

Formulating calcium carbonate masterbatches

Lucky Radebe, James Wesley-Smith, Walter W Focke* and Shatish Ramjee

Abstract

The effects of filler content, filler particle size and surface coating, as well as the natures of the wax and metal stearate lubricants on the properties of calcium carbonate-filled linear low-density polyethylene compounds were investigated. The elongation at break decreased exponentially with filler loading irrespective of whether the filler was surface coated or not. The corresponding decline in the impact strength was more gradual but it dropped abruptly on reaching a filler loading of 70 wt-%. The effect of shear rate on the apparent melt viscosity followed an empirically modified Carreau-Yasuda model which included the effect of filler content. It features the zero-shear viscosity and the flow consistency index as adjustable parameters. These characterize the viscosity trends at low- and high shear rates respectively. In the absence of additives, the melt viscosity at 60 wt-% filler exceeded that of the neat polymer by a factor of three. Adding 3 wt-% wax and 1.0 wt-% zinc stearate returned the melt viscosity to levels just above that of the neat polymer. Calcium stearate and magnesium stearate were less effective at reducing the apparent melt viscosity but a blend of the latter with zinc stearate performed particularly well.

Keywords: Fischer-Tropsch wax; polyethylene, calcium carbonate; masterbatch; rheology

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1 Introduction

Calcium carbonate (CaCO_3) is a low-cost inorganic filler used in polymer compounds [1]. It improves the processing behavior [2] and modifies the physical properties of the polymer [3, 4]. It increases the stiffness and the heat deflection temperature, reduces shrinkage and, in some cases, it even improves the impact strength [2, 5]. Furthermore, the filler helps to improve conversion efficiency [2] as it suppresses melt flow instabilities that lead to melt fracture during extrusion, for example, when converting polyolefins [3]. Consequently, calcium carbonate-filled linear low-density polyethylene masterbatches are widely used. Applications include extrusion of polyethylene film and polypropylene tape. In both cases cost reduction is achieved but in the latter case the filler also reduces the tendency of the tape to fibrillate.

Due to the polar nature of its surface, the filler particles are prone to agglomerate [6] with undesirable consequences [7]. The presence of agglomerates, in effect, decreases the apparent maximum volume fraction of the filler which increases the melt viscosity. This is caused, in part, by the effective solidification of the liquid portion trapped in the interstitial spaces. In the solid material, the agglomerates have a detrimental effect on tensile and impact properties [8]. Surface treatments with suitable dispersants, e.g. stearic acid coatings, reduce the tendency of calcium carbonate particles to agglomerate [7]. They lower the surface energy and thereby facilitate the breakdown of particle agglomerates and the dispersion of individual particles within the polymer matrix [9-12]. The coating renders the surface hydrophobic which 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 dispersion of the individual filler particles during the compounding process [13].

Neat synthetic waxes are long-chain hydrocarbons that typically lack functional groups. They include polyolefin waxes [14] and Fischer-Tropsch (F-T) waxes. The polyolefin waxes are commonly used in the formulation of highly filled calcium carbonate masterbatches. They reduce the melt viscosity and contribute to effective filler dispersion. This study considered the possibility of using a Fischer-Tropsch (F-T) wax as a drop-in replacement for the polyethylene wax commonly used in highly filled CaCO_3 masterbatch formulations. The F-T waxes are short-chain waxes that may help lower the melt viscosity.

Metal soaps are polymer processing additives that are also used in polyethylene [15]. They are important formulation ingredients used in the manufacture of highly-filled CaCO₃ masterbatches. Zinc stearate and calcium stearate are 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 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. In this study, calcium, magnesium and zinc stearates were considered as lubricants on their own. Mixtures of the latter with the former two metal stearates were also investigated. The lower melting temperatures of the metal stearate blends allows for early wetting of the filler particles and also for reduced melt viscosities of calcium carbonate-filled polyethylene compounds [17].

Based on these previous results [17] and information provided informally by a local masterbatch compounder, the effect of wax and metal stearate addition was 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 CaCO₃, its particle size distribution, as well as the filler loading on masterbatch properties were investigated. The results obtained may lead to improved CaCO₃ masterbatch formulations suitable for use in polypropylene tape extrusion or for producing low-cost polyethylene carrier bags. In South Africa, these bags are made from high-density polyethylene (HDPE) extended with calcium carbonate at levels as high as 20 wt-%.

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 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 kg·m⁻³ and the Melt Index was 20 g/10 min @ 190

°C/2.16 kg. This material was milled into a powder (< 400 µm) by Dream Weaver (Pty) Ltd., South Africa.

Table 1 summarizes the molecular mass descriptors for the two waxes and the polymer used in the present study. The molar mass distribution of the F-T wax was determined by Cirrebelle (Randburg, South Africa) using a standard Gas Chromatography (GC) method. Those of the PE wax and the polymer were determined by the Department of Chemistry and Polymer Science, University of Stellenbosch, using size exclusion chromatography (SEC).

Table 1: Number average (Mn), weight average molar mass (Mw) and polydispersity (Q= Mw/Mn) of the waxes and polymers employed.

Polymer/wax	Mn (kDa)	Mw (kDa)	Q (-)
F-T wax	0.776	0.786	1.01
PE wax	4.715	14.96	3.17
LLDPE	23.53	80.73	5.49

Serina (South Africa) supplied calcium carbonate grade Ascom 50 T. According to the supplier, the mean particle size was 2.2 µm with a stearic coating of 1.1 % on a weight basis. Idwala Holdings (South Africa) supplied a range of uncoated calcium carbonate powders of different nominal particle size.

2.2 Mixing and compounding

The masterbatches of this study were prepared in four separate compounding campaigns. These were planned in order to study the influence of the various formulation parameters on the mechanical properties and melt rheology of the filled compounds. 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 CaCO₃ particles. The third campaign evaluated the effect of filler particle size. The fourth considered the effect that the nature of the metal stearate lubricant might have.

Sample batches corresponding to a total mass of 2 kg were prepared. First the required amounts of the various powders were weighed out. They were mixed for one minute in a 20 L laboratory Jones (South Africa) dry-shear dry-dispersion mixer. The well-mixed powder blends were

compounded twice on a CFAM Technologies (South Africa) TX28P 28 mm corotating twin-screw laboratory extruder with L/D =18. The screw segment layout comprised several sets of intermeshing kneader blocks designed to impart a forward transport action. The temperature profile, from hopper to die, was set as follows: 100/180/200/220 °C. The extruder screw speed was varied from 80 to 100 rpm. The exiting strands were cooled in a water bath before pelletizing. The pellets were dried overnight at a temperature of 50 °C before re-compounding at the same conditions. During the first compounding operation, it was noted that the strands had a slightly rough outer surface. However, all the strands exiting during the second compounding operation featured smooth outer surfaces. This was taken as an indication that excellent mixing and dispersion of the filler in the polymer matrix was achieved.

2.3 Characterization

Particle size distributions (PSD) of the neat CaCO₃ 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.

Thermogravimetric analysis (TGA) scans were used to confirm the filler loading in the masterbatches. Samples of ca. 20 mg were placed in open alumina cups. They were analyzed in a TA Instruments SDT Q600 DSC-TGA instrument. Temperature was scanned up to 900 °C at a rate of 10 °C·min⁻¹ with nitrogen flowing at a rate of 20 mL·min⁻¹.

Mechanical properties were evaluated using ASTM D638-14 sub-size dog bone test specimens. These were injection molded on a BOY XS (100-140) machine. The temperature profile from hopper to nozzle was 80/120/150/190 °C. The screw speed was set at 150 rpm and the mound temperature was controlled at 40 °C. The stroke distance was 38 mm and the injection pressure was 80 bar.

The tensile properties were determined on an E-Z 50 LLOYD Instrument tensile machine. The crosshead speed was set 50 mm·min⁻¹ with the gauge length set 3 mm. Impact testing was

conducted on a Zwick impact tester machine fitted with a 4J Hammer. In both cases, the average of five test results are reported.

The melt fluidity of the filled compounds was determined on a Göttfert High Pressure Capillary Rheography 2000 rheometer. The 30 mm long die had a 180° entrance angle and the diameter of the capillary was 1 mm. The rheometer was equipped with a 100 bar pressure sensor and capable of applying shear rates in the range 10 - 20000 s⁻¹. The measurements were made at a temperature of 170 °C.

3 Results and discussion

3.1 Characterization

The particle size distributions of the different uncoated CaCO₃ powders were found to be multimodal in nature. Table 2 lists the D₁₀, D₅₀ and D₉₀ volume average particle sizes together with the BET surface areas.

Table 2: Physical properties of the calcium carbonate powders.

Nominal particle size	Particle size (µm)			BET surface area
	d ₁₀	d ₅₀	d ₉₀	m ² .g ⁻¹
2 C1 (surface coated)	0.73	2.51	6.93	2.99 ± 0.03
2 C2 (surface coated)	0.69	2.28	5.23	2.91 ± 0.03
2	0.66	2.25	6.31	2.95 ± 0.03
5	1.06	5.40	10.7	1.46 ± 0.02
10	1.43	9.23	23.0	0.49 ± 0.03
15	1.82	13.9	46.0	0.51 ± 0.02

The TGA mass loss curves, obtained in a nitrogen atmosphere, featured two major mass loss events. The first major mass loss step, commencing at about 400 °C, corresponds to the degradation and volatilization of the organic components present. The plateau values between 500 °C and 600 °C is indicative of the amount of CaCO₃ present. Above the latter temperature, the filler decarbonates and a second mass loss plateau is reached well below 900 °C. This corresponds to the amount of CaO remaining as residue. These two plateau values were used to confirm the actual filler levels of the masterbatches. In all cases the calculated values agreed to within 2 wt-%. Since the TGA measurements were based on very small samples in the milligram range, this was taken as confirmation that the actual filler levels present in the compounds agreed with the intended loadings.

3.2 Mechanical properties

Figure 1 shows the effect of filler loading level on the measured stress-strain curves of the molded test specimens made from the masterbatch compounds. The stress initially rises linearly with extension before a yield point is reached and sample necking ensues. This leads to a sudden drop in the applied stress. On further extension the stress rises again to a higher value before the sample fails in either a ductile or brittle fashion. As the filler level is increased, the elongation-at-break rapidly decreased from several hundred percent to just a few tens of a percent. The maximum stress before failure exceeded the yield stress for the masterbatches containing 30 wt-% filler. This was not the case for the most highly filled masterbatches.

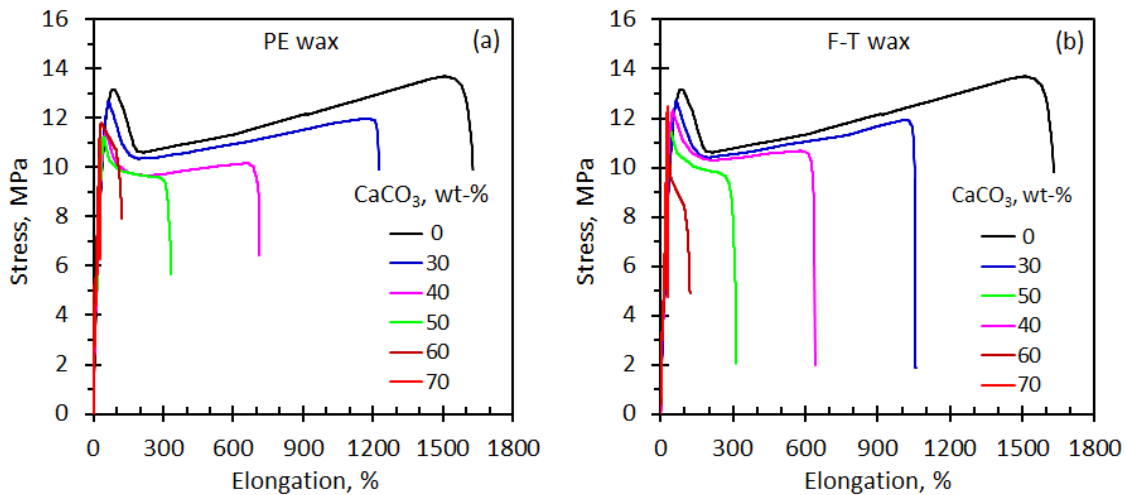


Figure 1. Typical stress-strain curves for masterbatches containing varying filler loadings.

The property values of elongation at break and impact strength are the most important from the perspective of indicating good particle dispersion in a composite [18]. This is because these two properties are most sensitive to the presence of agglomerates as they represent internal flaws that may initiate crack growth. Mechanical property data, for the masterbatches with varying filler loadings, are summarized in Figure 2 and in Table 3. In this campaign, zinc stearate was used as the lubricant. Perusal of these results indicates that comparable mechanical property values were realized for using the two different waxes. The effect of filler content was as follows for both data sets. The tensile strength declined slightly but the elongation at break decreased exponentially with filler content. The stiffness (Young's

modulus) increased while the impact strength decreased more gradually. The 70 wt-% filled samples were the exception as they featured very low impact strengths.

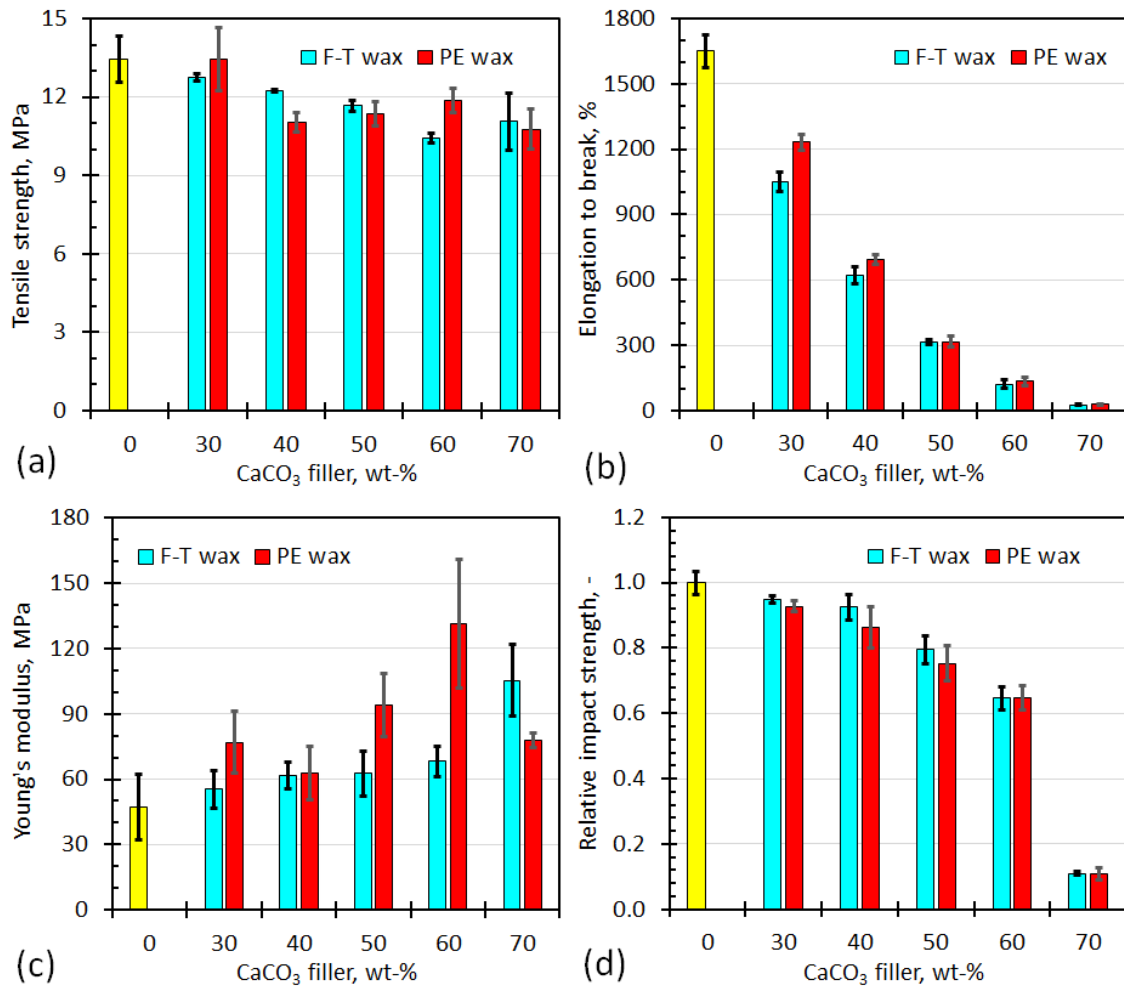


Figure 2. Effect of wax type and filler loading on the mechanical properties of the masterbatch compounds.

Table 3: The effect of filler loading and wax type on mechanical properties of compounds containing 2 μm stearic acid-coated calcium carbonate, 3.0 wt-% wax and 1.0 wt-% zinc stearate as lubricant.

Filler (wt-%) ^a	CaCO ₃ (wt-%) ^b	σ (MPa)	ϵ (%)	E (MPa)	Relative Impact strength
Neat LLDPE		13.4 \pm 0.9	1650 \pm 78	47 \pm 15	1.000 \pm 0.035
F-T wax-based compounds					
30	28.7	12.7 \pm 0.1	1051 \pm 45	55 \pm 9	0.939 \pm 0.012
40	37.8	12.3 \pm 0.1	620 \pm 40	62 \pm 6	0.925 \pm 0.039
50	47.5	11.7 \pm 0.2	316 \pm 11	63 \pm 10	0.794 \pm 0.043
60	56.9	10.4 \pm 0.2	122 \pm 18	68 \pm 7	0.646 \pm 0.034
70	67.1	11.1 \pm 1.1	27 \pm 3	105 \pm 16	0.109 \pm 0.006
PE wax-based compounds					
30	29.6	13.5 \pm 1.2	1233 \pm 37	77 \pm 14	0.927 \pm 0.017
40	34.4	11.0 \pm 0.4	693 \pm 23	63 \pm 12	0.864 \pm 0.021
50	45.8	11.4 \pm 0.5	315 \pm 25	94 \pm 14	0.753 \pm 0.019
60	55.9	11.9 \pm 0.5	134 \pm 21	131 \pm 30	0.647 \pm 0.020
70	66.9	10.8 \pm 0.8	29 \pm 1	78 \pm 3	0.107 \pm 0.014

^a Nominal filler content (wt-%); ^b CaCO₃ estimated from TGA results

Table 4 summarizes the effects of other formulation variables on the mechanical properties of the masterbatches. The effects of filler surface coating and particle size were explored for compounds containing 60 wt-% filler. In the absence of wax and lubricant, the properties obtained for coated and uncoated 2 μm -sized fillers were almost identical. This does not necessarily imply that there is no need for a stearic acid coating. This unexpected outcome might simply mean that the robust double-extrusion compounding procedure which was employed was just particularly effective at breaking down agglomerates and dispersing the individual filler particles in the polymer matrix. Including F-T wax and calcium stearate in the compound based on the uncoated filler did improve the impact strength by almost 60 % but the tensile properties did not change. In contrast, significant improvements in both the impact strength and the elongation at break were realized with the coated filler and zinc stearate as the lubricant.

Table 4: Effect of filler size and surface coating as well as the nature of the lubricant on mechanical properties. When present, the wax and lubricant contents were 3 wt-% and 1 wt-% respectively.

Effect	Filler D50 (μm)	Filler (wt-%)	Wax	Lubricant	σ (MPa)	ε (%)	E (MPa)	Relative Impact strength
Filler surface coating	2	60	None	None	14.1 ± 0.1	56 ± 2	66.2 ± 4.6	0.327 ± 0.062
	2 (coated)		None	None	14.5 ± 0.3	56 ± 1	71.3 ± 7.4	0.351 ± 0.053
	2		F-T	Ca St	12.6 ± 0.1	59 ± 2	66.0 ± 9.4	0.556 ± 0.004
	2 (coated)		F-T	Zn St	10.4 ± 0.2	122 ± 20	68.1 ± 7.8	0.646 ± 0.034
Filler particle size	2	60	F-T	Zn St	12.6 ± 0.1	59 ± 2	66.0 ± 9.4	0.556 ± 0.004
	5		F-T	Zn St	10.3 ± 0.3	126 ± 8	72.1 ± 7.9	0.735 ± 0.018
	10		F-T	Zn St	9.2 ± 0.3	166 ± 8	82.2 ± 13.9	0.525 ± 0.013
	15		F-T	Zn St	9.1 ± 0.3	156 ± 5	75.5 ± 10.6	0.434 ± 0.064
Lubricant nature	2 (coated)	70	F-T	Ca St	10.0 ± 1.3	25 ± 3	82.5 ± 8.3	0.112 ± 0.004
				Mg St	11.0 ± 1.6	27 ± 3	96.3 ± 20.8	0.111 ± 0.009
				Zn St	11.1 ± 1.2	27 ± 3	105.4 ± 18.4	0.109 ± 0.006
				Ca St/Zn St (2:3)	10.8 ± 1.6	26 ± 3	87.0 ± 18.8	0.111 ± 0.009
				MgSt/Zn St (2:3)	11.2 ± 0.7	25 ± 3	79.6 ± 4.7	0.090 ± 0.007

The next set of results listed in Table 4 show the effect of particle size when uncoated filler is used together with the F-T wax and zinc stearate as the lubricant. Here the results paint a rather complex picture which is difficult to rationalize. The elongation at break was least for the 2 μm particle size-based masterbatch. At 59 % this was less than half the value achieved by the other masterbatches. Interestingly, the tensile strength decreased with increase in particle size but the modulus was higher than that found for the uncoated 2 μm filler. Overall, the highest impact strength was obtained with the 5 μm filler and it also featured a high elongation at break.

Table 4 also summarizes the effect of the nature of the lubricant on the mechanical properties. These compounds contained 70 wt-% of the 2 μm stearic-acid coated calcium carbonate as the filler. The results are very similar irrespective of the lubricant employed: In most cases, the observed differences in the mechanical properties were not statistically significant.

3.3 Rheology

The flow curves for neat polymer melts feature a plateau value at low shear rates. This Newtonian-like behavior corresponds to so-called zero-shear viscosity η_o . At high shear rates, shear thinning behavior sets in. The apparent viscosity in this range is described by a power law on the shear rate. The Carreau-Yasuda viscosity model incorporates both trends. It was previously used to correlate data for calcium carbonate-filled linear low-density polyethylene [3]. The presence of filler particles has the effect of increasing the apparent viscosity of a polymer melt. For Newtonian fluids, containing non-interacting filler particles, the effect is well-described by the Krieger-Dougherty [19, 20] relation. Combining this model with the Carreau-Yasuda model leads to the following expression:

$$\eta = \eta_o \left[1 - \frac{\varphi}{\varphi_{max}} \right]^{-\beta\varphi_{max}} \left[1 + \left(\frac{K}{\eta_o} \right)^{\frac{a}{n-1}} |\dot{\gamma}|^a \right]^{\frac{n-1}{a}} \quad (1)$$

where η_o is the zero-shear viscosity of the liquid medium; φ and φ_{max} represent the volume fraction filler particles and their maximum value respectively, K is the flow consistency index and n is the flow behavior index; a and β are adjustable parameters and $|\dot{\gamma}|$ is the shear rate. At low shear rates, this expression reduces to the Krieger-Dougherty expression [19]:

$$\eta = \eta_o \left[1 - \frac{\varphi}{\varphi_{max}} \right]^{-\beta\varphi_{max}} \quad (2)$$

At high shear rates, and in the absence of fillers, it reduces to the conventional power law expression for the apparent viscosity:

$$\eta = K|\dot{\gamma}|^{n-1} \quad (3)$$

It has been suggested [21, 22] that the flow consistency index K should scale according to

$$K = K_o \left[1 - \frac{\varphi}{\varphi_{max}} \right]^{-n\beta\varphi_{max}} \quad (4)$$

However, Tanner, Qi and Housiadas [22] showed that, with this modification, the relationship does not reduce to the correct expression at low shear rates. Instead, in this study, the flow consistency index was treated simply as an adjustable parameter. Additionally, the presence of the waxes and lubricants also affect the flow behavior of the polymer melt in unknown ways. Therefore, the zero-shear viscosity η_0 was also treated as an adjustable parameter.

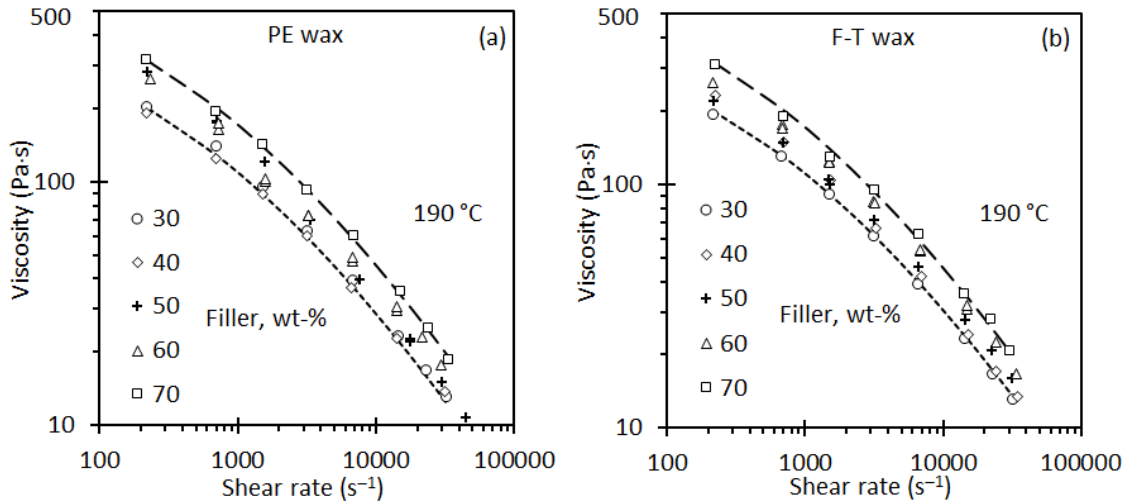


Figure 3. The effect of wax type and filler content on the flow curves measured at 190 °C with a capillary rheometer. The lines show the data fits of the modified Krieger-Carreau-Yasuda model (equation (5)) for the 30 wt-% and 70 wt-% filled compositions. All compounds contained 1.0 wt-% zinc stearate and 3 wt-% wax ((a) PE wax, and (b) F-T wax).

Figure 3 shows the shear rate dependence of the apparent viscosity of a set of filled masterbatches. In this set of experiments, the filler level was varied over a wide range and results for both of the two different types of wax were obtained. Therefore, these data were used for an initial fit of the Krieger-Carreau-Yasuda model, i.e. equation (1). Direct least squares regression resulted in parameter values of $\beta = 1$; $\varphi_{max} = 1.0$; $a = 0.380$ and $n = 0.0458$. The surprise was that the parameter values obtained for β and φ_{max} were very close to unity instead of the theoretical expected values near 2.5 and 0.64 respectively. These deviations

indicate that viscosity model is simply a convenient empirical expression, possibly due to lubricant effects. Consequently, the β and φ_{\max} parameters were assigned fixed values of unity. This meant that the actual model took the much simpler form:

$$\eta = \frac{\eta_o}{1-\varphi} \left[1 + \left(\frac{K}{\eta_o} \right) |\dot{\gamma}|^{0.38} \right]^{0.8795} \quad (5)$$

The implication is that only the zero-shear viscosity and the flow consistency index remained as adjustable parameters when regressing the data for all the other experiments. This is a convenient situation as it allowed the assessment of the effect of the diverse formulation constituents and their variation on the limiting values assumed by the flow curves at the low shear rate plateau (i.e. η_o) and in the high shear rate regime (i.e. K). The latter is particularly relevant at conventional plastics processing conditions.

The lines in Figure 3 and in Figure 4 are the predicted flow curves for the lowest and highest filler-content compounds shown. These, as well as the other curves agreed well with the actual experimental data. The least-squares values for η_o and K are presented in Table 5. The results show that at high shear rates, the apparent viscosity of the compounds containing the F-T wax was up to 10 % lower than the values for the compounds based on the PE-wax. Conversely, at low shear rates, in the Newtonian plateau, the F-T wax-based compounds were more viscous by about 6 %. Since these differences are relatively small, most additional experiments were conducted using the F-T wax only.

The next step was to explore whether the nature of the metal stearate had any effect. The results of this campaign are summarized in Table 5. Small differences in the performance of the different metal stearates were noted. However, using the blend of magnesium stearate with zinc stearate did result in a very significant reduction in the apparent viscosity in the high shear rate regime. Compared to the use of zinc stearate alone, the reduction reached 33 % (Figure 6). This result confirms a prediction made in a previous study [17] in which preliminary rheology measurements showed that true fluidification of magnesium stearate only happens well above the apparent melting point established from cooling curves. It proved possible to significantly lower this temperature by replacing part of the magnesium stearate with zinc stearate. It was then observed that calcium carbonate filled polyethylene containing metal stearate mixtures also featured lower melt viscosities than were achievable using only calcium- or magnesium stearate as lubricants.

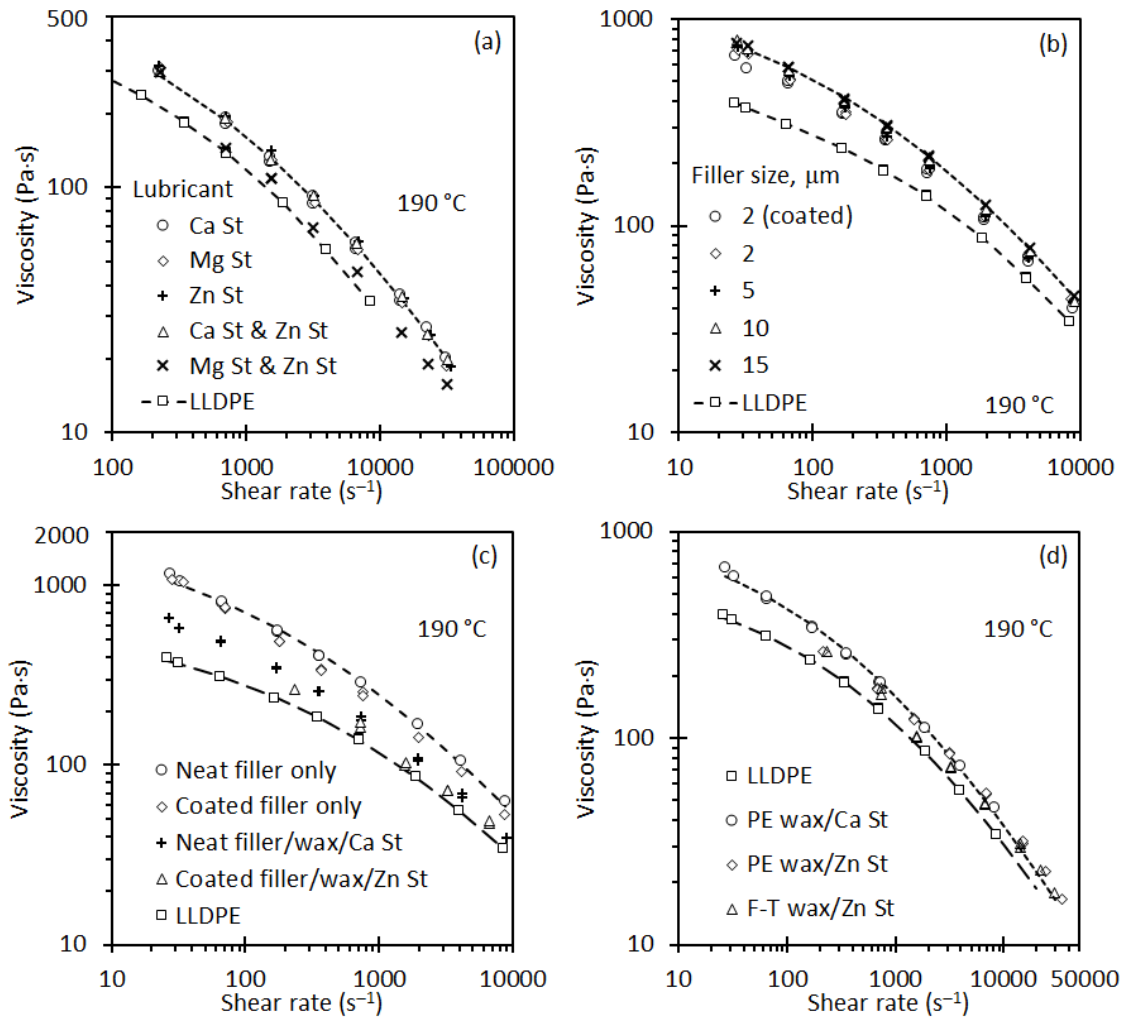


Figure 4. The result of various formulation parameters on the flow curves measured at 190 °C with a capillary rheometer. (a) Varying the lubricant nature in compounds, containing 3 wt-% F-T wax, and filled to 70 wt-% with coated CaCO₃; (b) Effect of filler particle size on compounds containing 3 wt-% F-T wax filled to 60 wt-% with uncoated CaCO₃; (c) Comparing the performance of uncoated filler with stearic acid coating filler for compounds filled to 60 wt-% in the presence and absence of a metal stearate lubricant, and (d) compounds filled to 60 wt-% with coated CaCO₃: Comparing the effects of the natures of the wax and the metal lubricant.

Table 5: Summary of rheological data reduction results.

Filler, μm	Filler, wt-%	Wax	Lubricant	η_0 , Pa·s	$K \times 10^{-6}$, Pa·s
2 coated	30 - 70	PE	Zn St	481	0.430
		F-T	Zn St	511	0.387
2 coated	70	F-T	Ca St	432	0.407
			Mg St	488	0.372
			Zn St	497	0.398
			Ca St/Zn St (2:3)	450	0.407
			Mg St/Zn St (2:3)	471	0.286
2 5 10 15	60	F-T	Ca St	802	0.307
				881	0.303
				948	0.298
				1006	0.326
2 coated 2 2 coated	60	none	none	1475	0.431
		none	none	1504	0.338
		F-T	Ca St	802	0.307
		F-T	Zn St	469	0.390
2 coated 2 coated 2 coated 15 15	60	PE	Ca St	768	0.328
		PE	Zn St	477	0.445
		F-T	Zn St	469	0.390
		F-T	Ca St	1006	0.326
		PE	Ca St	907	0.349
Neat LLDPE	none	none	none	432	0.305

Next, the effect of particle size was explored. Uncoated calcium carbonate was used and the filler level was fixed at 60 wt-%. The results are recorded in Table 5. The zero-shear viscosity increased with filler particle size from 802 Pa·s for the 2 μm -size powder to 1006 Pa·s for the 15 μm powder. This correspond to an increase of 25%. The effect of particle size on the flow consistency index was small except for the compounds containing the 15 μm powder. In these compounds the apparent viscosity was up to 15 % higher at high shear rates. The reasons for these observations are not presently known.

4 Conclusions

This study investigated the effects of particle size, filler stearate surface coating as well as the natures of the wax and metal stearate lubricants on the properties of calcium carbonate filled linear low-density polyethylene compounds. With wax added at 3.0 wt-%, the performance of a Fischer-Tropsch wax was comparable to that of a commercial polyethylene wax. The elongation at break decreased exponentially with CaCO_3 filler loading. The corresponding decline in the impact strength, the decline was more gradual but very low values were measured

at a filler loading of 70 wt-%. These observations held for both waxes, i.e. they performed similarly.

The effect of shear rate on the apparent melt viscosity followed a Carreau-Yasuda model empirically modified to include the effect of filler content. The only adjustable parameters, the zero-shear viscosity and the flow consistency index, characterized the viscosity trends at low- and high shear rates respectively. The melt viscosity increased rapidly with filler content. A stearic acid surface coating on the filler particles did not translate into lower melt viscosity. However, adding wax and, in particular zinc stearate as the lubricant, kept the melt viscosity of highly-filled compounds to levels closer to that found for the neat polymer. Calcium stearate and magnesium stearate were not as effective as zinc stearate with respect to reducing the apparent melt viscosity. However, the lowest melt viscosities were achieved using a blend of magnesium stearate and zinc stearate. Therefore, the main advantage offered by adding a wax at 3.0 wt-% and lubricant at 1.0 wt-% appears to be the facilitation of a significant reduction in the apparent melt viscosity.

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References

1. Barletta, M.; Puopolo, M., Thermoforming of compostable PLA/PBS blends reinforced with highly hygroscopic calcium carbonate. *Journal of Manufacturing Processes* **2020**, *56*, 1185-1192.
2. Roussel, M.; Guy, A.; Shaw, L.; Cara, J., The use of calcium carbonate in polyolefins offers significant improvement in productivity. *target* **2005**, *300*, 350.

3. Barczewski, M.; Lewandowski, K.; Schmidt, M.; Szostak, M., Melt fracture and rheology of linear low density polyethylene - calcium carbonate composites. *Polymer Engineering & Science* **2017**, *57* (9), 998-1004.
4. Viljoen, D.; Fischer, M.; Kühnert, I.; Labuschagné, J., The tensile behaviour of highly filled high-density polyethylene quaternary composites: Weld-line effects, die curiosities and shifted deformation mechanisms. *Polymers* **2021**, *13* (4), 1-39.
5. Lu, Q. C.; Dou, Q., Investigation of the microstructures, properties, and toughening mechanism of polypropylene/calcium carbonate toughening masterbatch composites. *Journal of Applied Polymer Science* **2017**, *134* (46), 45515.
6. Hostomsky, J.; Jones, A., Calcium carbonate crystallization, agglomeration and form during continuous precipitation from solution. *Journal of Physics D: Applied Physics* **1991**, *24* (2), 165.
7. Ersoy, O.; Köse, H., Comparison of the effect of reactive and nonreactive treatments on the dispersion characteristics of a calcium carbonate (calcite) filler in a polypropylene matrix composite. *Polymer Composites* **2020**, *41* (9), 3483-3490.
8. Švehlová, V.; Polouček, E., About the influence of filler particle size on toughness of filled polypropylene. *Die Angewandte Makromolekulare Chemie: Applied Macromolecular Chemistry and Physics* **1987**, *153* (1), 197-200.
9. Aliotta, L.; Cinelli, P.; Coltelli, M. B.; Lazzeri, A., Rigid filler toughening in PLA-Calcium Carbonate composites: Effect of particle surface treatment and matrix plasticization. *European Polymer Journal* **2019**, *113*, 78-88.
10. Osman, M. A.; Atallah, A.; Suter, U. W., Influence of excessive filler coating on the tensile properties of LDPE-calcium carbonate composites. *Polymer* **2004**, *45* (4), 1177-1183.
11. Suetsugu, Y.; White, J. L.; Kyu, T., Development of dispersion in the mixing of calcium carbonate into polymer blends in an internal mixer. *Advances in Polymer Technology: Journal of the Polymer Processing Institute* **1987**, *7* (4), 427-449.
12. Focke, W. W.; Molefe, D.; Labuschagne, F.; Ramjee, S., The influence of stearic acid coating on the properties of magnesium hydroxide, hydromagnesite, and hydrotalcite powders. *Journal of materials science* **2009**, *44* (22), 6100-6109.
13. Focke, W. W.; Molefe, D.; Labuschagne, F. J. W.; Ramjee, S., The influence of stearic acid coating on the properties of magnesium hydroxide, hydromagnesite, and hydrotalcite powders. *Journal of Materials Science* **2009**, *44* (22), 6100-6109.
14. Ciesińska, W.; Liszyńska, B.; Zieliński, J., Selected thermal properties of polyethylene waxes. *Journal of Thermal Analysis and Calorimetry* **2016**, *125* (3), 1439-1443.
15. Sherman, R. L., Jr. In *Use and utility of metal soaps in polyolefins*, Annual Technical Conference - ANTEC, Conference Proceedings, 2018.
16. Lee, C. D. In *Die lip build-up in the filled low density polyethylene wire and cable extrusion*, International Wire and Cable Symposium (50th), Lake Buena Vista, Florida, Anon, Ed. International Wire and Cable Inc.: Lake Buena Vista, Florida, 2001; pp 794-798.
17. Phillips, J.; Weldhagen, M.; Mhlabeni, T.; Radebe, L.; Ramjee, S.; Wesley-Smith, J.; Atanasova, M.; Focke, W. W., Thermal characterisation of metal stearate lubricant mixtures for polymer compounding applications. *Thermochimica Acta* **2021**, *699*, 178906.
18. Suetsugu, Y., State of Dispersion – Mechanical Properties Correlation in Small Particle Filled Polymer Composites. *International Polymer Processing* **1990**, *5* (3), 184-190.
19. Krieger, I. M., Rheology of monodisperse latices. *Advances in Colloid and Interface Science* **1972**, *3* (2), 111-136.
20. Mandersloot, W. G. B.; Scott, K. J., Rheology of particle suspensions. *South African Journal of Chemical Engineering* **1990**, *2*, 53-69.

21. Barnes, H. A., A review of the rheology of filled viscoelastic systems. *Rheology Reviews* **2003**, 1 – 36.
22. Tanner, R. I.; Qi, F.; Housiadas, K. D., A differential approach to suspensions with power-law matrices. *Journal of Non-Newtonian Fluid Mechanics* **2010**, 165 (23-24), 1677-1681.