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Characterizing CaCO₃ particle dispersion in blown film

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Abstract

A novel method for the visualization and quantification of the state of dispersion of calcium carbonate particles in thin blown polymer films is described. Particle imaging was achieved by elemental mapping using energy dispersive spectroscopy. This generated outlines of particles and agglomerates located close to the film surface. ImageJ software facilitated the extraction of the corresponding Feret diameters. Finally, the Bootstrap technique was used to estimate confidence intervals for the kurtosis of the Feret particle size distribution. Kurtosis is a statistic that describes the shape of a distribution's tails in relation to its overall shape. It therefore provides a measure that characterizes the degree of particle agglomeration. The proposed procedure was applied to analyze high-density polyethylene films prepared using different calcium carbonate masterbatches in which formulation parameters were varied.

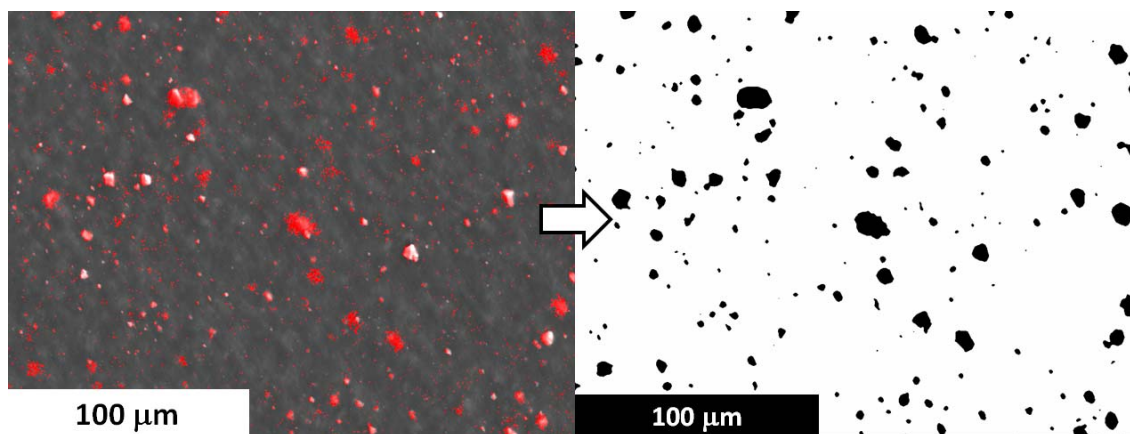
Keywords: Calcium carbonate; filler; agglomeration; imaging; kurtosis

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Graphical abstract



Visualizing the presence of calcium carbonate particle agglomerates in a thin plastic film using scanning electron microscopy (SEM) and elemental composition mapping with energy dispersive spectroscopy (EDS). Ferret diameter distribution determined using ImageJ data processing and Bootstrap-based statistical analysis.

1 Introduction

Calcium carbonate (CaCO_3) is a major-use low-cost functional filler for polyolefins. It decreases the overall material cost [1] while improving both the processing behavior [2] and the physical properties of the polymer [3, 4]. In molded structural components, its use reduces part shrinkage while improving the strength, stiffness, heat deflection temperature and, in some cases, even the impact strength [2, 5]. In extrusion-based applications, the calcium carbonate is incorporated into the final product via masterbatches which are dosed during the final conversion processes. For example, calcium carbonate is used as an extender in blown polyethylene film and in the extrusion of polypropylene tapes. In both cases cost reduction is a factor but in the latter case the filler also reduces the tendency of the tape to fibrillate.

For best performance, it is essential that the filler particles are individually and homogeneously dispersed in the polymer matrix of the final product. Unfortunately, due to the polar nature of the surface, calcium carbonate particles are prone to agglomerate [6]. Unless these structures are not broken down and removed, there will be unwanted consequences [7]. These include increased melt viscosities, reduced mechanical properties [8] and undesirable optical effects. Consequently, it is common practice to employ stearic acid-coated calcium carbonate fillers. This type of surface modification renders the surface hydrophobic and facilitates the

breakdown of particle agglomerates [7] and aids in the dispersion of individual particles within the polymer matrix [9-12]. The stearic acid coating also improves the compatibility of the fillers with non-polar polymers, e.g. linear low-density polyethylene (LLDPE). This reduces the shear forces required for disintegrating agglomerates and the dispersion of the individual filler particles during the compounding process [13].

Commercial calcium carbonate masterbatches usually contain very high loadings of the filler. This means that the formulations must include waxes and lubricants as processing aids. They help reduce the melt viscosity and contribute to effective filler dispersion. In practice, polyethylene wax [14] is commonly used but in this investigation a Fischer-Tropsch (F-T) wax was also considered. Waxes are long-chain hydrocarbons that typically lack functional groups. Compared to the polyethylene wax, the F-T waxes feature much shorter chains.

Metal soap-based processing additives are also used in the manufacture of polyethylene-based CaCO_3 masterbatches [15]. Zinc stearate and calcium stearate appear to be in common use [10]. During polymer compounding and processing, the metal stearates act as internal and external lubricants [10, 16]. It is believed that, together with the wax, they also assist with filler dispersion. They also function as external lubricants by forming a thin low-viscosity layer at the interface between the molten polymer and the metal surfaces of the polymer processing equipment. Calcium-, magnesium- and zinc stearate were considered as lubricants in this study. Mixtures of the latter with the former two metal stearates were also investigated. The lower melting temperatures of the blends allows for early wetting of the filler particles and also for reduced melt viscosities of calcium carbonate-filled polyethylene compounds [17].

Based on previous results [17], and information provided informally by a local masterbatch compounder, the effects of wax and metal stearate addition were examined at fixed loading levels of 3.0 wt-% and 1.0 wt-% respectively. Only the nature of these additives was varied. The effects of the presence or absence of a stearic acid coatings on the CaCO_3 , its particle size distribution, as well as the filler loading on masterbatch properties were investigated. High-density polyethylene (HDPE) films containing 5.0 wt-% of the LLDPE-based CaCO_3 masterbatch, on an add-on basis, were blown.

However, the primary purpose of this study was to develop a method that could reveal, and lead to the quantification of, the state of dispersion of the filler particles in polymer films.

Towards this goal, the suitability of a technique employing scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) was explored. This novel method is illustrated using the blown HDPE films described above. The proposed method could provide a useful tool for future optimization of calcium carbonate masterbatch formulations.

2 Materials and methods

2.1 Materials

Technical grade magnesium stearate [CAS No. 557-04-0] was purchased from Sigma-Aldrich. Sun Ace (South Africa) supplied commercial grades of calcium stearate (SAK-CS) [CAS no. 1592-23-0] and zinc stearate (SAK-ZS-TGF) [CAS no. 557-05-1]. The polyethylene wax (PE wax) used was a grade that is widely used in the local South African polymer compounding industry. Sasol (South Africa) supplied an experimental Fischer-Tropsch wax (F-T wax) for evaluation. Sasol also provided samples of linear low-density polyethylene (LLDPE) grade HM2420. The density of this masterbatch grade was $924 \text{ kg}\cdot\text{m}^{-3}$ and the Melt Index was 20 g/10 min @ 190 °C/2.16 kg. This material was milled into a powder ($< 400 \text{ }\mu\text{m}$) by Dream Weaver (Pty) Ltd. (South Africa). It was employed as the sole masterbatch carrier polymer in the present study. Safripol supplied HDPE Safrene M9255 F. The density of this film blowing grade was $953 \text{ kg}\cdot\text{m}^{-3}$ and the Melt Index was 0.3 g/10 min @ 190 °C/5 kg. Serina (South Africa) supplied calcium carbonate grade Ascom 50 T. According to the supplier, the mean particle size was $2.2 \text{ }\mu\text{m}$ with a stearic coating of 1.1 % on a weight basis. Idwala Holdings (South Africa) supplied a range of calcium carbonate powders of different nominal particle size.

2.2 Methods

Particle size distributions (PSD) of the neat CaCO_3 fillers were determined on a Malvern Mastersizer 3000. Proper dispersion of the powder particles was ensured with a Malvern LV Hydro. The ultrasound setting was 80 % and the shear mixer was set at 3500 rpm. The reported volume fraction-based distributions represent the average of five measurements. Single point BET surface area measurements were conducted on a Micromeritics Flowsorb II 2300 instrument.

Powder particle imaging was done as follows. Small quantities of the fillers were placed onto separated carbon tape on a metal sample holder. Excess powder was removed using a single

compressed air blast. The samples were rendered conductive with carbon using a Polaron E5200 coater. The samples were viewed on a JEOL 840 scanning electron microscope (SEM) at an accelerating voltage of 2 kV.

Table 1. Masterbatch formulations

Campaign and effect explored	Filler type (μm)	Filler (wt-%)	Wax	Lubricant
Filler loading and wax type	2 (C1)	30.0	F-T	Zn St
	2 (C1)	40.0	F-T	Zn St
	2 (C1)	50.0	F-T	Zn St
	2 (C1)	60.0	F-T	Zn St
	2 (C1)	70.0	F-T	Zn St
	2 (C1)	30.0	PE	Zn St
	2 (C1)	40.0	PE	Zn St
	2 (C1)	50.0	PE	Zn St
	2 (C1)	60.0	PE	Zn St
	2 (C1)	70.0	PE	Zn St
Filler coating on 2 μm powders	2	60.0	None	None
	2 (C2)	60.0	None	None
	2 (C2)	60.0	F-T	Zn St
	2 (C2)	60.0	PE	Zn St
	2	60.0	F-T	Ca St
Lubricant nature	2 (C2)	60.0	PE	Ca St
	2 (C2)	70.0	F-T	Ca St
	2 (C2)	70.0	F-T	Mg St
	2 (C2)	70.0	F-T	Zn St
	2 (C2)	70.0	F-T	Ca St:Zn St = 2:3
Filler particle size	2	70.0	F-T	Mg St:Zn St = 2:3
	2	60.0	F-T	Ca St
	5	60.0	F-T	Ca St
	10	60.0	F-T	Ca St
	15	60.0	F-T	Ca St
	2(C1):15 = 3:17	60.0	F-T	Ca St

The masterbatches formulated in this research are presented in Table 1. The experiments took the form of four separate compounding campaigns. These were planned in order to study the influence of masterbatch formulation parameters on the degree of filler particle dispersion in blown HDPE films. The first campaign explored the effects of filler loading and the type of wax employed. The second evaluated the importance of the stearic acid coating on the CaCO_3 particles. The third considered the effect that the nature of the metal stearate lubricant may have. According to Suetsugu, White and Kyu [11], smaller particles have a greater propensity

for agglomerating due to the larger surface area-to-volume ratio. Therefore, the fourth campaign evaluated the effect of filler particle size.

Details, relating to the mixing and compounding of the sample masterbatches were reported elsewhere [18]. In summary, the constituent powders were weighed out and mixed in a dry-shear dry-dispersion high-speed mixer before compounding on a corotating twin-screw laboratory extruder and pelletizing. After drying the pellets overnight, the compounding step was repeated. This exhaustive mixing approach was taken to ensure the disintegration of any agglomerates and the individual dispersion of the filler particles in the polymer matrix.

HDPE films, containing calcium carbonate filler, were prepared on a Collin BL 180/400 unit. This film blowing line comprised a 30 mm ϕ single screw extruder with an L/D ratio of 25. The diameter of the annular die was 60 mm. It featured a dual-lip cooling ring. The extruder was operated at a screw speed of 70 rpm. The temperature profile, from hopper to die, was set at 190/190/195/195/195/195/220/220 °C.

Two kg of the HDPE film grade pellets was weighed out. To this was added 100 g of the selected CaCO₃ masterbatch pellets, equivalent to an addition rate of 5 wt-%. The mixture was tumble-mixed before filling into the hopper of the extruder. Efforts were made to blow films as thin as possible but this was not always possible. In some cases, a film thickness of about 10 μm was achieved. However, for the most highly filled masterbatches, the film thicknesses reached 45 μm . Five pieces of film, widely separated in distance along the extruded tube, were cut and subjected to characterization by scanning electron microscopy.

Filler particle dispersion in the HDPE films was investigated as follows. A Zeiss Supra 55 V P Field Emission Gun SEM, fitted with an Oxford energy dispersive spectroscopy (EDS) system, was used to record elemental maps of Ca revealing the size and distribution of the calcium carbonate residues in the HDPE films. The analysis of the carbon-coated outer surface of the polymer films was performed side-on, at 25 kV and collecting 300k counts for quantitative EDS spectra, and over 500k for each X-ray map. The choice of such high accelerating voltage aimed to probe the polymer film to an approximate maximum depth of 6.5 μm [19]. To ensure statistical robustness, elemental maps were collected in triplicate from different regions of each of five samples from each treatment. Calibrated images were analyzed using ImageJ [20].

Images were segmented (Image > Adjust > Color Segmentation) using the default setting in the Color Thresholding RGB (ticking red channel only and "Dark Background" options). The threshold areas were "Selected" in the Threshold Color Panel, the image was converted to a binary image (Process > Binary > Make Binary), the "Fill holes" algorithm was applied (Process > Binary > Fill Holes), followed by "Analyze Particles" (Analyze > Analyze Particles), which generated a set of numbered outlines. From this, the Feret diameter was extracted as the measure of the size of the CaCO₃ agglomerates. Particles partially cut-off at the boundary of the images were excluded from the calculation. The results were exported to Excel and analyzed using the bootstrap-kurtosis method for agglomeration and dispersion.

3 Results

Figure 1 shows that the particle size distributions for the different uncoated CaCO₃ powders were multimodal in nature. Table 2 lists the BET surface area and the d₁₀, d₅₀ and d₉₀ volume average particle sizes together with the kurtosis of the various particle size distributions. The filler particles all featured similar irregular shapes as illustrated by the two samples shown in Figure 2.

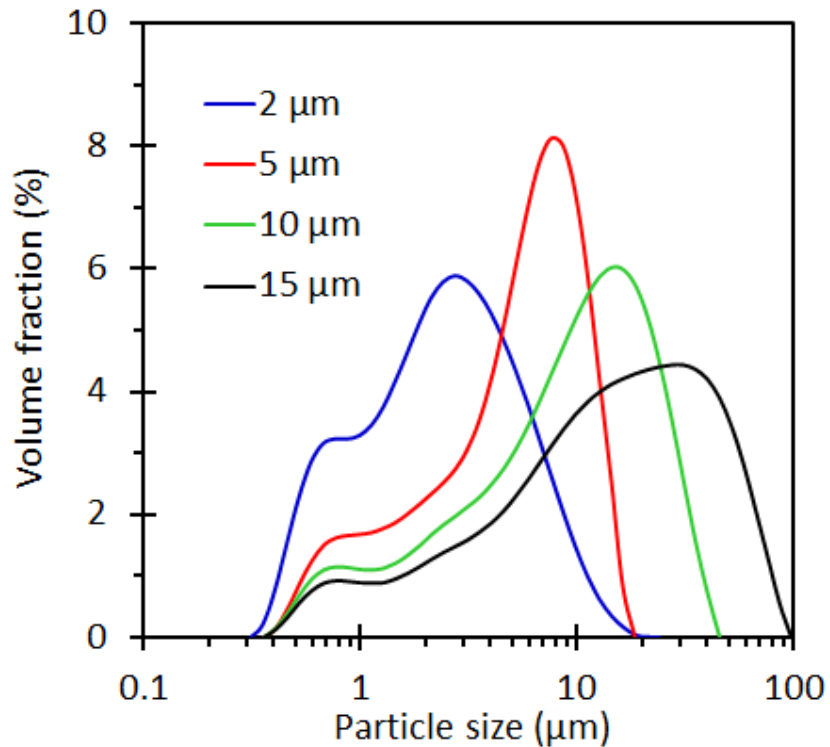


Figure 1. Calcium carbonate particle size distributions.

Table 2. Physical properties of the calcium carbonate powders

Nominal particle size	Particle size (μm)			Kurtosis -	BET surface area $\text{m}^2\cdot\text{g}^{-1}$
	d_{10}	d_{50}	d_{90}		
2 C1 (surface coated)	0.73	2.51	6.93	6.39	2.99 ± 0.03
2 C2 (surface coated)	0.69	2.28	5.23	3.14	2.91 ± 0.03
2	0.66	2.25	6.31	6.21	2.95 ± 0.03
5	1.06	5.40	10.7	2.44	1.46 ± 0.02
10	1.43	9.23	23.0	3.16	0.49 ± 0.03
15	1.82	13.9	46.0	3.77	0.51 ± 0.02

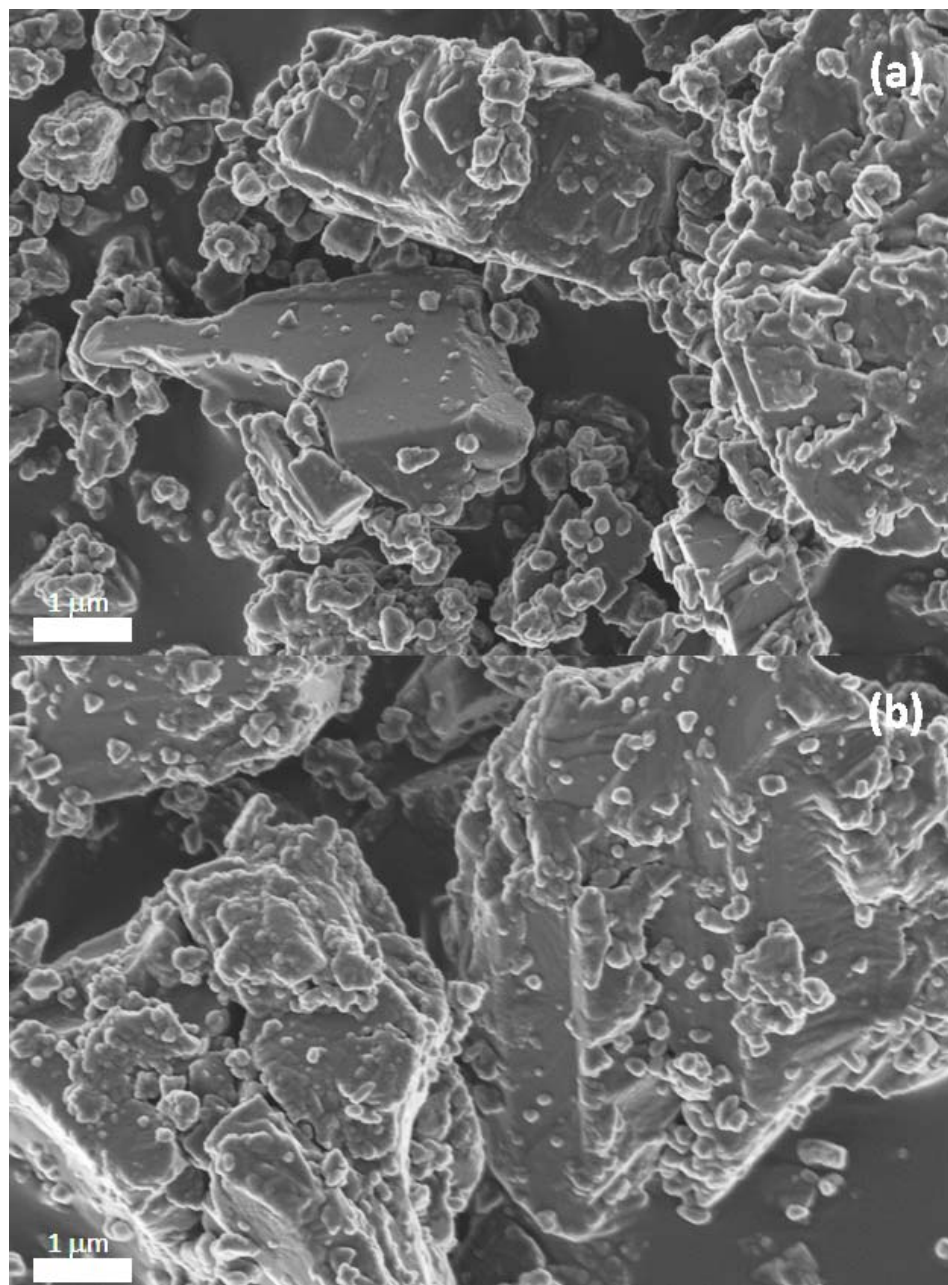


Figure 2. Scanning electron microscope image of uncoated calcium carbonate particles with nominal particle size (a) 2 μm , and (b) 15 μm .

Figure 3 illustrates a typical conversion of an EDS image to a binary black-and-white image. As described in the Experimental Section, ImageJ software was then applied to determine the maximum Feret diameter of each particle present in the image. Figure 4 shows a histogram of Ferret diameters in a typical sample. This distribution resembles an exponential distribution, but only approximately. Note that an agglomerate of a large number of small particles is counted as a single measurement. While such large, agglomerated “particles” are present, their number fraction is very small. Instead, the volume-mean Feret particle size (d_F) was calculated according to equation (6) shown below as it represents a kind of “volume fraction” distribution. In effect, this weighted distribution provides a better visualization of the agglomerates present (Figure 4). The actual particle size distribution of the CaCO_3 filler powder is also shown in Figure 4.

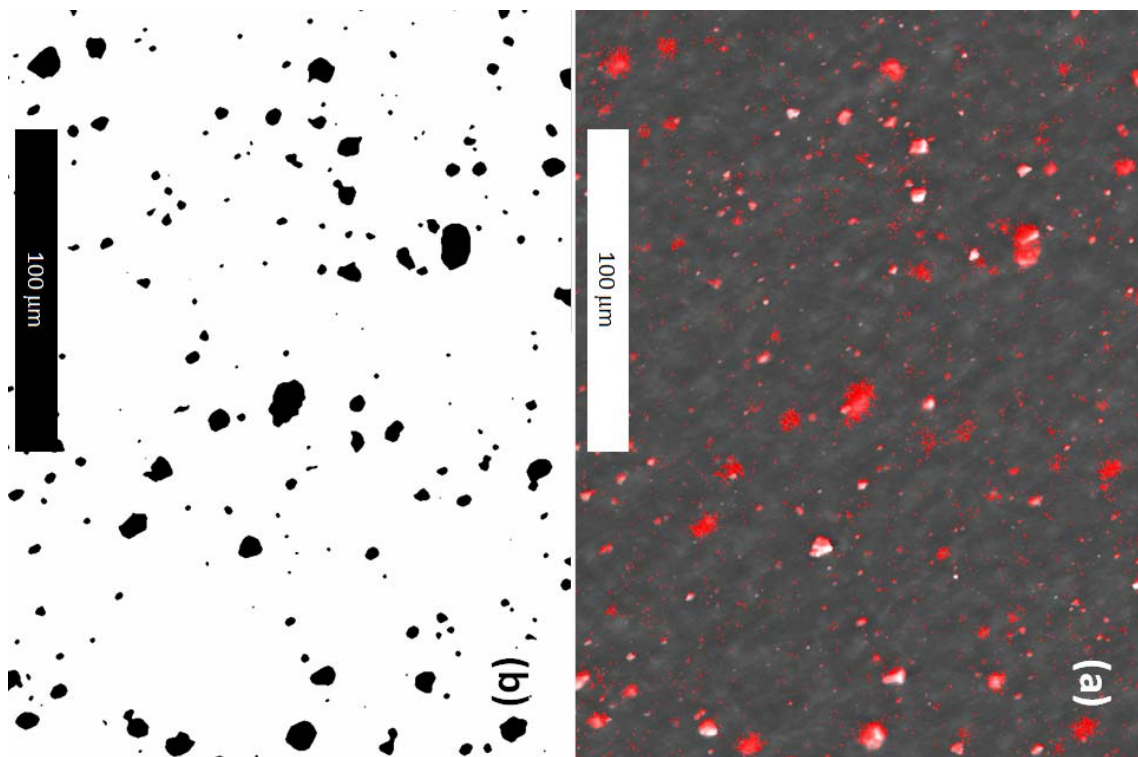


Figure 3. Typical image processing example showing how the EDS map was segmented and a binary mask created before particle Feret diameters were calculated.

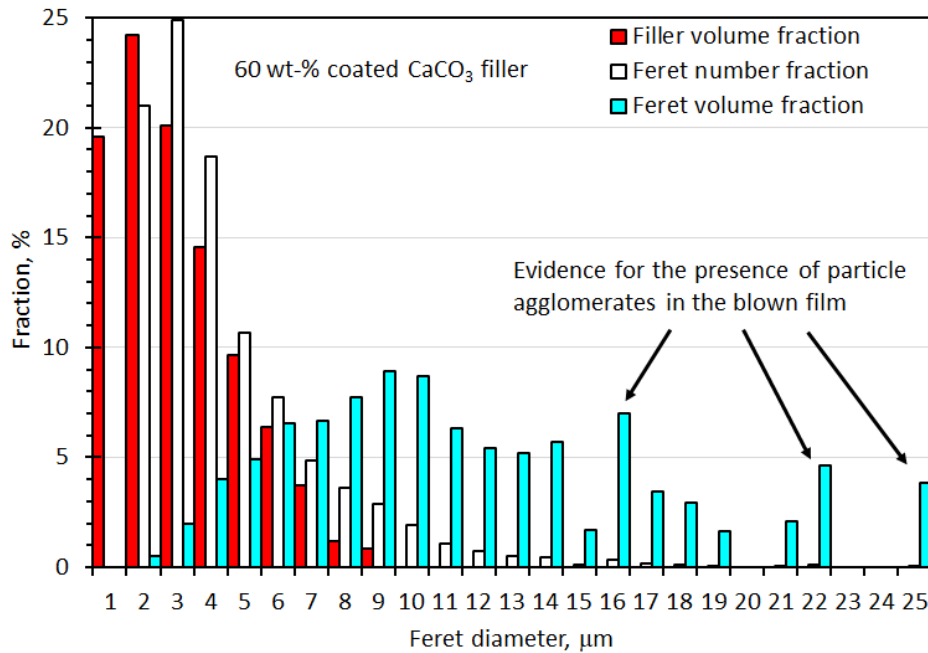


Figure 4. Typical particle size distributions. This particular one was obtained from a film prepared from a 60 wt-% masterbatch that contained only the 2 μm (C2) coated calcium carbonate, i.e. no wax nor metal stearate was present in the masterbatch.

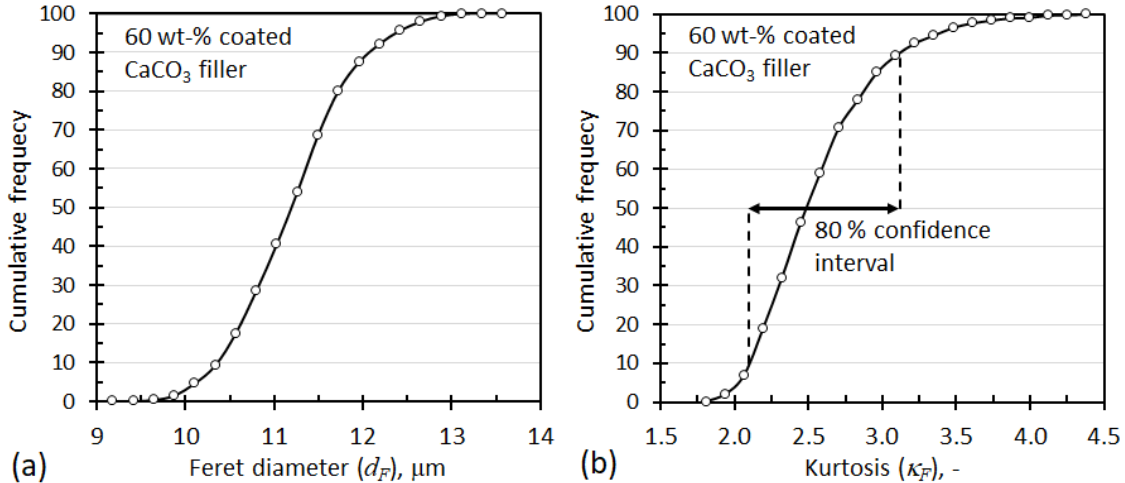


Figure 5. Bootstrap-generated distributions for the Feret volume mean diameter and the kurtosis of the corresponding distribution. These samples were obtained for the film prepared from a 60 wt-% masterbatch that contained only the 2 μm (C2) coated calcium carbonate, i.e. neither a wax nor a metal stearate were present in the masterbatch.

The larger agglomerates cause the distribution to have a “tail” that extends to larger diameters. In effect, the large agglomerates represent outliers with much larger diameters

than the actual particles present. The kurtosis of a statistical distribution provides a quantitative measure for the presence of such outliers. Therefore, it represents a statistic, i.e. a measure for the state of agglomeration of particles in a system. The following expressions were used to calculate the volume average Feret mean particle size (d_F), the standard deviation (s_F) and the kurtosis (κ_F):

$$d_F = \sum d_i^4 / \sum d_i^3 \quad (6)$$

$$s_F^2 = \sum d_i^3 (d_i - d_F)^2 / \sum d_i^3 \quad (7)$$

$$\kappa_F = \sum d_i^3 [(d_i - d_F) / s_F]^4 / \sum d_i^3 \quad (8)$$

Bootstrap was used to generate sample distributions that facilitated the estimation of confidence intervals for these parameters. The list of experimentally obtained Feret diameters were duplicated using a random sampling-with-replacement approach. This was repeated 697 times. The values of d_F , s_F and the kurtosis κ_F were then calculated for each of these resampled data sets and used to construct the corresponding mean parameter distributions. These, in turn, were used to determine 80 % confidence intervals for the volume-mean Feret diameter d_F and the kurtosis κ_F . The procedure is graphically illustrated in Figure 5 (b).

Figure 6 summarizes the effect of different formulation ingredients and the filler loading level on the estimated kurtosis values. There appear to be slight variations but (surprisingly!) the differences are not statistically significant at the 80 % confidence level. The implication is that the different masterbatch formulations delivered similar levels of calcium carbonate particle dispersion in the HDPE films. A plausible explanation for this unexpected result is the effect of the robust compounding process that was employed. It could be that the double-compounding approach was particularly efficient in generating masterbatches in which ultimate particle dispersion was achieved irrespective of the presence of the adjuncts (wax or lubricant).

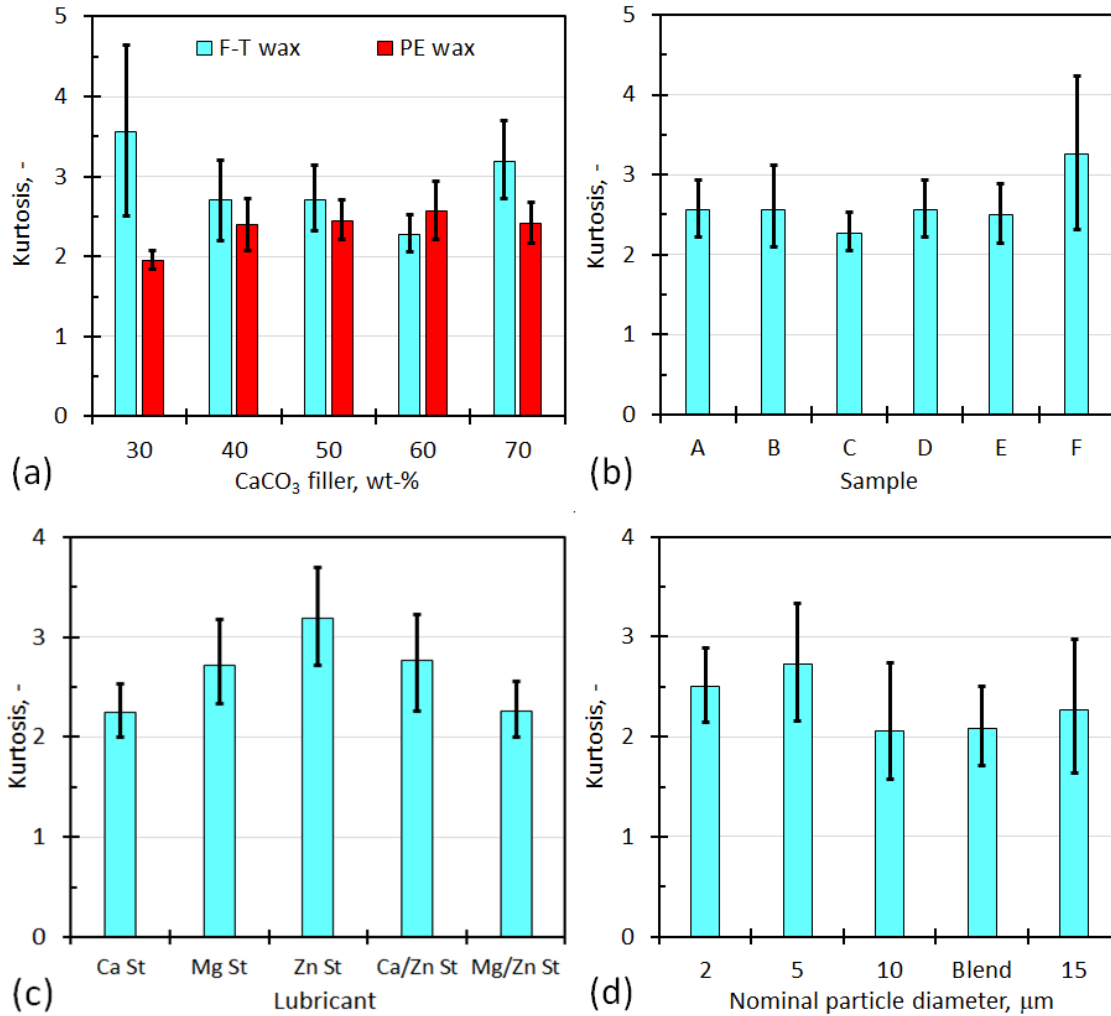


Figure 6. Effect of various formulation parameters on the estimated kurtosis values. (a) Effect of stearic acid coated (C1) CaCO_3 loading: The masterbatches contained 3 wt-% wax and 1 wt-% zinc stearate. (b) Formulations containing 60 wt-% filler with a nominal diameter 2 μm : A - uncoated filler only. B – stearic acid coated filler. C – Coated filler, 3 wt-% F-T wax and 1 wt-% Zinc stearate. D - as for C but replaced F-t wax with PE wax. E – Uncoated filler, 3 wt-% F-T wax and 1 wt-% calcium stearate. F - Coated filler, 3 wt-% PE wax and 1 wt-% calcium stearate. (c) Effect of the lubricant nature on formulations containing 70 wt-% coated CaCO_3 , 3 wt-% F-T wax and 1.0 wt-% metal stearate as lubricant. (d) Effect of filler particle size. All these formulations contained 60 wt-% uncoated filler, 3 wt-% F-T wax and 1.0 wt-% calcium stearate.

4 Conclusions

A novel method for characterizing the state of dispersion of calcium carbonate particles in thin polyethylene films was developed. It is based on elemental composition mapping using scanning electron microscopy with energy dispersive spectroscopy. This probes the polymer

film to an approximate maximum depth of 6.5 μm to yield an image of the particles present near the film surface. Image processing software was used to extract Feret diameters as the measure of the size of the CaCO_3 particles and agglomerates present. Finally, the intrinsic particle size distribution was determined using the Bootstrap method. The estimated value for the kurtosis represents a measure for the degree of particle agglomeration.

The proposed method was applied to HDPE films prepared with a range of different calcium carbonate masterbatches. They were formulated to gauge the effects of particle size, filler stearate surface coating as well as the natures of the wax and metal stearate lubricants on the masterbatch performance. Surprisingly, all of the formulations tested gave statistically similar particle dispersion results. This might be attributable to the aggressive double compounding technique that was employed in the preparation of the masterbatches. This ensured effective breakdown of agglomerates and individual particle dispersion even when using uncoated calcium carbonate and in the absence of any wax or metal stearate as lubricant.

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