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EXPRESS REGULAR ARTICLE

The Changes in Surface Properties of the Calcite Powder with Stearic Acid Treatment

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The chemisorption isotherm of stearic acid on a calcite powder was established by calculating the amounts adsorbed using a UV-Visible spectrophotometer. The changes in surface properties of the calcite powder with the surface treatment were examined using contact angle measurements and inverse gas chromatography (IGC) at an infinite dilution. The adsorption of stearic acid was available only at their dilute concentration. The contact angle with water and formamide increased with increasing amount of stearic acid adsorbed on the calcite powder. The adsorption of stearic acid onto the calcite powder surface resulted in a significant decrease in the dispersive component of the surface free energy, γ_S^D of calcite powder. The γ_S^D value of calcite powder with 90% surface coverage was 27.2 mJ·m^{-2} at 120°C, whereas that of untreated calcite powder was 103.3 mJ·m^{-2}. The standard adsorption enthalpy, $-\Delta H_A^0$ values of the non-polar probes (*n*-alkanes) for stearic acid-treated calcite powder had decreased to almost the heat of liquefaction of the corresponding probes. The specific component of the surface free energy, $-\Delta G_A^{SP}$ values of the polar probes for stearic acid-treated calcite powder were lower than those of untreated calcite powder.
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Keywords: *calcite, stearic acid, inverse gas chromatography (IGC), dispersive component of surface free energy (γ_S^D), standard adsorption enthalpy (ΔH_A^0), specific component of the surface free energy (ΔG_A^{SP})*

1. Introduction

Calcium carbonate ($CaCO_3$) containing calcite used in this study is the most widely used filler in the plastics, rubber, paper, paint and ink industry.[1)] It is usually obtained by grinding a natural mineral or synthetic $CaCO_3$ prepared by carbonatation of a calcium hydroxide solution. Indeed, the presence of filler enhances some of the technological properties of the resulting filled polymer. However, it very often decreases their impact strength because of agglomeration of filler. Accordingly, before incorporation into plastics, calcite powder is often surface treated in order to facilitate dispersion in the polymer matrix as well as to prevent the loss of mechanical performance.[2)]

When stearic acid is chemisorbed on the calcite powder surface, its adsorption mechanism is not established and its influence on the surface properties of calcite powder is not established quantitatively. Therefore, this paper examined the mechanism of the reaction between calcite powder and stearic acid using a UV-Visible spectrophotometer (UVS) and the changes in surface properties of calcite powder using contact angle and IGC measurement.

Inverse gas chromatography (IGC) at infinite dilution conditions be used frequently to determine the surface properties of various solids.[3–6)] Some results of an examination of the surface properties of precipitated calcium carbonate using IGC have been published.[7,8)]

In the present study, IGC was used to detect the possible differences in the dispersive component of surface free energy, γ_S^D, the standard adsorption enthalpy, ΔH_A^0, and the specific component of the surface free energy, ΔG_A^{SP}, of untreated and stearic acid-treated calcite powder. This paper reports the IGC results from this study.

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2. Experimental

2.1 Materials

Calcite powder was obtained with particle sizes ranging from 0.10 to 8.62 µm by crushing and grinding natural calcite. Table 1 shows the chemical composition and physical properties of the calcite powder.

2-propanol (C_3H_7OH) was used as the solvent for stearic acid ($CH_3(CH_2)_{16}COOH$), and water and formamide (CH_3NO) were used to measure the contact angle. A homologous series of *n*-alkanes, hexane (C_6H_{14}), heptane (C_7H_{16}), octane (C_8H_{18}), nonane (C_9H_{20}) and decane ($C_{10}H_{22}$) were used as the non-polar probes, and chloroform ($CHCl_3$), benzene (C_6H_6), toluene ($C_6H_5CH_3$) and p-xylene (C_8H_{10}) were used as the polar probes for the IGC experiment.

2.2 Adsorption experiment

The experiment designed to modify the calcite powder surface was carried out as follows: A solvent (100 mL), stearic acid (various concentration) and calcite powder (40 g) were stirred with a magnetic bar stirrer for 6–24 h. The mixture was then separated into solid and liquid components using a centrifugal separator. The concentration of the separated liquid was determined using a UV-Visible spectrophotometer (UVS). The separated calcite powder was dried for 12 h at 105°C, and used for the contact angle measurement and IGC experiment.

The amount of stearic acid adsorbed on the calcite powder and the degree of surface coverage was calculated by the following eqs. (1) and (2) using the difference in the concentration of stearic acid before and after the adsorption experiment.

$$q = (C_i - C_e) \cdot V \cdot \frac{1}{G} \cdot M \qquad (1)$$

Table 1 Chemical compositions and physical properties of calcite powder.

Chemical composition (mass%)	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	TiO_2	MnO	P_2O_5	Ig. loss
	54.61	0.40	0.38	0.12	0.05	0.07	0.38	0.02	<0.01	0.01	43.32

Physical properties	Max. diameter	Min. diameter	Average diameter	Specific surface area	Average pore size
	8.62 µm	0.10 µm	2.14 µm	1.70 m^2/g	19.37 nm

$$\theta = (C_i - C_e) \cdot V \cdot \frac{a}{G} \cdot \frac{n}{S} \tag{2}$$

where q (g/g) is amount of adsorption, θ is a degree of surface coverage, C_i (M) is the concentration of stearic acid in solvent before adsorption experiment, C_e (M) is the concentration of stearic acid in the separated solvent after adsorption experiment, V (L) is the volume of solvent, n is Avogadro's number, M (g/mol) is the molecular weight of stearic acid, G (g) is the weight of calcite powder used in adsorption experiment, a is cross sectional area of stearic acid (0.21 nm^2)[9] and S (m^2/g) is the specific surface area of calcite powder.

2.3 Contact angle measurement

The surface energies were readily evaluated on flat surfaces using classical liquid contact angle measurements. The determinations were also performed on powders compressed into discs. Moreover, for solids with high surface energy, it is preferable to use the two liquid technique.[10] However, this method is difficult to apply to agglomerated or compressed calcite particles due to surface hysteresis.[11] Hence, contact angle only was used to illustrate roughly the changes in surface properties of calcite powder when coated with stearic acid.

In practice, the discs were prepared by compression under controlled conditions: 100 mg of calcite powder and a pressure 10^9 Pa, in a typical IR die. The contact angle measurements were carried out using a goniometric telescope within 10 seconds after placing a drop of liquid on calcite powder disc.

2.4 IGC theory and experimental conditions

In IGC under infinite dilution conditions, the retention volume V_N can be calculated using the following eq. (3):

$$V_N = (t_R - t_0) j D_C \tag{3}$$

where t_R is the retention time of the probes, t_0 is the zero retention time measured with a nonadsorbing probe such as methane, j is the compressibility factor depending on the pressure at the column inlet and outlet, and D_C is the corrected flow rate. In practice, the retention time and retention volume, V_N can be determined in a current chromatographic experiment: a larger V_N will correspond to a higher affinity of a probe to the chromatographic support.

In eq. (3), j was calculated using the following eq. (4):[12]

$$j = 1.5\left[\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1}\right] \tag{4}$$

where p_i is the inlet pressure of the carrier gas, and p_0 is the outlet pressure of the carrier gas, which usually equal to atmospheric pressure.

For a test substance, the free energy of adsorption, ΔG_A is the sum of the energies of adsorption attributable to the dispersive and specific interactions. The adsorption of non-polar probes, such as n-alkanes, occurs through dispersive interactions, whereas, for polar probes, both London and acid-base interactions contribute to ΔG_A. In this study, the model reported by Donnet *et al.* was used because the injected probe is in the gas phase.[13] In this model, ΔG_A is given by the following equations:

$$[-\Delta G_A] = [-\Delta G_A^D] + [-\Delta G_A^{SP}] \tag{5}$$

$$= [RT \ln V_N + C] \tag{6}$$

$$= [K \cdot (h\nu_S)^{1/2} \cdot \alpha_{0S} \cdot (h\nu_L)^{1/2} \cdot \alpha_{0L}] + [-\Delta G_A^{SP}] \tag{7}$$

where ΔG_A^D and ΔG_A^{SP} are the dispersive and specific components of the free energy of adsorption, respectively. R is the ideal gas constant, T is the absolute temperature and the value of the constant, C depends on an arbitrarily chosen reference state of the adsorbed molecule in eq. (6). In eq. (7), K is a constant, $h\nu_S$ and $h\nu_L$ are the ionization potentials of the interacting materials, and α_0 the deformation polarizability of the molecules. Subscripts S and L refer to the solid and liquid phases, respectively. In the case of n-alkanes, ΔG_A is equal to the free energy of adsorption corresponding to the dispersive interactions only, ΔG_A^D, i.e., $[-\Delta G_A^{SP}] = 0$ in eq. (7). The term $[K \cdot (h\nu_S)^{1/2} \cdot \alpha_{0S}]$ is a characteristic of a given solid surface and is related to ΔG_A^D. Consequently, $[RT \ln V_N + C]$ between an adsorbate and an adsorbent is a linear equation of the parameter $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$ with a slope of $[K \cdot (h\nu_S)^{1/2} \cdot \alpha_{0S}]$. Table 2 shows the calculated $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$ values of the probes. Polar testing probes e.g. chloroform and benzene have their corresponding $[-\Delta G_A]$ values above the reference line. The $[-\Delta G_A^{SP}]$ value is determined by the vertical distance between the n-alkane plot and the data for the polar probe of interest.

The IGC experimental conditions performed in this study is the following. Since the particle size of the calcite powder was too small to be used as a chromatographic support, calcite powder discs were prepared by compressing the powders in an IR die at a pressure of 10^8 Pa. The discs were then hand-crushed and sieved to select the fraction of particles with sizes ranging from 250 to 425 µm. Particles of the correct size were introduced into a stainless steel column, which was 50 cm long and 3.17 mm in inner diameter. Approximately 1 g of each sample was used to fill the

Table 2 Characteristics of probes.

Probe	$\alpha_0 \cdot 10^{40}$ [Cm^2V^{-1}]	$h\nu \cdot 10^{19}$ [CV]	$(h\nu)^{1/2} \cdot \alpha_0 \cdot 10^{49}$ [$C^{3/2} \cdot m^2 \cdot V^{-1/2}$]
n-Hexane	13.24	4.84	9.2
n-Heptane	15.24	4.57	10.3
n-Octane	17.59	4.20	11.4
n-Nonane	19.75	4.00	12.5
Chloroform	10.57	5.45	7.8
Benzene	11.95	5.13	8.6
Toluene	13.68	4.82	9.5
p-Xylene	15.69	4.48	10.5

chromatographic column. Each column filled with the samples was attached to a gas chromatograph equipped with a highly sensitive flame ionization detector (FID), and then conditioned at 200°C for 15 hours to remove any impurities. The carrier gas was nitrogen (N_2) and the flow rate was 20 mL/min. The temperature of the injector and detector is controlled at 220°C. Measurements were carried out between 100 and 180°C. Very small amounts of the probes were injected using the following procedure. Ten to 20 µL of the probe was introduced through a septum into a 1L flask, which was filled with N_2. Subsequently, approximately 0.1 mL of the diluted probe was injected into the GC system. The physical and chemical properties of the probes were obtained from the CRC Handbook of chemistry and physics.[14)]

2.5 Analysis instruments

A Fluidized Bed Proposed Jet Mill 100 AFG from Alpin Co. was used for grinding of calcite, a Mastersizer from Malvern Co. was used for particle size analysis, an ASAP 2000 from Micromeritics Co. was used to determine the specific surface area and average pore size, a MXF-2001 XRF purchased from Shimatzu Co. was used for chemical composition analysis, an UVS-8452A from Hewlett Packard Co. was used to measure the concentration of liquid, an ERMA Contact Angle Meter from ERMA Optical Works Co. was used to measure contact angle and an HP 6890 GC (gas chromatography) of Hewlett Packard Co. was used for the IGC experiments.

3. Results and Discussion

Figure 1 shows the amount of stearic acid adsorbed, which was calculated using eq. (1) as a function of the equilibrium concentrations (C_e) of the solution determined by UVS. The adsorption isotherms indicate a stirring time of 6, 12 and 24 h, and 16 h aging after 8 h stirring, respectively. When it was stirred for 24 h, the maximum stearic acid adsorption was observed. Satisfactory agreement between the shape of each adsorption isotherm was observed. These adsorption isotherms correspond to a type III isotherm, which was classified by Schay for the adsorption of a nonelectrolytic solution.[15)] In Fig. 1, the adsorption of stearic acid on the calcite powder surface was only achieved successfully at low concentrations, and can be explained as follows.[16–18)] Alcohols form hydrogen bonds, as shown in Fig. 2(a). Fatty acids only form hydrogen bonds by two molecules, as shown in Fig. 2(b). A fatty acid liquid or solution exists in a state

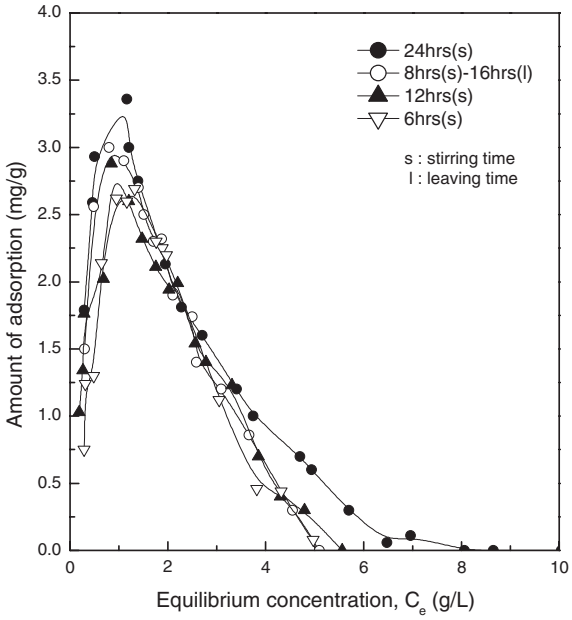

Fig. 1 Adsorption isotherm of stearic acid on calcite powder, determined from the change in concentration of the solution.

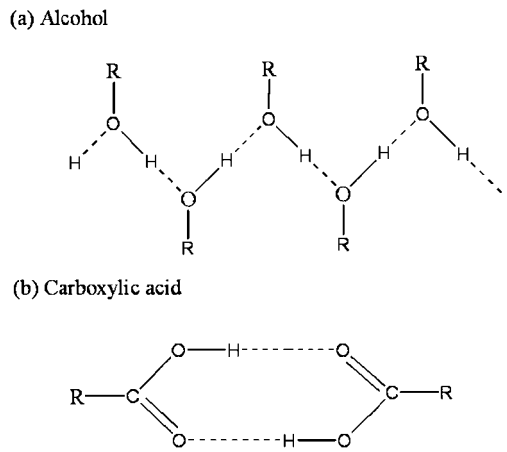

Fig. 2 Hydrogen bonds of alcohol and carboxylic acid.

of a double molecule but is a single molecule at very low concentrations. In addition, the hydrogen bond of a fatty acid is broken if a temperature is increased.[19)] Stearic acid forms hydrogen bond with hydroxyl sites on the surface of calcite powder. If a adsorption is controlled by the polarity of stearic acid and 2-propanol,[17)] stearic acid will be adsorbed on the calcite powder surface because the dipole moment of stearic acid is larger than that of 2-propanol.[14)] However, if the stearic acid concentration is increased sufficiently, a double molecule of stearic acid is formed, e.g. a hydrocarbon chain, in which in both ends of the stearic acid become nonpolar. Eventually, 2-propanol will be adsorbed preferentially on the calcite powder surface.

The amount of stearic acid adsorbed on the calcite powder surface and the degree of surface coverage were calculated by eqs. (1) and (2), respectively, using the measured stearic acid concentration before and after the adsorption experiment. Calcite powders with 0.10, 0.13, 0.18, 0.20, 0.26, 0.30 and 0.34 mass% of amount adsorbed were used as the

Table 3 The contact angle of water and formamide on calcite powder with various degree of coverage.

Degree of surface coverage	Contact angle (degree)	
	Water	Formamide
27%	30 ± 3	27 ± 2
35%	43 ± 1	33 ± 3
46%	52 ± 2	43 ± 2
53%	75 ± 1	58 ± 2
70%	97 ± 2	88 ± 2
80%	101 ± 2	95 ± 1
90%	103 ± 1	95 ± 1

standard samples for the contact angle measurement and IGC experiment. The cross sectional area of stearic acid is 0.21 nm^2.[9] Assuming stearic acid is fixed perpendicularly to the calcite powder surface, the above weight percents of stearic acid correspond to 27, 35, 46, 53, 70, 80 and 90% degree of surface coverage, respectively.

Table 3 shows the contact angle with water and formamide on calcite powder with various degree of coverage. The untreated calcite powder was wetted completely with the water and formamide used in the contact angle measurements. This means that the calcite powder surface has high surface energy. The contact angles with water and formamide on calcite powder increased with increasing level of stearic acid adsorption on the calcite powder surface. When the fatty acid was adsorbed as a complete monolayer, the maximum contact angle was 103° for water and 95° for formamide.[20] In this study, the contact angles for water and formamide had already reached the maximum value when the degree of surface coverage was 80%. Therefore, it is considered that an approximately 80% degree of surface coverage in the point of the surface free energy is similar to a complete monolayer.

IGC under infinite dilution conditions was used to determine the γ_S^D, ΔH_A^0 and ΔG_A^{SP} values of the surface of untreated and stearic acid-treated calcite powder.

The dispersive component of the surface free energy, γ_S^D, was obtained by injecting a homologous series of *n*-alkanes into the column and determining their retention characteristics. Dorris and Gray used the incremental amount of free energy of adsorption, which corresponds to the adsorption of a single CH_2 group, $\Delta G_A^{CH_2}$, to determine the value of γ_S^D:[21]

$$\gamma_S^D = \frac{1}{4\gamma_{CH_2}}\left[\frac{\Delta G_A^{CH_2}}{N \cdot a_{CH_2}}\right]^2 \tag{8}$$

where γ_{CH_2} is the surface energy of a solid composed solely of -CH_2- groups, i.e., a surface analogous to polyethylene, N is the Avogadro's number, and a_{CH_2} is the cross sectional area of an adsorbed -CH_2- group (0.06 nm^2).[21] The variation in γ_{CH_2} with temperature is given by the following equation:

$$\gamma_{CH_2} = 35.6 + 0.058(293 - T) \text{ in mJ}\cdot\text{m}^{-2} \tag{9}$$

where T is the temperature in K.

Generally, the logarithm of V_N varies linearly with the number of carbon atoms of the injected *n*-alkane. Therefore, it is possible to define the free energy of adsorption, $\Delta G_A^{CH_2}$, of a single methylene group, which no longer depends on the arbitrary choice of a reference state:

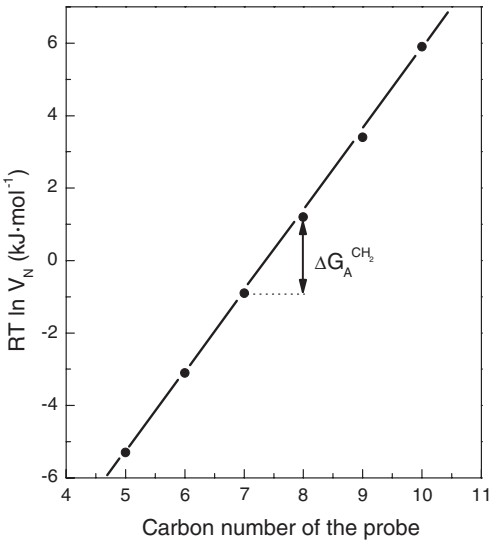

Fig. 3 Determination of the $\Delta G_A^{CH_2}$ value.

$$\Delta G_A^{CH_2} = -RT\ln\left(\frac{V_N^{n+1}}{V_N^n}\right) \tag{10}$$

where R is the ideal gas constant, T is the absolute temperature, and V_N^{n+1} and V_N^n are the net retention volumes of *n*-alkanes with $n + 1$ and n carbon atoms, respectively.

In the IGC experiment, the retention time and volume are associated with the γ_S^D of the solid. This means that $[RT \ln V_N]$ varies linearly with the number of carbon atoms in the injected *n*-alkane, as shown in Fig. 3.

In Fig. 3, $\Delta G_A^{CH_2}$ is the slope of the line obtained from eq. (10). Therefore, the γ_S^D values of the solid were calculated using eq. (8).

Figure 4 shows the change in $[RT \ln V_N]$ at 100°C as a function of the number of carbon atoms in the *n*-alkanes used to probe the surface properties of the untreated and stearic acid-treated calcite powder samples. Each line indicates the degree of surface coverage of the standard samples. Figure 4 shows that the $\Delta G_A^{CH_2}$ values decreased with increasing degree of surface coverage.

Figure 5 shows the change in γ_S^D values, which was calculated using slope of the lines in Fig. 4, as a function of the degree of surface coverage of the untreated and stearic acid-treated calcite powder. It is clear that the γ_S^D values decreased with increasing degree of surface coverage. The γ_S^D value decreased significantly in case of only 27% surface coverage. The γ_S^D value of calcite powder with 90% surface coverage was approximately 29 $mJ\cdot m^{-2}$, which is almost the same as the γ_S^D values reported for a solid surface composed solely of alkyl chains ($\gamma_S^D = 35$ $mJ\cdot m^{-2}$ for –CH_2– and $\gamma_S^D = 24$ $mJ\cdot m^{-2}$ for –CH_3–, at 20°C).[22]

Figures 6 and 7 show the change in $[RT \ln V_N]$ at various temperatures as a function of the number of carbon atoms in the *n*-alkanes used to probe the surface properties of the untreated and stearic acid-treated calcite powder, respectively. The treated calcite powder with 90% surface coverage was used to examine the change in γ_S^D values at different measuring temperatures. Each line indicates the variation with temperature of the IGC measurements. In Figs. 6 and 7,

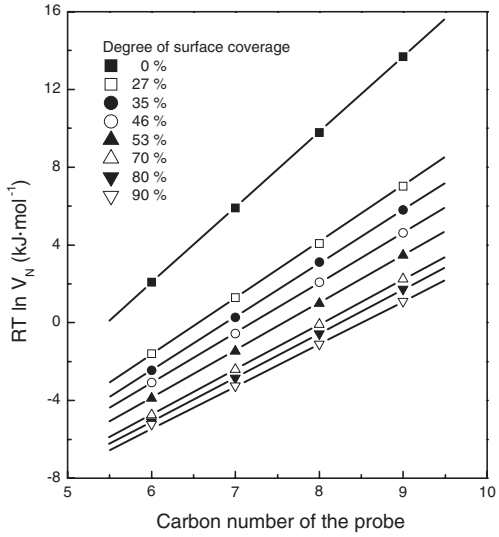

Fig. 4 Change in $[RT \ln V_N]$ of n-alkanes, on untreated and stearic acid-treated calcite powder samples measured at 100°C, as a function of the carbon number.

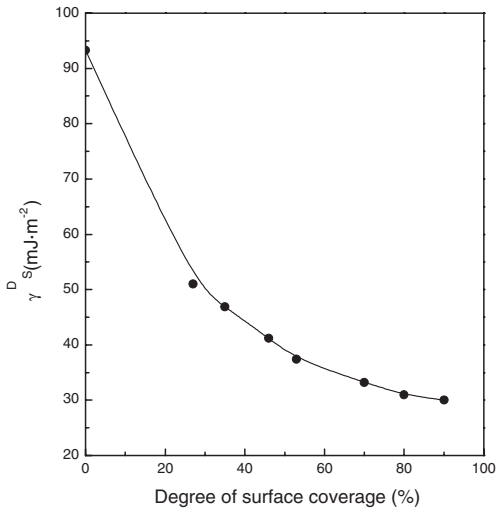

Fig. 5 Change in the dispersive component of surface free energy, γ_S^D, were measured at 100°C as a function of the degree of surface coverage of the stearic acid-treated calcite powder.

the $\Delta G_A^{CH_2}$ values were calculated from the slope of each line, and the γ_S^D values were calculated at various temperatures ranging from 120 to 180°C using eq. (8). Table 4 shows the calculated γ_S^D values for the untreated and stearic acid-treated calcite powder samples. The γ_S^D values decreased with increasing measuring temperature for all samples except for a few cases where γ_S^D increased slightly. The γ_S^D values of the treated calcite powder with 90% surface coverage were slightly lower than those of polyethylene. This means that the end of stearic acid facing out is $-CH_3-$, not $-CH_2-$, when it is adsorbed on the calcite powder surface, because the γ_S^D value for $-CH_3-$ generally is lower than that for $-CH_2-$ at the same temperature.[23)]

The standard adsorption enthalpy, ΔH_A^0, was determined by examining the temperature dependence of $[RT \ln V_N]$ for the same non-polar probe enables:[21)]

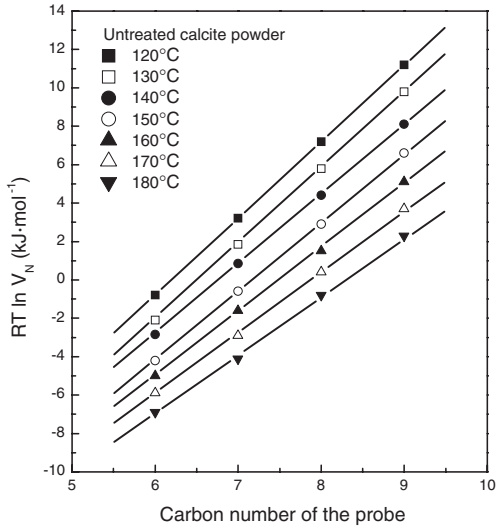

Fig. 6 Change in $[RT \ln V_N]$ of n-alkanes, on the untreated calcite powder measured at various temperatures, as a function of the carbon number.

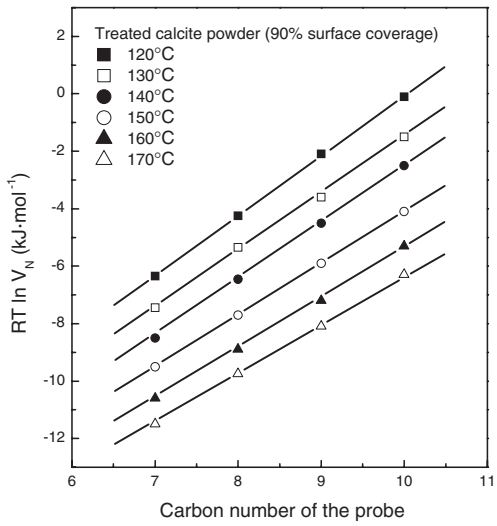

Fig. 7 Change in $[RT \ln V_N]$ of n-alkanes, on the stearic acid-treated calcite powder with 90% surface coverage measured at various temperatures, as a function of the carbon number.

Table 4 Dispersive components of the surface free energy, γ_S^D of untreated and stearic acid-treated calcite powder.

Sample	γ_S^D (mJ·m^{-2})						
	120°C	130°C	140°C	150°C	160°C	170°C	180°C
Untreated $CaCO_3$	103.3	101.6	87.8	85.4	77.1	76.2	72.9
Treated $CaCO_3$ (90% of coverage)	27.2	24.7	25.0	22.2	21.6	21.7	
Linear polyethylene*	30.0	29.4	28.8	28.3	27.7	27.1	26.6

*Calculated from Ref. 23).

$$\Delta H_A^0 = -R \frac{d(\ln V_N)}{d(1/T)} \tag{11}$$

where, the ΔH_A^0 value can be calculated using the slope of the line in the graph of $[-R \ln V_N]$, as a function of the reciprocal absolute temperature. Figures 8 and 9 show the change in

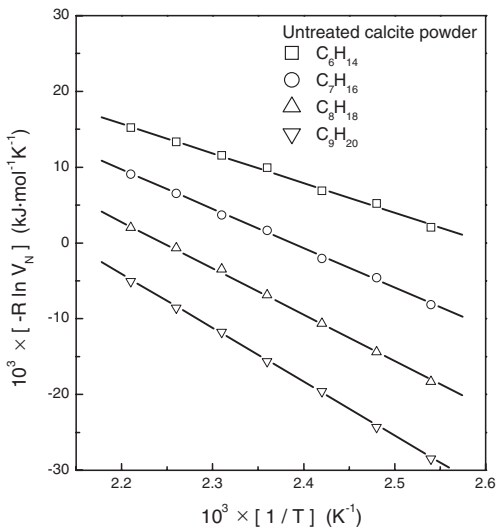

Fig. 8 Change in $[-R \ln V_N]$ as a function of $[1/T]$ (T in K) for n-alkanes adsorbed on the untreated calcite powder.

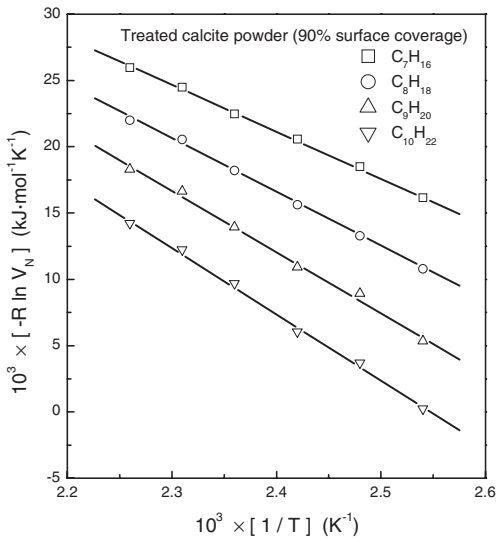

Fig. 9 Change in $[-R \ln V_N]$ as a function of $[1/T]$ (T in K) for n-alkanes adsorbed on the stearic acid-treated calcite powder with 90% surface coverage.

$[-R \ln V_N]$ of n-alkanes as a function of the reciprocal absolute temperature for the untreated and stearic acid-treated calcite powder samples. Each line indicates the change in $[-R \ln V_N]$ of n-alkanes according to the measurement temperature. In Figs. 8 and 9, the $-\Delta H_A^0$ values were calculated using the slope of each line using eq. (11). Table 5 shows the $-\Delta H_A^0$ values of the non-polar probes (n-alkanes) calculated using the above method and the heat of liquefaction of the corresponding probes.[14,24] The $-\Delta H_A^0$ value of n-alkanes increased with increasing carbon number of n-alkanes. The $-\Delta H_A^0$ values of n-alkanes for the treated calcite powder with 90% surface coverage were similar to the heat of liquefaction of the corresponding n-alkanes. This means that the interaction between n-alkanes and the treated calcite powder surface was similar to the interaction between n-alkanes. This means that the interaction between n-alkanes and treated calcite powder surface becomes weak because the

Table 5 The standard adsorption enthalpies, $-\Delta H_A^0$ of n-alkanes on untreated and stearic acid-treated calcite powder.

Probe	$-\Delta H_A^0$ (kJ·mol^{-1})		$-\Delta H_L$ (kJ·mol^{-1}) (Heat of liquefaction at 25°C)	
	Untreated $CaCO_3$	Treated $CaCO_3$ (90% of coverage)	CRC*	API** (at 25°C)
C_6H_{14}	39.0	·	31.9	31.7
C_7H_{16}	50.2	37.1	35.2	36.6
C_8H_{18}	62.0	40.1	38.6	41.5
C_9H_{20}	74.0	43.1	43.8	46.5
$C_{10}H_{22}$	·	46.1	45.7	51.4

*Calculated from Ref. 14).
**Calculated from Ref. 24).

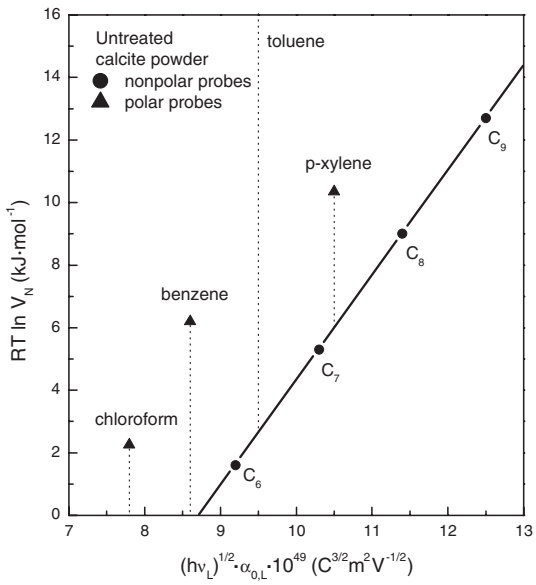

Fig. 10 Variation of $[RT \ln V_N]$ as a function of $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$ for different probes adsorbed on the surface of untreated calcite powder, measured at 100°C.

sites with high surface energy on the calcite powder surface are covered by stearic acid.

Figures 10 and 11 show the change in $[RT \ln V_N]$ as a function of $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$ for each probe used to evaluate the $-\Delta G_A^{SP}$ of the untreated and stearic acid-treated calcite powder (90% of surface coverage) from eq. (7), respectively. The $[RT \ln V_N]$ values of the n-alkanes used as the nonpolar probe varied linearly with $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$, and the $[RT \ln V_N]$ values of the polar probes of interest were above the reference line, as shown in Figs. 10 and 11. The vertical distance between the n-alkane plot and the $[RT \ln V_N]$ value for the polar probe corresponds to the $-\Delta G_A^{SP}$ value. In Fig. 10, the $[RT \ln V_N]$ of toluene could not be calculated because the retention time of toluene was too long to be measured. The $-\Delta G_A^{SP}$ values of the calcite powders were measured at 100°C.

Table 6 shows the calculated $-\Delta G_A^{SP}$ values. For the calcite powder with 90% of surface coverage, the $-\Delta G_A^{SP}$ values of all polar probes were lower than on the untreated calcite powder. It is believed that the alkyl chains of stearic

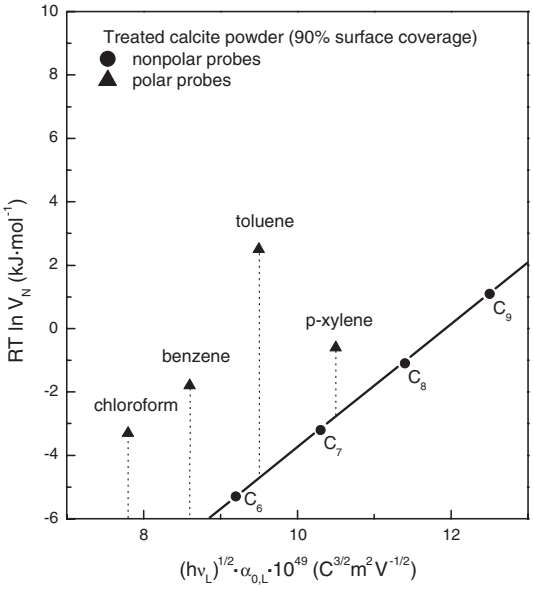

Fig. 11 Variation of $[RT \ln V_N]$ as a function of $[(h\nu_L)^{1/2} \cdot \alpha_{0L}]$ for different probes adsorbed on the surface of treated calcite powder, measured at 100°C.

Table 6 The specific component of the surface free energy, $-\Delta G_A^{SP}$, of polar probes on calcite powder.

Polar probes	$-\Delta G_A^{SP}$, kJ·mol^{-1}	
	Untreated $CaCO_3$	Treated $CaCO_3$ (90% degree of coverage)
Chloroform	5.09	4.71
Benzene	6.22	4.62
Toluene	Too high	7.25
p-Xylene	3.67	2.19

acid shield the calcite powder surface, which is in agreement with the conclusion from the contact angle, γ_S^D and ΔH_A^0 values.

4. Conclusions

Contact angle measurements and a well-established IGC method were used to evaluate the surface properties of untreated and stearic acid-treated calcite powder.

When stearic acid from a 2-propanol solution was adsorbed on the calcite powder surface, adsorption was only achieved quite slowly at low concentrations.

The adsorption of stearic acid on the calcite powder surface changed their hydrophilic surface into a hydrophobic surface. The contact angle on the calcite powder surface increased with increasing amount of adsorbed stearic acid. The maximum contact angles were 103° for water and 95° for formamide. These values correspond to the maximum contact angle for the monolayer with CH_3.

The stearic acid adsorbed on the calcite powder surface decreased γ_S^D value of the calcite powder dramatically (103.3 mJ·m^{-2} for untreated calcite powder and 27.2 mJ·m^{-2} for treated calcite powder with 90% surface coverage at 120°C). The γ_S^D values decreased with increasing degree of surface coverage and IGC measuring temperature. The $-\Delta H_A^0$ values of *n*-alkanes for the calcite powder with 90% surface coverage decreased and were similar to the heat of liquefaction of the corresponding *n*-alkanes. The specific component of surface free energy, $-\Delta G_A^{SP}$ of the polar probes on the calcite powder with 90% surface coverage decreased.

Above conclusions suggest that stearic acid covered the sites with high surface energy on the calcite powder surface. Therefore, treating the calcite powder with stearic acid will reduce the particle-particle interactions and hence facilitate the dispersion of the filler in some matrix. On the other hand, the surface treatment enhances the compatibility between the filler and matrix leading to better mechanical performance of the composite.

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