



An overview of iGC SEA – a new instrument for characterising the physico-chemical properties of polymers

Surface Measurement Systems Ltd

The surface properties of powders and fibres are important parameters in the handling and performance of a wide range of solid materials. iGC SEA has been specifically designed to address many of the issues faced by physical properties researchers, including fully automated operation and the ability to measure samples in a controlled humidity environment. This Application note gives a brief description of the technique, the instrument and some examples of its application to a range of polymeric materials analysis problems.

Introduction

iGC SEA - Introduction

Inverse gas chromatography (iGC SEA) is a gas phase technique, first developed over 40 years ago, to study the surface and bulk properties of particulate and fibrous materials. iGC SEA has the potential to unlock some of the more difficult to measure physico-chemical properties of solid materials such as powder surface energies, acid/base/polar functionality of surfaces and phase transition temperatures/humidities. However, until recently most iGC SEA studies have been carried out upon 'home-built' pieces of apparatus, often employing manual or semi-automated experimental methods. This has led to a diversity of results in the literature, often seemingly contradictory, due to the differences in instrument design, methodology, sample preparation and individual operator skill.

Surface Measurement Systems (SMS) has recently developed the world's first commercial inverse gas chromatography instrument – iGC SEA.



Figure 1. SMS iGC SEA instrument.



iGC SEA – The Technique

The principles of IGC SEA are very simple, being the opposite of a conventional gas chromatographic (GC) experiment. An empty column is uniformly packed with the solid material of interest, typically a powder, fibre or film. A pulse or constant concentration of gas is injected down the column at a fixed carrier gas flow rate and the retention behaviour of the pulse or concentration front is then measured by a detector. A series of IGC SEA measurements with different gas phase probe molecules allows access to a wide range of physico-chemical properties of the solid sample. The fundamental property measured by IGC SEA from which most of these properties are derived is known as the retention volume V_N . This is a measure of how strongly a given gas or vapour probe molecule interacts with the solid sample. From a series of measurements of V_N various thermodynamic and kinetic parameters can be readily calculated [1,2].

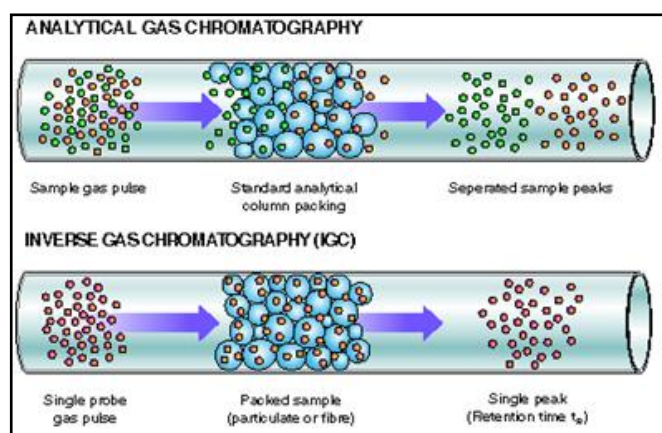


Figure 2. Schematic of IGC principle.

iGC SEA – The Instrument

A cutaway schematic of the SMS iGC SEA is shown in the figure below. The iGC SEA consists of a control PC, a flow control module, a probe gas oven, and a sample column oven. The instrument incorporates a number of innovative design features including the ability to use up to ten different probe molecules in any one experiment and the ability to condition the solid sample under a wide range of humidity (or solvent) and temperature conditions. The probe oven keeps all vapours at a specified temperature in order to facilitate accuracy and repeatability of injections. Another probe molecule, also located in the probe oven, can be used for a “background”

concentration. This can be any vapour. In the case of water, experiments at different relative background humidities are possible. A separate sample column oven allows the sample to be studied over a very wide temperature range. The instrument is designed for maximum flexibility, allowing both single peak and frontal injection methods to be employed, all with background concentration control. A flame ionization (FID) detector is fitted as standard, however it is also possible to add further detectors such as mass spectrometers for applications where volatile compounds are released from the sample being studied. SMS have also developed a column packing accessory which provides a significant advantage in both the time and repeatability of the packing of powdered samples into columns.

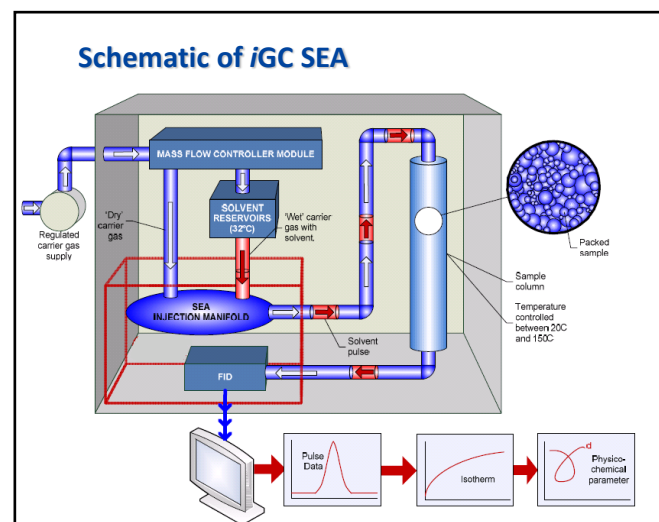


Figure 3. Schematic of SMS iGC-SEA instrument.

iGC SEA – Surface Energy and Fibre-Polymer Matrix Interactions

The quality and performance of carbon fibre/polymer composites depends strongly on the interaction of the components at their interface. To enhance the adhesion properties at the interface, fibres are often exposed to surface treatments such as oxidation and sizing. However, the sizing agent and polymer have to be mutually compatible to achieve an improved interaction. Polymer-fibre interactions are typically described by adhesion and cohesion phenomena. Both properties depend on the energetic situation on the surface of the individual compounds which is commonly expressed by the surface energy [3].

To measure the surface energy of solid materials with IGC SEA, a series of pulsed injections are

made through the column, packed with the solid under investigation, using different probe gas molecules. In the case of the dispersive (non-specific) component of surface energy (γ^D), these probe molecules will be a series of alkanes with different carbon chain lengths while the specific energy (γ^{SP}) is measured using polar probes. The retention time of each probe is related to the strength of interaction. The higher the retention time the stronger the interaction and the higher the surface energy. IGC SEA offers several benefits over conventional techniques such as contact angle measurements since it is more sensitive, the distribution of active sites can be investigated, the surface to bulk ratio can be controlled and samples can be investigated without having to undergo any physical changes (e.g. if the sample is a powder no compaction necessary).

In the current example three different treated carbon fibres (untreated, oxidised, sized and oxidised) and three thermoplastic polymers were investigated by IGC SEA [4]. The dispersive and specific surface energies obtained are shown in Figure 1. Experiments were carried out at infinite dilution (low concentrations of vapour interacting with high energy sites on the surface) which explains the relatively high total surface energies. However, the infinite dilution regime is highly sensitive to small changes and has therefore been successfully applied for the analysis of batch-to-batch problems [3].

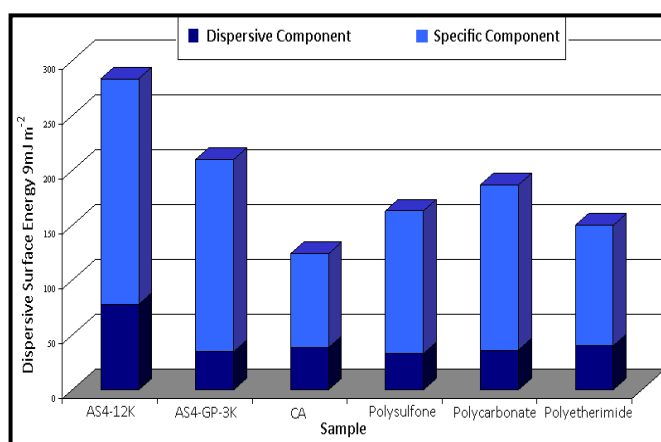


Figure 4. Dispersive, specific and total surface energies for carbon fibres and polymers.

The surface energy of the individual components can now be used to estimate the interaction between each polymer-fibre pair. Such an

estimation is obtained from the calculation of the work of adhesion, W^A by applying Eq.1.

$$W^A_{\text{total}} = 2(\gamma_1^d * \gamma_2^d)^{1/2} + 2(\gamma_1^{sp} * \gamma_2^{sp})^{1/2} \quad (1)$$

Numbers 1 and 2 denote polymer and fibre, respectively. For comparison practical adhesion measurements have been carried out by fibre pull out test. The results of these measurements (shear strength) have been correlated with the values for the work of adhesion estimated from surface energy measurements which is illustrated in Figure 2.

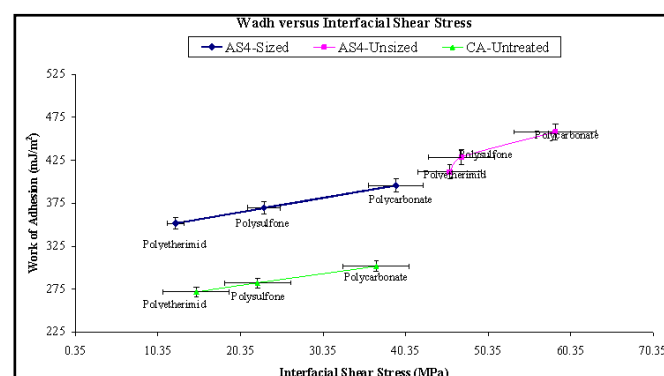


Figure 5. Correlation between work of adhesion values calculated for the different carbon fibre – polymer composites (based on the surface energies obtained by IGC SEA) and interfacial shear strength numbers (obtained from fibre pull-out tests).

For all three polymers predicted adhesion increases with shear strength when fibres are oxidized. Additional sizing does not increase the shear strength although predicted adhesion values are higher, most likely due to an incompatibility between polymer and sizing.

IGC SEA – Glass Transition Temperature of Polyvinylpyrrolidone (PVP)

IGC SEA is a sensitive technique for the detection and determination of first and second order phase transitions such as melting and glass transitions, respectively. Figure 3 shows schematically a typical glass transition event. Initially, at low temperatures the interaction between vapour probe and polymer is dominated by surface adsorption (A-B). When the temperature is increased there is more and more bulk absorption due to an increased molecular motion. The latter is a slow, kinetically controlled process and one

observes a deviation from linearity (B-C). This can be taken as the onset for a glass transition [5].

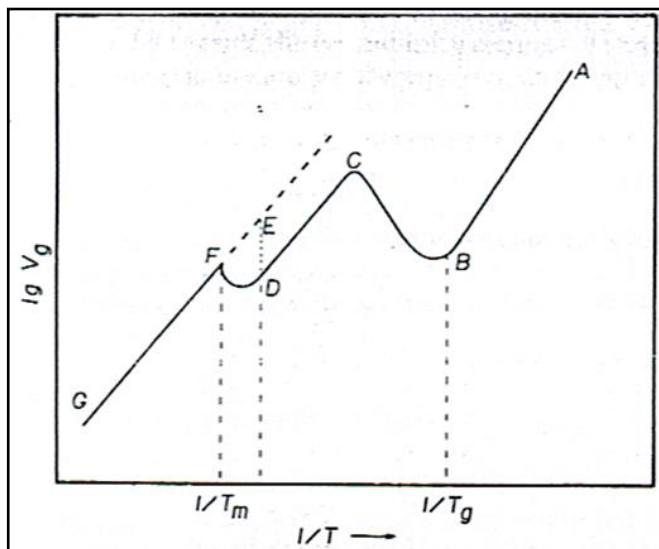


Figure 6. Schematic illustration of glass and melting transition in an IGC SEA retention diagram.

The glass transition temperature depends strongly on environmental conditions and material properties such as humidity and morphology. Water is well known to act as a plasticising agent for many organic materials. In contrast to the classical techniques for the characterisation of T_g , such as differential scanning calorimetry (DSC) and Dynamic Mechanical Thermal Analysis (DMTA), IGC SEA does provide an accurate and very sensitive method to investigate T_g under different relative humidity conditions [6].

In the current example the glass transition temperature of PVP K25 was determined at 45% RH. The retention curve in the vicinity of the glass transition is shown in Figure 4.

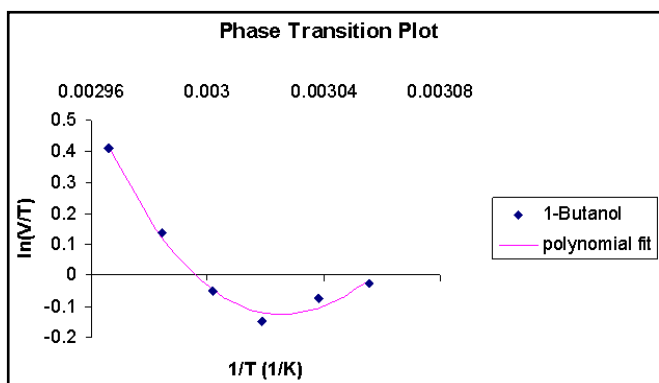


Figure 7. Glass transition of PVP K25 at 45% RH, measured with 1-butanol as vapour probe.

A glass transition temperature of 57.3 °C is obtained. This is in good agreement with the literature value, estimated by DSC to be 58.4 °C at the same humidity [7].

IGC SEA – Crystallinity (Amorphous Content) of Polyethylene

Discontinuities in the temperature variation of the retention volume have been related not only to glass transitions but also to melting of the stationary phase. This is typically observed as a shift in the linear portion of the retention curve above the glass transition (F-G in Figure 3).

Guilett and Stein showed that the retention behaviour in the melting transition can be quantified and related to the crystallinity of polymers [8]. In the current example high density polyethylene has been investigated. The melting curve is shown in Figure 5.

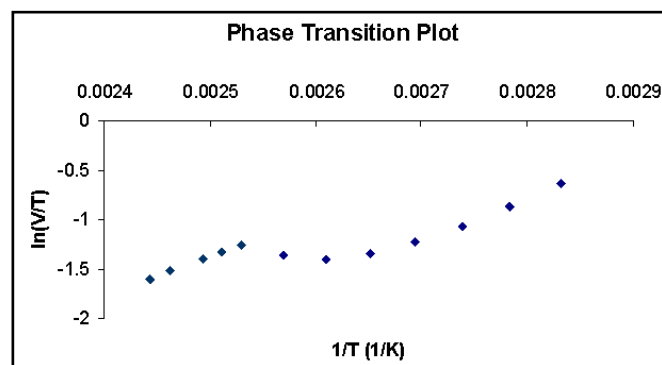


Figure 8. Melting transition of HD polyethylene measured with decane as vapour probe.

The onset of the melting point has been found to be 212 °C which is in good agreement with literature values [9]. To obtain the crystallinity of the polymer the linear region above the melting point is extrapolated backwards. The crystallinity is then calculated from the ratio between the theoretical retention volume Vg' (obtained from the extrapolated curve) and the retention volume before the melting transition Vg at the same temperature (Eq. 2).

$$\% \text{ crystallinity} = 100 * (1 - Vg/Vg') \quad (2)$$

This assumes that the melt is entirely amorphous and any deviation from linearity is a measure for the change in crystallinity. For the polyethylene sample in this study the crystallinity was found to be 64% which is consistent with the crystallinity



range of 60-80% for a typical high density polyethylene.

IGC SEA – Hildebrandt Solubility Parameters of PMMA

The solubility parameter was originally defined by Hildebrand and Scatchard to describe polymer-solvent interactions using thermodynamic theory of regular solutions. There are different approaches for the determination of the solubility parameters (sometimes also called cohesion parameters) which are usually either based on the Hansen theory (where it is split into dispersive (δ_d), polar (δ_p) and hydrogen-bonding (δ_H) contributions) or on the Hildebrandt theory to calculate the total solubility parameter.

In the current example the Hildebrand solubility parameter has been determined for polymethyl methacrylate (PMMA) [10]. In this experiment retention volumes are measured for various vapour phase probe molecules which have a considerable bulk interaction with the solid component. The retention volume can be transformed into an activity coefficient from which the Flory-Huggins interaction parameter χ can be calculated. If the solubility parameters of the probe molecules, δ_1 are known the solubility parameter of the sample, δ_2 can be calculated using Eq. 3.

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \left(\frac{2\delta_2}{RT} \right) \cdot \delta_1 - \left(\frac{\delta_2^2}{RT} - \frac{\chi_s}{V_1} \right) \quad (3)$$

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The other parameters in this equation are: the gas constant R , the measurement temperature T and the molar volume V_1 of the vapour probe. The linear form of this equation allows the solubility parameter of the polymer to be obtained from the slope of the plot shown in Figure 6.

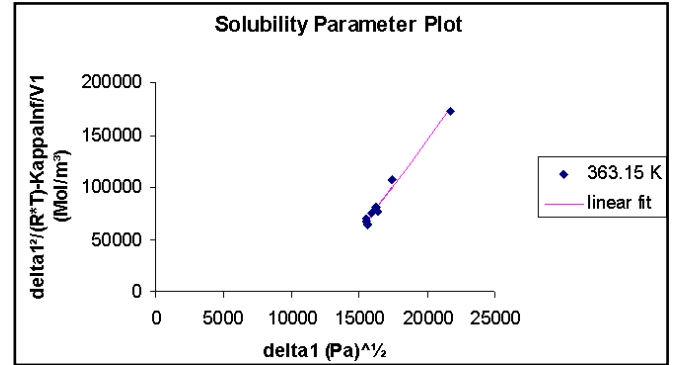


Figure 9. Solubility parameter plot for PMMA at 363 K. The different experimental points represent the various probe molecules used.

A solubility parameter of $17.6 \text{ MPa}^{1/2}$ was obtained which is in good agreement with literature values of 17.3 to $21.3 \text{ MPa}^{1/2}$ [11]. The Hildebrand approach can be taken even further for the study of polymer-polymer interactions in ternary systems [12].

IGC SEA – Degree of Cross Linking

Price *et al* utilised IGC to investigate the degree of cross-linking (cross-link density ν) by a finite concentration approach [13]. In short, a finite concentration of solvent (probe molecule) is injected through a column containing the material of interest. The Flory-Huggins interaction parameter, χ , is then determined from the probe molecule retention time [14]. Then, the Flory-Rehner equation (Equation 1) is used to determine the degree of crosslinking.

$$\nu = V_2 \left[\frac{\ln a_1 - \ln \phi_1 - [1 - (1/r)\phi_2 - \chi\phi_2^2]}{V_1[\phi_2^{1/3} - (\phi_2/2)]} \right] \quad (4)$$

In this equation V_1 and V_2 are the molar volume of the probe and the specific volume of the polymer, a is the activity coefficient, r the number of segments per polymer chain, ϕ_1 and ϕ_2 the volume fractions of probe and polymer and χ is the Flory-Huggins interaction parameter.

The clearcoat used in this study was a urethane acrylate with a starting (uncrosslinked) molecular weight around 1000 amu. The basecoat was a standard thermally cured automotive polyester basecoat. After curing the basecoat, the clearcoat was crosslinked by passing the sample



under a medium pressure mercury arc lamp. The total dose was approximately $1\text{-}2\text{ J/m}^2$. The resulting film was microtomed into slices measuring $2.5\text{ cm} \times 3.0\text{ cm} \times \sim 5\text{ }\mu\text{m}$. Slices were made through the clearcoat and basecoat layers. The reported density for the samples was 1.2 g/cm^3 .

For the iGC SEA experiments, the microtomed samples were cut into small strips and packed into silanized glass columns (30 mm long, 4 mm ID). Prior to measurement the sample was pre-treated at 368 K for 2 hours in situ.

Figure 7 displays the plateau degree of crosslink values as a function of coating depth. The error bars represent the standard deviation measured from repeat experiments ($n=2$). The results in Figure 7 indicate the degree of crosslink increases the further away from the surface. To illustrate, for the $0\text{-}5\text{ }\mu\text{m}$ sample a crosslink density of 2899 mol/g was measured, but for the $50\text{-}55\text{ }\mu\text{m}$ sample a crosslink density of 4065 mol/g was obtained. The error margins indicate the differences between the samples are greater than the measurement errors. For a thermoset clearcoat system, previous researchers measured a decrease in crosslink density with profile depth [15]. However, for this UV cured coating an increase in crosslink density with depth into the coating was observed. This has been observed

previously, and is likely due to the effects of oxygen inhibition during curing of the coating [16]. This effect is common in UV cured coatings, where the free radical nature of the curing process can be severely retarded by atmospheric oxygen scavenging the free radicals. This leads to a reduction in cure (crosslink density) in many UV cured coatings when cured in the presence of oxygen.

For the basecoat layer a similar trend was observed. The degree of crosslink increased slightly with profile depth. There were only two data points in this range, so additional studies are necessary to confirm this trend.

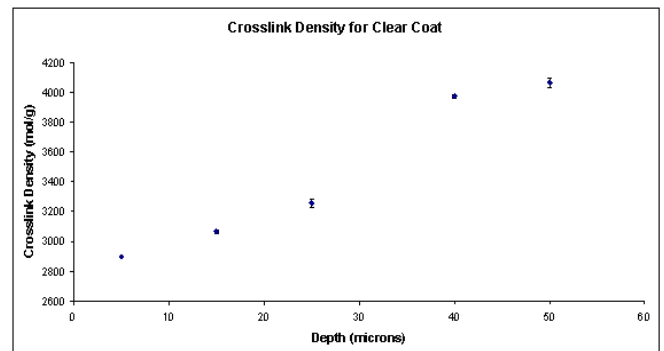


Figure 10. Crosslink density as a function of coating depth measured with decane at 368 K.



Conclusion

The above data demonstrates the potential of *iGC* as a technique available to researchers within the polymer industry. Advances in instrumentation have made it possible to measure physico-chemical properties of polymers which were previously very difficult or impossible to perform. In particular it is now possible to measure surface and bulk properties of polymers reproducibly and accurately in the presence of humidity. Such parameters include surface energies, acid-base numbers, enthalpies, entropies, glass transition temperatures, solubility parameters, degree of cross linking, crystallinity, Flory-Huggins interaction numbers, and many more. It is also possible to study polymers in different forms, whether as a powder or a coated film. A discussion of different coating methods is given in [17].

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