

## The Effects of Calcium Carbonate Filler on HDPE Pipe

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### ABSTRACT

The objective of this work is the preparation and the characterization of high density polyethylene /calcium carbonate (HDPE/CaCO<sub>3</sub>) composites. Polyethylene composites, containing 10–35 wt.% of CaCO<sub>3</sub> and HDPE with MFI (Melt Flow index) (0.550 g/10 mn) were prepared with co-extrusion process using extruder type Cincinnati 90D. Thermal and mechanical studies were made in order to determine the parameters for obtaining a material (corrugated pipe) with optimal properties. The composite viscosity increased with filler content, suggesting the formation of filler agglomerates. Thermal analysis shows that addition of 30% CaCO<sub>3</sub> increased the thermal stability of HDPE around 32°C, decreasing the processing temperature of composites in 15°C. Regarding to the mechanical tests, the ring stiffness of the composites decreased with the addition of CaCO<sub>3</sub> above 35 wt.%. According to the obtained results, we suggest that HDPE/CaCO<sub>3</sub> composites could be used in the pipe production where tensile strengths higher than 25 MPa are not required and for service temperatures between 30°C and 70°C.

**Keywords:** composite, HDPE, CaCO<sub>3</sub>, ring stiffness, MFI.

### INTRODUCTION

HDPE has many advantages such as good flexibility, resistance to chemical materials, low cost, high impact and toughness strength. ITP-Tubex Oran, is a company specialized in the transport of fluids. It produces high and low density polyethylene (PE) pipes (HDPE, LDPE) for fuel gas transport, irrigation and drinking water supply. The HDPE grade material used by this company is PE100 and PE80. These grades have low MFI and low permeability and also low thermal stability. However, for recover of this disadvantage inert mineral fillers are added. These fillers make it possible to significantly improve the mechanical [1, 2], thermal [3, 4] and morphological properties [5, 6]. Otherwise, simply reduce the cost price of the transformed material. It was observed that, despite the use of precipitated carbonate calcium as filler, particles have a very small nucleating effect on HDPE [7, 8]. There are no strong molecular interactions between the polymer matrix and this filler. Its inclusion in the

HDPE matrix can act only as a diluent. The first advantage of CaCO<sub>3</sub> filler is that calcium carbonate is an inorganic, low cost and non-toxic substance. Stiffness or Young's modulus can be readily improved by adding either micro or nano-particles since rigid inorganic particles generally have a much higher stiffness than polymer matrices [9, 10]. However, the impact strength of the composites is significantly increased with decreasing CaCO<sub>3</sub> particle size. But HDPE filled with CaCO<sub>3</sub> particles stay very brittle if interface adhesion between the HDPE matrix and the CaCO<sub>3</sub> filler is not good. To improve the interaction between HDPE and CaCO<sub>3</sub> it is necessary, either chemically modify the HDPE, or provide a surface graft treatment to the filler [3, 11–14]. The addition of CaCO<sub>3</sub> to HDPE can increase the crystallization and decrease the melting temperature and crystallization temperature using treated CaCO<sub>3</sub>. Very pure calcium carbonate can be obtained by synthetic methods. It is known as Precipitated Calcium Carbonate; the most frequently used form. This form has a fairly uniform particle

size which can vary from 0.03–0.05  $\mu\text{m}$  up to 8–10  $\mu\text{m}$ . On the technological side, in particular, the revision of the material flows as well as the technical improvement of the injection molds enables composites extrusion. Created in 2003 ITP-Tubex-Oran, (Innovation Transformation Polymer) is the first Algerian company to manufacture corrugated HDPE pipe reinforced for sanitation up to diameter 2500 mm. The reinforced corrugated HDPE pipe is made from HDPE and reinforced with a PP (Polypropylene) core pipe for better strength and flexibility and it is manufactured according to DIN 16961. It is a key product of the company, and for economic and technical reasons, it is currently manufactured by adding  $\text{CaCO}_3$  as filler. The objective of this work is to determine thermal and mechanical performances of HDPE/ $\text{CaCO}_3$  polymer composites of different compositions (10–35 wt.% of  $\text{CaCO}_3$ ).

## MATERIALS AND METHODS

Polymer matrix, HDPE (PE100) supplied by (ENIOS, Belgium) with HD 5030-UA trade name, was used as matrix resin. Specially adapted for extrusion, its molecular structure is simple and it contains no adjuvant (Table 1).

Pipes made from PE100 resin can withstand a minimum required stress (MRS) of 10 MPa at 20°C for more than 50 years. PE80 resin offers an MRS of 08 MPa at 20°C for more than 50 years and is intended for the manufacture of pipes, mainly for the transport and distribution of gas and drinking water, the transport of liquids under pressure and mobile irrigation. The use of PE100, instead of PE80, for the production of pipes has improved the following points: Higher pressure especially for large diameters; Tubes with thinner walls and therefore greater throughput; Better stiffness; higher long-term resistance.

Calcium Carbonate filler with an average particle diameter of 40 nm was supplied by Pasper Company, Spain (Ref E131C based on PE). The filler was surface treated with a coupling agent.

Melt-extrusion technique was applied to produce different compositions of PEHD/ $\text{CaCO}_3$  by a (Cincinnati 90D – Germany) co-rotating twin-screw extruder with a barrel temperature profile ranging from 160°C near the hopper to 200°C at the die and a screw speed of 400 rpm. The optimum values of different settings were obtained to produce samples free of defects.

The preparation of the test pieces intended for mechanical characterization was carried out on a manual press. Mechanical properties (Ring stiffness index), ITP-Tubex-Oran is renowned for its products which comply with European standards: EN ISO 13476, ISO 12201, DIN 16961. A permanent quality control process is set up from the arrival of the raw material to the delivery of the finished products. Ring stiffness index (RS) of HDPE/ $\text{CaCO}_3$  composites was determined according to EN ISO 9969.

The presence of calcium carbonate leads to varying the setting of the machines to a greater or lesser extent because of its influence on the viscosity and / or the rheology of the melts. For this, the study of the MFI of filled polymers in the molten state is of great importance for the plastics industry. The presence of the particles of  $\text{CaCO}_3$  filler increases the viscosity of the molten phase. MFI of HDPE and its HDPE/ $\text{CaCO}_3$  composites are determined according to ISO 1133, NA 357 and measured using a Changed JINGMI Testing fluidimeter, type XRL-400A. The principle of this test is to measure the mass of the thermoplastic material passing through a die with 2.09 mm in diameter and 8 mm long, under the action of pressure exerted by a defined force applied to the piston. The test was carried out at a temperature of 80°C under a load of 2.16 kg. The hot melt flow

**Table 1.** Characteristics of the PE100 polymer

Properties	Standards	Units	Values PE100	Values PE80
Density	DIN 53479 ISO 1183	$\text{g/cm}^3$	0.960	0.950
Elastic modulus (Short-term)	ISO178	N/mm	1200	1000
Melt flow index	ISO 1183 (190 °C, 5 kg)	$\text{g/10 mn}$	0.45	0.43
Breaking elongation	DIN53495	%	>600	>600
Thermal expansion factor	DIN53752	1/C	$1.8 \cdot 10^4$	$1.8 \cdot 10^4$

**Table 2.** Characteristics of CaCO<sub>3</sub> filler

Properties	Standards	Units	Values	Limits
MFI (190 °C / 2.16 kg)	ISO 1133	g/10 mn	0.53	0.25–0.75
Ashes	IT-005	%	82.52	82.00–84.00

index by mass is obtained in grams per 10 minutes according to the following formula:

$$MFI = 600 * M/t \quad (1)$$

where: *M* = the mass of material in grams flowing out;

*t* = constant time for all samples in seconds. The time used in this case was 45 seconds.

### RESULTS AND DISCUSSIONS

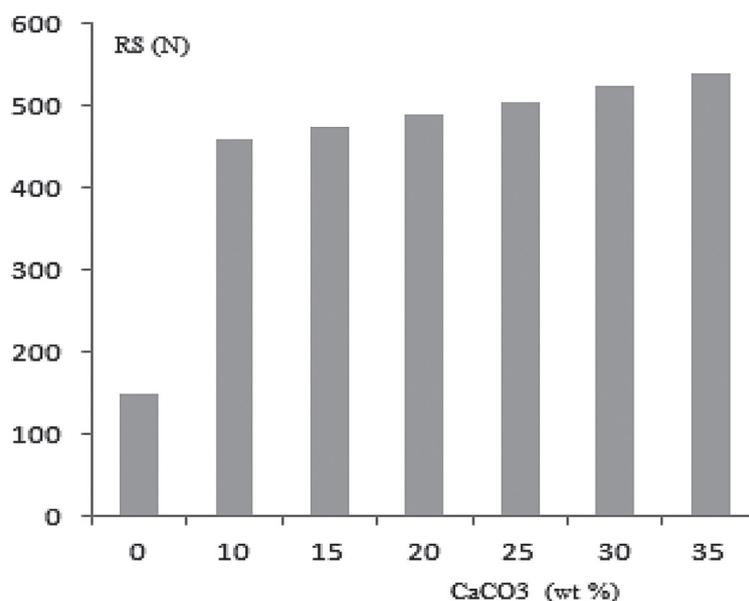
A marked increase in the rigidity of the pipe is noticed according to the the increase in the CaCO<sub>3</sub> filler content. This is explained by the impact of the filler on the mechanical properties of the system. By increasing the percentage of CaCO<sub>3</sub> greater than 35%, we have noticed a gradual regression of the rings stiffness and a clear decrease in the flexibility of the product which is explained by the negative effect of the filler. The filler content limit set at a value of 35% allowed us to have a 25% reduction in the production cost in terms of raw material (PEHD) (Figure 1).

Figure 2, indicates that the addition of CaCO<sub>3</sub> considerably reduce the melt flow index. The decrease of MFI can facilitate the injection molding and can lead to the reduction of energy consumption of molding process. The melt flow index (MFI) is a physical parameter that is widely used to evaluate the ability of a polymer to low when melted. With the addition of 10% by weight of CaCO<sub>3</sub>, the MFI decreased by 0.9%, while for a filler content of 25% wt the decline was 13%.

The density is determined according to standard NF EN 1183, NA7706. The variation of density of composite with filler content is shown in Figure 3.

Density increases when the filler content increases, that means an improvement in physical and mechanical properties.

FTIR spectra are obtained using a Perkin Elmer spectrometer in transmission mode. The transmittance measurements are carried out in the range of 450–4000 cm<sup>-1</sup>. For calcium carbonate filler presence in HDPE matrix is revealed by the appearance of peaks characteristic of calcite (CaCO<sub>3</sub>) at 717 cm<sup>-1</sup>, 875 cm<sup>-1</sup> and 1471 cm<sup>-1</sup>, corresponding to the  $\nu_{3-3}$  vibration and  $\nu_{3-4}$  vibration of the CO<sub>3</sub><sup>-2</sup> group. The



**Figure 1.** Ring stiffness index of composites HDPE/CaCO<sub>3</sub>

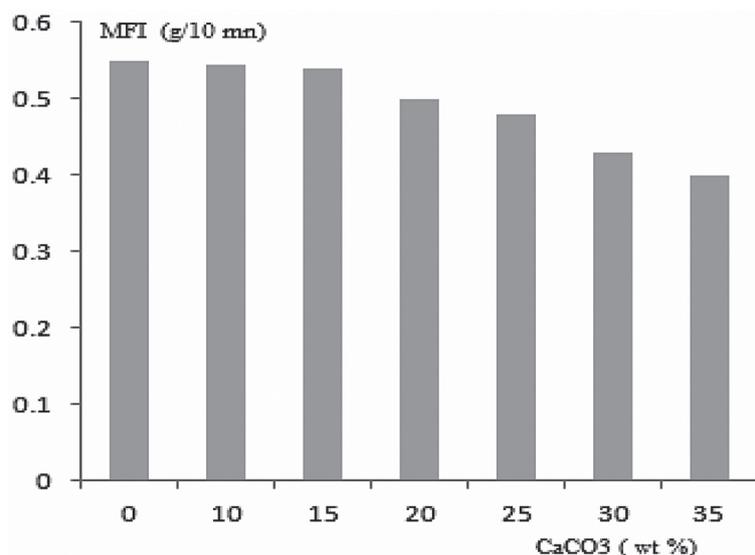


Figure 2. MFI of composites HDPE/CaCO<sub>3</sub>

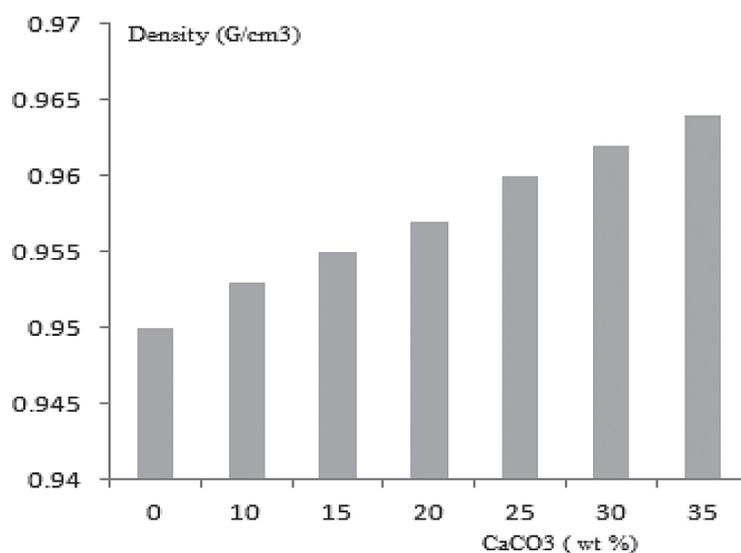


Figure 3. Density of composites PEHD/ CaCO<sub>3</sub>

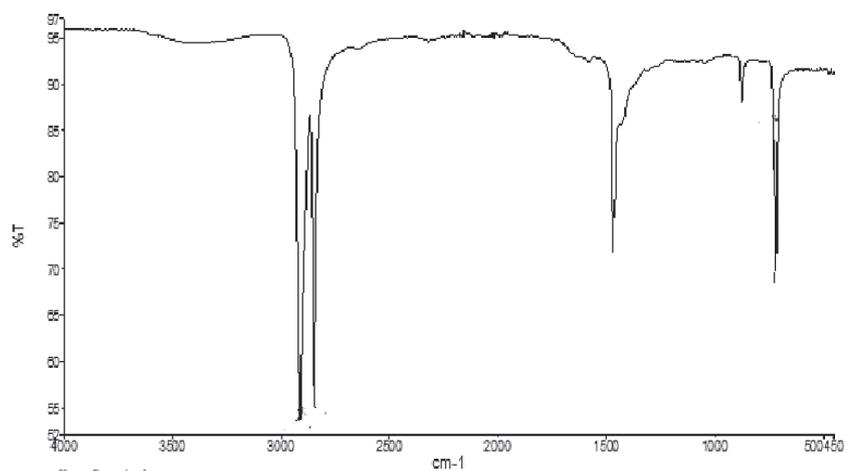
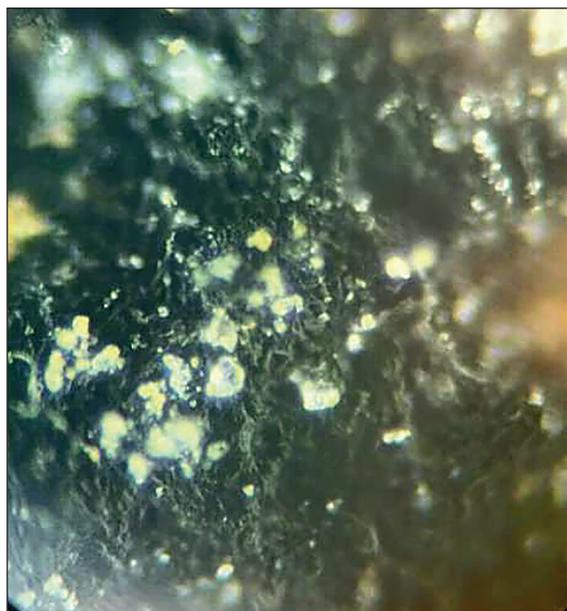


Figure 4. PEHD/CaCO<sub>3</sub> (15%) composite FTIR spectr

appearance of a band between 1709–1740  $\text{cm}^{-1}$  corresponds to the carbonyl group ( $-\text{C} = \text{O}$ ) of calcium carbonate. The infrared spectra of modified  $\text{CaCO}_3$  show intense bands at 2940 and 2848  $\text{cm}^{-1}$ , these are attributed to the alkyl groups ( $-\text{CH}$ ,  $-\text{CH}_2$ ,  $-\text{CH}_3$ ) (Figure 4).

The optical microscopy analyzes in this study are performed on films obtained by compression molding of a few sample granules. This technique does not change the state of filler dispersion; the thickness of the sections in this case is greater. Sections were observed on an optical microscopy occupied by a portable phone camera. This study allowed us to observe the presence of agglomerates on the surface sample HDPE/ $\text{CaCO}_3$  (15%)(Figure 5).



**Figure 5.** Optical micrographs of HDPE/ $\text{CaCO}_3$  (15%) composites (magnification x100)

## CONCLUSIONS

HDPE pipe industries are always trying to reduce the production costs. An alternative could be the use of inorganic fillers. Composites of polyethylene/calcium carbonate are currently very popular. It is confirmed that the calcium carbonate can improve preparation and mechanical properties effectively with of reduction in the production cost (in terms of raw material). The 30 wt.% calcium carbonate additive could effectively improve the melt fluidity of the composites and reduce the energy consumption in the processing. We suggest that HDPE/ $\text{CaCO}_3$  composites (30 wt.%  $\text{CaCO}_3$ ) could be used in the pipe production where tensile strengths higher than 25 MPa are not required and for service temperatures between 30°C and 70°C.

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