EFFECT OF THERMO KINETIC MIXER AND TWIN-SCREW EXTRUDER ON MORPHOLOGICAL AND THERMAL BEHAVIOR OF HIGHLY FILLED CaCO$_3$/LLDPE COMPOSITES

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Keywords
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Calcium carbonate,
Processing,
Melt extrusion,
Mixer.

Abstract
The goal of this study consists of examining the mixing effect of thermo kinetic mixing and melt extrusion methods on structural characteristics of the linear low density polyethylene (LLDPE) and its uncoated/coated calcium carbonate (CaCO$_3$) filled composites. The influence of mixing power of both methods on morphological and thermal properties of the LLDPE/CaCO$_3$ composites was investigated. According to the results, it was revealed that the LLDPE/CaCO$_3$ composites processed by melt extrusion contained more CaCO$_3$ particles in comparison to the composites obtained by thermo kinetic mixer. In addition, the melt extrusion method delivered a more homogeneous distribution of calcium carbonate particles within the matrix polymer. Incorporation of uncoated/coated calcium carbonate affected the thermal behavior of the composites to a large extent. And, more severe changes were observed on the composites generated on the thermo kinetic mixer.

1. Introduction
Calcium carbonate (CaCO$_3$) is commonly found and abundant inorganic material in nature, and used frequently in many areas, especially in the plastic industry [1-6]. Polyethylene (PE) is a thermoplastic material commonly used in the production of polymer composites. CaCO$_3$ is often preferred to use in thermoplastic composites that have a widespread usage in recent years, and classified as a functional filler. In various studies, the effects of calcium carbonate incorporation into thermoplastic polymers are given in detail [7-22]. In the related studies, only the melt extrusion method was used for composite generation due to its uncomplicated and all-purpose features of this method.

More recently, thermo kinetic mixer has begun to be used to achieve a better filler dispersion in the polymer matrix for crucial compounding applications. According to the literature, this method has been only used for the production of polyethylene/clay, polyethylene/graphite, and polyethylene terephthalate (PET)/clay nanocomposites so far [23-30]. Özen et al. [30] compared thermo kinetic mixing and melt extrusion methods in the application of PET/organoclay nanocomposites. It was observed that working on the thermo kinetic mixing maintained faster processing steps in comparison to the melt extrusion method, due to the elimination of drying step before melt processing, and provided less thermal degradation owing to short processing times, and more homogeneous and better dispersion of the clay particles in PET matrix phase.

The purpose of this study is to generate linear low density polyethylene (LLDPE)/calcium carbonate (CaCO$_3$) composites by two different methods, i.e. thermo kinetic mixing and melt extrusion and to investigate their mixing effects on the morphological and thermal behavior of the composites generated. To achieve this goal, uncoated and coated calcium carbonates were used as filler. Thus, it was also possible to study a possible effect of coating.

2. Materials
Two types of uncoated and coated calcium carbonates were used. Calcium carbonates were obtained from Mikron’s A.Ş., Niğde (C1: uncoated, C1C: coated) and Aydın Madencilik A.Ş., Bursa, Turkey (C2: uncoated, C2C: coated). Particle size distributions of the uncoated/coated CaCO$_3$ are shown in Table 1. Particle size is defined as equivalent diameter of a spherical...
particle and given as d50 and d98 values. (d50: Diameter where 50% of the population lies below this value (mean particle size) and d98: Diameter where 98% of the population lies below this value (the biggest particle size)). Linear low density polyethylene (LLDPE, Sabic 218W, Tm: 122°C, MFI 2.16 kg/190°C = 2 g/10min) as the polymer matrix, Irganox® 1010 (Ciba Speciality Chemicals) as antioxidant, and calcium stearate (Ca-St, Melos A.Ş.) as the internal lubricant were used in production of the LLDPE/CaCO3 composites.

Table 1. Particle size distribution of uncoated (C1, C2) and coated (C1C, C2C) calcium carbonates used [31, 32].

<table>
<thead>
<tr>
<th>CaCO₃</th>
<th>d₅₀</th>
<th>d₉₈</th>
<th>&lt;2µm (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>1.8</td>
<td>7.8</td>
<td>57.0</td>
</tr>
<tr>
<td>C2</td>
<td>1.2</td>
<td>3.3</td>
<td>79.9</td>
</tr>
<tr>
<td>C1C</td>
<td>1.6</td>
<td>9.3</td>
<td>57.6</td>
</tr>
<tr>
<td>C2C</td>
<td>1.2</td>
<td>3.5</td>
<td>80.2</td>
</tr>
</tbody>
</table>

3. Methods

3.1. Production of LLDPE/CaCO₃ Composites

Uncoated and coated CaCO₃ were compounded with LLDPE using two different types of melt processing equipment: a thermo kinetic high shear mixer with a volume capacity of 100 cm³ (Lab model, Gelimat G1, Dreiswerke Inc., USA) and a co-rotating intermeshing twin screw extruder (PTLE 2744, Polimer Technics Bursa, Turkey, Ø: 27 mm, L/D ratio: 44). The general parts of the equipment used in generating the composites are shown in Figure 1. In order to judge the dispersion state of the high amount of filler, polyethylene/coated calcium carbonate ratio was selected as 60/40 w/w. LLDPE/CaCO₃ composites produced by thermo kinetic mixer and twin-screw extruder were designated as follows: T/LLDPE-C1, T/LLDPE-C1C, T/LLDPE-C2, T/LLDPE-C2C for the thermo kinetic mixer and E/LLDPE-C1, E/LLDPE-C1C, E/LLDPE-C2, E/LLDPE-C2C for the twin screw extruder.

Thermo kinetic mixer

LLDPE/CaCO₃ composites were produced by the help of special blades in a completely stainless steel chamber of the thermo kinetic mixer called Gelimat mixer. Total amount of the material was determined as 120 g in the study. Gelimat was operated with at shaft speed of 3500, 4000, 4500 and 5000 rpm for 20 s at each step until the material reached a temperature value of 220°C. The molten composite was taken and pressed between two metal plates. Finally, it was cut by using a crusher. Details related to the thermo kinetic mixing can be found elsewhere [33-38].

Figure 1. Thermo kinetic mixer and twin screw extruder used for the production of LLDPE/CaCO₃ composite.

Twin-screw extruder

The temperature of the twin screw extruder barrel zones was set to 170°C, 180°C, 210°C and 9 x 220°C and LLDPE/coated CaCO₃ compounds were generated at a screw speed of 300 rpm. Throughput was adjusted to 10 kg/h so that a torque value of 50% was achieved.

3.2. Characterization

Morphology

Morphology analysis was performed to determine distribution behavior of uncoated/coated calcium carbonates (aggregation/agglomeration) in the polymer matrix. For this purpose, produced composites were cryogenically fractured and cross-sections of the samples were examined by employing a Leo G34-Supra 35VP scanning electron microscope (SEM) operating with an accelerating voltage of 20 kV. Before the SEM analysis, surface of the samples was coated with the help of a carbon evaporator (Emitech K950X).

Melt flow index (MFI)

Melt flow index of the composites was measured to determine the melt processability of the composites. The melt flow index values (MFI) of the neat LLDPE and LLDPE/CaCO₃ composites were detected according to ASTM 1238 using an MFI analysis instrument (Devotrans EA3, Istanbul, Turkey). The flow measurement was conducted by pushing the samples through a 2 mm diameter die at 190°C with 2.16 kg mass. The results were expressed in grams per 10 min (g/10 min).

Thermal analyses

In order to determine the CaCO₃ content in the LLDPE/CaCO₃ composites, the samples were weighed, later on held in an ash-oven (Protherm PLF-110/6) at 450°C for 1 h. Afterwards, the amounts of calcium carbonate in the composites were determined by weight loss measurements. Perkin Elmer PYRIS Diamond™ differential scanning calorimeter was used for determining peak melting temperature (Tₘ), crystallization temperature (Tₓ).
and % degree of crystallinity ($\chi_c$) of the LLDPE/CaCO$_3$ composites produced. Heating and cooling scans were carried out under nitrogen atmosphere at 10°C/min over the temperature range from 20 to 200°C. The first heating scans were considered for the evaluation. Crystallinity value of the samples was calculated by using the formula written below [39, 40]:

$$\chi_c = \left(\frac{\Delta H_f}{\Delta H_{f0}}\right) \times 100$$  

(1)

Here, $\chi_c$ represents degree of crystallinity, $\Delta H_f$ is the enthalpy of fusion in the thermogram, and $\Delta H_{f0}$ the enthalpy of fusion of the completely crystalline material at the equilibrium melting temperature, $T_m$. The value of 293 J/g has been taken as the enthalpy of melting of 100% crystalline PE [39, 41-47].

4 Results and discussion

4.1 Morphology and CaCO$_3$ particle size distribution

Particle size and particle size distribution of uncoated/coated calcium carbonate in the polymer matrix were performed visually by counting the calcium carbonate particles in the SEM images. The number of calcium carbonate was classified according to particle size. Three categories were used for classification of the CaCO$_3$ as follows:

- smaller than 1 µm,
- between 1-3 µm and,
- bigger than 5 µm.

The morphological analysis results of the composites prepared using different processing (thermo kinetic mixing and melt extrusion) methods are exhibited in Figure 2, and categorized in Figure 3. It was determined that the number of CaCO$_3$ particles smaller than 1 µm in the composites prepared by using thermo kinetic mixer is generally less than the others prepared by using extruder. In the case of using uncoated CaCO$_3$, it was observed that the difference in the number of CaCO$_3$ particles in sizes 1-3 µm between a composite produced on the thermo kinetic mixer (T/LLDPE-C1) and extruder (E/LLDPE-C1) is quite small. The number of uncoated CaCO$_3$ particles (C1) having bigger than 5 µm in the composite materials produced on the extruder is slightly more than in the composite produced by the thermo kinetic mixer. Similar variations were observed when coated CaCO$_3$ (C1C) was used. The same situation occurred for the uncoated (C2) and coated (C2C) CaCO$_3$ containing composites produced by both methods (T/LLDPE-C2, E/LLDPE-C2 and T/LLDPE-C2C, E/LLDPE-C2C). Processing on the extruder provided a better particle size distribution than the thermo kinetic mixer without aggregation or agglomeration. Thus, a more homogeneous CaCO$_3$ distribution was obtained in the polyethylene/CaCO$_3$ composites by melt extrusion process. The dispersion of CaCO$_3$ in the polyethylene matrix processed on the thermo kinetic mixer was worse than the twin-screw extruder. Generally, thermo kinetic mixers are expected to provide a better distribution of the filler materials thanks to its very high processing speeds in comparison to the conventional extrusion method. But, high amount of CaCO$_3$ probably acted as a hindrance for a better distribution within a very short processing time. Significant growth in particle size, aggregation or agglomeration were not observed in both processing types considering the measured particle sizes and particle size distributions of CaCO$_3$. In addition, the particle sizes of CaCO$_3$ in the produced composites were determined to be consistent with the initial particle sizes.
filled LLDPE composites processed on the extruder; and (E/LLDPE-C2C) C2C filled LLDPE composites processed on the extruder.

![Image](image-url)

**Figure 3.** Particle size distribution of CaCO₃ in the LLDPE/CaCO₃ (60/40 w/w) composites prepared on the thermo kinetic mixer and twin-screw extruder.

### 3.2. Melt flow index (MFI)

MFI values of LLDPE/CaCO₃ composites produced by mixing and extrusion processes are exhibited in Table 2. Independent of calcium carbonate type and quality (uncoated or coated), MFI values of all the produced composites decreased in comparison to the reference samples (E-LLDPE and T-LLDPE). The T/LLDPE-C2 composite containing uncoated CaCO₃ (C2) delivered the largest MFI value being 1.37 g/10min in all composites prepared on the mixer.

**Table 2.** MFI values of LLDPE/CaCO₃ composites generated on the mixer and twin-screw extruder.

<table>
<thead>
<tr>
<th>Notation</th>
<th>MFI (g/10min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-LLDPE</td>
<td>1.52</td>
</tr>
<tr>
<td>T/LLDPE-C1</td>
<td>1.21</td>
</tr>
<tr>
<td>T/LLDPE-C1C</td>
<td>1.05</td>
</tr>
<tr>
<td>T/LLDPE-C2</td>
<td>1.37</td>
</tr>
<tr>
<td>T/LLDPE-C2C</td>
<td>0.97</td>
</tr>
<tr>
<td>E-LLDPE</td>
<td>1.59</td>
</tr>
<tr>
<td>E/LLDPE-C1</td>
<td>1.10</td>
</tr>
<tr>
<td>E/LLDPE-C1C</td>
<td>1.22</td>
</tr>
<tr>
<td>E/LLDPE-C2</td>
<td>1.20</td>
</tr>
<tr>
<td>E/LLDPE-C2C</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Considering processing on the mixer MFI values of polyethylene/calcium carbonate composites containing uncoated CaCO₃ decreased when coated CaCO₃ was added into the polymer matrix instead of the uncoated one (MFI(T)/LLDPE-C1: 1.21 g/10min, MFI(T)/LLDPE-C1C: 1.05 g/10min). Despite the fact that the usage of coated calcium carbonate in the extruded composites led to an increase in MFI value (MFI(E)/LLDPE-C1: 1.10 g/10min, MFI(E)/LLDPE-C1C: 1.22 g/10min), there has been no large discrepancy observed among them.

The composites prepared by using the extruder delivered higher MFI values, when the same quality of the coated calcium carbonate was used. This situation indicates that working with melt extrusion process provides lower viscosity, and thus the torque to be generated during processing could be reduced.

### 3.3. Thermal analyses

The amounts of CaCO₃ in the composites produced range between 39 and 44 wt.%, and are listed in Table 3, which is in accordance with the initial loading amount of 40 wt.%. The DSC curves of the neat LLDPE (T-LLDPE and E-LLDPE) and the LLDPE/CaCO₃ composites are depicted in Figure 4, and their corresponding thermal behavior parameters such as melting temperature (Tₘ), crystallization temperature (Tc), and degree of crystallinity (χc) are listed in Table 4. According to DSC results, Tₘ values of the neat LLDPE (T-LLDPE and E-LLDPE) were determined to be 119.3 and 118.9 °C, respectively, while it ranged between 122.6 and 125.0 °C for the all composites filled with CaCO₃. Similar variation was observed for...
crystallization temperatures as well. Addition of uncoated/coated CaCO$_3$ to the neat LLDPE led to an increase in $T_c$ from 106.1 °C up to 111.2 °C for the composites generated on the mixer, from 104.2 °C up to 109.7 °C for the composites generated on the twin-screw extruder despite the reduction of degree of crystallinity ($\chi_c$) for all composites. Uncoated CaCO$_3$ (C1) filled LLDPE composite produced by the extrusion method showed the lowest degree of crystallinity (8.1%). In the case of using the composites filled with coated calcium carbonates (C1C and C2C) processed on the high shear mixer, it was observed that the degree of crystallinity was higher when compared with those of composites containing the uncoated CaCO$_3$. There was no distinctive difference observed on the degree of crystallinity between uncoated or coated filled composites when processed on the twin screw extruder. Changing the type of calcium carbonate (C1 and C2) affected the degree of crystallinity of the composites prepared by the mixing method to a small amount.

From DSC results, it was revealed that the addition of uncoated/coated calcium carbonate to the polymer matrix by using either mixer or twin-screw extruder affected the melting temperature ($T_m$), crystallization temperature ($T_c$), and degree of crystallinity ($\chi_c$), significantly. Besides, it was shown a relationship between the crystallization temperature and the degree of crystallinity. The presence of uncoated/coated calcium carbonate in the polymer matrix caused an increase in the crystallization temperature. This change led to a decrease in the degree of crystallinity.

Table 4. Thermal behavior of LLDPE/CaCO$_3$ composites generated on the thermo kinetic mixer and twin-screw extruder.

<table>
<thead>
<tr>
<th>Notation</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\chi_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/LLDPE</td>
<td>119.3</td>
<td>106.1</td>
<td>18.3</td>
</tr>
<tr>
<td>T/LLDPE-C1</td>
<td>123.0</td>
<td>110.3</td>
<td>8.1</td>
</tr>
<tr>
<td>T/LLDPE-C1C</td>
<td>123.3</td>
<td>109.8</td>
<td>14.5</td>
</tr>
<tr>
<td>T/LLDPE-C2</td>
<td>122.6</td>
<td>111.2</td>
<td>11.7</td>
</tr>
<tr>
<td>T/LLDPE-C2C</td>
<td>122.8</td>
<td>111.2</td>
<td>12.7</td>
</tr>
<tr>
<td>E/LLDPE-C1C</td>
<td>123.2</td>
<td>108.0</td>
<td>12.2</td>
</tr>
<tr>
<td>E/LLDPE-C2</td>
<td>125.0</td>
<td>109.7</td>
<td>12.2</td>
</tr>
<tr>
<td>E/LLDPE-C2C</td>
<td>122.7</td>
<td>109.5</td>
<td>12.4</td>
</tr>
</tbody>
</table>

The degrees of crystallinity of LLDPE/CaCO$_3$ composites prepared by the mixing method scattered in a wide range by showing unexpectedly high values although the crystallization temperatures are close to each other. It could be explained with the short processing time for melting of the materials on the high shear mixer.

DSC results distinctly revealed that the thermal behavior of LLDPE/CaCO$_3$ composite materials generated by both methods are greatly influenced by the addition of inorganic material. Higher melting temperatures for all the composites processed by thermo kinetic mixing and melt extrusion methods could be explained as follows: Calcium carbonate is an inorganic material, which reduces heat transfer within the matrix polymer.

4. Conclusions

The aggregation of coated CaCO$_3$ particles (>10 µm) in the composites produced by thermo kinetic mixing and extrusion processes was not detected, while the uncoated CaCO$_3$ filled composites contain bigger
CaCO₃ particle sizes. It was shown that the composites produced by melt extrusion have more number of CaCO₃ particles independent of particle size and coating state when compared with the thermo kinetic mixing.

The outcomes of the study showed that melting temperatures of all composites prepared using both methods decreased, while the crystallization temperatures increased. In addition, the degree of crystallinity values decreased significantly. Furthermore, it was seen that the small changes in melt flow index values did not affect the thermal and morphological properties of the composites. A worse mixing effect was observed in the composites prepared on the thermo kinetic mixer. High amount of CaCO₃ probably acted as a hindrance for a better distribution within a very short processing time. A better mixing effect could be achieved when a twin-screw extruder is used for generation highly filled LLDPE/CaCO₃ composites. Twin-screw extruder is also useful for a continuous process.

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Conflict of Interest

No conflict of interest was declared by the authors.

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