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CORRELATION OF MATERIAL PROPERTIES OF CALCIUM CARBONATE FILLED POLYPROPYLENE WITH THE FILLER SURFACE ENERGIES

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ABSTRACT

The physical and mechanical properties of a polypropylene, PP, have been measured and compared with those of PP composites filled with calcium carbonates that were modified with sodium polyacrylate and/or stearic acid. The variation in mechanical properties shows a high degree of correlation with the surface energies of the fillers as determined by inverse gas chromatography. The results confirm the usefulness of the IGC method for characterising the compatibility of polymer-filler combinations.

Keywords: Inverse Gas Chromatography; Calcium Carbonates; surfaces; fillers; polypropylene.

INTRODUCTION

The majority of common household or automotive applications of thermoplastics involves their use in conjunction with mineral fillers. The ability to tailor-make composites by surface modification has changed the emphasis from the mineral being considered as a simple filler, giving cost reduction but little else, to providing additional benefits in terms of processing and end properties^{1, 2}. Particulate composites can have improved mechanical properties and stability compared with the polymer alone. The benefits obtained depend critically on the surface properties of each component being appropriate to ensure good bonding and compatibility between them and also to ensure that the filler material can be well dispersed in the polymer matrix. In particular, this requires the surface energetics of the mineral and polymer to be carefully matched.

A number of methods can be used for measuring the surface properties of polymers³,^{4, 5} although recently inverse gas chromatography, IGC, has been shown to be a robust and reliable method for the study of surface characteristics of a wide range of minerals and polymers^{6, 7}.

A commonly used filler mineral, particularly in polyolefins, is calcium carbonate, CaCO_3 , where its addition confers improved toughness and rigidity to the composite. However, it usually needs to be modified before it can be successfully incorporated into the polymers. Treatment with stearic or other acids is often used to assist wetting and dispersion of the filler. Ahsan and Taylor⁸ measured the impact strength of PP- CaCO_3 composites where the filler had been treated with varying levels of stearic acid. They found that the surface free energy measured by IGC fell with SA treatment up to monolayer coverage and that there was a corresponding increase in impact strength. Some years ago, Schreiber and co-workers⁹ used IGC to investigate the plasma modification of CaCO_3 in polyethylene and PVC.

The IGC characterisation of a pure calcium carbonate and the effect of treatment with a dispersing agent, sodium polyacrylate, and with stearic acid was recently completed¹⁰. In this paper, we describe a range of mechanical properties of polypropylene composites prepared with these CaCO₃ materials and demonstrate their correlation with the polymer and filler surface energies as measured by IGC.

EXPERIMENTAL

Materials: 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, tensile yield stress of 34.5 MPa and a flexural modulus of 1.50 GPa. In order to avoid the compositional uncertainties involved in calcium carbonates obtained from natural sources, pure samples of calcite with a BET surface area of $2.68 \pm 0.05 \text{ m}^2 \text{ g}^{-1}$ were prepared in the laboratory. The preparation and properties have been described previously as have the conditions under which surface modification was carried out¹⁰. In summary, three samples of CaCO₃ were used: a pure precipitated calcite, denoted PCC; PCC coated with a monolayer of stearic acid, PCC-SA and finally PCC treated with sodium polyacrylate and then stearic acid, PCC-PAc-SA. SEM analysis showed the average particle size to be approximately 1 µm.

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 plaque colour was measured with a Minolta Chrometer to give L (whiteness), a (blue/green) and b (red/yellow) values; plaque gloss was measured at 20, 60 and 85 ° with a Gardner BYK haze-gloss meter. The falling-weight impact strength of the plaques was measured with a Rosand IFIW5 impact tester. The notched and un-notched Izod strength of the bars was measured with a Ceast pendulum tester. The flexural modulus was measured with a Monsanto T10 tensometer by the three-point bend technique.

Chromatography: To prepare IGC column packings, the homopolymer and composites were pelleted and ground in a Janeke and Kunkel mill under liquid nitrogen. The material was sieved to produce 425 – 850 µm fractions, and packed into the GC column in the usual manner⁶ for analysis. The chromatography system was based on a Perkin-Elmer Autosystem XL gas chromatograph and has been described in detail previously¹⁰.

After loading into the chromatograph, the columns were pre-conditioned at 120 °C for 24 hr under a flow of the nitrogen carrier. A series of 0.1 µL aliquots of the probe vapours was injected by Hamilton syringe over a range of temperatures. Each retention time was the result of at least three elutions agreeing to within experimental uncertainty. The usual checks⁷ were made to confirm that the measurements were being made under infinite dilution conditions.

RESULTS AND DISCUSSION

Physical testing of polypropylene injection mouldings

The characterisation of each of the filled polymers is given in Table 1. The polypropylene-calcium carbonate composites had a lower surface gloss than the parent homopolymer at all three measuring angles due to the particles at the surface scattering light and reducing the reflected light measured. This effect can be directly correlated to particle size provided the filler is well dispersed, with larger, coarser particles giving greater scattering and thus lower

gloss. Poorly dispersed particles form large coarse aggregates and also reduce the gloss. This accounts for the fact that the gloss is reduced most when unmodified CaCO_3 was used. No significant differences were seen between plaques where sodium polyacrylate, added to aid dispersion, was used, confirming that both PP-SA and PP-PAc-SA were well dispersed in the polypropylene matrix. Similarly, treatment with sodium polyacrylate made no significant difference in the colour results compared with stearic acid.

The mechanical properties of the polymer were significantly altered with addition of the filler. Each of the falling weight impact strength, the Izod impact strength and the flexural modulus markedly increased. 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 propagation¹. Addition of the filler to PP 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, these results 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.

Gas Chromatography measurements

In order to achieve good impact properties, the differences between the polymer matrix and mineral surface should be minimal^{11, 12}. IGC allows convenient measurement of surface energies. 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 between 80 – 130 °C are shown in Figure 1. As

expected from adsorption onto the surface below the glass transition of the polymer, the relationship is linear. The retention volume, V_n , is the volume of carrier gas required to elute the probe under standard conditions⁶ and is related to the standard free energy of adsorption, ΔG_a° by:

$$\Delta G_a^\circ = \Delta H_a^\circ - T\Delta S_a^\circ = -RT \ln V_n + k \quad (1)$$

where k is a constant term related to the choice of standard states⁹. The plot yields the isosteric enthalpy of adsorption, ΔH_a° . The data gives values 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.

Consideration of the surface free energy of the polymer is more instructive. The free energy change for the adsorption of a single methylene group, $\Delta G_a^{\circ, CH_2}$, can be determined from the difference in free energies of adsorption for successive alkanes in an homologous series

$$\Delta G_a^{\circ, CH_2} = -RT \ln \left(\frac{V_g^\circ(n+1)}{V_g^\circ(n)} \right) \quad (2)$$

where n is the number of carbons in the alkane. $\Delta G_a^{\circ, CH_2}$ is found at constant temperature from a linear plot for a series of alkane probes of $RT \ln(V_n)$ versus the number of carbon atoms.

The dispersive component of the surface free energy, γ_s^d , can then be calculated from^{13, 14}

$$\gamma_s^d = \frac{1(-\Delta G_a^{\circ, CH_2})^2}{\gamma_{CH_2}(2Na_{CH_2})} \quad (3)$$

where N is Avogadro's number; γ_{CH_2} is the surface tension of a hypothetical surface containing only methylene groups and a_{CH_2} is the cross-sectional area of a methylene group (≈ 0.06 nm²). The plots according to equation (2) is shown in Figure 2 and, in conjunction

with equation (3) yield values of γ_s^d of $36 \pm 2 \text{ mJ m}^{-2}$ between 110°C and 80°C . These agree well with literature values measured by other techniques quoted between 30 to 35 mJ m^{-2} ¹⁵.

The aim of this work was to correlate the physical property results with the surface energies of the polymer and fillers. The former are summarised briefly with reference to the unfilled PP in Table 2. Also shown in the table are the IGC measured surface free energies of the fillers¹⁰. It is apparent that the PCC and PCC treated only with sodium polyacrylate have significantly higher surface energies than the polymer while those treated solely with stearic acid have a somewhat lower surface energy. Our previous work¹⁰ showed that the PAc treated surfaces retained appreciable polarity and the dispersant prevented interactions with some parts of the surface. Complete coverage with stearic acid produced a surface that was effectively alkane-like in its interactions. It is clear from Table 2 that incorporation of this filler into PP gave the best enhancement of its physical properties,

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 composite¹⁶. Pukanzsky¹⁷ studied interfacial interactions in polypropylene composites and correlated their yield stress with interaction strengths measured 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 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 angles.

CONCLUSIONS

We have demonstrated a good correlation between the physical properties of polypropylene-calcium carbonate composites with the surface energies of the filler, as measured by IGC.

The optimum mechanical properties of those studied were obtained when the filler was completely coated so as to mask any polar interactions so that the surface free energy of the filler was comparable with (slightly lower than) that of the polymer matrix.

Our results further demonstrate the utility of IGC for measuring the surface properties of composite materials and show how such results may be used to engineer the surfaces of fillers so as to give the desired properties to a composite system.

Table 1: 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
Colour	L		87 (3)	85 (2)	84 (3)
	a		0.5 (0.01)	-0.5 (0.02)	-0.5 (0.03)
	b		3.0 (0.2)	2.5 (0.1)	2.3 (0.1)
Gloss	20 °	81 (1)	40 (3)	59 (2)	54 (4)
	60 °	106 (4)	58 (3)	74 (2)	71 (2)
	85 °	101 (1)	86 (2)	97 (1)	95 (2)
Falling weight impact strength	Peak force (N mm⁻¹)	167 (37)	500 (15)	1220 (60)	970 (40)
	Peak Energy (J mm⁻¹)	1.7 (0.2)	3.5 (1.2)	8.3 (1.3)	5.2 (2.1)
	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)
	Un-notched (kJ m⁻²)	60 (1)	30 (3)	45 (3)	32 (2)
Flexural properties	Modulus (MPa)	1480 (110)	2840 (125)	2710 (102)	2920 (117)
	Yield strength (MPa)	32 (1)	38 (2)	44 (1)	46 (1)

Table 2: Summary of physical testing results of PP mouldings with 40 wt% filler.

	Relative properties of mouldings (PP=1)					
System	Notched Izod strength	Impact strength (Fail energy)	Impact strength (Peak force)	Yield strength	Modulus	Surface free energy* (mJ m⁻²)
PP	1	1	1	1	1	36 ± 2**
PP + PCC	1.9	2.8	3.0	1.2	1.9	39 – 48
PP + PCC –SA	3.3	7.0	7.3	1.4	1.8	24 – 31
PP + PCC-PAc-SA	2.4	3.5	5.8	1.4	2.0	35 - 43

* Values measured at 80 – 110 °C. ** Surface energy of PP homopolymer

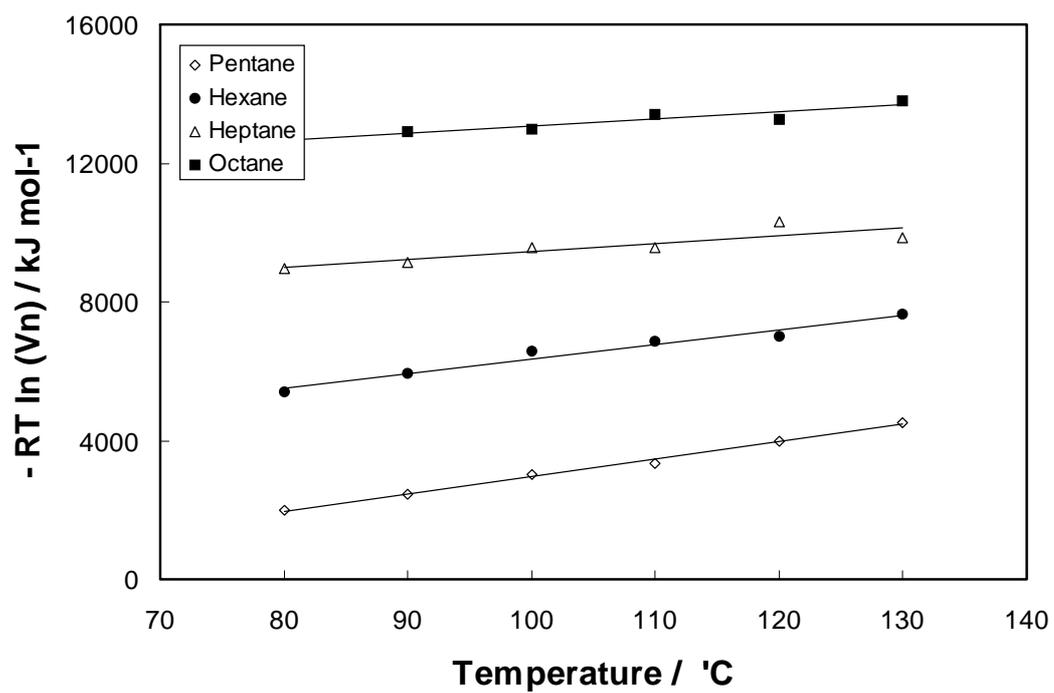


Figure 1: Retention diagrams for alkane probes on PP.

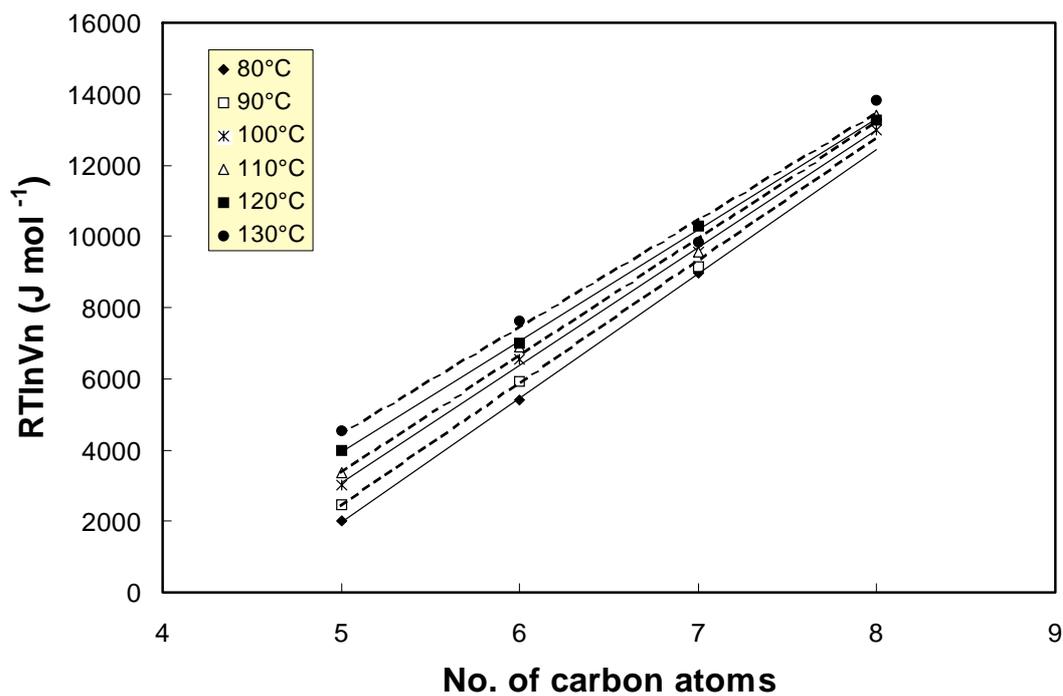


Figure 2: Plot of $RT \ln V_n$ versus number of carbon atoms for alkane probes on polypropylene.

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