Chem. Mater. **2002,** *14,* 4408−4415

Surface Treatment of Calcite with Fatty Acids: Structure and Properties of the Organic Monolayer

Maged A. Osman and Ulrich W. Suter*

Department of Materials, Institute of Polymers, ETH Center, CH-8092 Zürich, Switzerland

Received June 3, 2002. Revised Manuscript Received July 25, 2002

Thermogravimetric analysis was used to investigate the surface cleanliness of calcite fillers and to determine the optimal amount of fatty acid needed to coat the particles with an organic monolayer. The use of excess surfactant led to the formation of a bilayer as well as to the presence of free acid molecules. Both species could be detected by TGA. Optimal coating of calcite with stearic acid gave a monolayer of calcium stearate bicarbonate in which one acid molecule is attached to every Ca^{2+} present on the surface. The alkyl chains in the monolayer are vertically oriented to the surface and are restricted in their motion. ^{13}C NMR and IR spectroscopy revealed that the chain conformation shows a high trans population, which leads to an ordered solidlike phase. Monolayers of saturated fatty acids with long alkyl chains ($\geq C_{10}$) showed similar behavior, while the lower homologues ($\geq C_{10}$) gave monolayers with dynamically disordered phases. The immobilization of oleic acid molecules by tethering them to the calcite surface rendered them liable to thermal polymerization at relatively low temperatures. In other words, calcite can be coated with a monolayer of oleic acid molecules, which is polymerized later to give a polymeric monolayer.

1. Introduction

Polymers are popular household articles as well as construction and engineering materials; however, they are seldom used in their pure state. Usually, polymers (amorphous or semicrystalline) are filled with crystalline minerals to reduce price (extenders) or improve their solid-state properties (functional fillers). In the latter case, advantage is taken of both material properties; that is, existing properties are enhanced or new ones induced.[1−4] Calcite is the most abundant mineral on earth and finds increasing application in the polymer industry. However, the incompatibility of its high energetic hydrophilic surface with the low-energy surface of hydrophobic polymers is a problem to be solved before it can be used as a functional filler. For this and other reasons, the surface of calcite is often rendered organophilic by a variety of surface modifiers such as fatty acids, phosphates, silanes, titanates, or zirconates.[2−5] In this way, improved wetting and dispersion as well as uniform spatial distribution of the particulates are reached.[6] Better processability of the composites as well as enhanced mechanical and surface properties can also be achieved through proper surface treatment.[7,8] The most widely used calcite surface coating is the treatment with fatty acids, usually stearic acid. As a result, a monolayer of hydrophobic organic molecules is attached to the mineral surface. The structure and properties of such an ultrathin organic film have a strong influence on the final properties of the composites because this film represents the interface between the two phases of the heterogeneous material. It also determines the particle−particle as well as the particle−matrix interactions and controls the buildup of the interphase.

Ground natural calcite is one of the oldest manufactured powders and precipitated calcium carbonate was first prepared almost a hundred years ago. A tremendous number of patents and publications on carboxylate modification of both types of fillers have been reported.[2−5] Despite that, little is known on the structure and properties of the organic film created on the mineral surface and the existing scarce information is often contradictory. It is generally accepted that carboxylic acids or their salts react with calcium carbonate to produce a layer of the corresponding calcium salt (calcium stearate in the case of stearic acid) on the surface.[9−11] For example, Sutherland et al.[11] studied the surface reaction of calcite with ammonium stearate by diffuse reflection infrared Fourier transformation (DRIFT) and X-ray photoelectron spectroscopy (XPS) and concluded that this reaction leads to a surface layer

---

* To whom correspondence should be addressed. Phone: +41 1 6323127. Fax: +41 1 6321096. E-mail: suter@ifp.mat.ethz.ch.

(1) Katz, H. S., Milewski, J. V., Eds. *Hand Book of Fillers for Plastics*; Van Nostrand Reinhold Company: New York, 1987.

(2) Rothon, R. N., Ed. *Particulate-Filled Polymer Composites*; Longman Scientific and Technical: Harlow, 1995.

(3) Krager-Kocsis, J., Ed. *Polypropylene: Structure, Blends and Composites*; Chapman and Hall: London, 1995.

(4) Jancar, J., Ed. *Mineral Fillers in Thermoplastics I, Raw Materials and Processing*; Advances in Polymer Science 139; Springer: Berlin, 1999.

(5) Nakatsuka, T. In *Molecular Characterization of Composite Interfaces*; Plenum Press: New York, 1985.

(6) Pukánsky, B.; Fekete, E. *Polym. Polym. Composite* **1998**, *6* (5), 313.

(7) Schlumpf, H. P. *Kunststoffe* **1987**, *77*, 1092.

(8) Ahsan, T.; Taylor, D. A. *J. Adhesion* **1998**, *67*, 69.

(9) Szczypa, J.; Chibowski, St.; kuspit, K. *Trans. Inst. Min. Metall., Sect. C* **1979**, *88*, 11.

(10) Ivanishchenko, O. I.; Gladkikh, Y. P. *Colloid. J. USSR* **1979**, *41*, 660.

(11) Sutherland, I.; Maton, D.; Harrison, D. L. *Compos. Interfaces* **1998**, *5* (6), 493.

10.1021/cm021222u CCC: $22.00

of calcium stearate. Yet, Sharifkhodzhaeva et al.[12] suggested that the fatty acids react only with the $Ca(OH)_2$, omnipresent on the calcite surface,[13−15] but not with the $CaCO_3$ itself to give the corresponding calcium stearate. On the other hand, Papirer et al.[16] and Fekete et al.[17] found that only one stearic acid molecule is attached to each Ca^{2+} and suggested that the alkyl chains in a complete monolayer are vertically oriented to the calcite surface. The perpendicular orientation of the alkyl chains was confirmed by X-ray scattering techniques.[18] The thickness of the stearate monolayer was found to be ≈2.6 nm, which corresponds to the molecular length of stearic acid. Papirer et al.[16] did not investigate the chemical structure of the calcium salt formed on the calcite surface, while Fekete et al.,[17] on the basis of XPS measurements, suggested that Ca(OH)(OOCR) is created, accompanied by hydrolytic degradation during the stearic acid reaction with calcite. Both groups proved by contact angle measurements and inverse gas chromatography (IGC) that coating calcite with a fatty acid monolayer reduces its surface energy and diminishes the particle−particle interactions, a result which was confirmed by Ahsan and Taylor.[8] They also showed that the use of excess acid (to ensure complete surface reaction) leads to multilayer adsorption in which only a monolayer is chemisorbed, while the other is physisorbed in a tail-to-tail arrangement.[16,17]

The use of an optimal amount of surface modifier is not only of economic importance but also technically advantageous because excessive amounts of surfactant lead to processing problems and inferior mechanical properties.[8,17,19] A similar result was obtained in a detailed study on the effect of the coating level of magnesium hydroxide on the mechanical properties of its polyethylene composites.[20] The amount of chemically bonded surfactant has been determined by a so-called "dissolution technique," which consists of treating the filler with an excess of surfactant, then washing away the nonbonded part, and determining the amount of surfactant remaining in solution by HPLC, IR, UV, or liquid-scintillation β spectrometry.[16,17,19] In this way, the adsorption isotherms of stearic acid were measured in different solvents. Gilbert et al.[21] tried to determine the optimal coating level of magnesium hydroxide and calcium carbonate by DRIFT and XPS, but obtained different results from the two techniques. Thomas and Clouse[22] showed that thermogravimetric analysis (TGA), which is a much simpler technique, can be used to determine the amount of organic material on the surface of calcite but the method was not used to determine the amount of acid necessary for an optimal coating. To our knowledge, no method has been reported yet, which can differentiate between chemisorbed and physisorbed molecules.

The goal of the present study was to investigate the structure and properties of the organic monolayer formed on a calcite surface upon coating with a fatty acid. To achieve a pure chemically bonded organic monolayer, it was necessary to find a simple method to differentiate between chemisorbed and physisorbed molecules and to determine the optimal amount of surfactant necessary to cover the calcite surface with an organic monolayer.

2. Experimental Section

2.1. Materials. All chemicals were purchased from Fluka (Buchs, Switzerland). The calcite powder (VP1018) was courtesy of Omya (Oftringen, Switzerland) in which a pristine marble from Gummern was wet-milled in a Dyno-Mill without any additives. The so-obtained slurry was dried at 105 °C and the resulting powder deagglomerated in an Alpine 160Z mill. Omyacarb 1AV (marble, dry-milled, D50% = 1.8 μm) and Omyalite 90 (chalk, wet-milled, D50% = 1 μm) are commercial products of Omya, while Socal U1 (precipitated, D50% = 0.08 μm) is a product of Solvay (Ebensee, Austria). The D50% values given are supplier data.

2.2. Particle Size. The particle size distribution of the calcite powder VP1018 was measured in dilute aqueous suspension (ammonium polyacrylate was added to help the dispersion) by centrifugal sedimentation using a cuvette photocentrifuge, Horiba CAPA-700 (Kyoto, Japan).[23] The suspension was sonicated prior to the measurement to ensure complete dispersion of the powder.

2.3. Surface Area. The specific surface area (SSA) of the calcite powder was determined by the Brunauer−Emmett−Teller gas adsorption method (nitrogen) using a Gemini III 2375 surface area analyzer (Micromeritics Instrument Corporation, Norcross, GA). Prior to the measurement, the powder was dried at 80 °C under vacuum overnight and then scavenged with nitrogen on a FlowPrep 060 Degasser (Micromeritics) at 100 °C for 2−3 h.

2.4. Scanning Electron Microscopy (SEM). Samples of the calcite powder were deposited on a carbon-coated EM-grid from a dilute alcoholic suspension, which was previously sonicated. The samples were sputter-coated with 5 nm of Pt before they were observed in a Hitachi S-900 "in-lens" field emission scanning electron microscope (FESEM) at 10 kV.

2.5. Thermal Analysis. Thermogravimetric analysis (TGA) was carried out in an air stream at a heating rate of 20 °C/min on a TGA Q500 (TA Instruments, New Castle, DE) and a Perkin-Elmer 7 thermal analysis system (Perkin-Elmer, Norwalk, CT). Differential scanning calorimetry (DSC) was carried out under nitrogen at a rate of 10 °C/min on a MDSC Q1000 (TA Instruments) and a DSC 7 (Perkin-Elmer).

2.6. Surface Treatment. The required amount of fatty acid was added to a mixture of 20 g of calcium carbonate VP1018 and 20 mL of toluene in a centrifuging tube and the suspension shaken for 30 min at room temperature. The slurry was then centrifuged and the supernatant liquid decanted. The product was washed by shaking with toluene, separated by centrifugation, and then dried at 80 °C under reduced pressure. Oleic acid coated calcite was alternatively washed with ether and dried at room temperature under reduced pressure.

2.7. IR Spectroscopy. Infrared transmission spectra were collected on a Bruker IFS 66V FTIR spectrometer (Bruker

---

(12) Sharifkhodzhaeva, Kh. A.; Ryabova, N. D.; Aripov, E. A. Deposited Doc. 1975; VINITI 101-75; *Chem. Abstr.* **1977**, *87*, 4780y.

(13) Morimoto, T.; Kishi, J.; Okada, O.; Kadota, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1918.

(14) Keller, D. S.; Luner, P. *Colloids Surf. A* **2000**, *161*, 401.

(15) Stipp, S. L. S.; Hochella, M. F., Jr. *Geochim. Cosmochim. Acta* **1991**, *55*, 1723. Stipp, S. L. S.; Eggleston, C. M.; Nielsen, B. S. *Geochim. Cosmochim. Acta* **1994**, *58* (14), 3023.

(16) Papirer, E.; Schultz, J.; Turchi, C. *Eur. Polym. J.* **1984**, *20* (12), 1155.

(17) Fekete, E.; Pukánsky, B.; Toth, A.; Bertoti, I. *J. Colloid Interface Sci.* **1990**, *135* (1), 200.

(18) Fenter, P.; Sturchio, N. *Geochim. Cosmochim. Acta* **1999**, *63* (19/20), 3145.

(19) Fekete, E.; Pukánsky, B. *J. Colloid Interface Sci.* **1997**, *194*, 269.

(20) Haworth, B.; Raymond, C. L.; Sutherland, I. *Polym. Eng. Sci.* **2001**, *41* (8), 1345.

(21) Gilbert, M.; Sutherland, I.; Guest, A. *J. Mater. Sci.* **2000**, *35*, 391.

(22) Thomas, M. M.; Clouse, J. A. *Thermochim. Acta* **1989**, *140*, 245.

(23) Bowen, P.; Hérard, C.; Humphry-Baker, R.; Sato, E. *Powder Technol.* **1994**, *81*, 235.

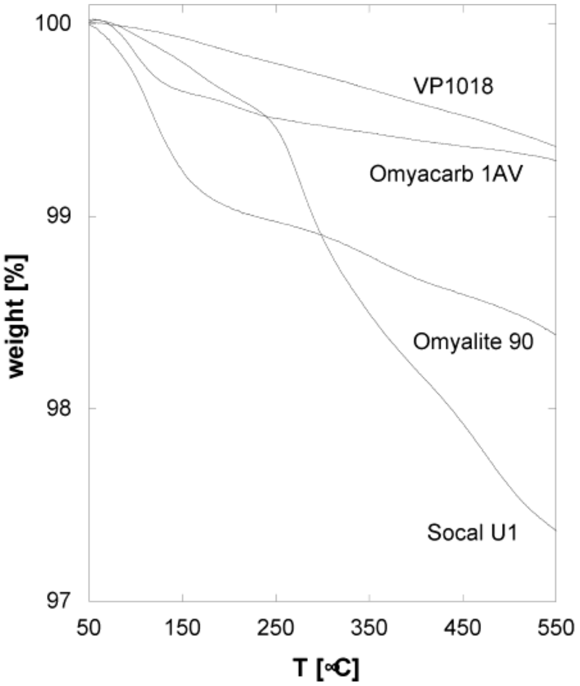

Figure 1. TGA traces of some commercial calcite fillers in comparison to that of a milling additive-free product, VP 1018.

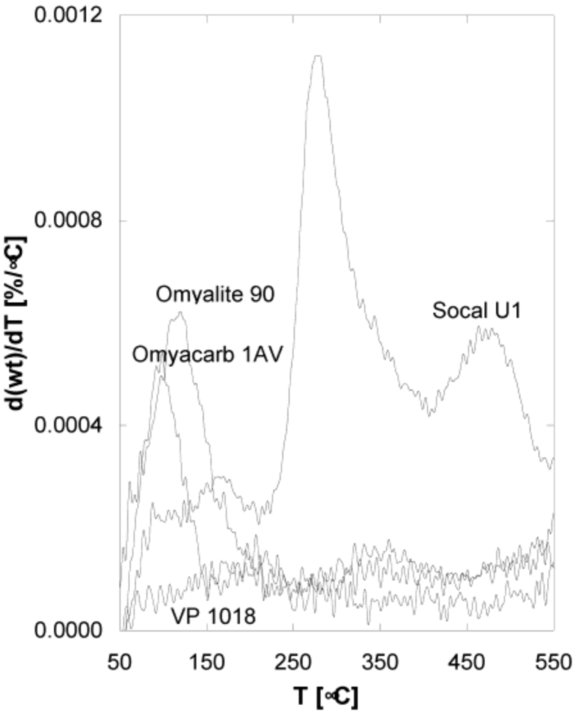

Figure 2. DTG traces of some commercial calcite fillers compared with that of VP 1018.

Optics Inc., Billerica, MA) equipped with a liquid nitrogen cooled MCT (Hg−Cd−Te) detector, operating at a resolution of 0.5 cm^{-1} with an unpolarized beam striking the powder sample held between CaF$_2$ windows at normal incidence. The resolution was better than 2% of the bandwidth. The noise was filtered from the spectra by fast Fourier transformation (FFT) and the peak maxima were taken as the band position. The accuracy of the measured band frequencies was estimated to be ±0.4 cm^{-1}. The spectra were normalized to the carbonyl absorption band at 1795 cm^{-1}.

2.8. NMR Spectroscopy. Solid-state ^{13}C NMR spectra (100.65 MHz) were recorded at room temperature on a Bruker Avance 400-MHz spectrometer equipped with a standard 7-mm double-resonance magic-angle spinning (MAS) probe. A spinning rate of 5 kHz, pulse delays of 5 s, and 16 000 scans were typically used to acquire the ^{13}C CP-MAS spectra. For the ^{1}H−^{13}C cross polarization (CP) experiments, ^{1}H 90° pulse widths between 4 and 4.5 μs and a contact time of 2 ms were used.

Oleic-coated calcite (cold- and hot-dried) was dissolved in a mixture of DCl and CDCl$_3$ and the organic phase separated. ^{1}H NMR spectra of the organic phase were recorded on a Bruker DPX 200-MHz spectrometer.

3. Results

3.1. Powder Characterization. A prerequisite for studying surface phenomena is a clean surface to start with. However, practically all commercially available calcite fillers (dry ground, wet ground, or precipitated) contain additives in different quantities, although nominally uncoated. The presence of organic carbon on the surface of such uncoated calcium carbonate has been detected by XPS.[20] The additives contaminate the calcite surface and reduce the number of reactive sites available for coating. Therefore, pristine marble was specially milled for this investigation without any additives and is denoted VP1018. Figure 1 compares TGA traces of some commercially available uncoated calcite fillers with that of VP1018. As can be seen, the commercial fillers contain different amounts of additives depending on their manufacturing process and particle size, that is, specific surface area. Obviously, the fillers with large surface area contain larger amounts of additives and the wet-milled fillers are more contaminated than those dry-milled. However, wet milling is necessary to obtain small-sized particles. Figure 2 shows the derivative thermograms (DTG), that is, the change in decomposition rate of the adsorbed organic material with temperature, of the same fillers. As can be seen, the decomposition rate maxima occur at different temperatures, indicating that the additives in both milling processes are different. The precipitated calcium carbonate also seems to contain completely different additives than those used in both milling processes. The minimal weight loss observed for VP 1018 is probably due to gradual loss of the adsorbed moisture inevitably present on the calcite surface.[13−15]

The particle size distribution of VP1018 was measured by centrifugal sedimentation (Figure 3) and was found to be broad ($D_{v0.9}/D_{v0.1} = 3.60/0.34$) with a volume median equivalent spherical diameter $D_{v0.5}$ of 1.85 μm. This is in accordance with the microscopic observations (Figure 4). The SEM micrographs also show that the primary particles are irregular in shape but are nearly isometric and can be approximated by a tetragon or a sphere. The SSA was measured by the gas (nitrogen) adsorption method to be 3.6 m^2/g, which is in agreement with the measured particle size.

3.2. Surface Treatment. The most widely used calcite-coating techniques, on a laboratory scale, are dry coating and the solution method. The economic dry coating consists of blending the calcite with a surfactant in a high-intensity mixer at temperatures above 100 °C, but this often leads to inhomogeneous products due to the small amount of surfactant used. In the solution method, which was preferred in this study to ensure the uniformity of the coating, the calcite is treated with a solution of the acid in a nonpolar solvent. VP1018 was

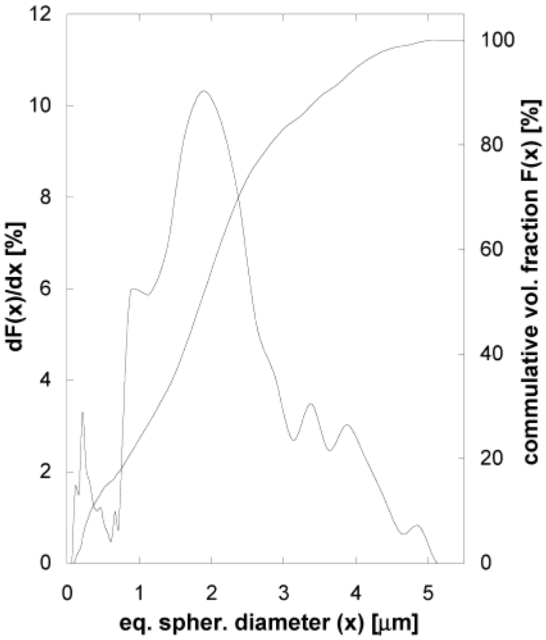

Figure 3. Volume frequency distribution of VP 1018 measured by centrifugal sedimentation.

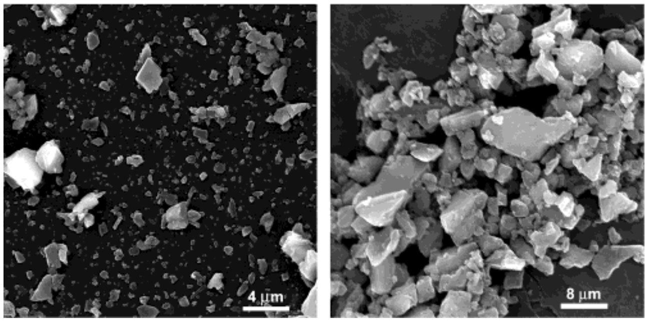

Figure 4. SEM micrographs of VP 1018.

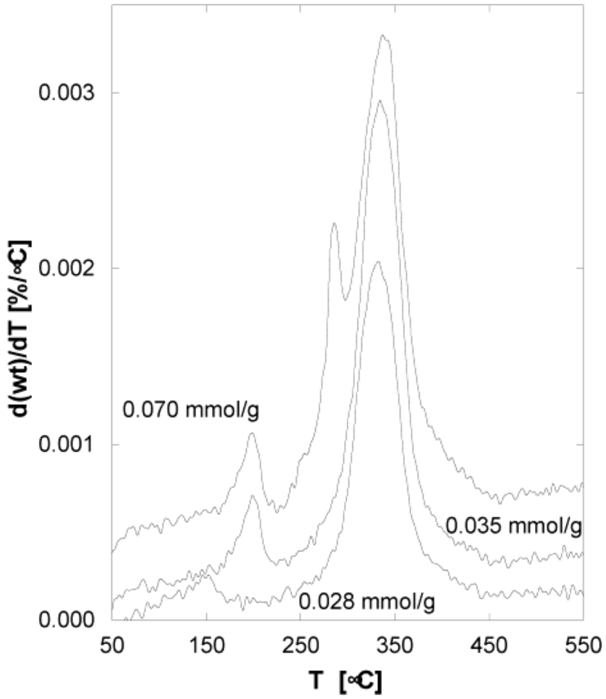

Figure 5. DTG traces of VP 1018 coated with different amounts of stearic acid.

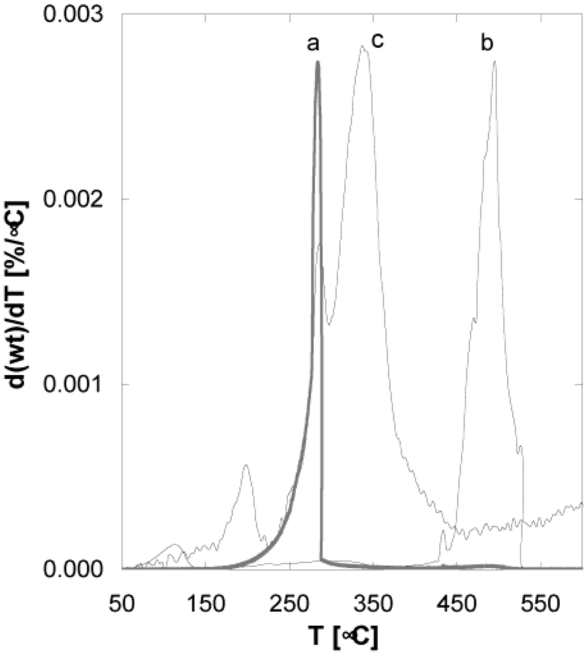

Figure 6. DTG traces of (a) stearic acid, (b) calcium stearate, and (c) VP1018 coated with 0.07 mmol/g stearic acid.

coated with different amounts of stearic acid dissolved in toluene and the product subjected to thermogravimetric analysis. The DTG traces of the coated products are recorded in Figure 5, showing that, with 0.028 mmol/g, only one decomposition step with a peak maximum at 335 °C was observed (the minimal weight loss at 150 °C is probably due to moisture adsorbed on the partially coated calcite surface), while with 0.035 mmol/g an additional decomposition step with a peak maximum at ≈200 °C takes place. When the amount of stearic acid was increased to 0.07 mmol/g, a third decomposition step with a peak maximum at 285 °C was recorded. A comparison of the DTG trace of the coated calcite with those of stearic acid and calcium stearate (Figure 6) suggests that, in contrast to what has been often stated in the literature, no calcium stearate results from the stearic acid treatment. It can also be seen that the peak at 285 °C, which resulted from the use of an excessive amount of surfactant, is identical to that of the pure acid. On repeated shaking with fresh toluene or ethanol, this peak quickly disappeared, while that at 200 °C gradually decreased and was more difficult to get rid of. Therefore, the peak at 200 °C can be attributed to the presence of stearic acid molecules, which are intercalated between the chemisorbed molecules (local bilayer). This intercalation takes place at the end of the surface-coating process, where the molecular packing becomes dense. Due to the attraction forces between the alkyl chains, the intercalated molecules probably adopt a tail-to-tail arrangement as postulated by Papirer et al.[16] and Fekete et al.[17] Such densely packed molecules are expected to be difficult to wash out, even if they are not chemically bound. Similar behavior has been observed with alkane monolayers self-assembled on a mica surface.[24] The above results show that the optimal amount of stearic acid needed to cover the surface of VP1018 with a monolayer of organic molecules lies between 0.028 and 0.035 mmol/g, that is, 7.8 and 9.7 μmol/m^2 surface area.

---

(24) Osman, M. A.; Seyfang, G.; Suter, U. W. *J. Phys. Chem. B* **2000**, *104* (18), 4433.

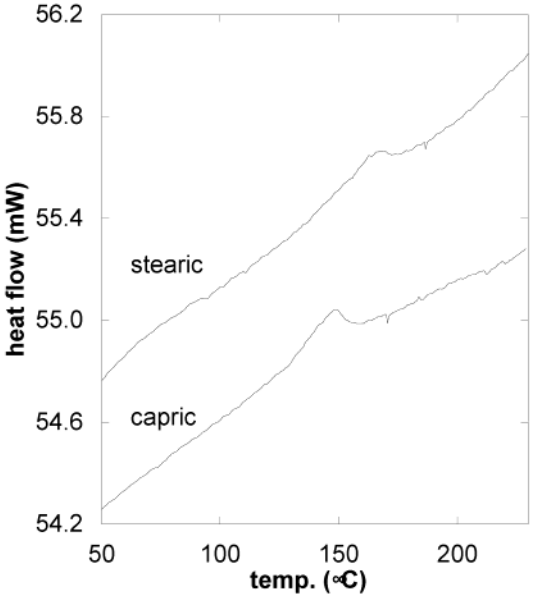

Figure 7. DSC traces of stearic- and capric-coated calcite.

Table 1. Calorimetric Behavior of the Fatty Acid Monolayers Self-assembled on a Calcite Surface

fatty acid	transition temperature (°C)	transition enthalpy (J/g)
stearic $CH_3(CH_2)_{16}COOH$	167	0.37
palmitic $CH_3(CH_2)_{14}COOH$	158	0.35
myristic $CH_3(CH_2)_{12}COOH$	149	0.36
lauric $CH_3(CH_2)_{10}COOH$	146	0.37
capric $CH_3(CH_2)_8COOH$	149	0.34
caprylic $CH_3(CH_2)_6COOH$	none	
caproic $CH_3(CH_2)_4COOH$	none	
valeric $CH_3(CH_2)_3COOH$	none	
butyric $CH_3(CH_2)_2COOH$	none	

3.3. Differential Thermal Analysis. The calorimetric behavior of the fatty-acid-coated calcite (0.03 mmol/g) was scanned between 25 and 250 °C at a rate of 10 °C/min and an endothermic peak could be detected for those coated with the higher homologues ($\geq C_{10}$). The DSC traces of stearic- and capric-coated calcite are shown in Figure 7 as examples and the transition temperatures are listed with their enthalpies in Table 1. The transition temperature decreased with decreasing length of the alkyl chain and was not observed in the calcites treated with acids shorter than capric acid. All transition enthalpies were similar, typically 0.35 J/g, which corresponds to $\approx$12 kJ/mol stearic acid in the monolayer. This value is quite similar to the melting enthalpy found for an ODTA monolayer ionically bonded to a mica surface.[24] However, the transition temperatures are much higher than those observed in monolayers assembled on mica or gold.

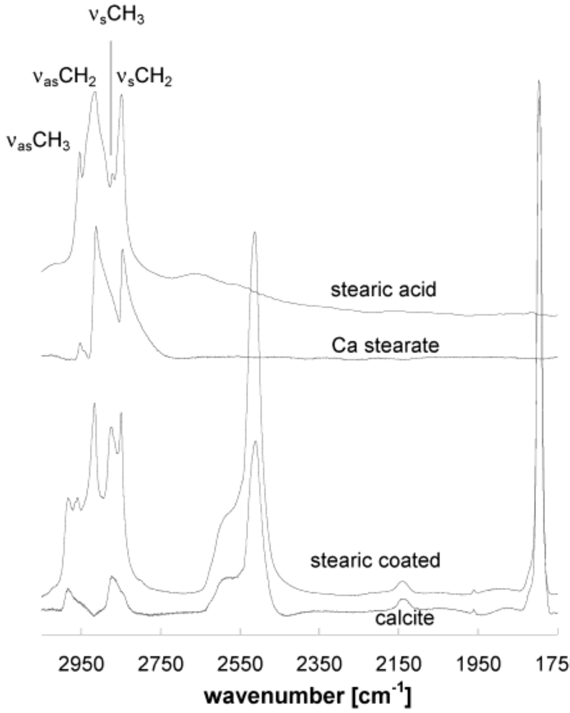

Figure 8. IR spectra of VP 1018 before and after coating with stearic acid in comparison to those of the acid and its calcium salt.

3.4. IR Spectroscopy. FTIR spectroscopy has often been used to probe the conformation and orientation of alkyl chains.[25–30] The frequency, width, and intensity of the asymmetric (ν_{as} CH_2) and symmetric (ν_s CH_2) methylene stretching bands near 2920 and 2850 cm^{-1}, respectively, were found to be sensitive to the gauche/trans conformer ratio. Therefore, these vibrational modes were used to monitor changes in the ordering and packing of the chains. For example, ν_s CH_2 shifted from 2848 to 2853 cm^{-1} and ν_{as} CH_2 shifted from 2916 to 2923 cm^{-1} on melting nonadecane, due to the increase in gauche population and the loss of order.[24]

The high-frequency absorption spectrum of stearic-coated calcite is compared to those of calcite, stearic acid, and calcium staerate in Figure 8. Four distinct peaks can be observed in the spectrum of crystalline stearic acid at 2849, 2872, 2916, and 2954 cm^{-1}, which were straightforwardly assigned to the CH_2 symmetric, CH_3 symmetric, CH_2 antisymmetric, and CH_3 asymmetric stretching C−H vibrations, respectively.[30,31] In the case of calcium stearate, only the methylene stretching bands were sufficiently resolved and their frequencies were shifted lower, indicating denser packing of the alkyl chains. Unfortunately, the C−H stretching vibration bands in stearic-coated calcite are superimposed on the first ($2\nu_3$) overtone bands of the carbonate anion, thus hindering a quantitative estimation of the surface coverage.[32] However, the spectrum shows a fingerprint similar to that of crystalline stearic acid with a very slight shift to higher frequencies, that is, 2850, 2873, 2917, and 2959 cm^{-1}, thus indicating a high trans

---

(25) Scheuing, D. R. In *Fourier Transform Infrared Spectroscopy in Colloid and Interface Science*; ACS Symposium Series 447; American Chemical Society: Washington, DC, 1990.

(26) Dubois, L. H.; Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558.

(27) Snyder, R. G.; Hsu, S. L.; Krimm, S. *Spectrochim. Acta, Part A* **1978**, *34*, 395.

(28) Snyder, R. G.; Strauss, H. L.; Elliger, C. A. *J. Phys. Chem.* **1982**, *86*, 5145.

(29) MacPhail, R. A.; Strauss, H. L.; Snyder, R. G.; Elliger, C. A. *J. Phys. Chem.* **1982**, *88*, 334.

(30) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, Ch. F. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(31) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: San Diego, 1991.

(32) Gilbert, M.; Sutherland, I.; Guest, A. *J. Mater. Sci.* **2000**, *35*, 391.

conformational population and a solidlike packing of the alkyl chains similar to that of crystalline stearic acid. The maximum at 2983 cm^{-1} belongs to the first ($2\nu_3$) overtone band derived from the fundamental stretching (ν_3) vibration, while that at 1795 cm^{-1} is a ($\nu_1 + \nu_2$) combination band of the carbonate anion.[33,34]

The surface chemistry of calcite has been studied by XPS and evidence was found for the presence of bicarbonate and hydroxyl groups.[15] IR studies on the adsorption of CO_2 on metal oxide surfaces and of alkali bicarbonates also showed that the hydrogen carbonates exist as dimers in the solid state and that the absorption band centered at $\approx$2550 cm^{-1} is attributable to ν_{OH} and characterize the hydrogen bonding in those dimmers.[35-37] The calcite spectrum (Figure 8) shows an absorption band at 2510 cm^{-1}, supporting the existence of CO_3H^- anions on the surface. The spectrum of the stearic-treated calcite, which was normalized to the 1795-cm^{-1} absorption band of pure calcite, reveals an increased absorption at 2510 cm^{-1}, indicating an increase in the hydrogen carbonate concentration during surface treatment.

In Figure 9 the normalized (1795 cm^{-1}) spectra of valeric-, stearic-, and oleic-treated calcite (hot-dried) are recorded, showing that the intensity of the 2510-cm^{-1} band is the same in all coated calcites, while the frequencies of the C$-$H vibrations vary. It can also be seen that in all cases the position of ν_s CH_3 does not change, while that of ν_s CH_2 in valeric- and oleic-coated calcites are shifted to higher frequencies so that ν_s CH_2 appears as a shoulder to ν_s CH_3. The asymmetric methylene stretching is also shifted to higher frequency in the oleic-coated calcite and is not resolved in the valeric acid treated product. These observations indicate higher gauche conformational population in the valeric- and oleic-coated (hot-dried) calcites and suggest that their alkyl chains are not as densely packed as those of the stearic-coated product.

3.5. NMR Spectroscopy. NMR spectroscopy has been used to probe the structure, conformation, and dynamics of alkyl chains self-assembled on solid surfaces (SAMs) and the results obtained not only are complementary to FTIR but also give insight into the conformational heterogeneity and packing differences of the molecules.[38-40] The conformational assignment is based on the fact that the ^{13}C chemical shift of methylene groups in the all-trans conformation (pure crystalline alkanes) is 33$-$35 ppm, whereas in solution, dynamic averaging of all possible conformations leads to an average shift of 29$-$30 ppm.

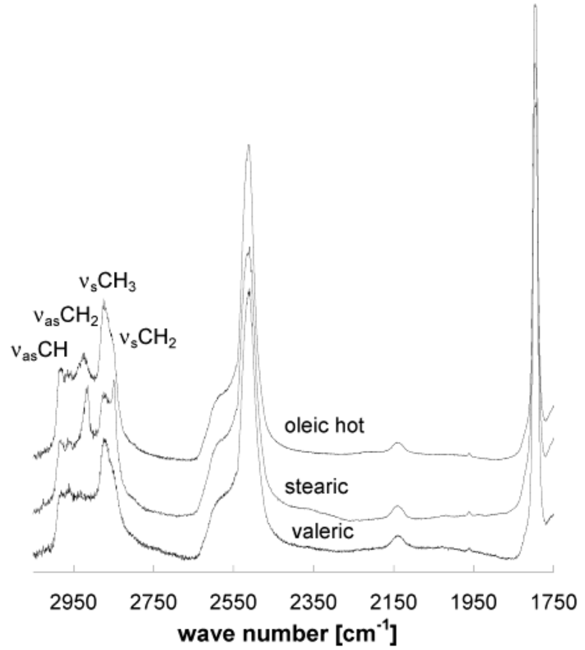

Figure 9. Normalized IR spectra of valeric-, stearic-, and oleic-coated calcite.

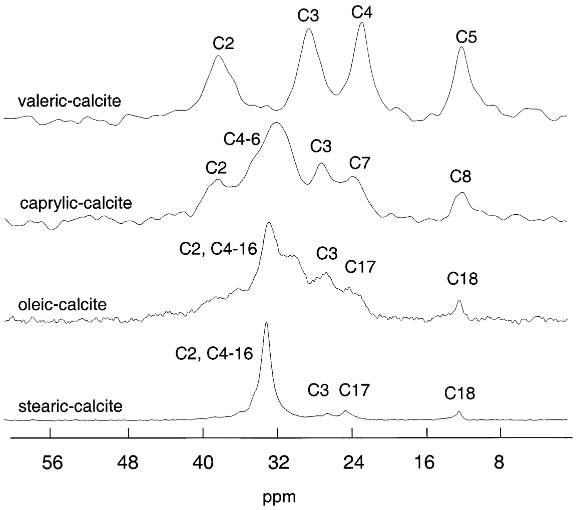

Figure 10. Solid-state ^{13}C CP-MAS NMR spectra of stearic-, oleic-, caprylic-, and valeric-coated calcites.

In Figure 10, the ^{13}C CP-MAS NMR spectra of valeric-, caprylic-, oleic-, and stearic-coated calcite are shown. The assignment given for the carbon resonance frequencies is in agreement with that reported for alkanoic acid SAMs on zirconium oxide.[41] The changes observed in the solid-state ^{13}C chemical shifts and line widths of the surfactant molecules after adsorption are typical of SAMs. After adsorption, stearic acid shows a carbonyl carbon (C1) signal at 177 ppm and the two adjacent methylene groups (C2 and C3) are also shifted and broadened, indicating the binding of the carboxyl headgroup to the calcite surface. The terminal methyl group (C18) exhibits a resonance frequency of about 12.5 ppm (all frequencies are given with respect to TMS), while the C17 carbon (last methylene group) resonates at a frequency of $\approx$24.5 ppm. The C3 signal is also broadened and shifted slightly downfield (26.5 ppm). The other CH_2 groups (C2, C4$-$C16) are not resolved

---

(33) Schroeder, R. A.; Weir, C. E.; Lippencott, E. R. *J. Res. Natl. Bur. Stand. A* **1962**, *66*, 407.

(34) Neagle, W.; Rochester, C. H. *J. Chem. Soc., Farday Trans.* **1990**, *86* (1), 181.

(35) Novak, A.; Saumagne, P.; Bock, L. D. C. *J. Chim. Phys.* **1963**, *60*, 1385.

(36) Bertoluzza, A.; Monti, P.; Morelli, M. A.; Battaglia, M. A. *J. Mol. Struct.* **1981**, *73*, 19.

(37) Busca, G.; Lorenzelli, V. *Mater. Chem.* **1982**, *7*, 89.

(38) Badia, A.; Gao, W.; Singh, L.; Demers, L.; Cuccia, L.; Reven, L. *Langmuir* **1996**, *12*, 1262.

(39) Badia, A.; Demers, L.; Cuccia, L.; Brown, G. R.; Lenox, R. B. *Chem. Eur. J.* **1996**, *2*, 359.

(40) Wang, L. Q.; Liu, J.; Exarhos, G. J.; Flangian, K. Y.; Bordia, R. *J. Phys. Chem. B* **2000**, *104*, 2810.

(41) Pawsey, S.; Yach, K.; Halla, J.; Reven, L. *Langmuir* **2000**, *16* (7), 3294.

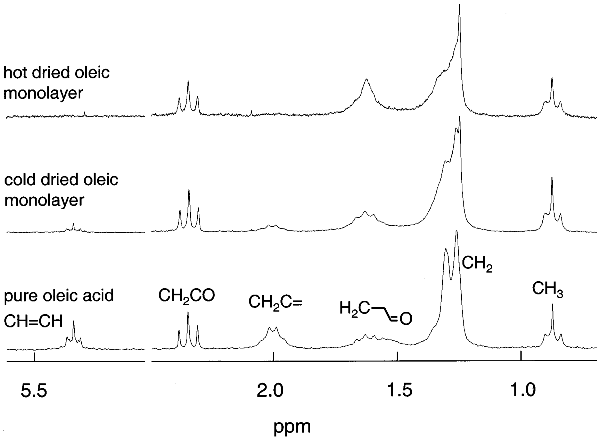

Figure 11. ^{1}H NMR spectra of pure oleic acid and oleic monolayers decoated from surface-treated (cold- and hot-dried) calcites in $CDCl_3$.

and give rise to a broad band at ≈33 ppm, indicating a high trans population. The width of the broad signals observed can be attributed to inhomogeneous line broadening. The hot-dried oleic-coated calcite showed the same band broadening and similar carbon resonance frequencies to those of stearic-coated calcite; for C18 (12.5 ppm), C17 (24.5 ppm), and C3 (27 ppm). However, a number of unresolved bands at 30.5, 33, and 36 ppm for the other carbons were observed, indicating a change in the structure of the monolayer. The caprylic-coated calcite also showed similar chemical shifts for C8, C7, and C3 but the C2 signal was better resolved and was shifted downfield (38.3 pp).The methylene group (C4–C6) signals were unresolved and gave rise to a broad band at 32 ppm, indicating higher gauche population than in the stearic-coated calcite. The ^{13}C CP-MAS NMR spectrum of the valeric SAMs showed the following carbon resonance frequencies: C5, 12.5 ppm; C4, 23 ppm; C2, 38 ppm. In contrast to stearic SAMs, valeric acid showed a carbon resonance frequency for the middle methylene group (C3) of 28.5 ppm, indicating a gauche conformation.

In Figure 11, the ^{1}H NMR spectrum of pure oleic acid in $CDCl_3$ is compared to those of oleic monolayers, decoated from surface-treated (cold- and hot-dried) calcites. A multiplet at 5.3–5.4 ppm, characteristic for the olefinic protons, can be observed in the pure acid and the cold-dried SAMs but not in the hot-dried oleic monolayer. The quartet of the CH_2 groups next to the double bond at ≈2 ppm is also absent in the spectrum of the hot-dried monolayer. These results indicate that the oleic acid molecules tethered to the calcite surface polymerized during hot drying.

4. Discussion

The TGA measurements (Figures 1 and 2) clearly show that the surface of the investigated commercial calcite fillers are partially covered by the additives used in the milling process and that VP 1018 has a clean surface. A comparison of the thermogravimetric behavior of calcite coated with increasing amounts of stearic acid with those of the reactants and of calcium stearate (Figures 5 and 6) revealed that the coating process most probably does not lead to the formation of a calcium stearate monolayer, as has been often postulated. Moreover, the presence of excess free acid or intercalated molecules (local bilayer) that usually occur in the presence of excess surfactant could be detected by TGA. Due to the attraction forces between the alkyl chains, the intercalated and chemisorbed molecules adopt a tail-to-tail arrangement.[16,17] Such an arrangement leaves the carboxyl groups of the intercalated molecules sticking out of the organic monolayer, which explains the lower decomposition temperature observed for the bilayer molecules.

Since a surface area of 3.6 m^2/g was measured (BET) for VP 1018, an area of 0.20 nm^2/molecule can be calculated for a surface coverage of 0.03 mmol/g (complete coating determined by TGA) by approximating the particle shape to a sphere. This is exactly the area/Ca^{2+} (4.97 Ca^{2+}/nm^2) which was calculated from the crystal structure of calcite.[13] In other words, the optimal coating amount of stearic acid measured by TGA perfectly matches a monolayer coverage. An area of 0.20 nm^2/molecule allows only a vertical orientation of the chains to the surface and has been reported to be typical for an alkyl chain with restricted motion. It is also indicative of an ordered phase like those found in liquid-crystalline smectic B and rotator (α) phases.[42] The C–H vibration ($\nu_s + \nu_{as}$ CH_2) frequencies (Figure 8) also indicate the presence of a high trans conformational population and dense packing in the stearic monolayer. Additional proof for the presence of an ordered phase was obtained from the solid-state ^{13}C NMR spectrum (Figure 9), which shows a chemical shift of 33 ppm for the methylene carbons, indicating a high trans population. The calorimetric measurements (Figure 7) revealed an energy uptake peaking at 167 °C for the stearic monolayer. Unfortunately, this high transition temperature did not allow us to investigate the degree of order in the high-temperature phase by IR or NMR spectroscopy. Similar behavior has been observed in alkane SAMs chemisorbed on mica and gold nanoparticles; however, the transition temperatures were much lower.[24,39,43] The shorter alkyl chains ($\leq C_{10}$) did not show such transition and their $\nu_s + \nu_{as}$ CH_2 were shifted to higher frequencies (Figure 9), indicating a disordered phase. The chemical shift of the methylene groups (C4–C6) was 32 ppm, which indicates the presence of a higher gauche population.

It has been pointed out by several authors that, through partial hydration, the calcite surface usually carries OH^- and HCO_3^- groups beside the carbonate anions.[13–15] In agreement with previous investigations, we could show that on coating calcite, one acid molecule is attached to every calcium surface cation regardless of the type of anion present.[16,17] IR spectroscopy (Figure 8) also showed that the intensity of the HCO_3^- absorption band at 2510 cm^{-1} increases on coating calcite with stearic acid. Therefore, we suggest that one molecule of stearic acid reacts with each Ca^{2+} on the calcite

---

(42) Small, D. M. *The Physical Chemistry of Lipids*; Plenum Press: New York, 1986.

(43) Osman, M. A.; Ernst, M.; Meier, B. H.; Suter, U. W. *J. Phys. Chem B* **2002**, *106* (3), 653.

surface to give calcium stearate bicarbonate, irrespective of the anion originally present.

$$Ca(OH)HCO_3 + C_{17}H_{35}COOH \rightarrow Ca(HCO_3)OOCC_{17}H_{35} + H_2O$$

$$2Ca(CO_3)_2 + 2C_{17}H_{35}COOH \rightarrow 2Ca(HCO_3)OOCC_{17}H_{35} + 2CO_2 + O_2$$

The ^{1}H NMR spectra in Figure 11 also show that the immobilization of the oleic acid molecules by tethering them to the calcite surface enhances their susceptibility to thermal polymerization so that they already polymerize during drying. This is supported by the ^{13}C NMR spectrum (Figure 10) and the shift of $\nu_s + \nu_{as}$ CH_2 (Figure 8) to higher frequencies.

5. Conclusion

TGA is an adequate technique for detecting organic contaminations of the calcite surface and to determine the optimal amount of surfactant necessary to coat it with an alkyl monolayer. This technique is also able to differentiate between chemisorbed, intercalated (local bilayer), and free acid molecules, which may be present on the surface of calcite fillers.

Stearic acid reacts with calcite particles and coats it with a monolayer of calcium stearate bicarbonate. One acid molecule reacts with every Ca^{2+} on the surface irrespective of the anion present and the chains are vertically oriented to the surface. The long alkyl chains show a high trans population and are closely packed, building an ordered solidlike phase. Fatty acids with 10−18 carbon atoms show similar behavior, while shorter homologues form dynamically disordered phases. The immobilization of oleic acid molecules on the calcite surface leads to their polymerization at relatively low temperatures without an initiator. In other words, calcite particles are coated with a monolayer of oleic SAMs, which can be polymerized under moderate conditions to give a polymeric ultrathin coating.

Acknowledgment. We would like to thank P. Bowen for the particle size measurement and Omya for supporting this work. We also gratefully acknowledge financial support from the Swiss Commission for Technology and Innovation (CTI) as well as from TOP Nano 21 of the Board of the Swiss Federal Institutes of Technology.

CM021222U