



# Vital importance of moisture level in all stages of processing from calcium carbonate coating through polyethylene/calcium carbonate compounding to film generation



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## ABSTRACT

The scope of this work consists of studying the effects of powder premixing and drying conditions on the production of linear low density polyethylene (LLDPE) films containing calcium carbonate ( $\text{CaCO}_3$ ) particles surface treated with stearic acid, which are intended for use in breathable film applications. Coated calcium carbonates and powdered LLDPE were physically premixed and dried in different conditions and polymer compounds containing 45 and 55 wt.% coated calcium carbonate were generated using a twin screw extruder. The effects of coating conditions, filler amount, and drying conditions on the prepared compounds were studied by thermal and morphology analyses. In the final stage, cast films were produced and then evaluated in terms of physical appearance. It was revealed that a precise drying regime is required not only for the calcium carbonates before and after coating but also for the polyethylene/calcium carbonate mixtures before compounding and film generation to ensure that films that were free of macropores could be manufactured.

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## 1. Introduction

Calcium carbonate ( $\text{CaCO}_3$ ), being one of the most abundant minerals in nature, is produced according to two methods, i.e., ground (GCC) and precipitated calcium carbonate (PCC). It is frequently used in a wide range of applications including the paper, paint, food, ceramic, construction, ink, adhesive, drug, cable, and plastic industries [1,2]. Calcium carbonate is traditionally used in plastics as a filler to reduce the cost of expensive polymers [3]. More than 80% of the fillers used in thermoplastics are based on calcium carbonate minerals. For use in the plastics industry calcium carbonate needs to be coated with suitable chemicals such as stearic acid and its salts before mixing into plastics. There are many reasons for coating, e.g. to provide calcium carbonate with a hydrophobic structure and an improved brightness, and to distribute it within a plastic material homogeneously so that the absorption of moisture and agglomeration are prevented. The coating process may be conducted by chemical dissolving (dry coating) or spraying. It may also be carried out in emulsion, or in the form of aqueous solution application [4,5].

Calcium carbonate plays a specific role in the plastics industry when breathable films possessing a microporous structure are considered. Breathable films are produced with very high levels of the particulate

mineral (calcium carbonate) to create an interconnecting pathway for the transport of water vapor through the film by stretching, while preventing permeation or leakage of liquid water out of the film [5,6]. Hence, the breathability of a material is usually measured by its water vapor permeability (WVP) [7]. Breathable films are used in many fields such as roof covering, greenhouse coverings, bandages, surgical clothes, sportswear, children's and adults diapers and sanitary towels [8–11].

The moisture content of calcium carbonates to be used in breathable film applications is of great importance and hence, proper drying is of great significance. Low moisture content calcium carbonate enables better interactions between the thermoplastic polymer and inorganic filler and also imparts breathability to the produced films. Otherwise, residual moisture contained in the particles of inorganic filler and/or in the thermoplastic polymer evaporates at high extrusion temperatures and forms macrovoids or holes in the film resulting in rupture during stretching instead of microvoid generation.

In many patents on breathable films, the importance of moisture content has been emphasized. US Patent No. 6,682,775 deals with calcium carbonate drying by two steps before coating, which should be less than 0.35 wt.% and preferably less than 0.1 wt.% [12]. WIPO Patent No. 050,167 proposes that the surface moisture content of coated  $\text{CaCO}_3$  should be less than about 0.1 wt.% even after exposure for 40 h at 20 °C to an atmosphere having a relative humidity of 97% [13]. According to EP Patent No. 0,979,838,  $\text{CaCO}_3$  particles and thermoplastic polymer should have a moisture content of less than 500 ppm, when they are blended to provide a mixture [14]. U.S. Patent Nos. 5,008,296 and

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5,011,698 present a method of maintaining the moisture level of a melt blended polymer/calcium carbonate composition at preferably below 300 ppm [15,16]. In order to achieve the target moisture content, the related patents only mention drying conditions superficially. One or two-step drying is recommended, in which the materials may be dried in an air circulating oven or under vacuum. However, a detailed drying procedure has not been reported, although the drying step is one of the most critical parameters in breathable film production. This uncertainty in the literature together with the importance of drying in processing stages such as coating and compounding led us to investigate the effect of moisture level in all stages of processing from CaCO<sub>3</sub> coating to film generation and thus to determine the optimized drying conditions. Pursuing this goal, uncoated and coated calcium carbonates were dried as follows: i) hot air drying (HAD), ii) vacuum drying (VD), iii) static bed contact drying (SBCD), and iv) stirred contact drying (SCD). Calcium carbonate coating and polymer/coated calcium carbonate compounding processes were carried out according to the optimum drying conditions, which were established with the help of moisture analyses. Afterwards, cast films were generated. The materials produced in each step were characterized in terms of surface area, coating efficiency, zeta potential, particle size distribution, physical appearance, thermal behavior and morphology.

## 2. Experimental

### 2.1. Materials

Two types of uncoated CaCO<sub>3</sub> were obtained; UC1 from Mikron's/Niğde and UC2 from Aydın Madencilik/Bursa. Their chemical compositions and particle size distributions are given in Tables 1 and 2 [17,18]. The other blend components are stearic acid (Sigma-Aldrich) as the coating chemical, linear low density polyethylene (Sabic 218W LLDPE, *T<sub>m</sub>*: 122 °C, MFI<sub>190 °C, 2.16 kg: 2 g/10 min</sub>) as the thermoplastic polymer, Irganox® 1010 (Ciba Speciality Chemicals) as antioxidant, and calcium stearate (Ca-St, Melos A.Ş.) and Dynamar™ FX9613 (3 M) as processing aids. In order to facilitate a good physical premixing of calcium carbonate together with the thermoplastic polymer, LLDPE was supplied in powder form.

### 2.2. Methods

#### 2.2.1. Drying conditions

It should be emphasized that the moisture level of the materials was controlled in all stages of processing until film casting. In order to achieve this, drying of the materials was studied in three sections: i) CaCO<sub>3</sub>, ii) LLDPE/coated CaCO<sub>3</sub> physical mixtures, and iii) LLDPE/coated CaCO<sub>3</sub> compounds.

**2.2.1.1. CaCO<sub>3</sub>.** In order to determine the optimum drying conditions, uncoated and coated calcium carbonates were dried as shown in Fig. 1. Drying was carried out at 80 °C and 110 °C for 24 h by employing convection and contact regimes. Within each regime the materials were dried using two different modes. In the convection regime, the materials were dried through heat convection under hot air (HAD) or vacuum mode (VD). A conventional oven was used in the convection regime. The contact regime also had two modes of operation. In stirred mode

**Table 2**

Particle size distribution of the uncoated (UC1, UC2) and stearic acid coated (CC1, CC2) calcium carbonates.

	<i>d</i> <sub>50</sub> (µm)	<i>d</i> <sub>97</sub> (µm)	<2 µm (%)
UC1 <sup>a</sup>	1.80	7.80	57.00
UC2 <sup>a</sup>	1.19	3.35	79.91
CC1	1.65	9.34	57.60
CC2	1.17	3.48	80.23

<sup>a</sup> Data for the particle size distribution are from [17,18].

(SCD), the materials were kept in continuous motion during drying. In static bed mode (SBCD), the materials were stationary. Heated plates and a high shear mixer operated at 1000 rpm (Cyclomix 5, Hosokawa Mikron B.V., The Netherlands) were employed for SBCD and SCD, respectively. After establishing the most suitable drying method and temperature, drying time was optimized.

The Cyclomix 5 is a versatile high shear mixer, which is used in the drying, coating, mixing, agglomeration, and densification of particulate materials. The mixer has four pairs of flat-bladed impellers placed from the bottom to the top (Fig. 2). A centrally located high-speed rotating shaft is driven from the mixer cover. The high-speed rotation (up to 2500 rpm) of the paddles and the conical shape of the vessel force the product from the bottom to the upper part of the vessel. Upon reaching the top, the product flows downwards into the center of the vessel. This flow pattern results in fast macromixing. During the upward motion, the particles are accelerated by the paddles and intensively mixed by friction with the vessel walls [19].

**2.2.1.2. LLDPE/coated CaCO<sub>3</sub> physical mixtures.** The LLDPE/coated CaCO<sub>3</sub> physical mixtures were prepared and dried in the high shear mixer (stirred contact drying, SCD) before compounding (Fig. 3). For this purpose, coated calcium carbonates were dry blended into powdered LLDPE in two different amounts (45 and 55 wt.% [7,13,20,21]) in the high shear mixer. Besides, minor components (150 ppm Irganox® 1010, 0.1 wt.% Ca-St, and 100 ppm Dynamar™ FX9613) were also added to the high shear mixer since the physical mixtures were used for the compounding process. In order to determine the effect of drying on film appearance, the physical mixtures were prepared as follows:

- Uncoated CaCO<sub>3</sub> SCD dried before coating + coated CaCO<sub>3</sub> SCD dried together with LLDPE before compounding,
- CaCO<sub>3</sub> undried before coating but SCD dried before compounding + SCD dried LLDPE,
- CaCO<sub>3</sub> undried before coating but SCD dried before compounding + undried LLDPE,
- CaCO<sub>3</sub> SCD dried before coating but undried before compounding + undried LLDPE, and
- CaCO<sub>3</sub> SCD dried before coating but undried before compounding + SCD dried LLDPE.

Additionally, CaCO<sub>3</sub> SCD dried before coating but HAD dried before compounding + HAD dried LLDPE was also studied.

**2.2.1.3. LLDPE/coated CaCO<sub>3</sub> compounds.** The LLDPE/coated CaCO<sub>3</sub> compounds generated from the previously prepared physical mixtures were dried only at 80 °C for 1 h in a conventional oven.

#### 2.2.2. CaCO<sub>3</sub> coating process

The quality of the coating significantly affects compounding and film generation conditions and the mechanical and barrier properties of the final product. For this reason, calcium carbonate coating has to be performed properly, if to be used in breathable film applications. In order to meet this requirement, the amount of stearic acid was calculated based on the assumption of 100% surface coverage of CaCO<sub>3</sub> particles with a monolayer of stearic acid particles. It was calculated that the optimal amount of stearic acid needed to cover the calcium carbonate surface with a monolayer of organic molecules lies between 7.8 and

**Table 1**

Chemical content of the calcium carbonates used [17,18].

Sample	Content (wt.%)					
	CaCO <sub>3</sub>	Mg	Fe	Si	Al	P
UC1	>99.5	<0.20	<0.01	<0.01	<0.02	–
UC2	>99.0	<0.20	<0.10	<0.10	<0.20	–

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