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Polymer 45 (2004) 1177–1183

polymer

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Influence of excessive filler coating on the tensile properties of LDPE–calcium carbonate composites

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Received 17 April 2003; received in revised form 17 October 2003; accepted 2 December 2003

Abstract

Calcium carbonate fillers are usually coated with stearic acid to reduce their surface energy and improve their dispersion in polymers. Commercial products are often over-coated and contain an excess of surfactant. It was found that stearic acid linearly increases the modulus and yield stress of LDPE but reduces its tensile strength, yield strain, and ultimate elongation. The influence of surfactant excess on the tensile properties of low-density polyethylene (LDPE)–$CaCO_3$ composites was investigated. Compounds of LDPE and optimally coated filler or with excess surfactant were prepared and their properties compared. $CaCO_3$ increased the stiffness and yield stress of the polymer but reduced all its other tensile properties. Over-coating the filler did not lead to linear accumulation of the effects of filler and stearic acid on the polymer matrix. In fact, surfactant excess amplifies the reinforcing effect on the stiffness but reduces all other mechanical properties of the composite. Calcium stearate, which is sometimes used as acid scavenger, lubricant or processing aid, has the same effect on the polymer properties as stearic acid, but to a smaller extent. It is concluded that it is most advantageous to coat the filler with the optimal amount of surfactant necessary to cover its surface with an organic monolayer unless the influence of excessive coating is required for a certain application. Care must also be taken in interpreting some of the published results, where the quality of the filler coating was not investigated.

Keywords: Tensile properties; Over-coating; Polyethylene–calcite composites

1. Introduction

Thermoplastic polymers and especially polyolefins are produced and consumed today in vast quantities. However, they are seldom used as neat polymers and are usually compounded with mineral fillers. Initially, fillers were used as 'extenders' for polymers to reduce cost but as the polymer price decreased and the requirements of modern applications increased, attention has been more and more focused on functionality enhancement [1–3]. Nowadays, 'functional fillers' find application in the polymer industry almost exclusively, e.g. to improve stiffness, toughness, dimensional-stability, electric-insulation or to decrease the dielectric-loss. A prerequisite for functional fillers is full dispersion (break-up of agglomerates into their primary particles) and uniform spatial distribution in the polymer matrix because agglomerates entrap air and act as sites for fracture initiation, thus leading to premature material failure [4–6].

Calcium carbonate is one of the most abundant materials on our planet and has been quite early used in ground form to produce polymer composites. There are no less than three minerals or phases of $CaCO_3$ (calcite, aragonite and vaterite), but calcite is that most widely found in nature. In contrast to precipitated calcium carbonate, ground natural calcite is usually micron-sized (easier to disperse) with a broad size distribution and irregular shape. To reduce its high surface energy and its particle–particle interactions, which lead to agglomerates, it is often coated by a variety of surface modifiers such as fatty acids, phosphates, silanes, titanates or zirconates [2,3,7,8]. The most widely used calcite coating is the surface treatment with stearic acid or one of its salts. As a result, an ultra thin layer of hydrophobic alkyl chains is chemically bonded to the surface. The coated organic film represents the interface between the filler and the polymer matrix, and hence influences the wetting and adhesion properties of the two phases involved. It also influences the growth of the interphase and consequently

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0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2003.12.020

determines the final properties of the composite besides reducing the particle–particle interactions and the filler surface energy. Studies on the structure and properties of the coated organic thin film have shown that one stearic moiety is attached to each surface Ca^{2+} [9–11]. This results in a vertical orientation and close packing of the alkyl chains, leading to a high trans population and an ordered state. To ensure complete surface coverage, an excess of the surfactant is often used in commercial products. It has been reported that surfactant excess often leads to processing problems and inferior mechanical properties but no detailed study on the influence of over-coating on the tensile properties of polyolefin–calcite composites can be found in the literature [4,10–13].

Several studies on the influence of increasing volume fraction of ground micron-sized calcite fillers (submicron precipitated calcium carbonate, which can have different shapes and narrow size distribution, is not included) on the mechanical properties of polyolefins, especially polypropylene have been reported [3,4,7,14–32]. Generally, the elastic modulus increases with augmenting filler volume fraction. Often a linear dependence of modulus on composition is observed, although theoretical models predict a nonlinear behavior and a discrepancy exists between the theoretical correlations and the experimental results [4,16,21,26]. The discrepancy between theory and experiment and within the experimental results can be attributed to the presence of aggregates, agglomerates or voids as well as to the adsorption of the polymer chains on the filler surface, leading to its immobilization and to changes in morphology [4,14,16–19,21,22,24,26]. All other tensile properties such as the yield stress and strain, or ultimate stress and strain, almost invariably deteriorate with increasing filler volume fraction [4,19,21,26,27,30–32]. In contrast to the modulus, which is determined at very low deformation, simplifying both measurements and modeling, yield and ultimate properties are measured at considerable deformations leading to more controversy. All the above-mentioned studies were carried out with commercial fillers, which were sometimes stearic coated, but the quality of the surface treatment was not investigated. Until recently a method to analyze the surface coating and detect surfactant excess was lacking and the influence of nonbonded surfactant molecules on the mechanical properties was ignored [11]. Although, it is well accepted that lack of filler dispersion has a detrimental effect on the composite properties, the efficiency of the compounding conditions used in dispersing the filler was often not assessed and the presence of aggregates or agglomerates cannot be ruled out, making the reported results ambiguous.

The goal of the present study was to investigate the influence of excessive stearic acid on the tensile properties of low-density polyethylene (LDPE)–$CaCO_3$ (stearic-coated) composites.

2. Experimental

2.1. Materials

The LDPE used in this study was Lupolen 2420H, which was supplied by Elenac (Ludwigshafen, Germany). It had a density of 0.922–0.926 g/cm^3 and a melt flow index of 1.9 g/10 min (2.16 kg at 190 °C). The calcite filler (Omyacarb 1TAV) was obtained from Omya (Oftringen, Switzerland) and was a dry-milled white marble from Avenza-Carrara (Italy) that was surface treated with stearic acid by the supplier. Its median particle diameter as determined by sedimentation (Sedigraph 5100) $D_v0.5$ was 1.8 μm and its specific surface area (BET) = 4 m^2/g. The characteristic data of the polymer and the filler are supplier's data. The two other fillers analyzed thermogravimetrically were Superpflex 200, supplied by Specialty Minerals Inc., USA and Supercoat, supplied by Imerys, USA. The first was precipitated calcium carbonate, while the second was ground $CaCO_3$ but both were stearic-coated products. Stearic acid and calcium stearate were purchased from Fluka (Buchs, Switzerland).

2.2. Sample preparation

Composites containing 0.1 or 0.2 volume fraction of filler with and without stearic acid were homogenized in a Brabender internal mixer 'Plasti-Corder W 50 EH' (Brabender, Duisburg, Germany) equipped with a 60 cm^3 bowl and counter-rotating blades. The polymer pellets were molten at 170 °C and mixed with the required amount of stearic acid or calcium stearate, then the filler was gradually added within 10 min at 40 rpm. The speed was then increased to 50 rpm and the mixture homogenized for further 10 min. Care was taken to fill the mixer cell completely with material to ensure optimal mixing and avoid incorporation of air in the composite. After compounding, the material was quickly removed from the cell and pressed to middle-sized flat lumps.

The compound was compression molded to 1.5 mm thick plaques in a brass frame between two aluminum plates at 180 °C. Not more than 2% in excess of the amount necessary to fill the frame was used (otherwise the polymer will be squeezed out of the mould, leaving the filler in the frame, thus changing the composition). To ensure the absence of microvoids, the molding process was carried out under reduced gas pressure (0.01 mbar) in a brass chamber, specially constructed for this purpose. The mold was left to cool slowly in the press without active cooling to ensure reproducible crystallization. Dumbbell-shaped tensile bars were stamped out of the resulting plaques, using a cutting press (H. W. Wallace, Croydon, Surrey, England) with a die conforming to type 5B of the ISO 527-2 norm.

Compounds and plaques of LDPE with different amounts of stearic acid or calcium stearate were prepared as described above.

2.3. Scanning electron microscopy (SEM)

To study the morphology of the composites, the face of a sample cut perpendicular to the horizontal plane (the plane parallel to the plaque flat surface) was planed with a diamond knife of a microtome (Reichert Jung Ultracut E). The sample face was etched with cold oxygen plasma for 3 min to enhance the contrast. Excessive etching was avoided because it uncovers particles lying underneath the surface, giving wrong information on the concentration and the morphology. The sample surface was sputter coated with 5 nm of Pt and observed in a Hitachi S-900 'in-lens' field emission scanning electron microscope (FESEM) at 10 kV accelerating voltage. The morphology of all composites prepared in this study was controlled by SEM even if the micrographs are not shown here. The fracture surface of the tested tensile bars was also sputter coated with 5 nm of Pt and microscopically examined. All samples were initially observed under low magnification to obtain an overall impression and then higher magnifications were adopted.

2.4. Tensile measurements

Engineering stress–strain curves were obtained from uniaxial tension tests carried out according to the ISO 527-2 norm on dumbbell-shaped tensile bars of type 5B at room temperature with a Zwick 1474 tensile tester (Zwick, Ulm, Germany). Displacement was measured with a Video-Extensometer ME-46 (Messphysik, Fürstenfeld, Austria). The elastic modulus was determined at 0.5 mm/min cross-head speed, while all other tensile characteristics were measured at 6 mm/min. An average of at least five measurements for each sample is reported.

2.5. Thermal analysis

The thermogravimetric analysis (TGA) was carried out in an air stream (50 cm^3/min) at a heating rate of 20 °C/min on a Perkin–Elmer 7 thermal analysis system (Perkin–Elmer, Norwalk, CT, USA) and the first derivative of the mass-loss with temperature was plotted (DTG). The differential scanning calorimetry (DSC) was carried out under nitrogen at a rate of 10 °C/min on a MDSC Q1000 (TA Instruments, New Castle, DE, USA). The samples weight was kept constant (10 mg) and the melt enthalpies were measured over the same temperature range. The peak maximum was taken as the melting point.

3. Results and discussion

To illustrate the fact that some commercial CaCO$_3$ fillers are over-coated and contain an excess of surfactant, the DTG traces of Omycarb 1TAV, the same filler mechanically mixed with stearic acid, Supercoat and Superpflex 200 are plotted in Fig. 1. As can be seen, 1TAV does not contain excessive stearic acid as evidenced by the absence of the peaks at ca. 200 °C (local bilayer) and ca. 270 °C (free acid) [11]. Mechanical mixing of stearic acid (melting point 70 °C) with 1TAV led to the formation of a local bilayer during mixing and thermal analysis as well as to the presence of free acid molecules as in over-coating the filler (Fig. 1) [11]. 'Supercoat' contains an excess of surfactant in the form of a bilayer, while 'Superpflex 200' contains not only a bilayer but also a large amount of free acid or other surfactant. The small difference between the decomposition temperature of the latter filler coating and that of the others is probably due to the fact that it is a precipitated calcium carbonate (submicron size), while the others are ground natural calcites.

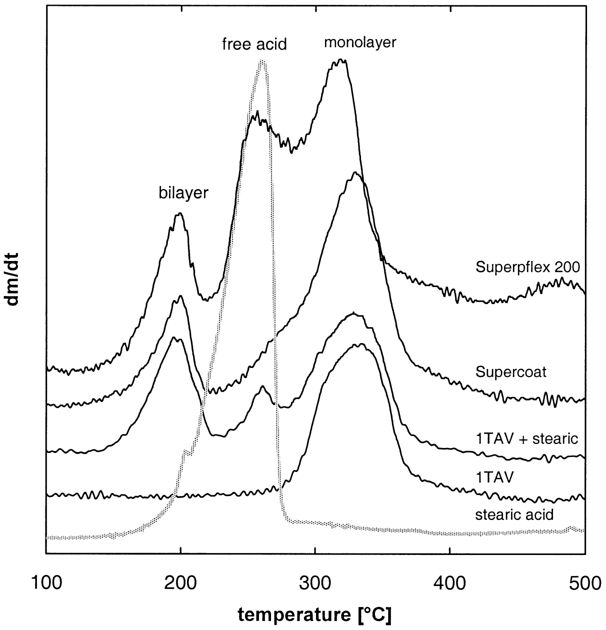

Fig. 1. DTG traces of Omyacarb 1TAV, same filler mechanically mixed with stearic acid, Supercoat and Superpflex 200.

To study the influence of surfactant excess on the mechanical properties of LDPE–CaCO$_3$ composites, a calcite filler which is not over-coated (Omyacarb 1TAV) was chosen in order to be able to add excess surfactant to it later. Composites of this filler and LDPE containing 0.1 and 0.2 filler volume fraction were prepared and their tensile properties measured. The dispersion and spatial distribution of the filler were assessed by SEM. A micrograph of the 20 vol% composite is given in Fig. 2, showing that the compounding conditions used were adequate to disperse and uniformly distribute the filler in the polymer matrix. It can also be seen that the particle size distribution is quite broad, which is typical for milled powders. In the 10 vol% composite, the filler was even better dispersed due to the smaller number of particles and the large interparticle distances. Table 1 shows that the elastic modulus increased monotonically with increasing filler volume fraction as observed in most particulate filled polymers [4,16,21,26]. The presence of the filler also nucleated the crystallization

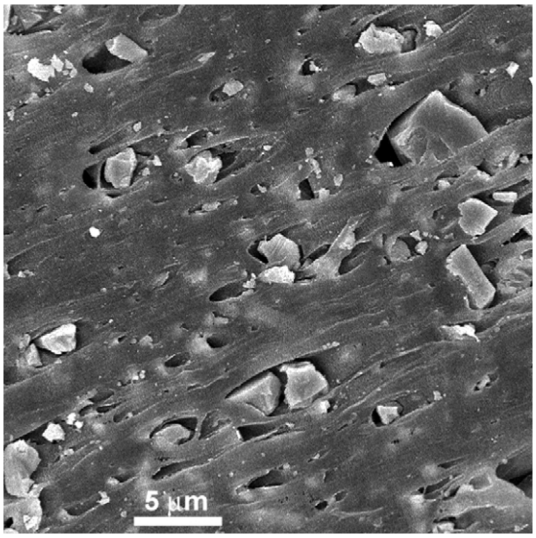

Fig. 2. SEM micrograph of the 20 vol% 1TAV–LDPE composite.

of the polymer, reducing its melting point by 1 and 2 °C and increasing its melt enthalpy by 3.5 and 6% at 10 and 20 vol% loading, respectively (Table 2). This suggests that the nucleation effect of the filler and the change in crystallinity of the polymer is modest, which is in accordance with previous investigations [33–35]. The tensile yield stress also increased with augmenting filler volume fraction, while the stress at break initially decreased then increased to exceed the original value of the matrix in the 20 vol% composite. This behavior is in contrast to what is usually observed in filled semi-crystalline polyolefins like PP or HDPE, where both properties often invariably decrease with increasing filler content [4,19,21,26]. The yield strain decreased monotonically, while the ultimate elongation decreased to reach a plateau value as often reported for HDPE and PP composites [19,26]. A SEM micrograph of a fracture surface of the 20 vol% composite is given in Fig. 3, showing the plastic deformation of the matrix and the debonding (dewetting) of the filler from the matrix before fracture. The sharp edges of the filler particles indicate that the adhesion between the two phases is weak.

Composites containing the same filler volume fraction and different additional amounts of stearic acid were also prepared and their tensile properties measured. In the 10 vol% composite, the modulus increased linearly with increasing amount of stearic acid, thus enhancing the modulus by 11% at 2 wt% stearic acid with respect to the polymer weight (Fig. 4). In case of the 20 vol% composite, the modulus increased asymptotically to reach a plateau (13% increment) at ca. 1 wt% stearic acid based on the amount of polymer present (Fig. 5). It seems that there is a maximum stiffness that can be reached by the addition of stearic acid at this loading. The influence of surfactant excess on the yield stress and tensile strength is also shown in Figs. 4 and 5. Stearic acid had little effect on the yield stress of the composites but increased the stress at break linearly in the 10 vol% composite and asymptotically in the 20 vol% composite. The reinforcement of the 10 vol% composite was appreciable (20%). The yield strain and ultimate elongation, which strongly deteriorated in presence of the filler, decreased further on adding stearic acid. In both composites, plateau values were reached at ca. 1 wt% stearic acid with respect to the amount of LDPE. As can be seen from Table 2, the presence of excess stearic acid, at all concentrations used, had no sizable effect on the crystallization behavior of the polymer. From these results, it becomes clear that surfactant excess (over-coating) has a remarkable influence on the tensile properties of the composites, which cannot be attributed to a change in crystallinity of the polymer. The reinforcement effect may be due to the presence of free surfactant molecules in the polymer matrix as a heterogeneous phase or to the presence of local bilayer (Fig. 1). Fig. 6 shows a SEM micrograph of a fracture surface of the 20 vol% composite containing 1.2 wt% stearic acid. It can be seen that the ductility of the matrix is still preserved (compare Fig. 3) in spite of the increase in stiffness and that the filler was debonded (dewetted) from the matrix before fracture.

To compare the influence of the surfactant on the pure

Table 2
Effect of filler and surfactant on the melting point and enthalpy of LDPE

	Melting point (°C)	Melting enthalpy (J/g polymer)
LDPE	114	82.5
LDPE + stearic acid	113	86.8
LDPE + Ca stearate	113	88.0
LDPE + 10 vol% 1TAV	113	85.4
LDPE + 10 vol% 1TAV + stearic acid	113	85.1
LDPE + 20 vol% 1TAV	112	87.6
LDPE + 20 vol% 1TAV + stearic acid	112	88.9

Table 1
Mechanical properties of LDPE–Omycarb 1TAV composites

Volume fraction	Tensile modulus[a] (MPa)	Yield stress[b] (MPa)	Yield strain[b] (%)	Stress at break[c] (MPa)	Ult. elongation[c] (%)
0	281	10.9	15.8	10.1	617
0.1	428	12.3	14.0	7.1	72
0.2	530	12.7	10.1	11.1	17

[a] Relative probable error 5%.

[b] Relative probable error 3%.

[c] Relative probable error 10%.

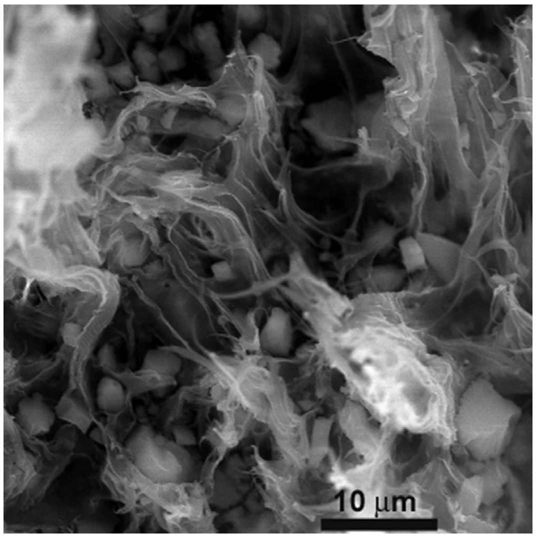

Fig. 3. SEM micrograph of a tensile fracture surface of the 20 vol% 1TAV–LDPE composite.

polymer with that on the composites, the tensile properties of LDPE compounds with stearic acid were measured. Fig. 7 shows that the modulus increases linearly with augmenting stearic acid concentration. The reinforcement reaches 20% at 2 wt% stearic acid concentration. The yield stress also increases linearly with the addition of stearic acid (Fig. 8). Table 2 shows that the effect of stearic acid on the crystallization behavior of the polymer is quite modest. That is, the reinforcing effect of excess surfactant cannot be solely ascribed to change in crystallinity of the polymer. By

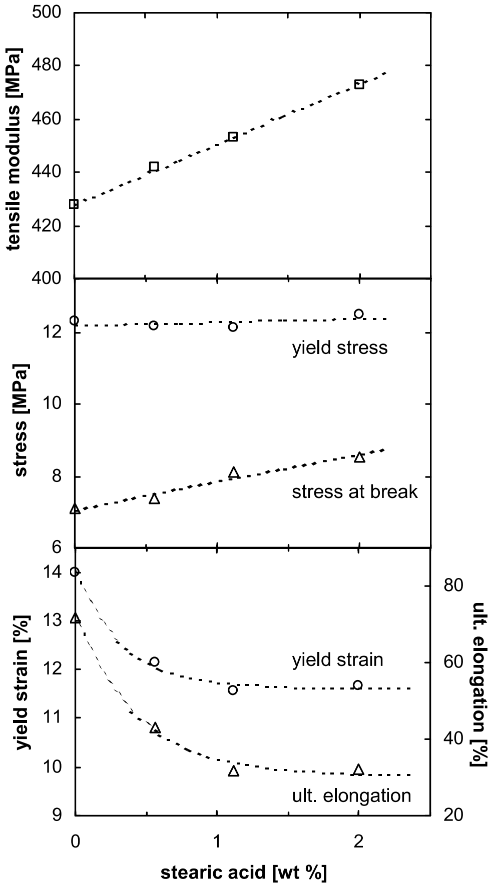

Fig. 4. Influence of stearic acid on the mechanical properties of 10 vol% 1TAV–LDPE composites. The dotted lines are guides for the eye.

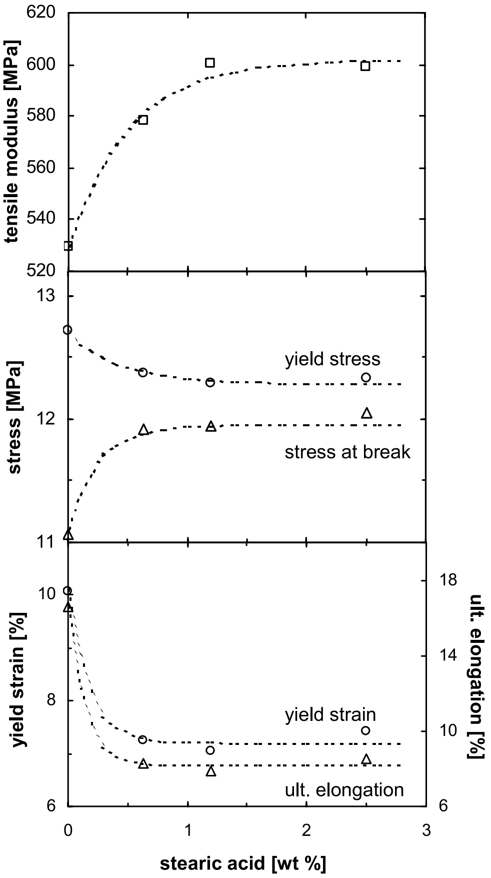

Fig. 5. Influence of stearic acid on the mechanical properties of 20 vol% 1TAV–LDPE composites. The dotted lines are guides for the eye.

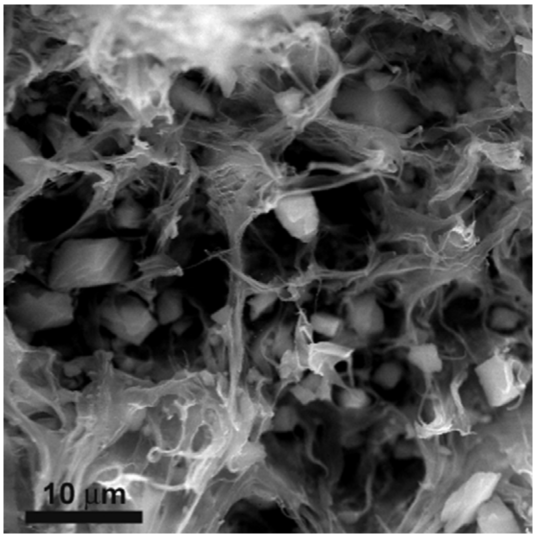

Fig. 6. SEM micrograph of a tensile fracture surface of the 20 vol% 1TAV–LDPE composite containing 1.2 wt% stearic acid.

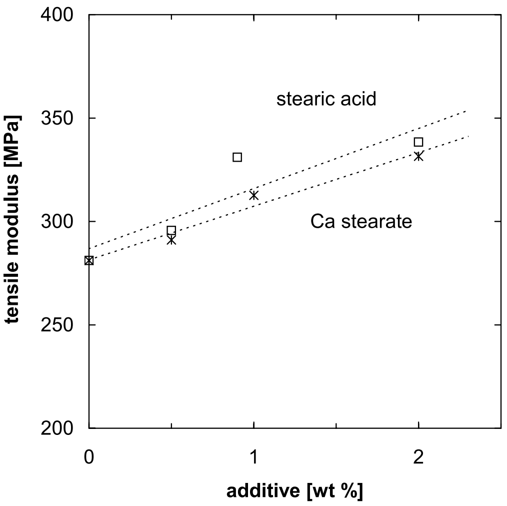

Fig. 7. Influence of stearic acid and calcium stearate on the stiffness of LDPE. The dotted line is a guide for the eye.

comparing the effect of both, surfactant (Figs. 7 and 8) and filler (Table 1) on the stiffness and yield behavior of the polymer with that of their combination (Figs. 4 and 5), it can be seen that the reinforcing effects are not additive. The excess surfactant actually amplifies the modulus reinforcement but its effect tops at 600 MPa in the 20 vol% composite. Although both, filler and surfactant enhance the yield stress of the polymer, their combination does not lead to linear accumulation of both effects (Figs. 4 and 5). All other tensile properties of the polymer decrease monotonically on adding stearic acid (Figs. 8 and 9). However, stearic acid in presence of the filler leads to reinforcement of the tensile strength (Figs. 4 and 5).

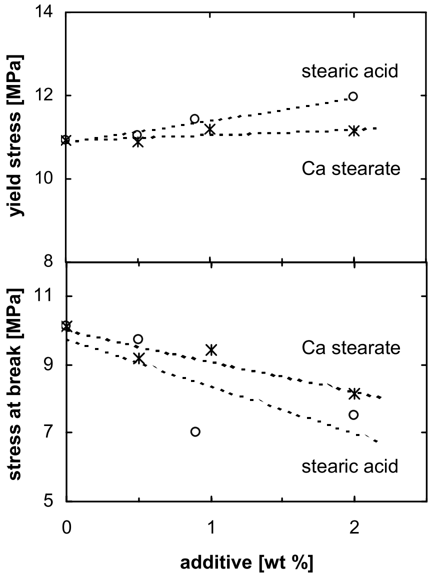

Fig. 8. Influence of stearic acid and calcium stearate on the yield stress and tensile strength of LDPE. The dotted lines are guides for the eye.

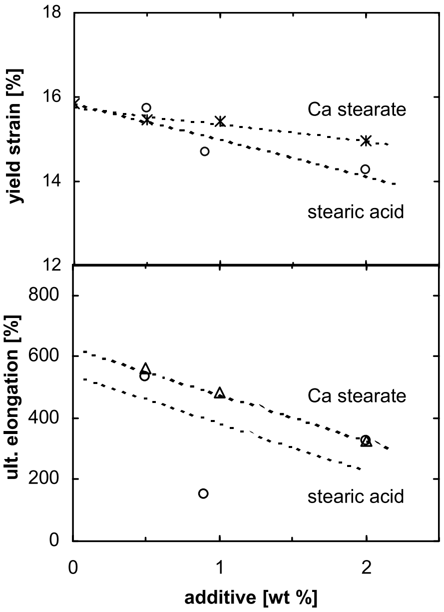

Fig. 9. Influence of stearic acid and calcium stearate on the yield strain and ultimate elongation of LDPE. The dotted lines are guides for the eye.

In Figs. 7–9 the influence of calcium stearate, which is some times used as acid scavenger, lubricant or processing aid, on the tensile properties of LDPE is also shown. It can be seen that calcium stearate has practically the same but less pronounced effect on the tensile properties of the polymer as stearic acid. The influence of calcium stearate on the mechanical properties of the polymer can be explained by the fact that the calcium salt is present as a heterogeneous phase (particulates) in the polymer matrix. Fig. 10 shows a SEM micrograph of a 2 wt% compound of calcium stearate and LDPE, in which it can be seen that the calcium salt is incorporated in the polymer as submicron particles. The nucleation effect of these particulates on the crystallization of the polymer is small as can be seen from Table 2. Stearic acid, which is molten at the crystallization temperature of LDPE, can be expected to build micelles in the molten state,

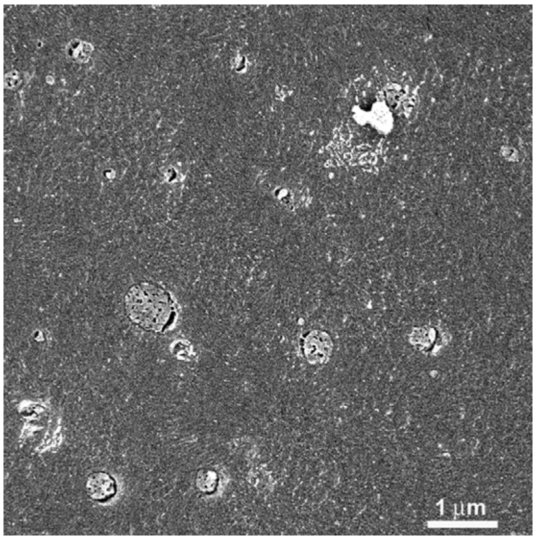

Fig. 10. SEM micrograph of a 2 wt% calcium stearate–LDPE compound.

leading to a heterogeneous structure in the solid state similar to that observed in particulate filled polymers. This may explain the influence of stearic acid on the mechanical properties of LDPE and the composites containing excessive surfactant. Unfortunately, it was not possible to prove this hypothesis by electron microscopy due to the lack of contrast between stearic acid and polyethylene.

4. Conclusions

Stearic acid linearly increases the modulus and yield stress of LDPE but reduces its tensile strength, yield strain and ultimate elongation. Calcium stearate has the same effect on the polymer but to a smaller extent. Stearic-coated calcite also increases the stiffness and yield stress of LDPE but decreases all its other tensile properties. Over-coating the filler does not lead to linear accumulation of the effects, and the influence of surfactant excess on the composite properties cannot be simply predicted. Surfactant excess amplifies the reinforcement of the stiffness but decreases all other tensile properties of the composite. It is probably more advantageous to coat the filler with the optimal amount of surfactant necessary to cover its surface with an organic monolayer unless the influence of excessive coating can be exploited in certain applications.

Acknowledgements

We gratefully acknowledge financial support from the Swiss Commission for Technology and Innovation (CTI) and the Swiss National Science Foundation (SNF).

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