
Production and Characterization of Polyethylene/Calcium Carbonate Composite Materials by Using Calcium Carbonate Dry and Wet Coated With Different Fatty Acids

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SUMMARY

In this study, calcium carbonate (CaCO_3) was coated by suitable chemicals using aqueous or dry coating methods in the optimum conditions. Uncoated calcium carbonate having a mean particle size (d_{50}) of 1.6 microns and a top cut (d_{98}) of 8 microns was provided commercially and it was dry and wet coated with saturated fatty acids whose carbon numbers vary between 14 and 18. Coating amount was adjusted to 0.5-2%. Particle size and particle size distribution of the calcium carbonates before and after coating were investigated. After characterization of the coated calcium carbonates, they were incorporated into linear low density polyethylene (LLDPE) in changing amounts using a twin screw extruder. The effects of coating chemicals, coating conditions and filler amount on composite materials were studied by evaluating the thermal (DSC and TGA) and appearance (Scanning Electron Microscope (SEM)) analyses.

Keywords: Calcium carbonate; Fatty acid; Stearic acid; Compounding; Particle size

1. INTRODUCTION

Calcium carbonate being one of the most abundant minerals in nature, which is available in 4 different qualities (marble, limestone, chalk and travertine) in nature, has been produced according to two methods, i.e., ground (GCC) and precipitated calcium carbonate (PCC) and used frequently in a wide range of applications including paper, paint, food, ceramic, construction, ink, adhesive, drug, cable, and plastic industries¹⁻².

Calcium carbonate has been used as a filler in plastics since it is abundant in nature and a very cheap mineral. More than 80% of the fillers used in thermoplastics are based on calcium carbonate minerals. Calcium carbonate is traditionally used in plastics as bulking agent to

substitute the expensive polymers⁴. It is difficult to distribute calcium carbonate homogeneously in plastic materials since it has a hydrophilic and a lyophilic character. Therefore, calcium carbonate to be used in plastic industry is coated generally with stearic acid and its salts. Coating process may be chemical dissolving (dry coating) or spraying and it also carried out in emulsion, or in the form of aqueous solution application⁵. There are a lot of reasons for coating, e.g. to provide calcium carbonate a hydrophobic structure and an improved brightness, to distribute it within a plastic material homogeneously without taking moisture and agglomeration. One of the recent developing application fields of calcium carbonate in plastics industry is also breathable films. Breathable films have many microvoids, which permit to pass water vapor but do not

allow the water passage⁶⁻⁷. Breathable films are used in many fields such as roof covering, greenhouse coverings, bandages, surgical clothes, sportswear, children's and adult diapers and sanitary towels⁸⁻¹¹.

The main purpose of present study is to investigate the effects of different coating chemicals (fatty acids), coating conditions (dry, aqueous solution) and the filler amount on the LLDPE/ CaCO_3 composite materials.

2. MATERIALS AND METHODS

Uncoated and coated calcium carbonate, technical grade stearic acid, and linear low density polyethylene (LLDPE, MFI_{2.16kg/190°C} = 2 g/10 min) were provided from Mikron's A.Ş. Uncoated calcium carbonates (CC and CA) were dry and wet coated with saturated fatty acids whose carbon numbers vary between 14 and 18 (**Table 1** and **Table 2**). As characterization procedures, particle

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Figure 1. SEM images of calcium carbonate in different qualities (a) chalk, (b) limestone, (c) marble³

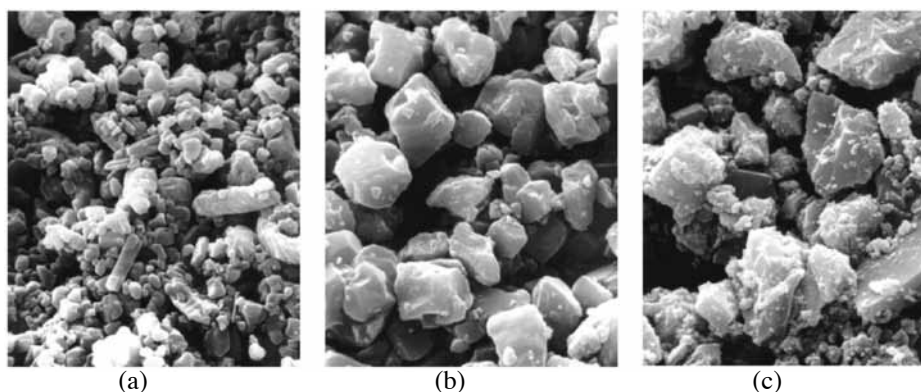


Table 1. Coated calcium carbonates from uncoated calcium carbonate (CC)

Materials (CaCO ₃)	Coating ratio	Coating agent (fatty acid)	Coating method
CC	Uncoated calcium carbonate		
CC1	%1,1	Technical stearic acid	Dry
CC2	%1,1	Pure stearic acid	Dry
CC3	%1,1	Palmitic acid	Dry
CC4	%1,1	Myristic acid	Dry
CC1W	%1,1	Sodium stearate (NaSt)	Aqueous
CC2W	%1,1	Stearic acid and sodium hydroxide (NaOH)	Aqueous
CC3W	%1,1	Palmitic acid and sodium hydroxide (NaOH)	Aqueous

Table 2. Coated calcium carbonates from uncoated calcium carbonate (CA)

Materials (CaCO ₃)	Coating ratio	Coating agent (fatty acid)	Coating method
CA	Uncoated calcium carbonate		
CA1	%1,6	Technical stearic acid	Dry
CA2	%1,6	Pure stearic acid	Dry
CA3	%1,6	Palmitic acid	Dry
CA4	%1,6	Myristic acid	Dry
CA1W	%1,6	Sodium stearate (NaSt)	Aqueous
CA2W	%1,6	Stearic acid and sodium hydroxide (NaOH)	Aqueous
CA3W	%1,6	Palmitic acid and sodium hydroxide (NaOH)	Aqueous

size and particle size distribution of the calcium carbonates before and after coating were investigated using Sympatech Helos particle size analyzer.

2.1 Characterization

2.1.1 Calcium Carbonate Powder

Thermal degradation was determined by thermogravimetric analysis (TGA)

using a Mettler Toledo TGA/DSC 1 Star. Thermogravimetric analysis was also performed to obtain quantitative information about coating. The thermal analyzer was run between room temperature (24 °C) and 1000 °C with 10 °C/min heating rate under air atmosphere.

In order to determine structure of crystallinity of the obtained materials

wide angle x-ray diffraction analyses (WAXD). The uncoated calcium carbonate (CC) and its commercial coated sample were studied by X-ray diffraction (XRD) using a Bruker AXS Advance D8 diffractometer (Cu K_α radiation, λ = 1.5406 Å, generator voltage = 40 kV, current = 30 μA). Samples were scanned in 2θ ranges from 1° to 60° at a rate of 1°/min.

Furthermore, Brunauer-Emmett-Teller (BET, Quantachrome, Nova 2200e) surface area analyses were performed with regard to gas adsorption method (nitrogen). Before measurements uncoated calcium carbonates were dried in vacuum oven at 80 °C during 72 hours and coated calcium carbonates were dried in vacuum oven at 40 °C during 72 hours.

Zeta potential measurements (Zetasizer Nano ZS) and moisture analyses were also performed.

2.1.2 Polyethylene/Calcium Carbonate Composite

After the coating of calcium carbonate it was compounded with LLDPE using a co-rotating twin screw extruder (diameter: 27 mm, L/D = 44, PTLE 2744, PolimerTechnics Bursa). Calcium carbonate amount was fixed at 45 and 55 wt.%. Morphologies of the cryo-fractured samples (from the composite) were studied using Scanning Electron Microscopy (SEM). Thermal analysis (DSC) was also conducted.

3. RESULTS AND DISCUSSION

Calcium carbonate powder and LLDPE/calcium carbonate composites were investigated and the results were evaluated.

3.1 Calcium Carbonate Powder

Particle sizes and particle size distributions were determined to remain constant after dry/wet coating with fatty acids having different carbon numbers (**Table 3**).

Uncoated calcium carbonate (CC) is also available commercially as coated calcium carbonate. Thermal analysis (TGA) of this material shows the coating amount and quality. The weight losses between 200-400 °C in the TGA results belong to surface agent. From **Figure 2** the coating ratio of calcium carbonate was determined as 0.8%.

Moisture was observed to drop to 0.1% especially in the case of coating with fatty acids bearing shorter carbon number, while moisture values were around 0.3% before coating (**Table 4**). Zeta potentials were -5 mV before coating but they raised up to 10-15 mV after coating independent upon the coating chemical and coating conditions. In other words, the tendency to agglomeration was reduced after coating (**Table 5** and **Table 6**).

The obtained calcium carbonates were studied by using Bruker AXS Advance D8 wide angle x-ray diffractometer (WAXD) to get information about their crystalline structure. According to WAXD analysis, uncoated the calcium carbonate (CC) contains mostly calcite and aragonite structure (**Figure 3**).

Before calcium carbonate coating its surface area should be known. Surface area of the uncoated calcium carbonate was found 4.0 m²/g. After coating the surface area was increased (4, 6-5, 5 m²/g).

Table 3. Particle size distribution of the uncoated and coated calcium carbonate used

	d ₅₀ (µm)	d ₉₇ (µm)	< 2 µm (%)
CC	1.8	7.8	57
CC1	1,63	8,56	58,02
CC2	1,66	9,18	57,23
CC3	1,61	8,42	58,4
CC4	1,64	9,16	57,55
CA	1,19	3,35	79,91
CA1	1,17	3,46	80,3
CA2	1,17	3,48	80,23
CA4	1,17	3,45	80,113

Table 4. Moisture analysis of uncoated and coated calcium carbonates after contact drying

	Moisture after drying (%)
CC	0,35
CC1	0,1
CC2	0,1
CC3	0,06
CC4	0,08
CC1W	0,20
CC2W	0,15
CC3W	0,29

Table 5. Zeta potential values of uncoated and coated calcium carbonates used

	ζ-Potential (mV)	Deviation (mV)	pH
CC	-5.5	8.9	8.04
CC1	-11.80	3.97	8.15
CC2	-10.10	3.15	8.22
CC3	-14.00	1.98	8.22
CC4	-6.75	2.82	8.40
CC1W	-13,6	5,61	8,28
CC2W	-16,5	5,48	8,38
CC3W	-15,3	4,56	8,32

Figure 2. TGA analysis of commercial coated calcium carbonate

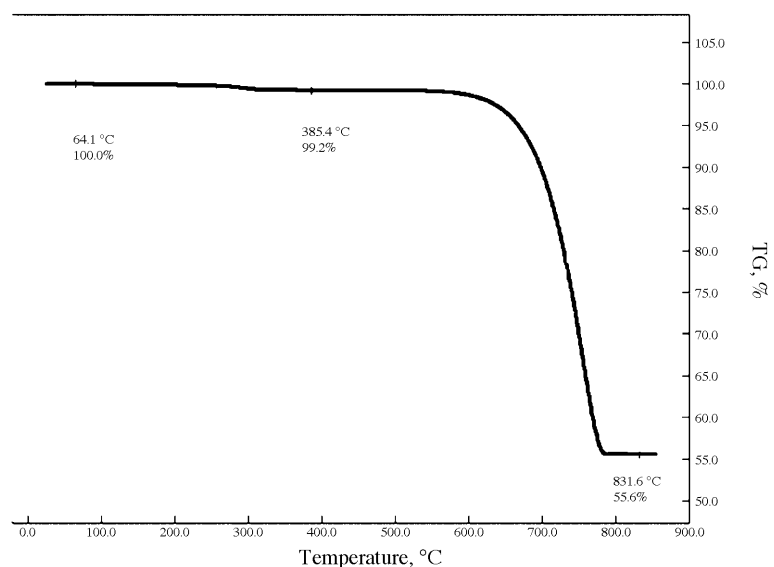
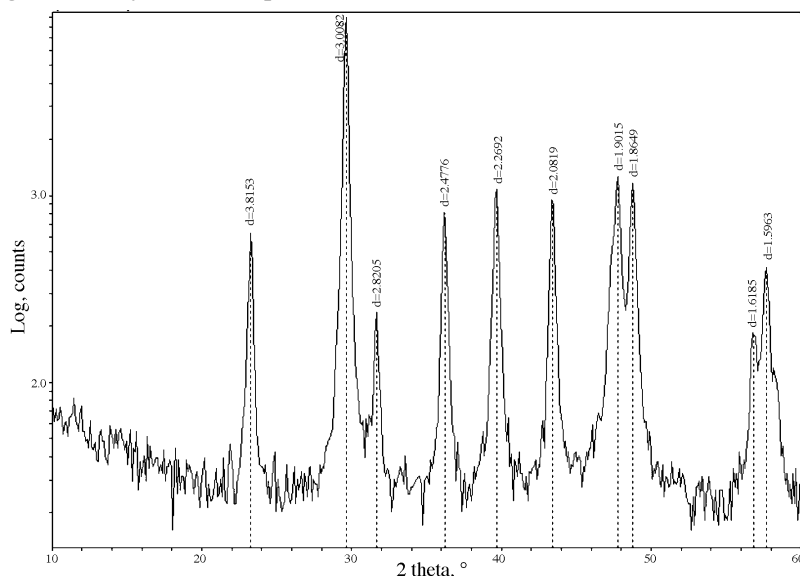


Table 6. Zeta potential values of the uncoated and the coated calcium carbonates used

	ζ -Potential (mV)	Deviation (mV)	pH
CA	-5.5	8.9	8.04
CA1	-10,70	4,03	7,8
CA2	-12	2,44	8,3
CA3	-10,9	2,62	7,18
CA4	-12,7	2,66	7,87
CA1W	-14,5	2,79	8,16
CA2W	-10,8	2,08	8,13
CA3W	-17,2	1,87	8,05

Figure 3. X-ray diffraction pattern of the uncoated calcium carbonate (CC)



3.2 Polyethylene/Calcium Carbonate Composite

After coating with stearic acid, its salts and other fatty acids which have 14-18 carbon numbers, calcium carbonate became hydrophobic. Thus dispersion quality of calcium carbonate in polymer matrix has been increased. The amount of coating in commercial products was found to be ranging between 1-2 wt.% and most of the calcium carbonate particles were < 1 μm . Polyolefin/calcium carbonate compounds contain 45-55 wt.% calcium carbonate. Particle sizes increased with increasing amount of the filler when considered the SEM images of the composites (**Figure 4** and **Figure 5**).

Crystallization temperatures of the composites decreased with increasing amount of the filler according to the thermal analyses (DSC).

4. CONCLUSIONS

In wet coated calcium carbonate the best results were obtained when used fatty acids bearing longer carbon

Figure 4. SEM images of LLDPE/CC2 (55 wt%-45 wt%) composites (x2000, x5000, x10000 magnification)

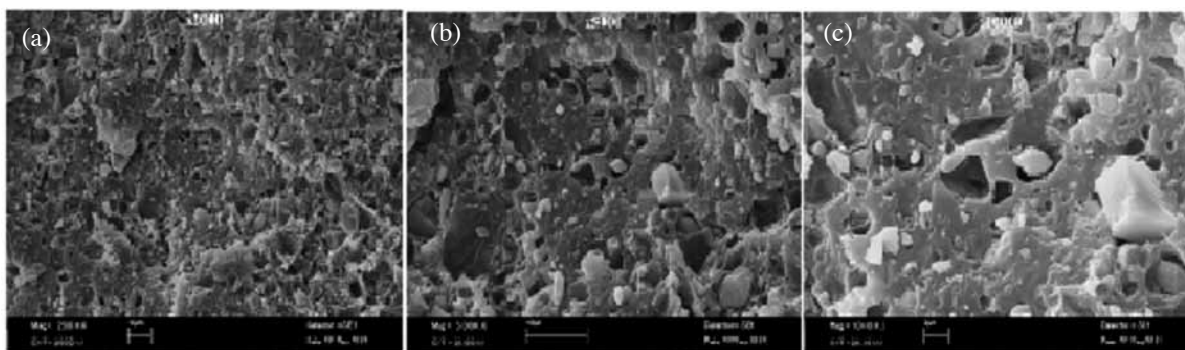


Figure 5. SEM images of LLDPE/CC2 (45 wt%-55 wt%) composites (x2000, x5000, x10000 magnification)

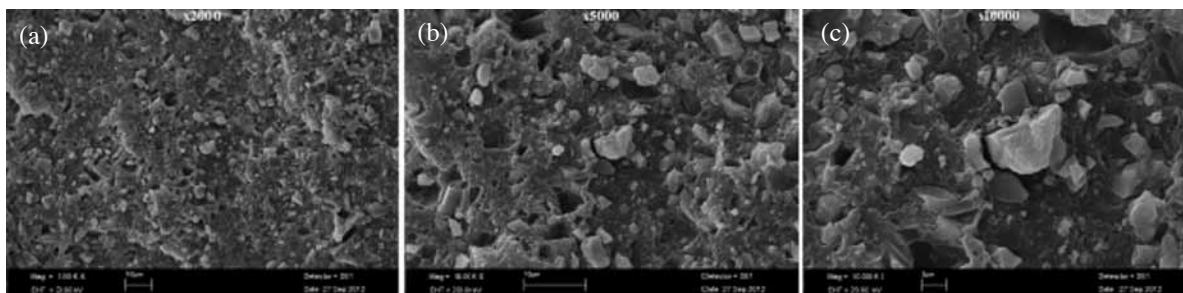
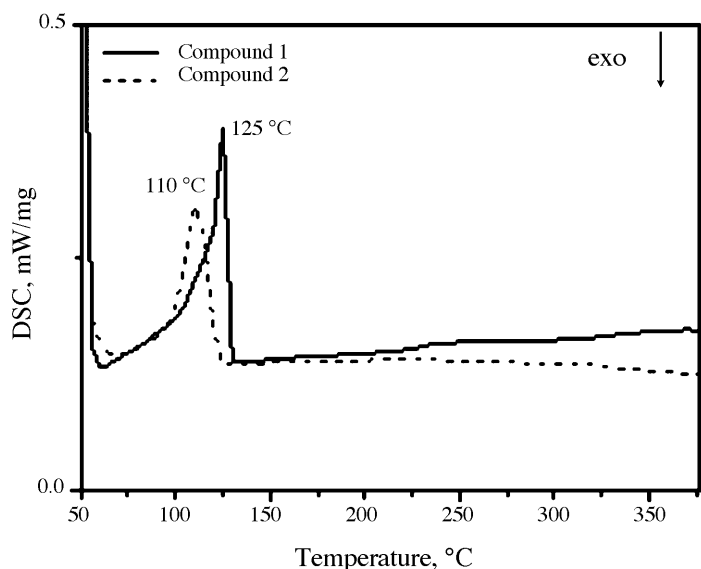


Figure 6. DSC thermograms of different compounds (compound 1: 41% calcium carbonate, compound 2: 45% calcium carbonate)



number. Particle sizes increased with increasing amount of the filler when considered the SEM images of the composites. Crystallization temperatures of the composites decreased with increasing amount of the filler according to the thermal analyses.

In this study, it has been shown that the coating plays a significant role in calcium carbonates for their dispersibility in polymer matrix. Using different chemicals changes the dispersion quality but processing type affected the dispersion quality considerably. Using different coating agents and methods for calcium carbonate were determined to have

no effect in terms of particle size and particle size distribution. Coating of calcium carbonate in aqueous solution delivers less moisture as dry coated calcium carbonates. In the second step of this work the wet coated CaCO_3 gave the best results were extruded with LLDPE and characterized. That means calcium carbonate can be also wet coated before using with polymer matrix without agglomeration.

ACKNOWLEDGMENTS

We thank Mikron'S for providing calcium carbonate and chemicals. This work was supported by Research Fund of the Erciyes University Project Number: FBY-12-4114.

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