Revised manuscript submitted, Jun. 2003

SURFACE MODIFICATION OF CALCIUM CARBONATES STUDIED BY INVERSE GAS CHROMATOGRAPHY AND THE EFFECT ON MECHANICAL PROPERTIES OF FILLED POLYPROPYLENE

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ABSTRACT

IGC has been used to characterise the surfaces of a pure calcitic calcium carbonate as well as samples that had been treated with sodium polyacrylate and/or stearic acid. The dispersive components of the surface free energy for the pure material agreed well with related Literature data. Polar contributions to the surface interactions with a range of probes were determined. The results show that the surface treatments reduced the polarity of the surface and that modification with stearic acid produced a non-polar, low energy surface. Some mechanical properties of polypropylene composites containing the modified calcium carbonates were found to correlate well with the filler surface energies.

Keywords: Inverse Gas Chromatography; Calcium Carbonates; surface energy; surface modification, filled polypropylenes.

INTRODUCTION

Calcium carbonate, $CaCO_3$, is a commonly used filler mineral, a major use being in filled polyolefins such as polyethylene and polypropylene where its addition leads to materials with improved toughness and rigidity. The property improvements in filled materials depend critically on the surface properties of each component being appropriate to ensure good bonding and compatibility between them as well as to ensure that the filler can be well dispersed in the polymer matrix. Hence, the surface properties of the mineral usually need to be modified before it can be successfully incorporated into a polymer. Many applications use natural or precipitated calcium carbonates with surfaces modified by treatment with carboxylic acids such as stearic acid to assist wetting and reduce the surface energy. This improves the dispersion of the filler into the polymer and prevents aggregation but also affects the mechanical properties. Thus an understanding of the surface characteristics of both polymer and filler is necessary [1].

Surface interactions depend on the thermodynamic nature of the components and can be quantified by calorimetric methods or adsorption studies. Each method has its advantages and disadvantages [2]. Inverse gas chromatography, IGC, has been shown to be a robust and widely applicable method for the study of surface characteristics of polymers and a wide range of other materials [3, 4] and was therefore chosen for this work. Calcium carbonates have previously been studied by IGC. Papirer and co-workers compared the surface energies for varying stearic acid coverage determined by contact angle techniques with chromatographic data [5]. They found that IGC at infinite dilution could be used to measure the dispersive component of the mineral and its modification. Schmitt *et al*. [6] found that the adsorption behaviour of n-alkanes was similar for stearic acid and non-treated calcium carbonates although the entropic contributions to the interactions were different. Ahsan and co-workers [7, 8] also measured the surface energetics of calcium carbonates, and showed that the enthalpy of adsorption of alkane probes was reduced after treatment with stearic acid. Ahsan and

Taylor [8] measured the impact strength of PP-$CaCO_3$ composites where the filler had been treated with varying levels of stearic acid and found a correlation with the surface free energy measured by IGC.

Various forms of calcium carbonate were studied by Keller and Luner [9], [10]. The surface energies of chalk, marble and a laboratory-prepared material were characterised in terms of the dispersive component of the surface free energy and the differential enthalpy of adsorption. The results were equated to physisorbed and chemisorbed water bound at the surface and within the porous structure. Other modifying agents for calcium carbonate were scrutinised by Balard *et al.* [11]. Calcite was treated with stearic, undecylenic and linoleic acids which were found to markedly change the dispersive or non-specific component of the surface free energy. Values for stearic acid-treated calcite were strongly dependent upon surface coverage, whereas those for undecylenic and linoleic acids were less dependent.

The aim of this study was to apply IGC to a number of modified calcium carbonate systems and to determine the effect that the surface modifications had on the mechanical properties of filled polypropylenes. To remove uncertainties due to variations in naturally occurring minerals, a pure calcium carbonate with known, well defined structure was prepared in the laboratory. Surface properties have been characterised in terms of both dispersive and specific components of the surface Gibbs free energy allowing the effect of the surface treatment with a dispersing agent, sodium polyacrylate, and with stearic acid on a range of properties of polypropylene composites to be monitored.

EXPERIMENTAL

Materials: A pure, precipitated calcium carbonate, PCC, was prepared by chemical precipitation [12]. Equimolar equivalents of 0.5 mol dm^{-3} solutions in de-ionised water of BDH AnalR sodium carbonate and calcium chloride were combined slowly with stirring,

maintaining the mixture between 25 and 30 °C. The resulting precipitate was filtered through a 541 Whatman filter, and the supernatant through a 50 Whatman filter. The solids were combined and dried in a vacuum oven at 60 °C to a constant weight. The PCC was analysed by X-ray diffraction (XRD) with a Siemens D5000 diffractometer utilising a Braun position sensitive detector, and by scanning electron microscopy (SEM), with a Philips-Electroscan 2020 SEM as shown in Figure 1. From the XRD data the crystal structure was determined as calcite with only trace amounts (< 0.1 %) of vaterite and no aragonite observed.

Figure 1 near here

A sample of the PCC was diluted to a 60 wt.% solids aqueous suspension in a Heidolf mixer and sodium polyacrylate (N40 Dispex from Allied Colloids) was added to give a level of 0.4% (w/w) and the sample mixed for fifteen minutes. This treated material, referred in this paper as PCC-PAc, was removed and pressure filtered under nitrogen through a 0.2 μm Millipore filter. The filtered material was dried to a constant weight at 60 °C in a vacuum oven. Separate samples of PCC and PCC-PAc were each coated at 80 °C with 2 wt.% stearic acid (Pristerene 1870) using a Steele and Cowlishaw high shear mixer. This additive level corresponded to a theoretical surface monolayer[13] from the BET surface area of 2.68 ± 0.05 $m^2\ g^{-1}$. Each was mixed for ten minutes to ensure surface homogeneity and conditioned at 23 °C, 50 % relative humidity, for one week.

The polypropylene used was a commercially available grade GWE 27 PP from ICI. It had a melt flow index of 4.2 at 230 °C, a density of 905 kg m^{-3}, a melting range of 165 – 175 °C.

To prepare IGC column packings with the appropriate particle sizes, the solids were compacted into 1 mm diameter pellets using a press at 20 tonnes pressure. The pellets were pressed and then crumbled and sieved to retain aggregates of 425 – 850 μm. The resulting particles were packed with the aid of mechanical agitation into stainless steel columns, ¼”

o.d., which had been washed with de-ionised water, acetone and n-hexane (AnalR grade) before drying in an oven at 80 °C. The surface areas of each of the stationary phases were determined by the single point BET nitrogen absorption method with a Micromeritics Flowsorb II 2300. The values and the column characteristics are shown in Table 1.

Gas Chromatography: A Perkin-Elmer Autosystem XL gas chromatograph employing FID detection was used. The instrument was modified to allow independent gas flow, pressure and oven temperature control and readings. A Chrompack RDT thermometer was calibrated by comparison against an NPL calibrated Tinsley Type 5840 platinum resistance thermometer, between 313 K and 353 K and placed inside the oven to give an independent temperature measurement. Looped-valve tubing before the column inlet permitted inlet pressure and flow to be measured with a FP-407 (Chrompack) solid state calibrated dual flow and pressure meter. The accuracy of temperature measurement was within ± 0.2 °C, and gas flow measurement was within ± 0.3 cm^3 min^{-1}. The carrier gas used was oxygen-free nitrogen (BDH, 99+ %) passed through a Perkin-Elmer three-stage drying and purification system, before entering the chromatograph. Flow rates of 10 – 20 cm^3 min^{-1} were used; there was no significant dependence of the results on the flow rate. Barometric pressure was measured at the beginning and end of each run using a BDH precision aneroid barometer. The mean of the two was used for all calculations. The instrument was located in a temperature-controlled laboratory, maintained at 23 °C ± 1 °C.

After loading into the chromatograph, the columns were pre-conditioned at 120 °C for 24 hr. A series of 0.1μL aliquots of the probe vapour was injected by Hamilton syringe over a range of temperatures. All probes were chromatographic grade (BDH). Retention times were recorded and processed by the PE-Nelson Turbochrom data management software. Methane was used as a non-interacting probe to determine the void volume of the column. Each value reported is the result of at least three elutions agreeing to within experimental uncertainty. In

order to confirm that the results were collected at infinite dilution, injections of n-pentane were made with varying sample sizes in the range 0.01 – 0.1μL . There was no significant variation in the retention times.

The method was repeated at 5 °C intervals, up to 110 °C, with the column (PCC1) being conditioned for 12 hours between each temperature change. The column was then held at 110 °C for 250 hours before repeating the measurements. This was done to quantify any surface modifications caused by heating during the initial study. In addition, a quantity of the original, compacted PCC was placed in the GC oven at the start of the experiment. On completion, this was removed and re-examined by XRD and SEM to determine whether the heating cycles caused changes to the $CaCO_3$ structure. No changes from the original material were observed.

Polymer property characterisation: The fillers were compounded into the polypropylene at a loading of 40 wt.% on an APV MP2030 twin screw extruder at a constant 50 % torque. The die temperature was 210 °C with a screw speed of 250 RPM. After drying overnight at 60 °C in a Conair Churchill desiccant dryer, each compound was injection moulded in an Arburg 320M Allrounder injection moulder with a mould temperature of 60 °C and a die temperature of 230 °C to give 80 x 80 x 2 mm plaques or 80 x 10 x 4 mm bars. Test specimens, also produced for the unfilled polypropylene, were conditioned for four days at 23 °C and 50 % relative humidity before testing.

The falling-weight impact strength (BS2782 – 306C) of the plaques was measured with a Rosand IFIW5 impact tester. The Izod strength (ISO 180) of the bars was measured with a Ceast pendulum tester and the flexural modulus (ISO 178) with a Monsanto T10 tensometer by the three-point bend technique.

RESULTS AND DISCUSSION

Data treatment

The primary measurement in IGC is the net retention volume, V_n, given [14] by

$$V_n = J\, f\, (t_r - t_0) \qquad (1)$$

where t_r is the retention time taken for the probe and t_0 that for the non-interacting marker and f is the carrier gas flow rate corrected to S.T.P. J is the correction factor for pressure drop across the column and carrier gas compressibility, given with the column inlet and outlet pressures, p_i and p_o respectively by:

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

For solid minerals, absorption into the bulk is negligible and retention is solely due to adsorption onto the solid surface so that

$$V_n = K_s\, W_s\, S_a$$

where S_a is the specific surface area of adsorbent and W_s the weight of sample in the column. K_s can be defined as a surface partition coefficient

Calculating the enthalpy, entropy and free energy of adsorption

For isothermal adsorption of one mole of the probe molecule from the standard gaseous state to a standard adsorption state, the change in Gibbs free energy is

$$\Delta G_a^{\circ} = -\, RT\, ln\left(\frac{p_s}{p_g}\right)$$

where ΔG_a° is the standard free energy change of adsorption, p_s is the vapour pressure of the adsorbate in its adsorbed state in equilibrium with the vapour and p_g is its equilibrium vapour pressure. By introducing the Gibbs equation to account for the surface concentration, Γ, it can be shown [10] that

$$\Delta G_a^\circ = - RT\, ln\left(\frac{V_n p_g}{\pi W_s S_a}\right) \quad \text{or} \quad \Delta G_a^\circ = -RT\left[ln(V_n) + ln\left(\frac{p_g}{\pi W_s S_a}\right)\right] \tag{2}$$

To determine ΔG_a°, p_g and π, the surface pressure of the adsorbate, must be known. De Boer [15] first proposed that the standard surface pressure was that where the distance of separation between molecules in the adsorbed state was equal to that in the standard state liquid, giving $p_g = 1.013 \times 10^5$ Pa and $\pi = 3.38 \times 10^{-4}$ Nm^{-1}. Hence, ΔG_a° can be calculated over a series of temperatures from measurement of V_n. All the bracketed components in Equation (2) with the exception of V_n, are constants so that

$$\Delta G_a^\circ = \Delta H_a^\circ - T\Delta S_a^\circ = -RT \ln V_n + k \tag{3}$$

Thus, if ΔG_a° is plotted *versus* T, ΔH_a° can be calculated from the intercept and ΔS_a° from the slope, with the assumption that neither parameter depends on temperature over the range investigated.

An alternative approach to determining ΔH_a° arises from a van't Hoff treatment of Equation (3). Considering the temperature dependence of V_n, gives:

$$\Delta H_a^\circ = -R\frac{\partial \ln V_n}{\partial\left(1/T\right)} \tag{4}$$

The non-specific or dispersive component of the substrate surface energy, γ_s^d can be calculated from the elution data for hydrocarbon vapours, which are assumed to interact only by dispersion intermolecular forces. The free energy change for the adsorption of a single methylene group, $\Delta G_a^{\circ,\,CH_2}$, is found from the difference in free energies of adsorption for succeeding alkanes in an homologous series, γ_s^d then being calculated from [16, 17]

$$\gamma_s^d = \frac{\left(-\Delta G_a^{\circ,CH_2}\right)^2}{\gamma_{CH_2}\left(2Na_{CH_2}\right)} \tag{5}$$

where N is Avogadro's number; γ_{CH2} is the surface tension of a hypothetical surface containing only methylene groups and is calculated from [15, 18]

$$\gamma_{CH2} = 35.6 + 0.058\ (293.13 - T)$$

and a_{CH2} is the cross-sectional area of a methylene group ($\approx 0.06\ nm^2$). Thus at constant temperature, for a series of alkane probes, a plot RT *ln* (V_n) *versus* the number of carbon atoms should give a straight line from which $\Delta G_a^{\circ,CH_2}$ can be found. It is clear that this will not give an exact value of γ_s^d under all circumstances since, for example, a_{CH2} will be somewhat temperature dependent. However, comparison of relative results across a series of systems should allow reasonable conclusions as to the surface behaviour to be made.

Calculating specific interactions

By using probes which can interact with the stationary phase by more specific interactions, further information as to the surface properties can be found. Following the work of Fowkes [18], Saint Flour and Papirer showed how IGC could be used for characterising surfaces in terms of their acid-base nature [19], [20]. Adsorption data for a range of acidic, basic and neutral probes can be used to determine specific adsorption components ($\Delta G°_{sp}$), where the total free energy is the sum of the separate contributions:

$$\Delta G_a° = \Delta G°_{non\text{-}polar} + \Delta G°_{sp}$$

Non-polar interactions are related to the surface area of the adsorbed species, a, and the dispersive components of the surface tension for the solid and adsorbate components, γ_s^d and γ_a^d, respectively.

$$\Delta G_a°_{non\text{-}polar} = -RT\ ln\ V_{n(alkane)} = -N\ a\ 2\ (\gamma_s^d \gamma_a^d)^{1/2} \qquad (6)$$

The slope of a plot of RT $lnV_{n(alkane)}$ as a function of $a(\gamma_a^d)^{1/2}$ therefore corresponds to the response of a non-polar (alkane) probe. If a polar probe with equivalent $a(\gamma_L^d)^{1/2}$ is used, the deviation from the slope on the RT *ln* V_n axis is a measure of a specific interaction, giving rise to $\Delta G°_{sp}$.

$$\Delta G_a°_{sp} = -RT\ ln\left(\frac{V_n}{V_{n\,(alkane)}}\right) \qquad (7)$$

To apply Equation (7), γ_L^d, the surface tension of the pure liquid, was obtained from published data and a, the area of the molecule when it is adsorbed on a surface, was estimated from: [15, 18]

$$a = 1.09 \times 10^{14} \left(\frac{M}{\rho N}\right)^{2/3}$$

where M is the molecular weight of the probe, ρ is the density of the liquid at STP and N is Avogadro's number. By using a range of probes with varying acceptor, donor, acidic and basic properties, a full characterisation of the surface can be carried out.

Experimental results

The enthalpies of adsorption for the alkane probes were calculated to give an initial assessment of the surface properties and effects of the treatments. Figure 2 shows the results for four probes adsorbed on PCC plotted in the van't Hoff format as in Equation (4). The expected linear relationship was obtained and the results recorded for the same probes on all four solids that were investigated gave similar plots. The $\Delta H_a°$ values calculated from these results are shown in Tables 2 and 3. Since the results were recorded at infinite dilution, this is the 'zero coverage' enthalpy of adsorption. The results show that $\Delta H_a°$ and $\Delta S_a°$ for a probe do not vary significantly with temperature over this range. Also shown in the tables for comparison are Literature results on related systems.

Figure 2 near here

Tables 2 and 3 near here

The $\Delta H_a°$ values for PCC and PCC-PAc calculated by both methods show excellent agreement, confirming the validity of the two approaches. In each case the isosteric enthalpy of adsorption was found to increase with increasing carbon number of the probe due to the increasing polarisability giving stronger interaction energies.

The measured results compare well with most of the Literature values. However, Schmitt *et al*. [6] cited much lower values under similar experimental conditions to those used here. Ahsan *et al*. [8] considered those differences to be due to water adsorption from the carrier gas, or surface modification of the cationic sites by the hydrocarbon probes. The former of these seems most likely. The equipment used in our work included a gas drying and purification system to remove water from the carrier gas and prevent any modification by impurities. Repeating the measurements on PCC after 250 hours conditioning resulted in a small but significant increase in $\Delta H_a°$ of 0.7 – 1.8 kJ mol^{-1}, probably related to the removal from the PCC of relatively weakly bound physisorbed water. The presence of adsorbed water on calcium carbonate surfaces is a widely recognised phenomenon and partial desorption of the water monolayer would result in the changes observed [21]. Both Ahsan *et al*. [8] and Keller and Luner [10] found physisorbed water could only be completely removed by prolonged heat treatment above 300 °C. In this work, conditions applicable to commercial practices were used and all samples were treated in the same manner so that comparative results should be valid.

The modification of PCC with sodium polyacrylate reduced the $\Delta H_a°$ by only a small amount, 0.1 – 2.0 kJ mol^{-1}. Similar results were found by Ahsan *et al*.[8] when modifying a colloidal PCC with sodium hexametaphosphate. The relatively small change suggests that only the very highest energy sites on the surface are being covered since sodium polyacrylate will interact most with these reducing interaction with the probes. However, it is clear that a high proportion of high energy sites remain and the polyacrylate coating retains a relatively polar nature of the surface. There are two contributions to this polarity. Some sites on the solid surface may not interact effectively with the polymer coating but an alternative explanation is that all the $CaCO_3$ polarity is masked but that the new surface contains a proportion of polar acrylate groups from the polymer.

The stearic acid coated PCC's both displayed significantly lower isosteric enthalpies of adsorption for the probes than the uncoated equivalents, as shown in Table 3. As might be expected, the change was smaller for the polyacrylate modified material. The sodium polyacrylate effectively masks some of the adsorption sites preventing stearic acid chemisorption. Complete coverage of stearic acid, as calcium stearate, must therefore result in a lower enthalpy of adsorption than coverage with calcium polyacrylate. Limited data from the Literature are available for comparison. Ahsan *et al*. [22] found a reduction in $\Delta H_a°$ of 0.7 – 5.3 kJ $mol.^{-1}$ with stearic acid addition.

The non-specific or dispersive component of the solid's surface energy, γ_s^d, was calculated according to Equation (5). An example plot for PCC is given in Figure 3. The equivalent plots for the modified solids had similar forms and were satisfactorily linear. The calculated values of γ_s^d are shown in Table 4.

Figure 3 near here

Table 4 near here

The measured value of the surface free energy of 41 mJ m^{-2} for PCC at 100 °C was somewhat lower than that observed by Schmitt *et al*. [6] (45 mJ m^{-2}) or Balard and Papirer [23] (52 mJ m^{-2}). Their work used commercially available, natural sourced $CaCO_3$ samples which may be considered less uniform than those prepared under rigorous laboratory conditions. These minerals will contain a proportion of silica, silicates and heavy metals which may not be completely removed during manufacturing and may give rise to variations in surface energy.

The coating of PCC with either sodium polyacrylate or stearic acid resulted in a lowering of γ_s^d although the effect is significantly greater with the latter compound. This again suggests that treatment of $CaCO_3$ with sodium polyacrylate masks the highest energy sites on the surface. It is interesting to note that further treatment of this material with stearic acid gives no significant change in γ_s^d wheras it causes a large reduction in unmodified

$CaCO_3$. This can be explained since the polyacrylate will coat the high-energy sites preventing interaction with stearic acid but still leave a relatively polar surface. Conversely, stearic acid alone will interact with these sites and leave a largely alkane-like surface with a γ_s^d value similar to polyolefins.[24]

In order to obtain further information on the nature of the surface, further calculations were performed in order to investigate more specific interactions. Adsorption data for several non-alkane probes were used to determine the specific energy of adsorption ($\Delta G°_{specific}$) on the calcium carbonates. An example of the plots obtained using Equation (8) for the four $CaCO_3$ samples is shown in Figure 4; those for the other solids again had similar forms. The differences in retention compared with the linear relation for the alkane probes are readily apparent.

Results for adsorption of specific probes on PCC and PCC-PAc are given in Table 5. Due to the very low retention time differences (compared with alkanes) for specific probes on the stearic acid-treated PCCs, only alkene probes were considered to yield reliable results.

Table 5 near here

Figure 4 near here

The isosteric enthalpy of adsorption for each alkene may be found by plotting $\Delta G°_a$ versus T, following the procedures outlined above for the alkane probes. The plots were satisfactorily linear and similar in form to those discussed above. The polar contribution to the adsorption may then be expressed as the difference between the values for the alkane and corresponding alkene. The differences in adsorption for the alkanes and alkenes on the SA treated materials are of the same order as the differences in the enthalpies of vaporization of the probes [25]. However, those for the other surfaces are higher and are indicative of polar sites on the surface.

This model is also borne out by consideration of the entropies of adsorption, $\Delta S°_a$, calculated from Equation 3. The values, shown in Table 6, show that adsorption onto PCC-SA occurs with the lowest entropy change, as expected where there are no strong interactions to induce ordering at the surface. The values for the alkanes on the other solids are somewhat higher. The alkene probes produce higher values than the corresponding alkane due to the polarizing interaction of the double bond with the surface. It is noticeable that coating the PCC with PAc produced a large increase in $\Delta S°_a$ although both materials coated with SA yielded similar values. The reasons for this are not totally clear but may be related to the charge centres on the polyacrylate being more accessible to interaction with the probe than the rougher PCC surface.

Table 6 near here

IGC data on surface adsorption is often considered in terms of the donor-acceptor (or acid-base) properties of the probes. The results for PCC1 and PCC-PAc reveal the extent to which surface modification of polar sites occurred on coating. Using alkene probes, the specific enthalpies of adsorption were lower for PCC-PAc compared with PCC. As the basic π -bonds of the alkenes will interact most readily with the active Ca^{2+} surface sites, sodium polyacrylate effectively masked these sites. This confirms the conclusions from the dispersive component energy results. The values were comparable with those for the stearic acid treated materials. Chloroform is moderately acidic, and its retention on PCC was reduced with polyacrylate treatment. Toluene, another acidic probe, interacted more strongly with PCC, but only moderately with PCC-PAc. Addition of sodium polyacrylate thus resulted in a net reduction in both basic and acidic sites. The very small difference in retention times between these probes and the alkane probes again suggests that there is little polar nature to the surface after stearic acid treatment. It was recently shown using computer simulation methods [26] that carboxylic acids could readily adsorb onto the most stable surfaces of calcite.

In the case of formic acid, one acid molecule interacted with two adjacent Ca^{2+} ions at the surface. The hydrogen atom of the carboxylate group interacted with carbonate oxygens at the surface. In this way, the surface polarity was masked. With the longer chain acids, the alkyl groups would then further mask the polarity at the solid surface yielding the low surface energy materials observed here.

Table 7 near here

Some of the measured mechanical properties of each of the filled polymers are given in Table 7. A fuller mechanical characterisation of the materials has been given elsewhere.[24] Each of the falling weight impact strength, the Izod impact strength and the flexural modulus markedly increased when the filler was incorporated. Polypropylene homopolymer is brittle and has a relatively low impact strength. Calcium carbonate addition modifies this by a "crack pinning" effect where the filler particles retard microcrack propagation.[27] Addition of unmodified filler doubled the impact fail energy although surface modification of the filler greatly enhanced the increase. The Izod impact strength results follow the same trend, with the mouldings containing the surface modified PCC's having considerably higher impact strength. It is perhaps surprising that the addition of sodium polyacrylate before the stearic acid reduced the beneficial effect of the latter. Flexural modulus increases with filler addition because of the greater rigidity of the filler compared with the polymer matrix. Taken together, the results from the current work strongly suggest that demonstrate that there is good dispersion of the PCC-SA material through the PP matrix and also that there is good adhesion between the polymer and the filler. However, to confirm this unambiguously, SEM analysis of fractured composites would be needed.

Since PP is a polyolefin, it would be expected to show only dispersive, non-polar contributions to the surface energy and to give negligible polar contributions. The IGC retention diagrams for alkane probes on PP had the expected linear form and yielded values of

$\Delta H_a°$ of 30 – 43 kJ mol^{-1} for pentane to octane respectively. These are close to the enthalpies of vaporisation of the probes and indicate that there is, as expected, little specific interaction between the alkane probes and the polypropylene surface. Further information can be achieved by consideration of the surface free energy of the polymer. The plots according to equation (2) yielded values for γ_s^d of 36 ± 2 mJ m^{-2} between 110 °C and 80°C. These agree well with literature[28] values measured by other techniques quoted between 30 to 35 mJ m^{-2}.

In a polymer matrix, good wetting of the filler surface is necessary for thorough dispersion. Any agglomerated filler will act as a defect which can initiate impact failure. However, the adhesion between filler and matrix should not be too strong as this will prevent de-bonding at the interface which is necessary for dissipating the energy in an impact and hence imparting toughness to the composite[29]. Pukansky [30] studied interfacial interactions in polypropylene composites and correlated their yield stress with interaction strengths measured as by contact angle. A stearic acid treated calcium carbonate gave a lower yield stress and lower interaction than untreated calcium carbonate in PP polypropylene.

The aim of the current work was to correlate the physical property results with the surface energies of the polymer and fillers. It is clear that the mechanical properties of the filled PP correlate with the surface energy of the $CaCO_3$ used. In particular, coating the filler with stearic acid produced a non-polar, alkane-like surface with a surface energy close to that of the polymer and this gave the best mechanical performance.

CONCLUSIONS

IGC at infinite dilution was confirmed as a suitable and robust technique for the characterisation of both specific and non-specific interactions of the surfaces of mineral fillers such as calcium carbonate. The effects of differing surface treatments may readily be quantified in terms of both dispersive and specific components of the surface free energy.

Measurements of the isosteric enthalpy of adsorption and the various contributions to the surface free energy of calcium carbonate demonstrate that coating with stearic acid effectively produces an "alkane-like" surface where the acid groups interact with the Ca^{2+} ions at the surface and the alkane groups shield these from interactions.

A good correlation between the physical properties of polypropylene-calcium carbonate composites with the surface energies of the filler was also demonstrated. The IGC method has the advantage that it can be applied to finely divided particulates such as fillers, the surface energies of which are difficult to measure by contact angle and related methods.

Table 1: Details of GC columns and packing materials

	PCC1	PCC-PAc	PCC-SA	PCC-PAc-SA
Length of column (cm)	150	100	100	100
Mass in column (g)	24.013	14.472	12.973	13.893
Surface area (m^2 g^{-1})	2.68	2.25	2.59	2.18
Stearic acid coating (wt.%)	0	0	1.95	1.93

Table 2: Comparison of $\Delta H_a°$ data for *n*-alkanes on calcium carbonates.

(Standard deviations given in parentheses)

	Isosteric Enthalpy of Adsorption / kJ mol^{-1}								
Probe	**PCC[1]**	**PCC[2]**	**PCC 250 hr[3]**	**PCC-PAc[1]**	**PCC-PAc[2]**	**Keller & Luner** (a)	**Schmitt *et al.*** (b)	**Ahsan *et al.*** (c)	**Okonkwo *et al.*** (d)
Pentane	32.1 (1.2)	32.5 (1.0)	32.8 (0.6)	32.0 (0.8)	32.0 (0.8)		9		
Hexane	37.3 (0.8)	37.3 (1.1)	39.1 (0.7)	36.2 (1.0)	36.2 (1.0)	41	11	36	38
Heptane	43.8 (0.8)	43.8 (0.5)	45.1 (1.3)	43.1 (1.4)	43.1 (1.4)	48	15	44	46
Octane	51.6 (0.4)	51.6 (0.5)	52.5 (0.9)	49.0 (0.6)	49.6 (0.6)	53	17	53	54

[1] Calculated from Equation 3

[2] Calculated from Equation 4

[3] after 250 hr conditioning at 110 °C

(a) Results for commercial, aragonitic PCC [10].

(b) Results for laboratory prepared, calcitic PCC [6].

(c) Results for re-precipitated colloidal PCC [22].

(d) Results for commercial, calcitic PCC [31].

Table 3: Comparison of $\Delta H_a°$ data for *n*-alkanes on stearic acid treated calcium carbonates.

(Standard deviations in parentheses)

	Isosteric Enthalpy of Adsorption / kJ mol^{-1}			
Probe	**PCC- SA**	**PCC-PAc-SA**	**Schmitt *et al.*** (a)	**Ahsan *et al.*** (b)
Pentane	26.9 (0.9)	28.0 (0.8)		
Hexane	31.5 (0.9)	33.6 (0.9)	28	35.3
Heptane	40.0 (1.2)	42.3 (1.2)	37	41.1
Octane	43.0 (1.3)	47.4 (1.4)	46	47.7

(a) Calcitic PCC treated with a monolayer of stearic acid [6].

(b) Colloidal PCC treated with ammonium stearate [22].

Table 4: Comparison of the dispersive component of surface free energy for calcium carbonates.

(Standard deviations in parentheses)

	Dispersive Component of Surface Free Energy / mJ m^{-2}			
Temp. (°C)	**PCC**	**PCC-PAc**	**PCC-SA**	**PCC-PAc-SA**
70	48 (1)	40 (1)		
80	46 (1)	42 (2)	31 (1)	43 (2)
90	46 (2)	38 (1)	29 (2)	40 (1)
100	41 (2)	35 (3)	29 (1)	37 (2)
110	39 (2)		24 (1)	35 (2)

Table 5: Isosteric enthalpies of adsorption for specific interactions on $CaCO_3$.

	$-\Delta Ha_{specific}$ / kJ mol^{-1*}			
Probe	**PCC1**	**PCC-PAc**	**PCC-SA**	**PCC-PAc-SA**
1-Pentene	6.3	2.3	2.4	2.9
1-Hexene	7.5	1.9	2.5	3.0
1-Heptene	7.8	2.2	2.0	3.2
1-Octene	8.3	2.4	2.2	3.6
Chloroform	4.0	1.6		
Toluene	11.1	2.5		
Cyclohexane	1.1	- 0.04		

* uncertainty ± 1 – 2 kJ mol^{-1}

Table 6: Comparison of entropy of adsorption data* for *n*-alkanes and n-alkenes on stearic acid treated calcium carbonates.

	$-\Delta S_a°$ / J K^{-1} mol^{-1}			
	PCC	**PCC-PAc**	**PCC-SA**	**PCC-PAc-SA**
Pentane	55	64	56	58
Hexane	61	67	63	67
Heptane	72	81	80	84
Octane	86	92	82	90
1-Pentene	89	103	69	66
1-Hexene	86	108	74	74
1-Heptene	92	116	95	88
1-Octene	106	126	96	94

* uncertainty ± 2 – 3 J K^{-1} mol^{-1}

Table 7: Mechanical and Physical property results of filled PP mouldings (standard deviation of measurements in parentheses)

		PP	PP + PCC	PP + PCC-SA	PP + PCC-PAc-SA
Falling weight impact strength	**Peak force ($N\ mm^{-1}$)**	167 (37)	500 (15)	1220 (60)	970 (40)
	Fail Energy ($J\ mm^{-1}$)	1.3 (0.2)	3.7 (1.1)	9.1 (1.5)	4.6 (1.3)
Izod strength	**Notched ($kJ\ m^{-2}$)**	1.4 (0.2)	2.6 (0.2)	4.6 (0.1)	3.4 (0.4)
Flexural properties	**Modulus (MPa)**	1480 (110)	2840 (125)	2710 (102)	2920 (117)
	Yield strength (MPa)	32 (1)	38 (2)	44 (1)	46 (1)

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CAPTIONS FOR FIGURES

Figure 1: SEM image showing the crystal structure of PCC.

Figure 2: van't Hoff plot for PCC to determine isosteric enthalpies of adsorption for alkane probes

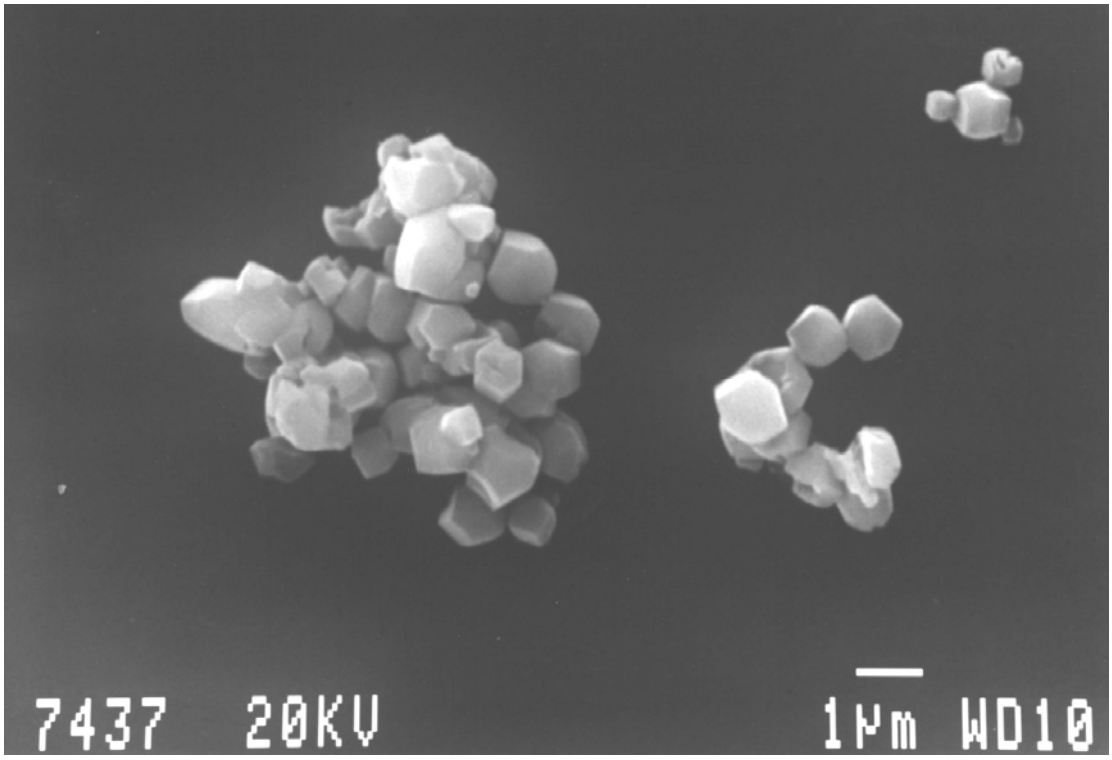
Figure 3: Temperature dependence of Gibbs free energy of adsorption for PCC to determine isosteric enthalpies of adsorption

Figure 4: Plot of $RT ln V_n$ versus number of carbon atoms for PCC to determine the dispersive component of surface free energy

Figure 5: Plot of $\Delta G_a°$ versus $a(\gamma_L^d)^{1/2}$ to determine specific interactions for PCC at 100 °C

Figure 6: Plot of $\Delta G_a°$ versus $a(\gamma_L^d)^{1/2}$ to determine specific interactions for PCC-PAc at 100 °C.

Figure 1: SEM image showing the crystal structure of PCC1.



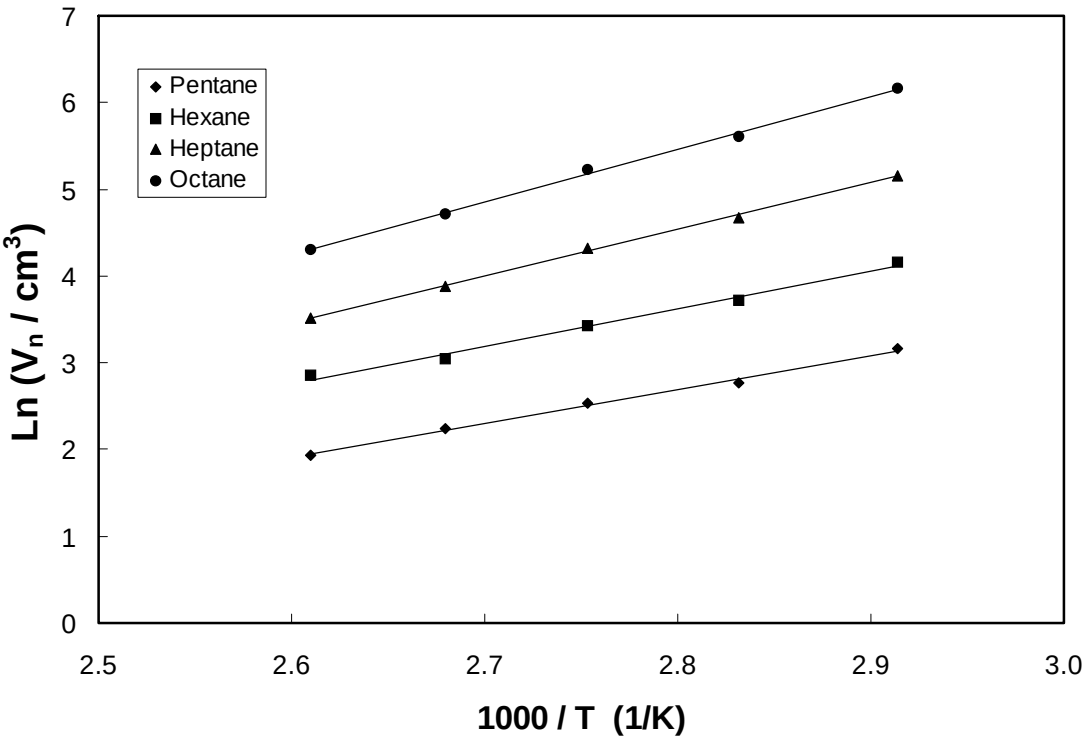


Figure 2 van't Hoff plot for PCC to determine isosteric enthalpies of adsorption.

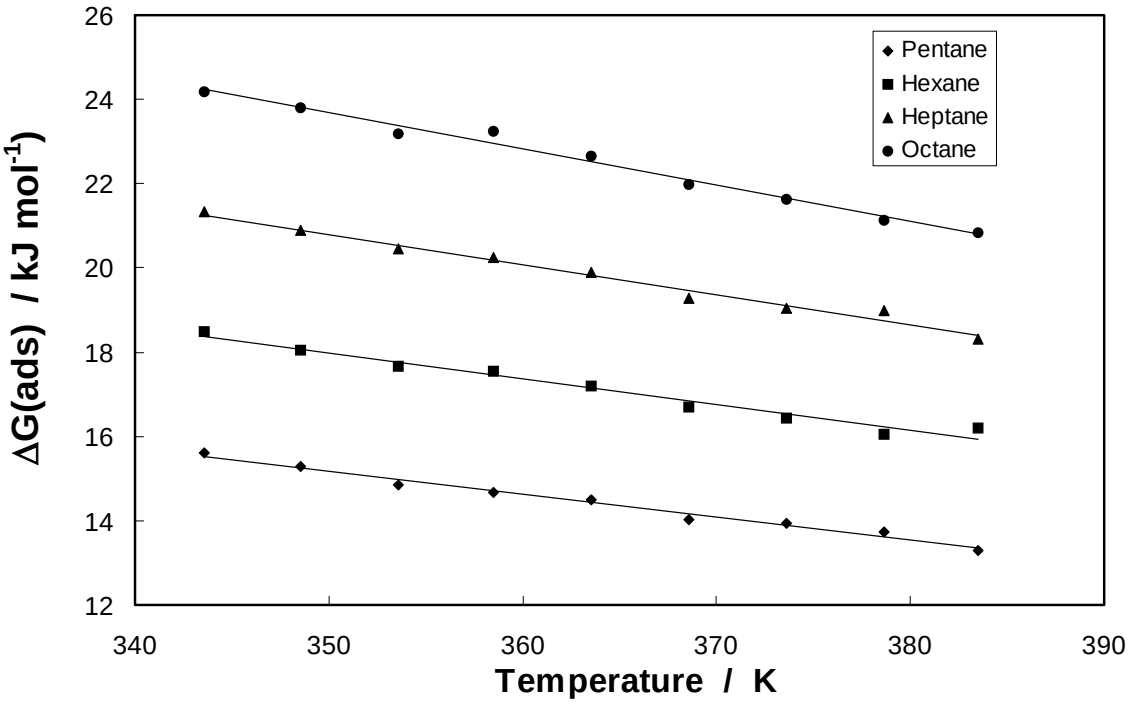


Figure 3 Temperature dependence of Gibbs free energy of adsorption for PCC to determine isosteric enthalpies of adsorption.

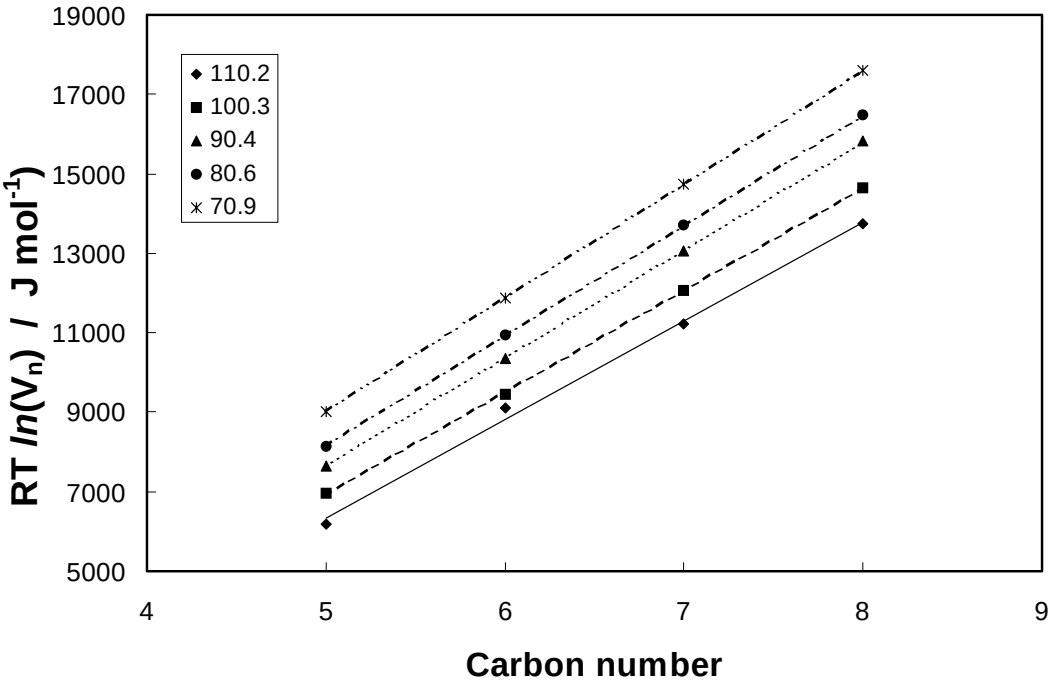


Figure 4 **Plot of RT*ln*V_n versus number of carbon atoms for PCC to determine the dispersive component of surface free energy.**

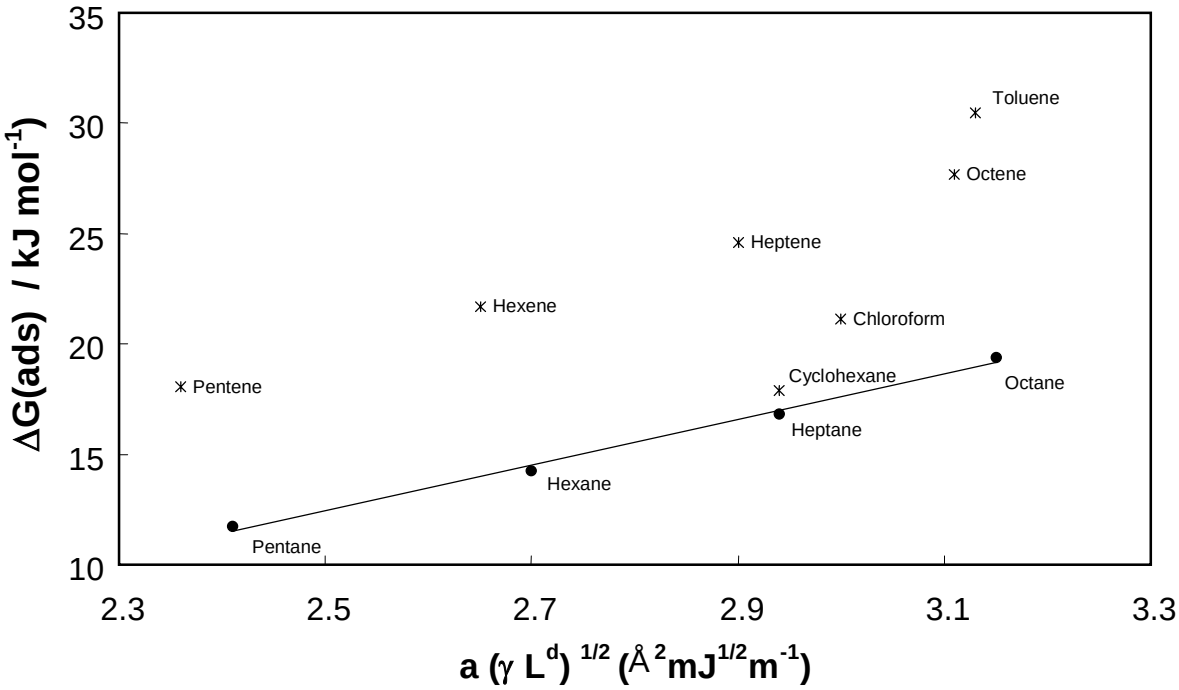


Figure 5 **Plot of ΔG_a^0 versus $a(\gamma_L^d)^{1/2}$ to determine specific interactions for PCC at 100 °C.**

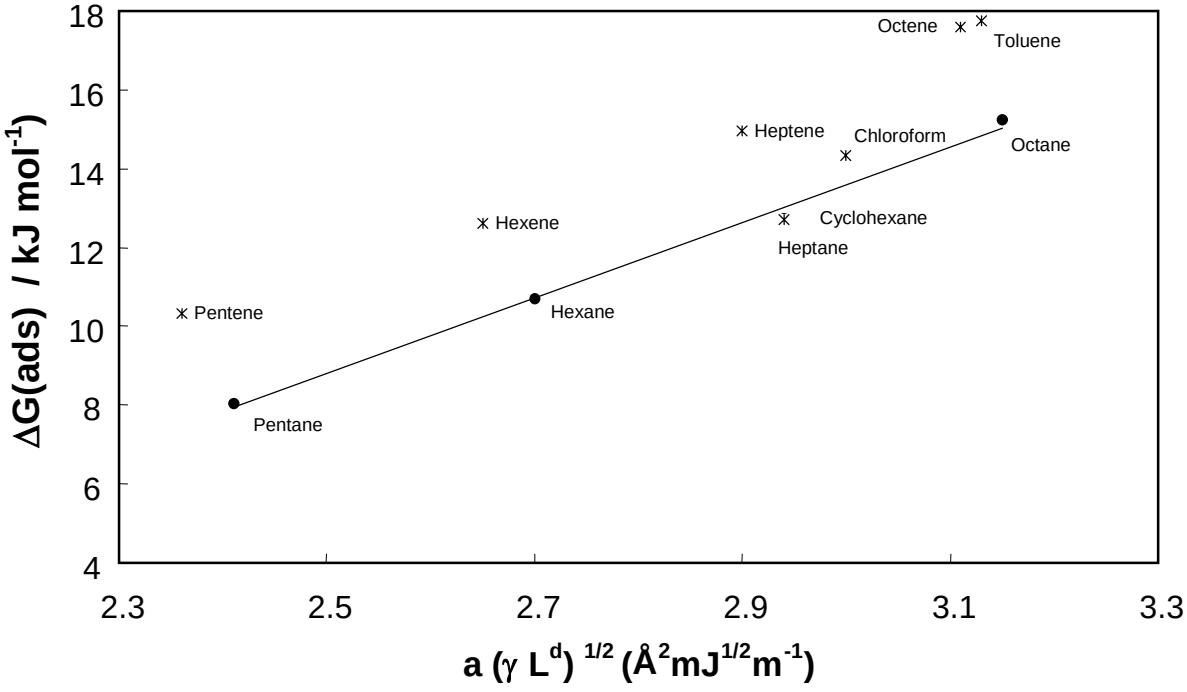


Figure 6 **Plot of ΔG_a^0 versus $a(\gamma_L^d)^{1/2}$ to determine specific interactions for PCC-PAc at 100 °C.**