

Influence of Calcium-Based Fillers and Vegetable Oil on the Processability and Yield Behavior of Polyolefins

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ABSTRACT: The mixing of different polyolefins, several calcium-based fillers, and a type of vegetable oil was investigated. The effect of viscosity and type of polyolefin on Young's modulus, yield stress, and elongation at yield has been determined. Tensile and machine torque properties have been studied for both mixing at 180°C and at 250°C as a function of the content of several types of calcium carbonate or calcium hydroxide filler. The influence of the addition of a sunflower oil as a lubricant has also been characterized. SEM micrographs indicate some problems of the formation of agglomerates and the influence of particle size on matrix morphology and filler/matrix adhesion. Physical and chemical interactions among high-density polyethylene (HDPE), vegetable oil, and calcium hydroxide was noticed. Spectra from infrared spectroscopy illustrate the formation of structures similar to metallic soaps, which integrate well within HDPE. Compared to calcium carbonate, results reveal excellent possibilities for the use of calcium hydroxide as a filler for polyolefins. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 2761–2772, 1997

INTRODUCTION

Incorporation of mineral fillers into polyolefins is not new and it is well known that in this way one can change all kinds of wanted properties of the thermoplastic.^{1–4} Among mechanical properties the yield stress and the elongation at yield, commercially most widely quoted, are of primary importance, since they provide information on the maximum load and elongation the material can endure.

More than 80% of the filler used in thermoplastics is based on calcium carbonate minerals (845 kt estimated as European consumption in 1986¹) and a lot of research work has been done on its

characterization as a filler. Calcium carbonate filler has developed from a poorly known low-cost particulate to a well-defined commercial product. Nowadays, the raw materials industry supplies many different kinds of engineered calcium carbonate particulates that are produced by chemical precipitation from calcium hydroxide. These particulates are often designed especially for use as filler in polymers.

Much less is known about the influence of the incorporation of calcium hydroxide as a filler. World literature only mentions the use of calcium hydroxide as an inferior filler candidate for retarding fires.^{5,6} However, it should be noticed that a bulk low-cost filler like calcium hydroxide can be highly competitive with precipitated calcium carbonate.

Usually polyolefins filled with calcium hydroxide exposed to weathering conditions tend to develop a white surface due to some carbonation

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Table I Polyolefins Used as Matrix

Sample Code	Commercial Name	Manufacturer	MFI, g/10 min (ASTM D 1238)
P1 (HDPE)	ERACLENE MP 94	Polimeri Europa	7.0
P2 (HDPE)	ERACLENE FB 61	Polimeri Europa	0.25
P3 (PP)	MOPLEN X 30 G	Montell	8.0
P4 (PP)	MOPLEN D 50 S	Montell	0.5

of calcium hydroxide on the surface. By using vegetable oil as a supplemental additive, a few try-out experiments showed that this kind of whitening can be avoided.

As no scientific information exists on the triples polyolefin/calcium hydroxide/vegetable oil, a first study was started to process several mixtures and to analyze their tensile properties in comparison with systems containing the usual calcium carbonate instead of calcium hydroxide.

EXPERIMENTAL

Materials

The materials used in this work are reported in Tables I and II together with some characteristics. Four types of polyolefins [a low- and high-viscosity high-density polyethylene (HDPE) and polypropylene (PP)] and four types of mineral filler (two different sizes of calcium carbonate, a stearate-coated calcium carbonate, and a building grade calcium hydroxide) were used as commercially available in bags. The sunflower oil was used as commercially available in liter cans.

Preparation of Specimens

Mixtures of polymer and filler were prepared by melt-mixing in a 48 cm³ Brabender PLE 330 Plasti-corder in conjunction with a cam mixing head. Torque was continuously measured during

mixing. Set temperatures were 180°C and 250°C. Full filling was done at 3 rpm, alternately filling with polymer and filler material. When both oil and filler had to be added, the oil and the filler were mixed before by hand. After filling, the rotor speed was set at 30 rpm and further mixing was done for 10 min. The mixed material was cooled and cut into smaller pieces. Sheets of composite materials 100 × 100 mm and 1 mm thick, were obtained by compression molding at 200°C in a Carver laboratory press. The compression cycle was preheated for 3 min under an iron bar load, 1 min heat compression, and cooled under compression by means of water until 30°C was reached. Samples for mechanical test size (100 × 5 mm) were punched out of the plates 1 mm thick using a punching machine. Thinner samples were used for FTIR measurements.

Characterization

Tensile stress–strain curves were obtained by using an Instron model 1122 at a cross-head speed of 50 mm/min. Strain values were derived from the displacement of the head. Average results are based on at least seven measurements and include tensile yield stress (TY), strain at yield (EY), and Young's modulus (*E*).

Unused tensile test samples of the composites, fractured under liquid nitrogen, were observed with a scanning electron microscope, Phillips model 505. The surfaces of the specimens were coated with gold.

Table II Fillers and Lubricant

Sample Code	Filler	Commercial Name	Manufacturer	Average Diameter (μm)
F1	CaCO ₃	OMYACARB 2 UM	Omya, Italy	10
F2	Stearate coated CaCO ₃	OMYACARB 2T UM	Omya, Italy	10
F3	CaCO ₃	OMYACARB 5 UM	Omya, Italy	30
F4	Ca(OH) ₂	—	AIGI, Italy	5
SO	Sunflower oil	—	DIETA, Italy	—

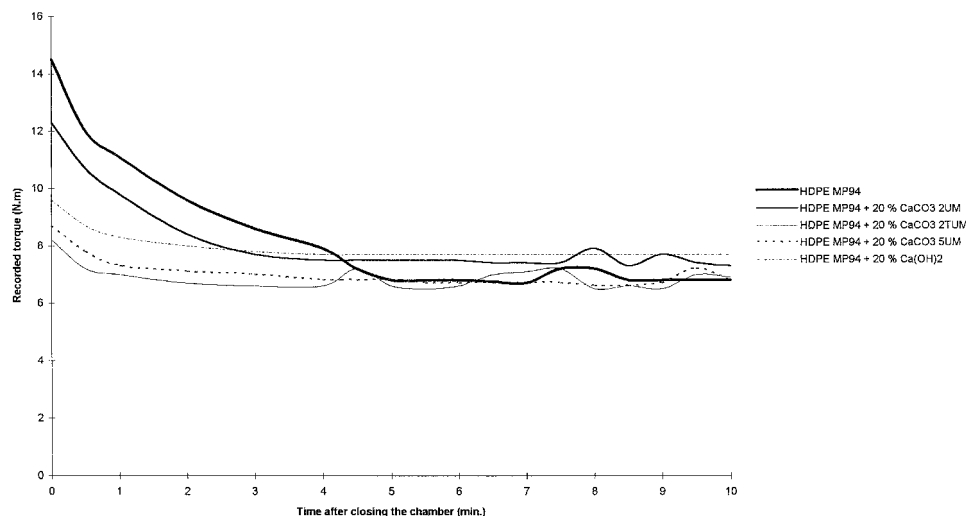


Figure 1 Influence of filler type on torque.

Infrared spectra were obtained with a FTIR Perkin–Elmer 2000. For the composites, films as thin as possible with the available press ($\sim 100 \mu\text{m}$) were used for analysis. For filler powders, 200 mg of KBr and 1 mg of filler were mixed and ground in a Wig-L-Bug for 3 min and dried 1 h at 110°C before pressing a pellet. Spectroscopy on the oil was done by putting a drop of oil between two 600-mg KBr pellets. For each spectrum, 16 scans with a resolution of 4 cm^{-1} were averaged.

RESULTS AND DISCUSSION

Flow Characterization

Figures 1–3 show some torque–time curves, recorded from the point of putting the rotor speed

to 30 rpm, for different low-viscosity HDPE/filler systems, whereas the influence of the mixing temperature on the torque of some low-viscosity HDPE/filler systems is reported in Figure 4. The equilibrium torque value gives a good indication of the viscosity of the melt: increases in final torque mean an increase of the viscosity of the material.

Figure 1 shows the influence of the filler type on torque–time behavior of filled low-viscosity HDPE mixed at 180°C . Considering the addition of untreated mineral filler, it was noticed that the recorded torque increased with smaller particle size, being the highest for the addition of calcium hydroxide. The recorded torque was lowest when adding the stearate-coated calcium carbonate.

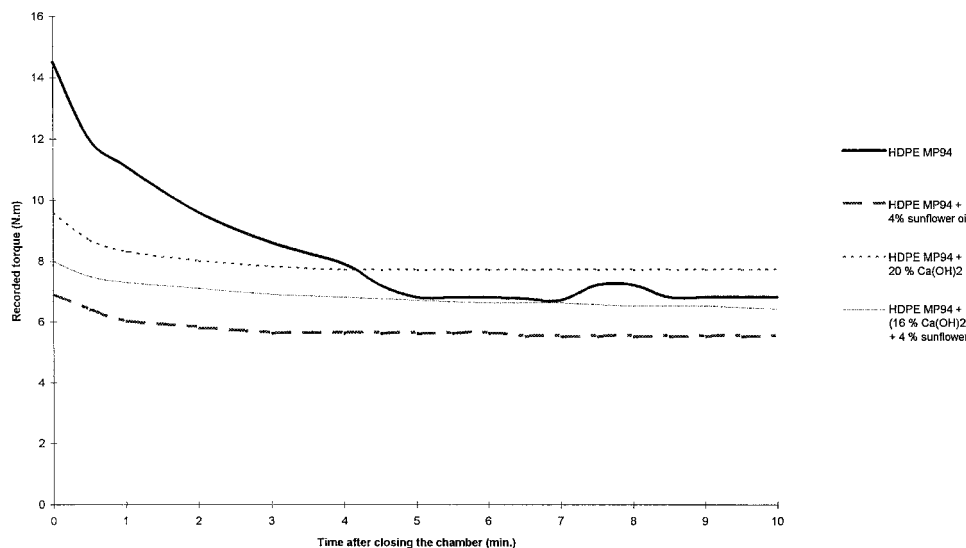


Figure 2 Influence of addition of oil and $\text{Ca}(\text{OH})_2$ on torque.

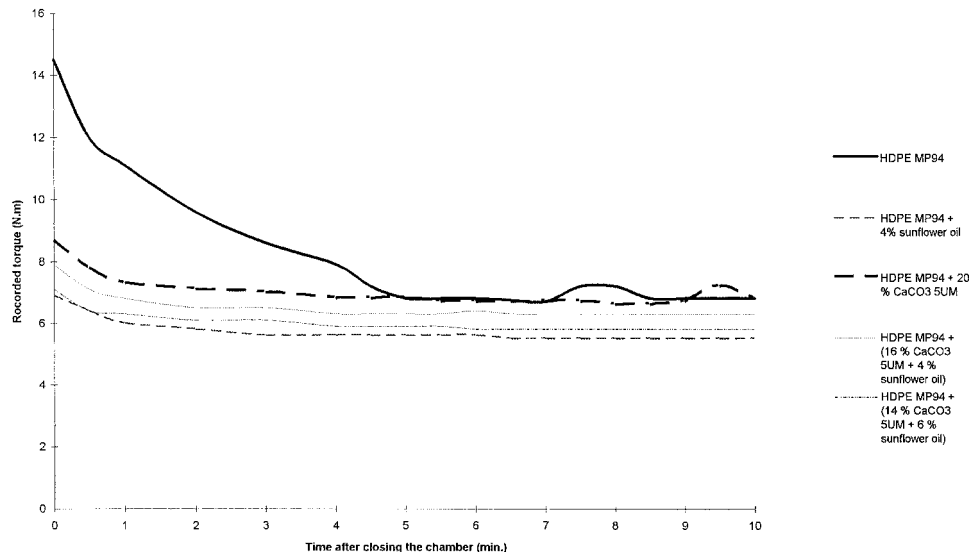


Figure 3 Influence of addition of oil and CaCO_3 on torque.

The increase of the torque, and then of the viscosity, with decreasing the particle size has been already reported in the literature,⁷ while the low torque value of the material filled with coated CaCO_3 could be attributed to some lubricating action of the coating. It is worth noticing, however, that the rise of the torque due to the fillers is quite modest, and the processability of the HDPE sample is only slightly worsened.

The processability of the other polyolefins shows similar features. One should notice, however, that under the processing conditions considered, unfilled low-viscosity PP tends to degrade

and that the high-viscosity polyolefins give final torque values ~ 4 times higher than the respective low-viscosity polyolefins.

The addition of 20 or 40 wt % filler particles gives rise to a rise of the torque with largest increase for the low-viscosity PP (e.g., $\sim 80\%$ at 40 wt % CaCO_3 2UM), and lowest increase for the low-viscosity HDPE (e.g., $\sim 25\%$ at 40 wt % CaCO_3 2UM).

Figures 2 and 3 show the influence of adding sunflower oil on the torque behavior of filled low-viscosity HDPE, mixed at 180°C . As expected, the addition of oil gives rise to lower torque moments,

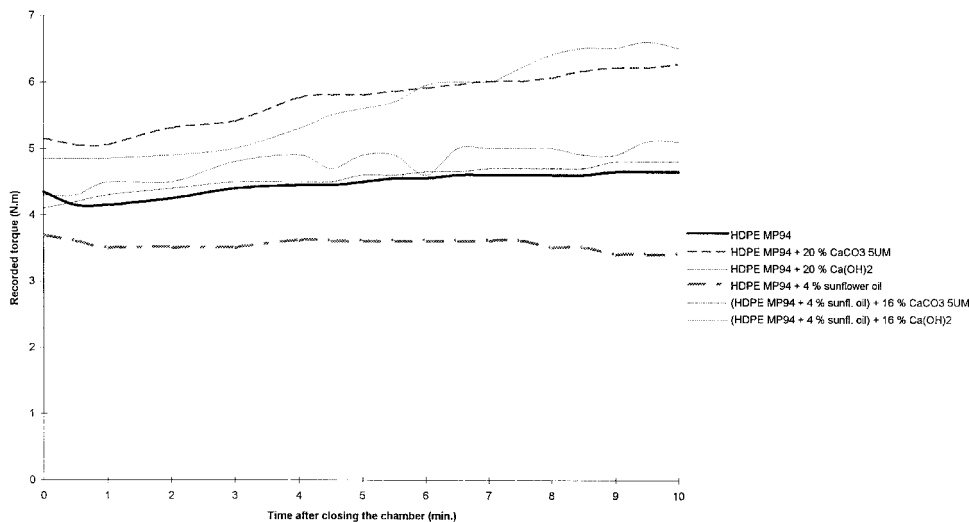


Figure 4 Influence of temperature on torque.

also for filled polyolefins. This aspect can be particularly interesting for injection molding operations where the low viscosity is the more important parameter for both energy saving and a good and rapid filling of the mold.

Figure 4 shows that mixing at higher temperatures gives rise to lower values of the torque, but a more complicated trend with time is observed. Indeed, the torque is almost constant and in some cases gradually increases with time, and this feature seems enhanced by the presence of the solid dispersed particles. During processing of HDPE two different phenomena, due to the thermomechanical degradation, occur: decrease of the molecular weight due to the chain scission and recombination of the radicals giving increase of chain length and formation of branching and crosslinking.⁸⁻¹⁰ This latter phenomenon, in competition with the decrease of molecular weight, occurs, in particular when the number of terminal insaturations is high. The drastic decrease of the torque and its next increase of the viscosity of HDPE can reflect this process. The chain scission reduces the molecular weight of the polyethylene, but with time formation of branching or crosslinking can increase the torque.

Mechanical Characterization

Influence of the Mixing Operation on Virgin Polyolefins

The mixing in the investigated processing conditions can give rise to some degradation phenomena, as already discussed. These processes induce a change of the structure and of the morphology of the polymers, causing some modifications of the mechanical properties. In Table III the elastic modulus, E , the yield stress, TY , and the strain at yield, EY , of the four polyolefins as measured on sheets prepared directly from the granules and from the processed material are reported. In the same table, and in all the other tables, the minimal and the maximal values measured are also reported. The results indicate that, for the materials processed at 180°C, modulus and yield stress slightly increase or remain constant while the strain at yield is slightly reduced. Only the low molecular weight HDPE shows an opposite trend, but the values of the mechanical properties are very near. The decrease of the molecular weight and the consequent increase of the crystallinity degree can explain these results. Some crosslinking can also arise during processing because of the thermomechanical stress in these

Table III Influence of Mixing on the Mechanical Properties of the Polyolefins

Material	E (MPa)	TY (MPa)	EY (%)
P1, virgin	1160 (1050–1260)	30.4 (29.8–31.3)	10.1 (8.8–10.8)
P1, mixed	1190 (1030–1240)	31.4 (30.9–32.4)	10.3 (9.5–11.3)
P1, mixed, 250°C	810 (720–970)	28.1 (26.1–28.6)	11.3 (8.2–14.3)
P2, virgin	690 (680–710)	21.7 (21.2–22.1)	11.8 (10.5–12.4)
P2, mixed	790 (730–940)	22.3 (21.5–23.0)	10.9 (10.4–11.7)
P3, virgin	1050 (970–1150)	34.8 (34.1–35.5)	11.7 (11.1–12.1)
P3, mixed	1150 (1070–1240)	35.7 (34.4–36.8)	10.4 (10.1–11.1)
P4, virgin	630 (570–660)	29.5 (29.1–29.7)	19.2 (17.7–21.5)
P4, mixed	620 (590–660)	29.1 (28.9–30.0)	17.6 (15.3–19.2)

Numbers in parentheses are minimal and maximal values.

Table IV Influence of the Filler Content, F1, on the Mechanical Properties of the Four Polyolefins

Material	Composition (wt %)	<i>E</i> (MPa)	TY (MPa)	EY (%)
P1	—	1190 (1030–1240)	31.4 (30.9–32.4)	10.3 (9.5–11.3)
P1/F1	80 : 20	1410 (1200–1480)	26.0 (24.7–26.5)	7.0 (6.0–8.1)
P1/F1	60 : 40	1780 (1210–2290)	24.8 (23.5–25.1)	3.8 (2.6–4.6)
P2	—	790 (730–940)	22.3 (21.5–23.0)	10.9 (10.4–11.7)
P2/F1	80 : 20	970 (910–1150)	20.0 (19.2–21.7)	10.8 (9.3–12.4)
P2/F1	60 : 40	1290 (1050–1540)	16.9 (15.7–18.7)	4.3 (2.0–5.6)
P3	—	1150 (1070–1240)	35.7 (34.4–36.8)	10.4 (10.1–11.1)
P3/F1	80 : 20	1450 (1280–1530)	30.3 (29.4–31.8)	7.7 (7.0–8.4)
P3/F1	60 : 40	1780 (1470–2150)	24.2 (23.3–24.6)	4.8 (4.4–5.0)
P4	—	620 (590–660)	29.1 (28.9–30.0)	17.6 (15.3–19.2)
P4/F1	80 : 20	780 (710–850)	24.6 (24.0–25.1)	15.0 (12.5–17.2)
P4/F1	60 : 40	1100 (1010–1320)	19.8 (18.3–21.3)	8.7 (5.8–10.2)

Numbers in parentheses are minimal and maximal values.

conditions.^{8–10} The processing at 250°C of the low molecular weight HDPE gives rise to more severe degradation with remarkable decrease of modulus and yield stress. The slightly larger average value of the strain at yield seems to confirm a predominance of the molecular scission, as already shown above.

In the following, the mechanical properties of the filled polymers will be compared with the values relative to the processed pure matrix.

Influence of the Filler Content

The influence of the filler content on the investigated mechanical properties can be noticed from Table 4, where *E*, TY, and EY are reported as a function of the content of F1 for all the polyolefins. The main features are common to all the matrices: the yield properties decrease with increasing the filler content, while the elastic modulus increases.

This aspect becomes particularly evident when the filler content is > 10%. One exception can be found in 20% filled high-viscosity HDPE, for which EY nearly does not change. One should notice that, under the conditions of the experiment, the spreading of the measured properties increases for an increasing filler content.

Influence of Filler Type on Low-Viscosity HDPE

The influence of the filler type on the low-viscosity HDPE (P1) is reported in Table V. Compared to the small size calcium carbonate filler, the stearate coating gave rise to a decrease of TY, an increase of EY, and to a decrease of *E*, as expected by the lubricating effect that the stearate has on the polymer chains.¹

Large particles are known to cause greater stress concentrations in the matrix than smaller ones, and this should result in lower TY. Small

Table V Influence of the filler Type on the Mechanical Properties of the Low-Viscosity HDPE

Material	Composition (wt %)	<i>E</i> (MPa)	TY (MPa)	EY (%)
P1	100	1190 (1030–1240)	31.4 (30.9–32.4)	10.3 (9.5–11.3)
P1/F1	80 : 20	1420 (1200–1560)	25.6 (24.7–26.9)	7.1 (6.0–8.1)
P1/F2	80 : 20	1130 (950–1380)	24.9 (23.7–25.9)	9.2 (8.4–10.1)
P1/F3	80 : 20	1180 (1000–1400)	25.6 (24.0–27.8)	8.8 (7.8–10.1)
P1/F4	80 : 20	1140 (1070–1240)	27.4 (26.7–28.1)	6.2 (5.4–7.2)

particles should be free to move within the matrix, and correspondingly the matrix should be free to stretch around them and EY should increase.² However, compared to the smaller size calcium carbonate, filling with the larger size particles gives similar TY and improved EY and *E* similar to the virgin polymer. Also, a larger spreading of the results can be noticed. Effects of increased aspect ratio with particle size might have had an influence.

Finally, the calcium hydroxide filler improves TY and decreases EY and *E* with respect to the smaller size calcium carbonate filler. TY improves because of the small size of the particles. A better

adhesion with the polyolefin matrix could also be invoked, as it will be clear in the following, to explain this behavior. The decrease in EY can be caused by the formation of calcium hydroxide agglomerates within the matrix.

Influence of Sunflower Oil Addition on Filled Low-Viscosity HDPE

The addition of the vegetable oil (Table VI) decreases TY, increases EY, and gives rise to a significant decrease of the modulus. This effect is attributable to the lubricating effect of the oil, which allows a more easy slippage of the macro-

Table VI Influence of Oil on the Mechanical Properties of HDPE and Filled HDPE

Material	Composition (wt %)	<i>E</i> (MPa)	TY (MPa)	EY (%)
P1	100	1190 (1030–1240)	31.4 (30.9–32.4)	10.3 (9.5–11.3)
P1/SO	96 : 4	660 (550–720)	23.7 (21.5–24.7)	11.6 (8.7–15.1)
P1/F3	80 : 20	1180 (1000–1400)	25.6 (24.0–27.8)	8.8 (7.8–10.1)
P1/F3/SO	80 : 16 : 4	900 (770–1120)	24.1 (23.2–25.1)	12.3 (10.7–15.7)
P1/F3/SO	80 : 14 : 6	730 (650–810)	23.5 (22.6–24.2)	14.6 (11.2–17.5)
P1/F4	80 : 20	1140 (1070–1240)	27.4 (26.7–28.1)	6.2 (5.4–7.2)
P1/F4/SO	80 : 16 : 4	820 (740–1020)	21.3 (19.8–22.3)	8.9 (7.6–10.7)

Numbers in parentheses are minimal and maximal values.

Table VII Influence of Mixing Temperature on the Mechanical Properties of Filled Low-Viscosity HDPE

Material	Composition (wt %)	Temperature (°C)	<i>E</i> (MPa)	TY (MPa)	EY (%)
P1/F3	80 : 20	180	1180 (1000–1400)	25.6 (24.0–27.8)	8.8 (7.8–10.1)
P1/F3	80 : 20	250	1150 (950–1390)	27.7 (26.2–28.8)	8.5 (7.2–9.7)
P1/F4	80 : 20	180	1140 (1070–1240)	27.4 (26.7–28.1)	6.2 (5.4–7.2)
P1/F4	80 : 20	250	1080 (970–1230)	28.8 (28.2–29.4)	8.1 (6.4–9.3)
P1/SO	96 : 4	180	660 (550–720)	23.7 (21.5–24.7)	11.6 (8.7–15.1)
P1/SO	96 : 4	250	660 (550–760)	23.4 (22.1–24.6)	13.9 (12.5–15.5)
P1/F3/SO	80 : 16 : 4	180	900 (770–1120)	24.1 (23.2–25.1)	12.3 (10.7–15.7)
P1/F3/SO	80 : 16 : 4	250	710 (640–770)	22.6 (21.5–23.5)	10.8 (9.5–11.9)
P1/F4/SO	80 : 16 : 4	180	820 (740–1020)	21.3 (19.8–22.3)	8.9 (7.6–10.7)
P1/F4/SO	80 : 16 : 4	250	940 (850–1050)	22.5 (22.0–23.1)	7.6 (8.4–9.6)

Numbers in parentheses are minimal and maximal values.

molecules. The same lubricating effect was also noticed for the filled HDPE.

Influence of Mixing Temperature on Filled Low-Viscosity HDPE

The mechanical properties of P1 filled with F3 and F4 (80% of P1) also in presence of oil (4%) are reported for two mixing temperatures in Table VII. The increase of the mixing temperature on filled P1 without oil gives rise to a small increase of TY and a small increase of EY for calcium hydroxide. The modulus remains about unchanged.

The increase of the mixing temperature for oil-filled HDPE gives rise to a small increase in the average EY, resulting from a smaller scattering of the results. This can be explained by the evaporation of the most volatile (low molecular weight) oil components.

When adding oil in calcium carbonate-filled HDPE all mechanical properties degrade. This can be explained when considering physical adsorption

of oil on calcium carbonate, which gives rise to a completely zero adhesion between filler and polymer.

On the contrary, the addition of oil proved to be beneficial for the mechanical properties of calcium hydroxide-filled HDPE. These results can be ex-

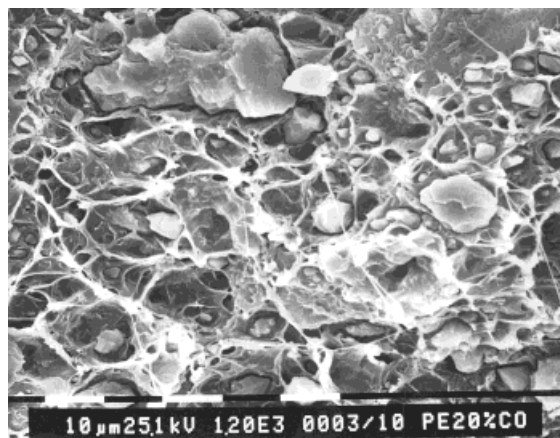


Figure 5 SEM micrograph of 80% P1 + 20% F1.

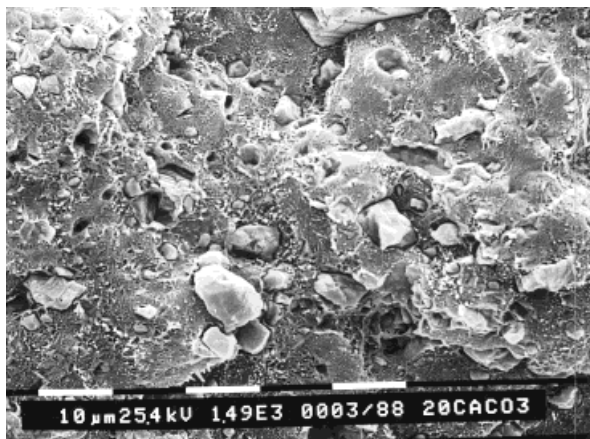


Figure 6 SEM micrograph of 80% P1 + 20% F3.

plained considering an increased chemical and physical interaction among the polymer, the oil, and the calcium hydroxide (as it will be seen from the IR spectroscopy results).

Scanning Electron Microscopy

Figures 5–8 show four SEM micrographs of filled materials. Figures 5 and 6 show that the calcium carbonate particles have a homogeneous distribution within the matrix, but a large variation in size. The adhesion is very scarce and increasing the particle size (Fig. 6), the larger particles are less well embedded within the matrix.

Figure 7 confirms that building-grade calcium hydroxide forms agglomerates within low-viscosity polyethylene. The particulates are less well dispersed because of their smaller size. However, the agglomerates still have a smaller size than the calcium carbonate particles considered. Next



Figure 7 SEM micrograph of 80% P1 + 20% F4.

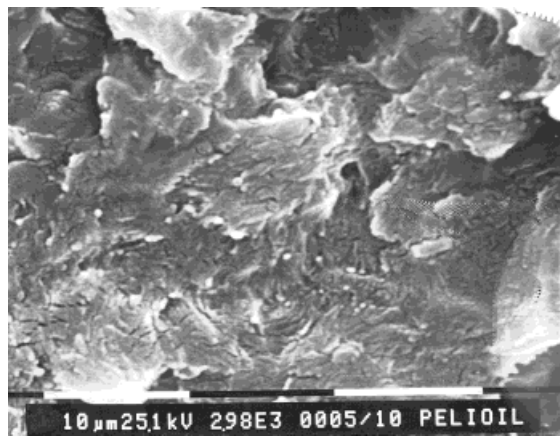


Figure 8 SEM micrograph of 80% P1 + 16% F4 + 4% SO, prepared at the mixing temperature of 250°C.

to the agglomerates a distribution of particulates at submicron level can be noticed with very good adhesion to the matrix.

Figure 8 shows a sample of P1, F4, and SO, mixed at 250°C. It can be noticed that agglomerates disappear, the ratio of calcium hydroxide particulates decreases, and the adhesion with the polyolefin matrix is improved. As it will be more clear in the following, the reaction product of calcium hydroxide and vegetable oil is a polymer which integrates well within HDPE, improving the adhesion.

Infrared Spectroscopy

Infrared spectroscopy spectra were recorded for all mixtures containing low-viscosity HDPE. Some results are illustrated in Figures 9–12. Figures 9–11 show the FTIR spectra of some virgin materials used, while Figure 12 shows spectra of two composite products.

All FTIR graphs of composites were more or less recognized as superpositions of the spectra for the polymer, the filler, and/or the sunflower oil. Specimens prepared at a higher mixing temperature did not show significant differences in the recorded spectra. However, deviations were noticed for the mixture of HDPE, calcium hydroxide, and sunflower oil at 250°C. Figure 12(b) shows the appearance of a new strong absorption peak at 1554 cm^{-1} , together with the disappearance of the sharp peak at 1747 cm^{-1} . The peak at 1747 cm^{-1} corresponds to the ester function of the vegetable oil and 1554 cm^{-1} corresponds to the formation of carboxylate ions.^{11,12} Under the influence of $\text{Ca}(\text{OH})_2$ the vegetable oil probably has

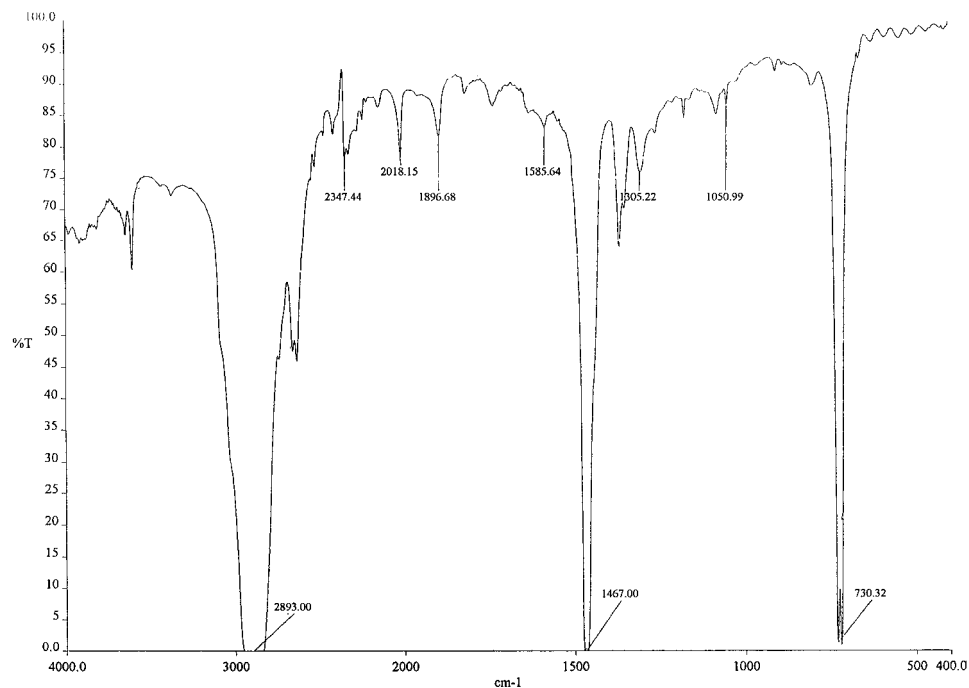


Figure 9 IR spectrum of low-viscosity HDPE (P1).

dissociated into glycerol and fatty acids.^{13,14} The fatty acids can form structures similar to metallic soaps with the remaining calcium. The absorption peak at $\sim 1554 \text{ cm}^{-1}$ is, for example, found in the

IR spectra of common metal stearates.¹¹ However, the interaction among calcium hydroxide, glycerol, and unsaturated fatty acids is more difficult to characterize.¹⁵ A further polymerization of un-

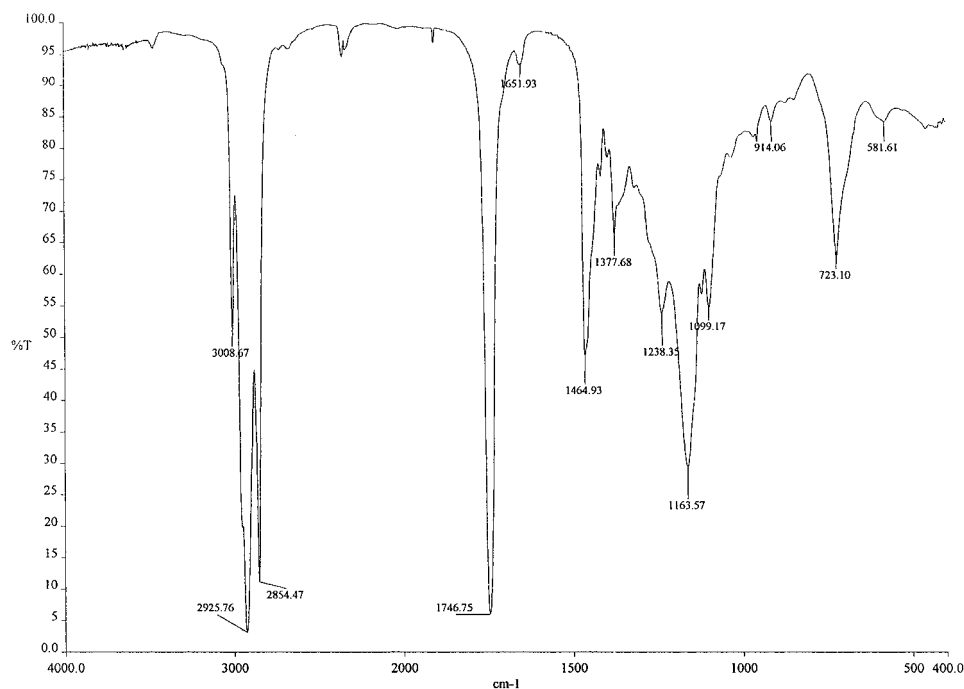


Figure 10 IR spectrum of sunflower oil DIETA (SO).

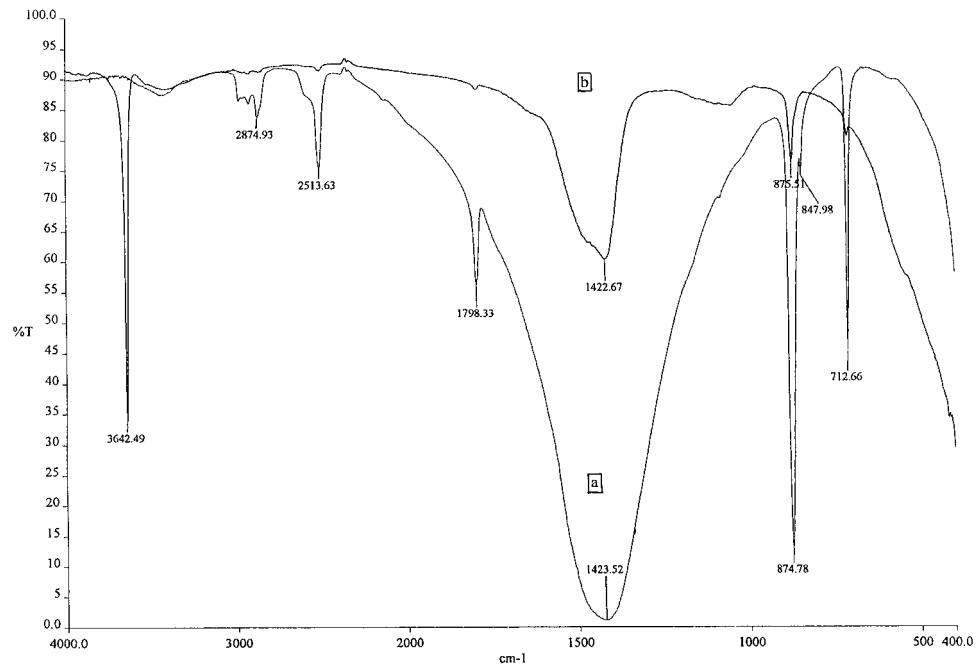


Figure 11 IR spectra of (a) CaCO₃ OMYACARB 5 UM (F3), and (b) Ca(OH)₂ (F4).

saturated fatty acids due to Ca(OH)₂ might create molecules that are sufficiently long for physical entanglement with HDPE from the matrix bulk. Also, as torque properties indicate the chemical recombination of HDPE-chains caused by thermo-

mechanical action during mixing, interaction of free radicals with the insaturations of the oil can be expected. The presence of these new molecules can explain the deviation in mechanical properties and the observation in Figure 8.

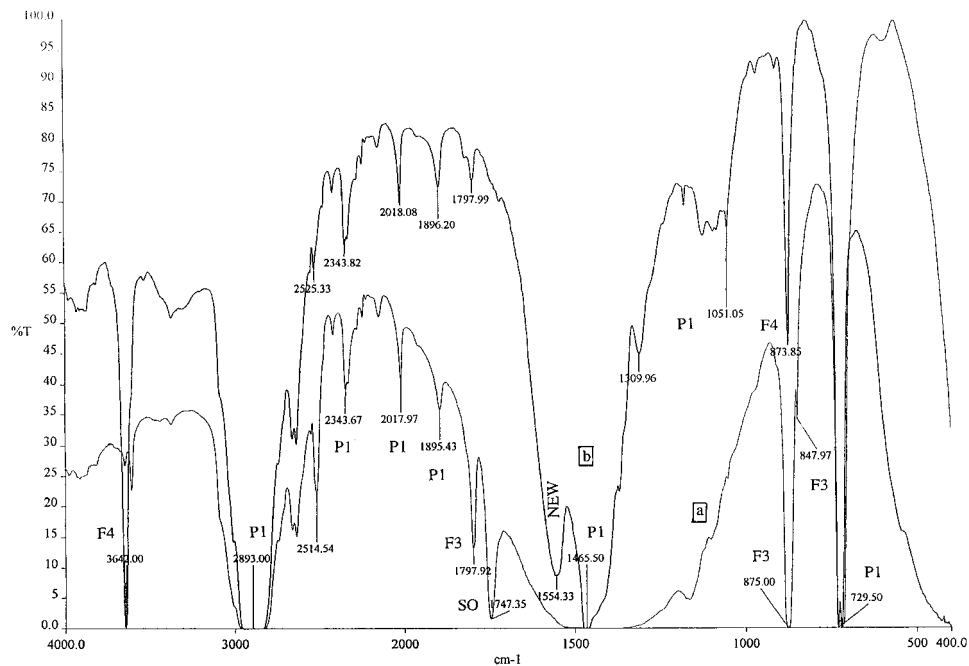


Figure 12 IR spectra of (a) 80% P1 + 16% F3 + 4% SO, and (b) 80% P1 + 16% F4 + 4% SO mixed at 250°C.

CONCLUSIONS

One should take into account that the prediction of tensile properties of polyolefins from theoretical mixture rules is not always adequate. The chemical recombination of polymer molecules can give rise to some crosslinking and chemical and thermomechanical interaction with fillers. Results can be different according to the viscosity of the polymer or the mixing procedure that was used. Common plasticizers and/or lubricants can have an effect on particle distribution and filler/matrix adhesion. This is especially true for carbon acid-containing components which can form carboxylates that adhere to certain metallic components. Proof was given for the chemical interaction between vegetable oil and calcium hydroxide in a low-viscosity HDPE matrix. Possibly structures similar to calcium soaps are formed which integrate well within the matrix.

The fact that precipitated calcium carbonate as a filler is often derived from calcium hydroxide and that calcium hydroxide has a lower density than calcium carbonate makes $\text{Ca}(\text{OH})_2$ an interesting alternative as a filler material for polymers. Its reactivity with fatty acids makes it also a possible candidate as a filler with full adhesion to the matrix material. Metallic soap functions can provide a chemical or physical link between calcium hydroxide particulates and polymers, and should avoid carbonatation of composite products.

Further research will be done on the recycling of polymer waste contaminated with vegetable oil and on the development of (building) products from polymers, calcium hydroxide, and fatty acids.

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