown films, extrusion coatings, sheet extruded/ thermoformed parts and blowmolded containers. The balance of physical properties and functional productivity can be tailored by the selection of calcium carbonate, total mineral loading level, and the matrix polymer used to produce the mineral – resin masterbatch.

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References

1. Guy, A.R., "Calcium Carbonates For Polyolefin Extrusion Coating Applications", *TAPPI Polymers, Laminations, and Coatings Conference Proceedings 2004*, Indianapolis, IN.
2. Ruiz, F.A., "Mineral Enhancement of Extrusion Coated Polyethylene", *TAPPI Polymers, Laminations & Coatings Conference Proceedings 1994*, TAPPI Press, p.89 – 95.
3. Ruiz, F.A., "Optimizing the Benefits of Film Mineral Reinforcement: Interactions of Film and Concentrate Base Resins", *TAPPI Polymers, Laminations & Coatings Conference Proceedings 1996*, TAPPI Press, p. 535 – 544.
4. Batiste, J.L.H, Shaw, L.G., and Ballard, R.R, "Benefits and Performance Mechanisms of Fine Treated Calcium Carbonate in Blown Polyethylene Films", *TAPPI Polymers, Laminations, and Coatings Conference Proceedings 2000*.
5. Bartzcak, Z, Argon, A.S., Cohen, R.E., and Weinberg, M., "Toughness Mechanism in Semi-Crystalline Polymer Blends: II. HDPE Toughened with Calcium Carbonate Filler Particles", *Polymer*, **40**, 2347 (1999).
6. Ruiz, F.A., "High Performance Mineral Reinforcement Concentrate for LLDPE and HMW-HDPE Blown Film Extrusion", *TAPPI Polymers, Laminations & Coatings Conference Proceedings 2001*.
7. Weindenfeller, B., Höfer, M., and Schilling, M., "Thermal Conductivity, Thermal Diffusivity, and Specific Heat Capacity of Particle Filled Polypropylene", *Composite: Part* A, **35**, 423 – 429 (2004).

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The Physiochemical Aspects of Calcium Carbonate Use in Polyolefins Provides Significant Productivity Improvements

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Calcium Carbonate – A Functional Mineral Additive

- Show calcium carbonate produces productivity gains in polyolefin extrusion processes
- Highlight delivery technology concept via masterbatch additive
- Illustrate performance benefits of calcium carbonate to respective processes

Application Processes Studied

Blown Film
Extrusion Coating
Polyolefin Sheet Extrusion / Thermoforming
Blowmolding

$CaCO_3$ in Polyolefins – Advantages Previously Established

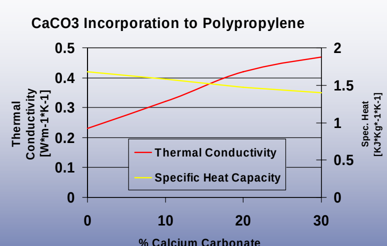
Productivity
- Increased output
- Higher line speeds
- Lower melt pressure and motor load
- Improvements in bubble stability

Physical Properties
- Higher toughness
- Flexural stiffness
- Adhesion
- Printability
- Barrier Properties

Introduction - Material Constants

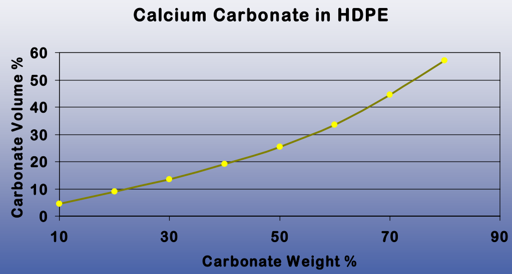
Material	Thermal Conductivity $[W*m^{-1}*K^{-1}]$	Spec. Heat Capacity $[KJ*Kg*^{-1}*K*^{-1}]$
PP	0.23	1.68
HDPE	0.51	2.70
LLDPE	0.40	2.50
$CaCO_3$	2.70	0.86
Talc	2.10	0.86

Introduction - Material Constants



$CaCO_3$ in PP provides faster heat transfer and the needed energy to heat up or cool down the mixture lower.

Introduction – Weight to Volume Relationship



Mineral Properties

$CaCO_3$ (1) - Omyacarb® FT

- Marble derived calcite
- Wet ground and fully beneficiated
- Median particle size – 1.4 micron
- Top Cut (d98) – 10 micron
- Stearic Acid Surface Treated

Experimental– Blown Film Impact Performance

LLDPE Film

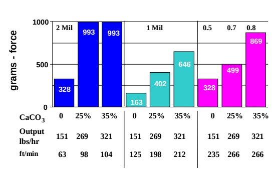
Resin (A)

- Equistar Petrothene® GA 601-030
- Melt Index – 1.0 dg/min
- Density – 0.918 g/cm^3

Mineral Additive (M1)

- Resin (A) – 25% wt.
- $CaCO_3$ (1) – 75% wt.

Figure 1. Dart Impact Strength ASTM D-1709, grams force 1MI Hexene LLDPE

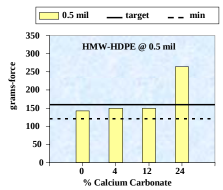


Experimental – Blown Film Impact Performance

HMW- HDPE Film Resin (B)
- Formosa E905
- Melt Index – 0.05 dg/min
- Density – 0.950 g/cm^3

Mineral Additive (M1)

Figure 2. Dart Impact ASTM D-1709, grams force HMW-HDPE Resin B and (M1) $CaCO_3$ masterbatch



Experimental – Blown Film Barrier Performance

LLDPE Film – Resin (A) w/ Mineral Additive (M1)

Figure 3. WVTR Barrier Properties

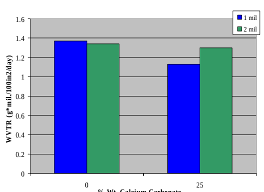
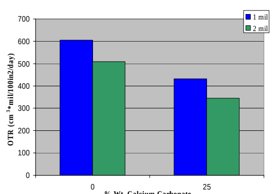


Figure 4. O_2 Transmission Rate



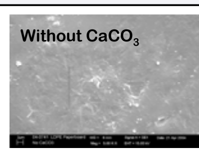
Experimental Discussion – Extrusion Coating

LDPE Coating

Unchanged Line Speed
- Improved Adhesion
- Better Heat Sealability
- Downguaged at same coating weight
- Improved Printability

Calcium Carbonate

Omyacarb® 2SST in a 75/25 wt% masterbatch



Experimental – Sheet Extrusion / Thermoforming

Polypropylene Sheet Extrusion

- Davis – Standard 4.5” Extrusion Line
- $CaCO_3$ (1) via PP Masterbatch

Table 1. Linear Output in Sheet Extrusion Trial

Calcium Carbonate (%Wt.)	0%	15	25
Homopolymer Output (Ft./Min.)	6.34	6.55	6.75
Copolymer Output (Ft./Min.)	6.64	6.64	7.09

Sheet Forming

- 25% Improvement in Cycle time
- Overall improvement in nominal wall

Experimental – Blowmolding Productivity

HDPE HIC Container

Resin (C)

- CPChem Marlex® HHM-5202-BN
- Melt Index – 0.35 dg/min
- Density - 0.951 g/cm³

Mineral Additive (M2)

- Resin CPChem Marflex® 7109 – 25% wt
- $CaCO_3$ (1) – 75%

Mineral Additive (M3)

- Resin CPChem Marlex ® 9004 – 25% wt.
- $CaCO_3$ (1) – 75%

Figure 6. Part Exit Temperature at Constant Wall Thickness & Constant Process Cycle Time

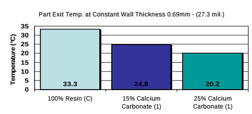
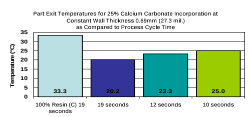


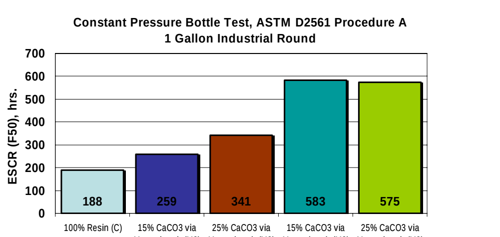
Figure 7. Part Exit Temperature at Constant Wall Thickness at Reduced Cycle Times



Experimental – Blowmolding ESCR Performance

HDPE HIC Container

Figure 8. Constant Pressure Bottle ESCR



Conclusions

Addition of Calcium Carbonate to Polyolefins

- Improves productivity from 5 – 25% or better
- Can enhance physical properties
- Provides opportunity to downgauge
- Economic saving ($/unit) possible

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Thank You

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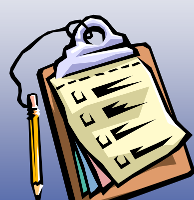

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