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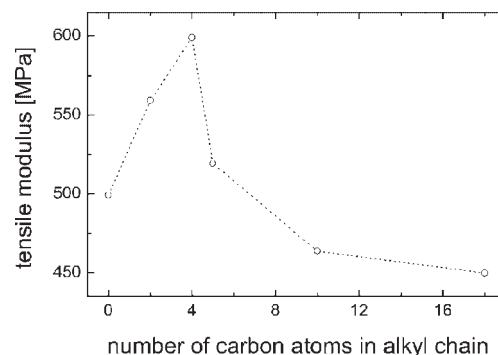
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Surfactant Chain Length and Tensile Properties of Calcium Carbonate-Polyethylene Composites

Maged A. Osman,* Ayman Atallah

Micron-sized CaCO_3 particles free of milling additives were coated with a monolayer of aliphatic carboxylic acids of different chain length (C2, C4, C5, C10, and C18). CaCO_3 was compounded with LDPE at different loading, and the tensile properties of the composites were measured and correlated to the length of the alkyl chains tethered to the particles' surface. SEM indicated that the particles are well dispersed (no agglomerates). The inclusions show little influence on the polymer crystallization, and the filler surface treatment leads to a slight decrease in polymer crystallinity that grows with increasing chain length of the fatty acid. The tensile modulus, yield stress, and maximum stress increase with increasing filler volume fraction ϕ , and the dependence is a function of the length of the alkyl chains tethered to the CaCO_3 surface. It seems that the interphase thickness and properties depend on the alkyl chain length and strongly influence the modulus and stresses measured. With increasing chain length in the coated organic layer, the interfacial adhesion between the inclusions and the polymer matrix decreases, and the fibril formation increases. The tensile properties are the result of a superimposition of all these effects. The yield and ultimate strains are dominated by the interfacial slippage (increases with growing alkyl chain length) that leads to debonding at high deformations. Surface treatment of CaCO_3 with valeric acid leads to the maximum possible tensile modulus, yield stress, and tensile strength combined with a relatively small loss in yield and ultimate strain.



Introduction

Polyethylene (PE) is one of the most widely exploited polymers and is often compounded with natural minerals to enhance its stiffness, toughness, dimensional stability, or electric-insulation properties.^[1,2] Calcium carbonate is

the most abundant mineral on earth, and therefore its PE composites are of considerable industrial and scientific interest. Like most of the natural minerals, CaCO_3 has a high energetic hydrophilic surface, whereas the PE surface is of low-energy and hydrophobic nature. This often leads to aggregation (hard clusters that need attrition to be disintegrated) and agglomeration (soft flocks) of the filler particles to clusters in the polymer matrix. The number and strength of the clusters depend on the particles size, i.e., specific surface area (SSA), production method, and compounding conditions. To reduce the CaCO_3 surface

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energy and the interparticle attraction forces, it is often coated with a variety of surfactants of which stearic acid is the most often used.^[2–4] Practically, all these surfactants have long alkyl chains and short chains have not been adequately investigated, although the filler surface tension and the work of adhesion between the inclusions and the polymer matrix are expected to depend on the chain length.^[5–8] The coated organic layer enhances the wetting of the filler by the polymer melt during compounding and reduces the particles' tendency to agglomerate. Reducing the surface energy of CaCO_3 leads not only to better particle dispersion (disintegration to the primary particles) but also decreases the interfacial tension and the work of adhesion between the particles and the polymer with consequences for the tensile and impact properties of the composite.^[4,8–12]

Nano- and sub-micron particles (large SSA) have strong tendency to aggregate, building strong clusters with different shapes, which cannot be disintegrated during compounding. Hence, they lead to special reinforcement effects (higher moduli) and are not going to be considered in this context.^[13,14] Filling a semi-crystalline polymer with micron-sized isotropic filler particles influences its tensile properties in different ways. In addition to the component properties, the composite mechanical characteristics are influenced by the adhesion forces at the filler-matrix interface and by the thickness and properties of the interphase, e.g., crystallite orientation and chain dynamics.^[11,12,15–17] Moreover, the particulates can influence the polymer crystallization, thereby increasing or decreasing the crystallinity and thickness of the crystallites.^[17,18] The crucial role of composite morphology in determining the mechanical properties is well recognized. During macroscopic deformation, numerous processes such as elastic deformation, yielding, crazing, orientation, debonding (dewetting), failure initiation, and propagation take place. These local processes, which occur at small or large deformations, are differently influenced by the above mentioned parameters that vary not only with the type of filler but also with the particles surface treatment.

Generally, the polymer's tensile modulus increases, whereas the deformability decreases with the increase in crystallinity and the reinforcing effect of solid inclusions increases with the decrease in matrix stiffness. In a weak matrix, the filler carries a significant part of the load, hence reinforces it. The extent of stress transfer depends on the adhesion strength at the interface and the SSA of the filler. The inclusion of micron-sized CaCO_3 in low-density PE (LDPE, low crystallinity) enhances its modulus and yield stress but decreases its elongation at break.^[19–21] The surface treatment of the particles with stearic acid reduces their reinforcing effect on the yield stress. In a stiff matrix, larger stresses develop around the inclusions and the probability of debonding increases, making this process

the dominant deformation mechanism. Bartczak et al.^[22] reported that the tensile modulus of high-density PE (HDPE, highly crystalline) increases with the increase in the volume fraction of stearic acid treated CaCO_3 particles, whereas the yield stress and strain as well as the stress and elongation at break decrease. Only few studies on the effect of CaCO_3 and its surface treatment on the tensile properties of PE are available in the literature; however, more investigations have been carried out with the more crystalline poly(propylene) (PP).^[11,17,19,23–25] The development of the tensile properties of PP- CaCO_3 composites with increasing filler volume fraction ϕ shows the same trend as that described for HDPE composites. The particulate surface treatment with stearic acid decreases the work of adhesion between the two phases, leading to decreased yield stress and tensile strength as well as to improved deformability but unchanged modulus. Neither in PE nor in PP, has the effect of the alkyl chain length in the organic coating on the mechanical properties of the composites been described.

In the present investigation, micron-sized nearly spherical (aspect ratio close to one) CaCO_3 particles were coated with a monolayer of aliphatic carboxylic acids of different chain length (C2, C4, C5, C10, and C18). The CaCO_3 powder (treated and untreated) was compounded with LDPE at different loading and the tensile properties of the composites were measured. LDPE was chosen as a matrix to emphasize the effect of the filler and its surface treatment. The influence of the alkyl chain length in the organic monolayer on the polymer crystallinity and the tensile properties of the composites were studied.

Experimental Part

Materials

All chemicals were purchased from Fluka (Buchs, Switzerland). The CaCO_3 powder (VP1018) was courtesy of Omya (Oftringen, Switzerland), for which a pristine marble from Gummern was wet-milled in a Dyno-Mill without additives to avoid surface contamination. The obtained slurry was dried at 105 °C and the resulting powder de-agglomerated in an Alpine 160Z mill. The particles volume median equivalent spherical diameter was found to be 1.85 μm and its SSA was measured by the nitrogen adsorption method (BET) to be 3.6 $\text{m}^2 \cdot \text{g}^{-1}$.^[26] The LDPE used in this study is Lupolen 2420H, which was supplied by Elenac (Ludwigshafen, Germany). It has a density of 0.924 $\text{g} \cdot \text{cm}^{-3}$ and a melt flow index of 1.9 g per 10 min (2.16 kg at 190 °C), as per supplier's data.

Filler Surface Treatment

Care was taken to coat the filler particles with a chemically bound monolayer of fatty acid, avoiding the presence of excess surfactant

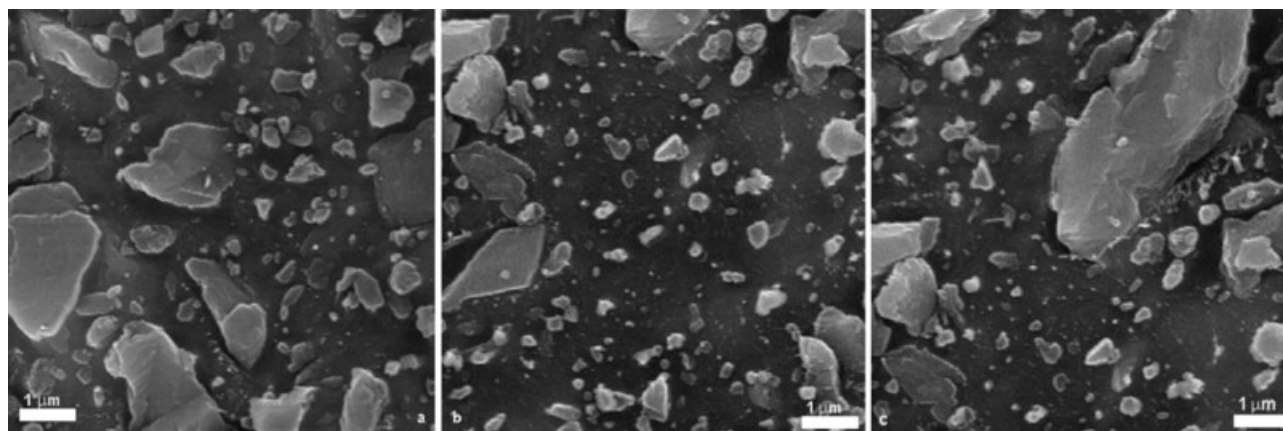


Figure 1. SEM micrographs of LDPE composites with 20 vol.-% filler loading: (a) untreated CaCO_3 (VP 1018), (b) C2, and (c) C18.

(over-coating), which influences the surface properties of the filler and the mechanical properties of the composites.^[27,28] The required amount (1.5 mmol) of carboxylic acid (acetic C2, butyric C4, valeric C5, capric C10, and stearic C18) was added to a suspension of 50 g VP1018 in 50 mL of toluene and the mixture was stirred for 30 min at room temperature. The slurry was centrifuged and the supernatant liquid decanted. The product was washed twice by shaking with toluene and separated by centrifugation, then dried at 80 °C under reduced pressure. Full surface coverage and the purity of the monolayer (presence of unreacted acid) were monitored by thermogravimetric analysis (TGA).^[26]

Composite and Sample Preparation

The composites were prepared in a twin-blade kneader “Plasti-Corder W 50 EH” (Brabender, Duisburg, Germany) equipped with a 60 mL bowl and counter-rotating blades. The filler volume fraction was calculated using the densities of CaCO_3 and LDPE. The polymer pellets were molten at 150 °C and the required amount of 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. The amount of material was chosen to fill the bowl completely and avoid incorporation of air that promotes the polymer degradation.

The compound was compression molded to 1.5 mm thick plaques in a brass frame between two aluminum plates at 180 °C. To ensure the absence of microvoids, the molding process was carried out under reduced gas pressure (0.01 mbar) in a brass chamber. The mold was left to cool slowly in the press without active cooling to ensure reproducible polymer crystallization. The neat polymer used for comparison was kneaded and compression molded under the same conditions. 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.

Differential Scanning Calorimetry

DSC measurements were carried out on a DSC 7 (Perkin-Elmer, Norwalk, CT) under nitrogen at a heating rate of 10 °C · min⁻¹, adopting the procedure used for measuring heat capacities.^[29] The temperature-dependent instrumental deviations were corrected by using aluminum pans (sample and reference) of the same weight; the calorimeter base line was also scanned and subtracted. A sapphire standard sample was used to calibrate the response of the calorimeter and the sample weight was kept constant (ca. 6 mg). The melting enthalpy (ΔH_m) of all samples was measured over the same temperature range (55–120 °C) and the enthalpy was related to the weight of LDPE in the sample.

Table 1. Effect of surface treated and untreated CaCO_3 on the crystallization behavior of LDPE in 20 vol.-% composites.

Filler	$T_{m, \text{onset}}^{\text{a)}$ °C	$T_m^{\text{b)}$ °C	ΔH_m $\text{J} \cdot (\text{g polymer})^{-1}$	Crystallinity $X_c^{\text{c)}$	$T_{c, \text{onset}}^{\text{d)}$ °C
Neat LDPE	103	111	105	0.358	96
Untreated	103	110	105	0.358	100
C2	103	110	101	0.345	99
C4	102	111	102	0.348	99
C18	103	110	99	0.338	98

^{a)}Melt onset temperature; ^{b)}Melt peak temperature; ^{c)}Degree of crystallinity calculated using ΔH of PE equilibrium crystals 293 J · g⁻¹^[34]; ^{d)}Crystallization onset temperature.

It has to be remarked that the above mentioned precautions are often ignored, which can lead to misleading results and interpretations.^[30,31]

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. 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 fracture

surface of the tested tensile bars was also sputter coated with 5 nm of Pt and microscopically examined.

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, Fürstentfeld, Austria). The elastic modulus was determined at $0.5 \text{ mm} \cdot \text{min}^{-1}$ crosshead speed, while all other tensile characteristics were measured at $6 \text{ mm} \cdot \text{min}^{-1}$. Prior to the measurement, the thickness and width of the specimen were measured with a micrometer and the cross-sectional area was calculated. An average of at least five measurements for each sample is reported.

Results and Discussion

The presence of filler clusters strongly influences the mechanical properties of composites because they act as sites for fracture initiation, thereby leading to premature material failure.^[17,32,33] With increasing ϕ , even micro-n-sized-particles (small SSA) tend to build agglomerates if

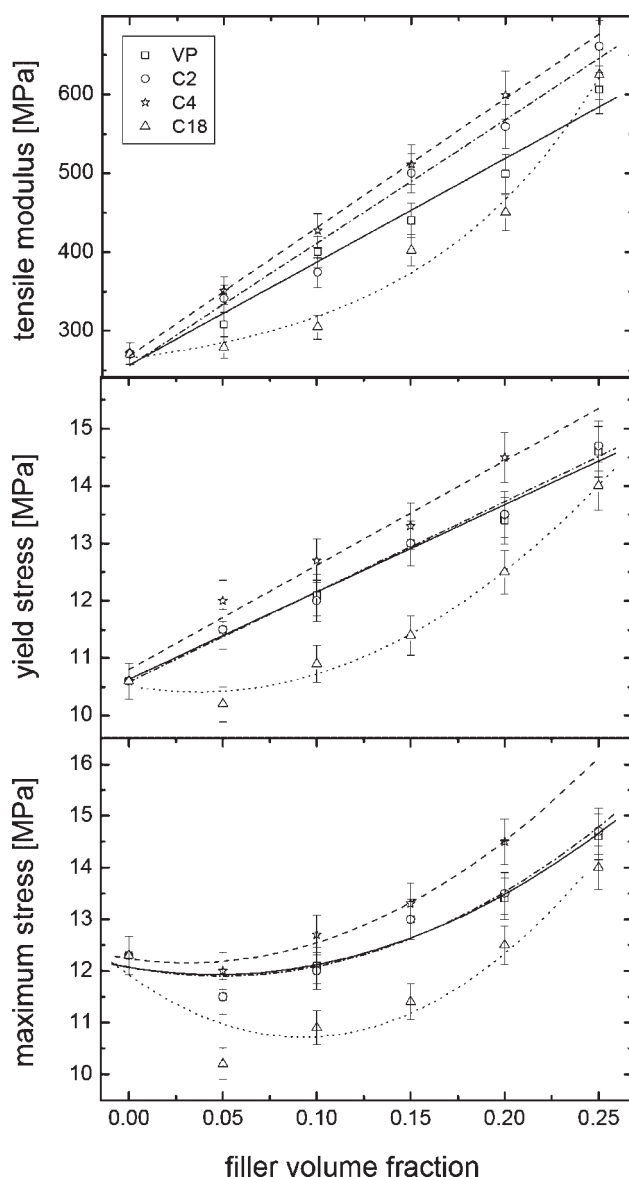


Figure 2. Tensile modulus, yield stress, and maximum stress of LDPE- CaCO_3 composites as functions of the filler volume fraction and surface treatment. The lines are simple guides to the eye.

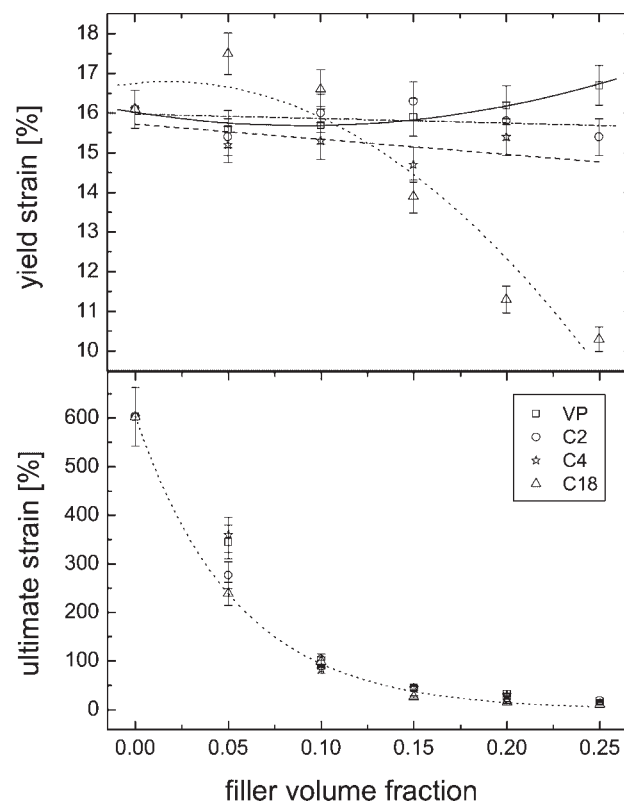


Figure 3. Yield and ultimate strain of LDPE- CaCO_3 composites as functions of the filler volume fraction and surface treatment. The lines are simple guides to the eye.

the compounding conditions do not ensure optimal dispersion and spatial distribution. The dispersion of the particulates in the prepared composites (treated and untreated CaCO_3) was assessed by SEM. The micrographs indicated that the compounding conditions used resulted in high dispersion levels of the particles even at high loading (Figure 1), i.e., differences in the mechanical properties of the composites cannot be attributed to the presence of filler clusters.

The effect of the surface treated and untreated CaCO_3 on the crystallization of LDPE was investigated by DSC and the results obtained for the 20 vol.-% composites are given in Table 1 (neat polymer was kneaded and compression molded under the same conditions as the composites). The presence of CaCO_3 as well as its surface treatment has little influence on the crystallization kinetics and the degree of crystallinity of LDPE. A modest increase in the crystallization onset temperature is observed, indicating that the inclusions induce heterogeneous nucleation. The effect is largest in the untreated CaCO_3 composite, decreases with the filler surface treatment and diminishes with increasing chain length of the carboxylic acid. The melt enthalpy of the polymer shows that the untreated filler has no influence on the degree of crystallinity although the crystallization process starts at a higher temperature. The filler surface treatment leads to a slight decrease in polymer crystallinity that increases with growing chain length of the fatty acid, so that the stearic acid surface treatment reduces the PE crystallinity from 35.8 to 33.8%.

The tensile properties of the composites are plotted against the filler volume fraction in Figure 2 and 3. The figures also show the effect of the alkyl chain length in the coated monolayer on these functions. The tensile modulus of the untreated CaCO_3 -LDPE composites increases with augmenting ϕ as expected.^[35] Treating the filler surface with acetic acid increases the slope of the ϕ -dependence and with butyric acid the slope increases further. In view of the observed slight decrease in polymer crystallinity with the filler surface treatment (Table 1), this result is unexpected. However, it can be explained by the formation of an interphase, whose properties and thickness depend on the alkyl chain length in the filler coating. In the stearic acid treated CaCO_3 composites, the tensile modulus increases at a

much lower pace at low loading then grows fast with the increase in ϕ . That is, at low loading, the modulus of the C18 composites is lower than that of the untreated CaCO_3 ones but higher than that of the polymer matrix, then exponentially increases to reach that of the other composites at 25 vol.-%. This is probably the result of superimposed effects: reduction in polymer crystallinity (Table 1), an interphase, with higher modulus than that of LDPE, increased thickness of the interphase and decreased interfacial adhesion with growing alkyl chain length. With increasing volume fraction of the inclusions that have a wide size distribution, the interparticle distance decreases and the interphase surrounding the inclusions interconnects.^[22,36,37] In the early stages, partial interconnection of the interphase leads to the formation of domains that percolate above a certain filler concentration. With increasing thickness of the interphase, the interconnection is reached at lower ϕ . The sum of these effects leads to the observed exponential increase in the modulus of C18 (Figure 2). The behavior of the tensile moduli strongly suggests that the thickness and properties of the interphase, which depend on the alkyl chain length in the coated monolayer, have a strong influence on the mechanical properties of the composites. It has to be emphasized that

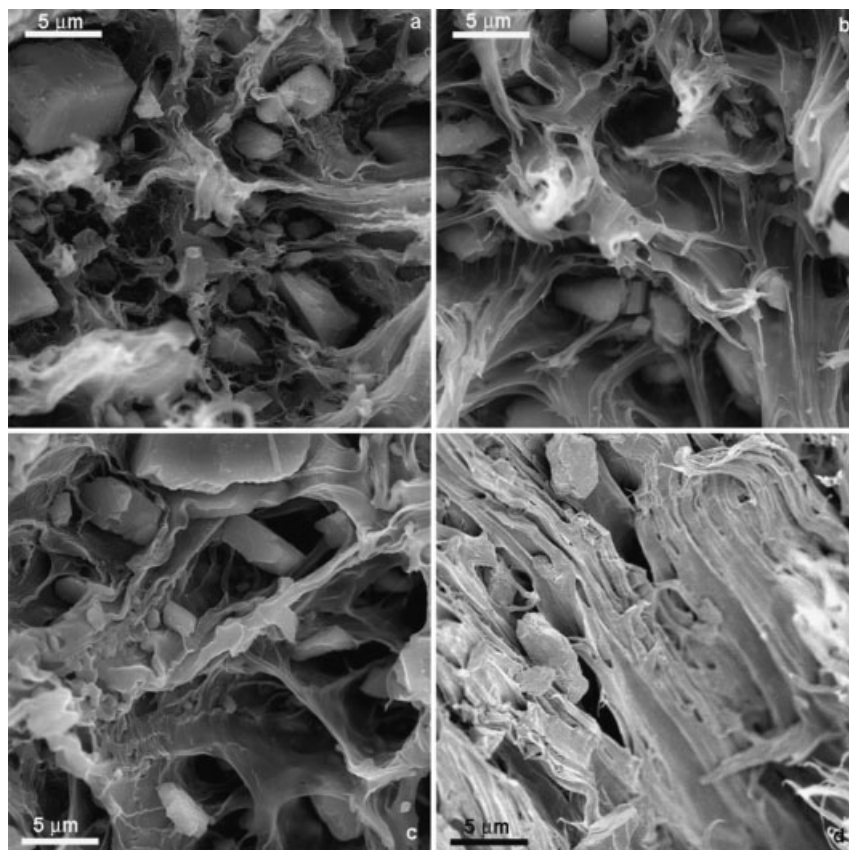


Figure 4. SEM micrographs of the fracture surface of tensile samples of 15 vol.-% LDPE- CaCO_3 composites: (a) non-treated, (b) C2, (c) C4, and (d) C18.

this is a plausible explanation for the measured tensile moduli without an explicit evidence, since it is not possible to directly measure the thickness or the mechanical properties of the interphase.

Similarly, the yield and maximum stresses increase with augmenting ϕ ; however the C2 and the untreated CaCO_3 composites functions are identical (Figure 2). The yield stress shows a linear dependence on ϕ for the untreated filler, C2 and C4 composites, but a nonlinear one for the C18 compound for the same reasons mentioned above. The maximum stress, which is measured at higher deformations, is a nonlinear function of ϕ in all the cases, and the C4 composites show higher values than those of C2 and the pristine CaCO_3 compounds, whereas those of C18 are lower. The interfacial adhesion between the two heterogeneous phases is significantly decreased in the C18 composites and its effect becomes noticeable at the high deformations applied. However, the yield and maximum stresses are dominated by the thickness and properties of the interphase, especially at high filler loading.

The yield strain (Figure 3) of the untreated CaCO_3 composites remains almost unaffected by the filler loading up to ca. 15 vol.-%, then increases slightly, whereas that of C2 and C4 slightly decreases with increase in ϕ . In contrast, the yield strain of the C18 composites strongly decreases at high filler loading (above 10%), suggesting that the adhesion forces are reduced with growing chain length of the fatty acid. The ultimate strain decreased exponentially with increasing ϕ for all the composites. This implies that interfacial slippage (relative movement of the matrix chains across the interface under the applied force) takes place, leading to debonding at high deformations, which dominates the ultimate strain.

SEM micrographs of the fracture surface after the tensile test of the 15 vol.-% composites (VP, C2, C4, and C18) are given in Figure 4, showing the effect of the filler surface treatment. The composite of the untreated CaCO_3 [Figure 4(a)] shows very little plastic deformation that increases to a small extent in the C2 and C4 composites [Figure 4(b) and (c)]. In contrast, the C18 compound [Figure 4(d)] shows extensive fibrillation of the polymer. Figure 4 also demonstrates that debonding between the inclusions and the polymer matrix takes place, resulting in elongated cavities as the matrix undergoes plastic deformation. These findings support the notion that the interphase thickness and properties are essentially influenced by the surface treatment of the filler and by the length of the alkyl chains tethered to its surface.

The dependence of the 20 vol.-% composites tensile properties on the length of the alkyl chains tethered to the CaCO_3 surface is shown in Figure 5. The modulus as well as the yield and maximum stress increase with growing chain length to reach a maximum at C5 then decrease to plateau values as the alkyl chains become longer than C10.

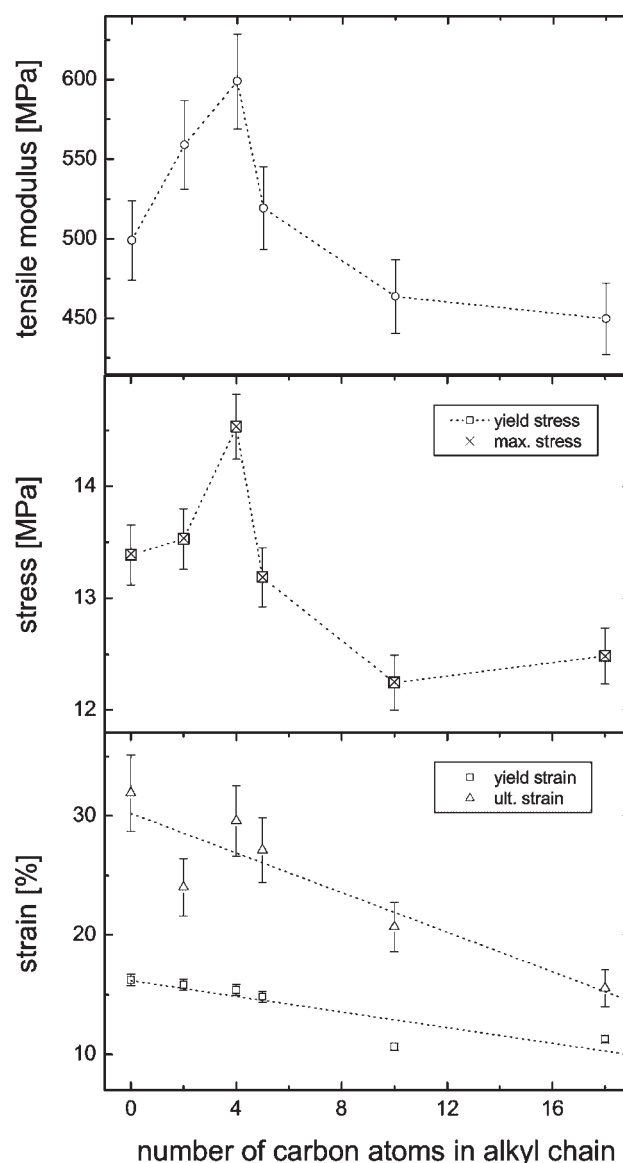


Figure 5. Tensile properties of 20 vol.-% LDPE- CaCO_3 (surface treated with carboxylic acids) as a function of the number of carbon atoms in the acid. The lines are simple guides to the eye.

In contrast, the yield and ultimate strain monotonically decrease with growing alkyl chain length and the dependence of the ultimate strain is stronger. In accordance with the explanation given above, the modulus and stresses mainly depend on the thickness and properties of the interphase which in turn depend on the length of the alkyl chains, leading to a maximum at C5. The strain is dominated by the interfacial slippage that monotonically increases with augmenting alkyl chain length and sample deformation. At high deformations, the interfacial slippage between the coated filler surface and the polymer matrix leads to debonding.

Conclusion

Surface treatment of solid inclusions in a polymer matrix affects the tensile properties of the composite. The alkyl chain length in the coated organic monolayer influences the thickness and properties of the interphase as well as the interfacial slippage that leads to debonding. The tensile modulus, yield stress, and maximum stress are strongly influenced by the interphase thickness and properties, whereas the yield strain and ultimate strain are dominated by the interfacial slippage. Surface treatment of CaCO_3 with valeric acid leads to composites with the maximum possible tensile modulus and strength combined with a relatively small loss in yield and ultimate strain.

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Keywords: calcium carbonate; chain; interphase; polyethylene; surface treatment; tensile properties

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