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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

Polyethylene,
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 used only for the production of polyolefine/clay, polyolefine/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

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particle and given as d_{50}, and d_{98} values. (d_{50}: Diameter where 50% of the population lies below this value (mean particle size) and d_{98}: Diameter where 98% of the population lies below this value (the biggest particle size)). Linear low density polyethylene (LLDPE, Sabic 218W, T_m: 122°C, $MFI_{2.16kg/190°C}$= 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].

$CaCO_3$	*d_{50}*	*d_{98}*	<2µm (%)
C1	1.8	7.8	57.0
C2	1.2	3.3	79.9
C1C	1.6	9.3	57.6
C2C	1.2	3.5	80.2

3. Methods

3.1. Production of LLDPE/$CaCO_3$ Composites

Uncoated and coated $CaCO_3$ were compounded with LLDPE using two different types of melt processing equipment: a thermo kinetic high shear mixer with a volume capacity of 100 cm^3 (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/$CaCO_3$ 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].

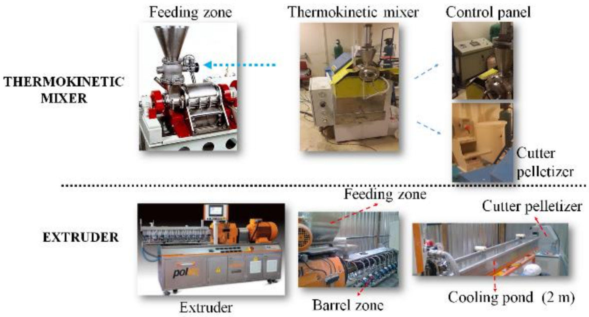

Figure 1. Thermo kinetic mixer and twin screw extruder used for the production of LLDPE/$CaCO_3$ composite.

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 $CaCO_3$ 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/$CaCO_3$ 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 $CaCO_3$ content in the LLDPE/$CaCO_3$ 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 (T_m), crystallization temperature (T_c), and % degree of crystallinity (χ_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]:

$$\chi_c = [(\Delta H_f)/(\Delta H_{f0})]x100 \quad (1)$$

Here, χ_c represents degree of crystallinity, ΔH_f is the enthalpy of fusion in the thermogram, and ΔH_{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 CaCO3 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 CaCO3 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.

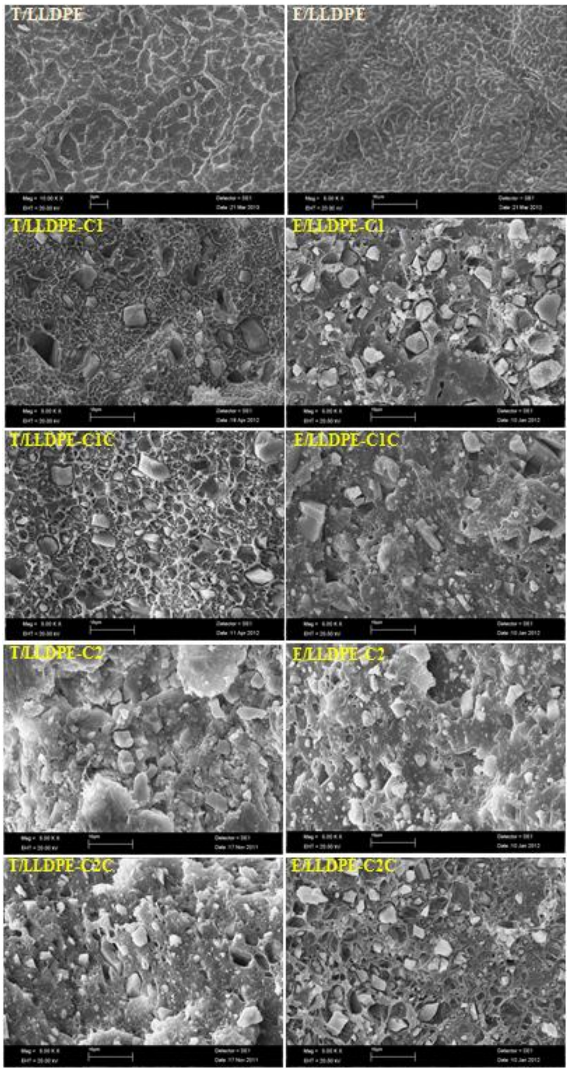

Figure 2. SEM images of LLDPE/$CaCO_3$ composites (60/40 w/w) generated on the mixer and twin screw extruder (Magnification: 5000X): (T/LLDPE) Reference sample (100% LLDPE) processed on the mixer; (T/LLDPE-C1) C1 filled LLDPE composites processed on the mixer; (T/LLDPE-C1C) C1C filled LLDPE composites processed on the mixer; (T/LLDPE-C2) C2 filled LLDPE composites processed on the mixer; (T/LLDPE-C2C) C2C filled LLDPE composites processed on the mixer; (E/LLDPE) Reference sample (100% LLDPE) processed on the extruder; (E/LLDPE-C1) C1 filled LLDPE composites processed on the extruder; (E/LLDPE-C1C) C1C filled LLDPE composites processed on the extruder; (E/LLDPE-C2) C2

filled LLDPE composites processed on the extruder; and (E/LLDPE-C2C) C2C filled LLDPE composites processed on the extruder.

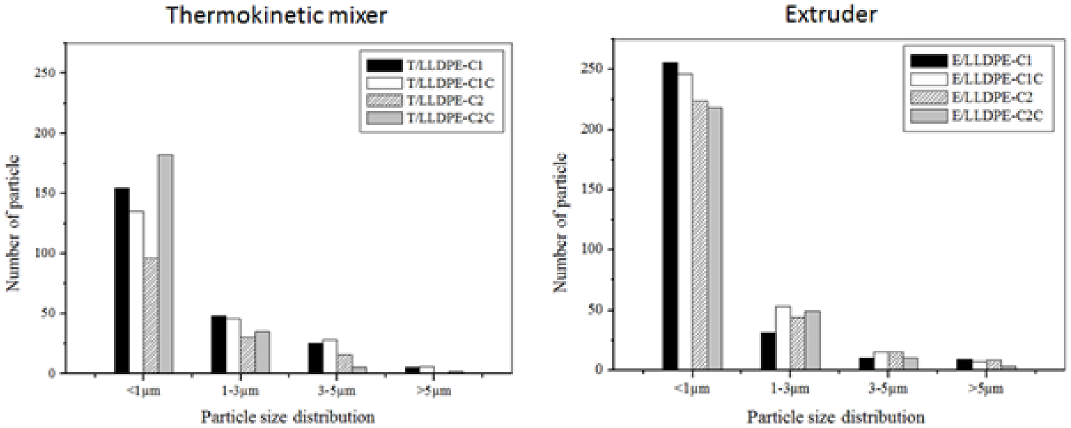

Figure 3. Particle size distribution of $CaCO_3$ in the LLDPE/$CaCO_3$ (60/40 w/w) composites prepared on the thermo kinetic mixer and twin-screw extruder.

3.2. Melt flow index (MFI)

MFI values of LLDPE/$CaCO_3$ 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 $CaCO_3$ (C2) delivered the largest MFI value being 1.37 g/10min in all composites prepared on the mixer.

Table 2. MFI values of LLDPE/$CaCO_3$ composites generated on the mixer and twin-screw extruder.

Notation	MFI (g/10min)
T-LLDPE	1.52
T/LLDPE-C1	1.21
T/LLDPE-C1C	1.05
T/LLDPE-C2	1.37
T/LLDPE-C2C	0.97
E-LLDPE	1.59
E/LLDPE-C1	1.10
E/LLDPE-C1C	1.22
E/LLDPE-C2	1.20
E/LLDPE-C2C	1.26

Considering processing on the mixer MFI values of polyethylene/calcium carbonate composites containing uncoated $CaCO_3$ decreased when coated CaCO3 was added into the polymer matrix instead of the uncoated one (MFIT/LLDPE-C1: 1.21 g/10min, MFIT/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 (MFIE/LLDPE-C1: 1.10 g/10min, MFIE/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 $CaCO_3$ 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.%.

Table 3. The amount of $CaCO_3$ in LLDPE/$CaCO_3$ composites prepared on the mixer and twin-screw extruder.

Notation	$CaCO_3$ (w/w%)
T/LLDPE-C1	40
T/LLDPE-C1C	43
T/LLDPE-C2	39
T/LLDPE-C2C	44
E/LLDPE-C1	41
E/LLDPE-C1C	39
E/LLDPE-C2	39
E/LLDPE-C2C	42

The DSC curves of the neat LLDPE (T-LLDPE and E-LLDPE) and the LLDPE/$CaCO_3$ composites are depicted in Figure 4, and their corresponding thermal behavior parameters such as melting temperature (T_m), crystallization temperature (Tc), and degree of crystallinity (χ_c) are listed in Table 4.

According to DSC results, T_m 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 $CaCO_3$. Similar variation was observed for crystallization temperatures as well. Addition of uncoated/coated $CaCO_3$ to the neat LLDPE led to an increase in Tc 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 (χc) 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.

Table 4. Thermal behavior of LLDPE/$CaCO_3$ composites generated on the thermo kinetic mixer and twin-screw extruder.

Notation	T_m (°C)	T_c (°C)	χ_c (%)
T/LLDPE	119.3	106.1	18.3
T/LLDPE-C1	123.0	110.3	8.1
T/LLDPE-C1C	123.3	109.8	14.5
T/LLDPE-C2	122.6	111.2	11.7
T/LLDPE-C2C	122.8	111.2	12.7
E-LLDPE	118.9	104.2	24.1
E/LLDPE-C1	123.2	108.0	12.2
E/LLDPE-C1C	123.0	107.0	12.6
E/LLDPE-C2	125.0	109.7	12.2
E/LLDPE-C2C	122.7	109.5	12.4

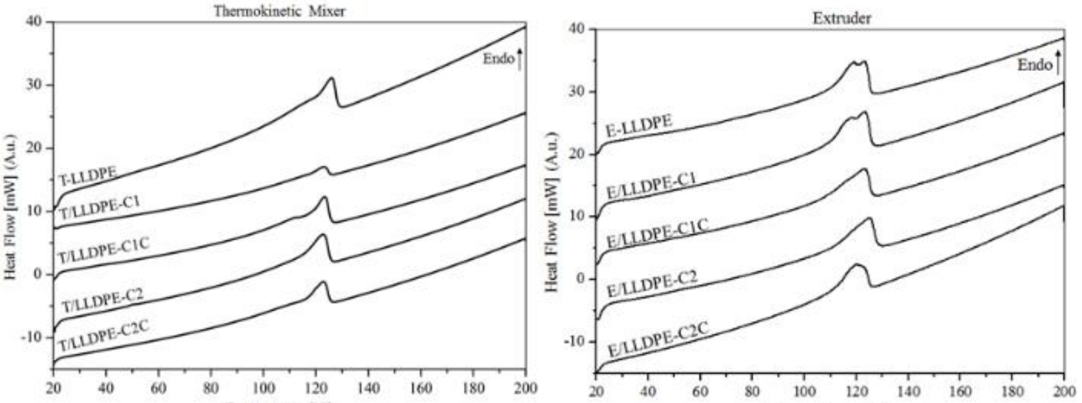

Figure 4 DSC curves of the neat LLDPE and LLDPE/$CaCO_3$ composites generated on the thermo kinetic mixer and twin screw extruder.

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 (χ_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.

The degrees of crystallinity of LLDPE/$CaCO_3$ composites prepared by the mixing method scattered in a wide range by showing and 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

$CaCO_3$ particle sizes. It was shown that the composites produced by melt extrusion have more number of $CaCO_3$ 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 $CaCO_3$ 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/$CaCO_3$ 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.

References

AŞ, Aydın Madencilik, AY103 Technical Datasheet, Bursa, Turkey, 2012.

AŞ, Mikron's, KK1 Technical Datasheet, Nigde, Turkey, 2012.

Atkinson, C., Richardson, M.T., 1969. Thermodynamic Properties of Ideally Crystalline Polyethylene. Transactions of the Faraday Society, 65, 1764-1773.

Baker W, Patel P, Catani A. SPE ANTEC Proceedings, 1986, 32, 1205.

Bravo VL, Hrymak AN, Wright J.D., 2004. Study of Particle Trajectories, Residence Times and Flow Behavior in Kneading Discs of Intermeshing Co-Rotating Twin-Screw Extruders. Polymer Engineering & Science, 44, 779-793.

Brough, C., McGinity, J.W., Miller, D.A., DiNunzio, J., Williams, R.O., US Patent 8486423 B2, 2013.

Busigin, C., Lahtinen, R., Martinez, G.M., Thomas, G., Woodhams, R.T., 1984. The properties of mica-filled polypropylenes. Polymer Engineering & Science, 24, 169-174.

Demjén, Z., Pukánszky, B., Nagy, J., 1998. Evaluation of Interfacial Interaction in Polypropylene/Surface Treated CaCO3 Composites. Composites Part A: Applied Science and Manufacturing, 29, 323-329.

Dole, M., Hettinger, Jr. W.P., Larson, N.R., Wethington, Jr. J.A., 1952. Specific Heat of Synthetic High Polymers. I. A Study of Polyethylene Including a Statistical Theory of Crystallite Length. The Journal of Chemical Physics, 20, 781-790.

Fu, S.Y., Lauke, B., 1998. Characterization of Tensile Behaviour of Hybrid Short Glass Fibre/Calcite Particle/ABS Composites. Composites Part A: Applied Science and Manufacturing, 29, 575-583.

Fu, S.Y., Lauke, B., 1998. Fracture Resistance of Unfilled and Calcite-Particle-Filled ABS Composites Reinforced by Short Glass Fibers (SGF) Under Impact Load. Composites Part A: Applied Science and Manufacturing, 29, 631-641.

Gao, W., Ma, X., Liu, Y., Wang, Z., Zhu, Y., 2013. Effect of Calcium Carbonate on PET Physical Properties and Thermal Stability Powder Technology, 244, 45-51.

Garcia, F., Bolay, N., Le Frances, C., 2002. Changes of Surface and Volume Properties of Calcite During A Batch Wet Grinding Process. Chemical Engineering Journal, 85, 177-187.

Ghalia, M.A., Hassan, A., Yussuf, A., 2011. Mechanical and Thermal Properties of Calcium Carbonate-Filled PP/LLDPE Composite. Journal of Applied Polymer Science, 21, 2413-2421.

Good, E., Brough, C., Taylor, J., Rice, D., Little, D., Patent CA 2417382 C, 2009.

Gopakumar, T.G., Pagè, D.J.Y.S., 2004. Polypropylene/Graphite Nanocomposites by Thermo-Kinetic Mixing. Polymer Engineering & Science, 44, 1162–1169.

Gopakumar, T.G., Pagè, D.J.Y.S., 2005. Compounding of Nanocomposites by Thermo kinetic Mixing. Journal of Applied Polymer Science, 96, 1557-1563.

Jancar, J., 1999. Mineral Fillers in Thermoplastics-I Raw Materials, Processing and I, Springer, Berlin.

Kao, Y.H., Phillips, P.J., 1986. Crystallinity in Chemically Crosslinked Low Density Polyethylenes: 1. Structural and Fusion Studies. Polymer, 27, 1669-1678.

Karger-Kocsis, J., 1995. Polypropylene: Structure, Blends and Composites, Chapman and Hall, London.

Kong, Y., Hay, J.N., 2003. The Enthalpy of Fusion and Degree of Crystallinity of Polymers As Measured by DSC. European Polymer Journal, 39, 1721-1727.

Krehula, L.K., Sirocic, A.P., Katancic, Z., Jelencic, J., Kovacevic, V., Hrnjak-Murgic, Z., 2012. Influence of Calcium Carbonate Filler and Mixing Type Process on Structure and Properties of Styrene-

Acrylonitrile/Ethylene-Propylene-Diene Polymer Blends. Journal of Applied Polymer Science, 126, 1257-1266.

La Mantia, F.P., Morreale, M., Scaffaro R., Tulone, S., 2013. Rheological and Mechanical Behavior of LDPE/Calcium Carbonate Nanocomposites and Microcomposites. Journal of Applied Polymer Science, 127, 2544-2552.

Leong, Y.W., Abu Bakar, M.B., Mohd Ishak, Z.A., Ariffin, A., Pukanszky, B., 2004. Comparison of the Mechanical Properties and Interfacial Interactions between Talc, Kaolin, and Calcium Carbonate Filled Polypropylene Composites. Journal of Applied Polymer Science, 91, 3315-3326.

Liang, J.Z., Duan, D.R., Tang, C.Y., Tsui, C.P., Chen, D.Z., 2013. Tensile Properties of PLLA/PCL Composites Filled with Nanometer Calcium Carbonate. Polymer Testing, 32, 617-621.

Little, D., Good, E., Brough, C., Taylor, J., Rice, D., EP Patent 1365853 B1, 2006.

Little, D., Rice, D., US Patent 6709146 B1, 2004.

Liu, Z., Yu, R., Yang, M., Feng, J., Yang, W., Yin, B., 2008. A Novel Approach in Preparing Polymer/Nano-CaCO3 Composites. Frontiers of Chemical Engineering in China, 2, 115-122.

Lyons, D., Baker, W.E., 1990. Dynamics of a High Speed Melter/Mixer. International Polymer Processing, 2, 136-141.

Martel, S., Murphy, S., WO Patent 2014063254 A1, 2014.

Mathot VBF. Polymer 1984, 25, 579-599.

Nowaczyk, G., Głowinkowski, S., Jurga, S., 2004. Rheological and NMR Studies of Polyethylene/CalciumCarbonate Composites. Solid State Nucl. Mag., 25, 194-199.

Osman, M.A., Atallah, A., Suter, U.W., 2004. Influence of Excessive Filler Coating On the Tensile Properties of LDPE–Calcium Carbonate Composites. Polymer, 45, 1177-1183.

Özen, İ., İnceoğlu, F., Acatay, K., Menceloğlu, Y.Z., 2012. Comparison of Melt Extrusion and Thermo kinetic Mixing Methods in Poly (Ethylene-Terephthalate) / montmorillonite Nanocomposites. Polymer Engineering & Science, 52, 1537-1547.

Özen, İ., Şimşek, S., 2015. Vital Importance of Moisture Level in All Stages of Processing From Calcium Carbonate Coating Through Polyethylene/Calcium Carbonate Compounding to Film Generation. Powder Technology, 270, 320-328.

Quinn Jr F, Mandelkern L., 1958. Thermodynamics of Crystallization in High Polymers: Poly-(ethylene). Journal of the American Chemical Society, 80, 3178-3182.

Richardson, M.J., 1972 Precision Differential Calorimetry and the Heat of Fusion of Polyethylene. Journal of Polymer Science Part C: Polymer Symposia, 38, 251-259.

Rothon, R.N., 2003. Particulate-Filled Polymer Composites, 2nd ed., iSmithers Rapra Publishing, Shawbury.

Sahin, A., Karsli, N.G., Sinmazcelik, T., 2015. Comparison of the Mechanical, Thermomechanical, Thermal, and Morphological Properties of Pumice and Calcium Carbonate-Filled Poly(Phenylene Sulphide) Composites. Polymer Composites, doi: 10.1002/pc.23513.

Şirin, K., Doğan, F., Balcan, M., Kaya, İ., 2009. Effect of CaCO3 Filler Component on Solid State Decomposition Kinetic of PP/LDPE/CaCO3 Composites. Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 46, 949-958.

Suwanprateeb, J., 2000. Calcium Carbonate Filled Polyethylene: Correlation of Hardness and Yield Stress. Composites Part A: Applied Science and Manufacturing, 31, 353-359.

Wang, G., Chen, X.Y., Huang, R., 2002. Nano-CaCO3/Polypropylene Composites Made with Ultra-High-Speed Mixer. Journal of Materials Science Letters, 21, 985–986.

Web page: http://www.ima-eu.org/fileadmin/downloads/publications/factsheets/Calcium_Carbonate_Mineral_ Factsheet_ EN_.pdf.

Wunderlich, B., Cormier, C.M., 1967. Heat of Fusion of Polyethylene. Journal of Polymer Science Part A-2: Polymer Physics, 5, 987-988.

Wunderlich, B., Dole, M., 1957. Specific heat of synthetic high polymers. VIII. Low pressure polyethylene. Journal of Polymer Science, 24, 201-213.

Zhu, Y.D., Allen, G.C., Jones, P.G., Adams, J.M., Gittins, D.I., Heard, P.J., Skuse, D.R., 2014. Dispersion characterisation of CaCO3 particles in PP/CaCO3 composites. Composites Part A: Applied Science and Manufacturing, 60, 38-43.

Zuiderduin, W.C.J., Westzaan, C., Huétink, J., Gaymans, R.J., 2003. Toughening of Polypropylene with Calcium Carbonate Particles. Polymer, 44, 261-275.