

Determination of Carbon Fibre-Polymer Interactions by Inverse Gas Chromatography

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Abstract

PAN based carbon fibres have a huge potential as reinforcement for fluorocarbon polymers. Fluorination of the carbon fibres is supposed to increase adhesion between fibres and PVDF matrix. Inverse Gas Chromatography was applied to measure surface energetics from which the theoretical work of adhesion can be derived. A comparison of these results with apparent interfacial shear strength measurements shows a limited improvement in practical adhesion for a fluorinated sample despite a more significant increase in the predicted work of adhesion. This discrepancy is due to an optimum F/C ratio for an improved adhesion which is smaller than the one of the sample investigated.

INTRODUCTION

The quality and performance of carbon fibre composites depends strongly on the interaction of the components at the interface.

Those interactions are typically described as adhesion and cohesion phenomena. Both properties depend on the energetic situation on the surface of the materials which is commonly expressed by the surface energy. Surface energies are classically measured by wettability (contact angle) methods. The main problem with this technique is the limited sensitivity making it less useful for sophisticated batch-to-batch variation studies. Inverse Gas Chromatography (IGC) has become a popular alternative due to its high sensitivity and reproducibility.

Inverse gas chromatography (IGC) is a well-known tool for the characterisation of particulates [1], fibres [2] and films [3].

IGC involves the sorption of a known adsorbate (probe molecule) onto an unknown adsorbent stationary phase (solid sample). This approach inverts the conventional relationship between mobile and stationary phase found in analytical chromatography.

Most IGC experiments are carried out in the pulse mode. This kind of experiment involves the injection of a certain amount of a vapour or gaseous probe molecule into an inert carrier gas

mobile phase. The probe molecule is transported by the carrier gas to the adsorbent in the column and in the ideal case an equilibrium state is reached. The adsorbed substance will then be eluted by the carrier gas. This elution is detected as a peak by a conventional chromatographic detector. The retention time can be obtained from the peak maximum. The net retention volume V_N is computed using Equation 1.

$$V_N = j / m \cdot w \cdot (t_R - t_0) \frac{T}{T_{Ref}} \quad (1),$$

where T is the column temperature, T_{Ref} is the reference temperature for the flow rate measurement, m is the sample mass, w is the exit flow rate, t_R the retention time for the adsorbing probe and t_0 is the mobile phase hold-up time (dead time). “ j ” is the James-Martin correction, which corrects the retention time for the pressure drop in the column bed.

One of the most commonly measured parameters for the description of the energetic situation on the surface of a solid is the surface energy. The surface energy is defined as the energy required to form (or increase the surface by) a unit surface under reversible conditions and is the analogue to the surface tension of a liquid. This means in practical terms that the higher the surface energy the more reactive the surface. This parameter can be divided into a dispersive and a specific component. The dispersive surface energy can be obtained from a plot of the logarithm of the retention volume of a series of alkane probe molecules (multiplied by the column temperature and the gas constant) versus the product of (square root of the) liquid tension and molecular area [4]. The result is a straight line and the dispersive surface energy γ_S^D is calculated from the slope according to Equation 2.

$$RT \ln V_N = 2N_A (\gamma_S^D)^{1/2} a_m (\gamma_L^D)^{1/2} + C \quad (2)$$

In this equation γ_L^D the liquid tension of the probe molecule and a_m its cross sectional area, C is a constant. The other parameters have the same meaning as above.

The specific contribution of the surface energy is obtained indirectly the specific free energy of a range of polar probe molecules. Points representing a polar probe are located above the alkane straight line. The difference is equal to the specific component of the free energy of desorption ΔG_{SP} (Equation 3).

$$\Delta G_{SP} = RT \ln V_N - RT \ln V_N^{ref} \quad (3)$$

From the specific free energy acid-base numbers can be calculated if an appropriate concept is applied.

The study of acid-base properties by IGC has the benefit that changes in the orientation of surface groups can be studied. Those changes are not necessarily related to variations in composition. For this reason spectroscopic methods are less appropriate for the study of these effects [5].

The most common approach for acid-base calculations used in IGC is the Gutmann concept [6]. Equation 4 gives an approximation:

$$\Delta G_{SP} = K_a \cdot DN + K_b \cdot AN^* \quad (4)$$

where the constants K_a and K_b represent the acid and base contribution of the solids surface while DN and AN* are the donor and acceptor number of the probe molecule.

Although this is very useful for semi-quantitative studies it suffers from the fact that the acid-base numbers obtained are dimensionless and can only be used for relative comparison.

An alternative is the van Oss concept [7], which provides acid and base numbers in the same unit as the surface energy.

$$\Delta G_{SP} = N_{A^*} a_m \cdot 2 \cdot ((\gamma_L^+ \cdot \gamma_S^-)^{1/2} + (\gamma_L^- \cdot \gamma_S^+)^{1/2}) \quad (5)$$

In this equation γ_S^+ and γ_S^- are the electron acceptor and donor parameters of the surface and γ_L^+ and γ_L^- are the electron acceptor and donor parameters of the probe molecule.

Unfortunately, in its original form this equation can only be used for relative comparison due to inaccurate starting parameters leading to an overestimation of the basicity [8].

Once the individual surface energetics are determined the work of adhesion between the individual solids can be calculated according to Equation 6.

$$W_{total}^A = 2(\gamma_1^d \cdot \gamma_2^d)^{1/2} + 2((\gamma_1^+ \cdot \gamma_2^-)^{1/2} + (\gamma_1^- \cdot \gamma_2^+)^{1/2}) \quad (6)$$

with: $\gamma_s^{SP} = 2 \cdot \sqrt{\gamma_s^+ \cdot \gamma_s^-}$.

The scope of this study is the investigation of the impact of carbon fibre fluorination on the adhesion and mechanical strength of single fibre PVDF-composites.

EXPERIMENTAL

The carbon fibres used in this study were PAN based high tensile strength carbon fibres C320.00A, Sigril SGL Carbon, Germany. The commercial PVDF material was Kynar 711 in powder form, Atofina, France. All samples were kindly provided by Imperial College, London. Two fibres were investigated: a non-fluorinated sample C0 and a fluorinated fibre C3 with an F/C ratio of 1.8.

For an IGC experiment the samples were packed into silanised glass columns (30 cm long, 3 mm ID). Prior to measurement the sample was pre-treated at 303 K for 2 hours in situ.

IGC measurements were carried out using the SMS-IGC 2000 system. The samples were measured at 303 K with a carrier gas flow rate of 10 ml/min. Probe molecules were decane, nonane, octane, heptane, dichloromethane, acetone, ethyl acetate, ethanol and acetonitrile. The probe molecules were injected from the head-space via a loop with 250 μ l volume. The injection concentration was 0.03 p/p₀ to obtain infinite dilution conditions. The deadtime was determined by a methane injection.

Mechanical strength results (practical adhesion), based on single fibre pull-out tests to obtain the apparent shear strength τ_{IFSS} were taken from [9].

RESULTS AND DISCUSSION

Figure 1 shows the dispersive surface energies for the two carbon fibre samples and the PVDF.

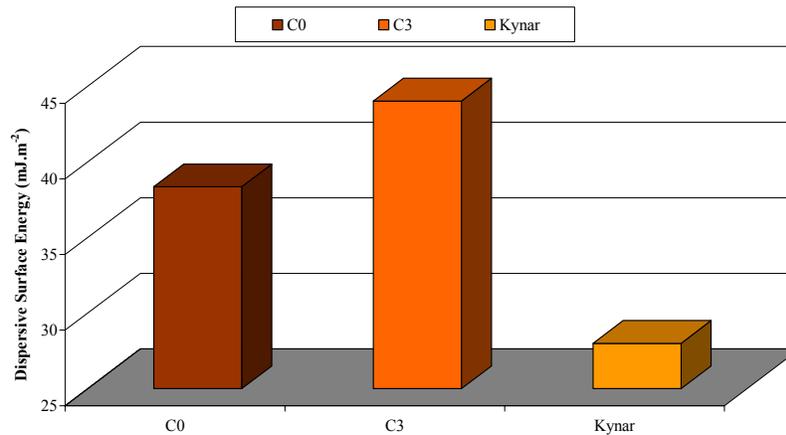


Fig. 1. Dispersive surface energies from IGC measurements at infinite dilution.

Figure 2 shows the specific free energies of the same materials. It can be seen that the numbers for the fluorinated carbon fibres are higher than for the non-fluorinated samples in both cases. It is interesting to note that the PVDF sample shows unexpectedly strong specific interactions while the dispersive surface energy is rather low. This might be due to chemical impurities of the polymer.

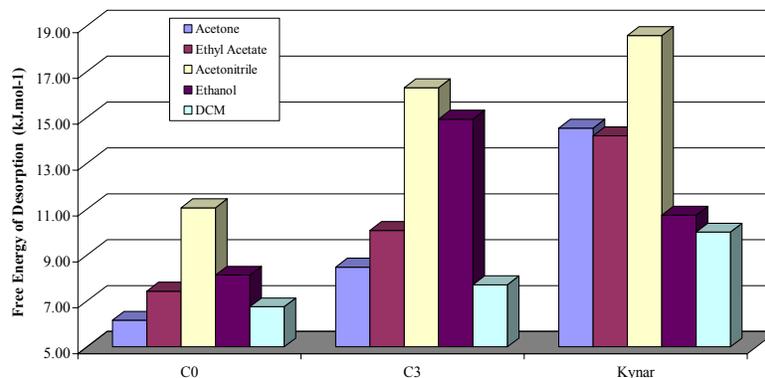


Fig. 2. Specific free energies from IGC measurements at infinite dilution.

A similar trend is visible in the acid-base numbers, which were calculated from the specific free energies using the Gutmann concept. Figure 3 suggests that the fibre surface is dominated by basic surface groups while the polymer is predominately acidic.

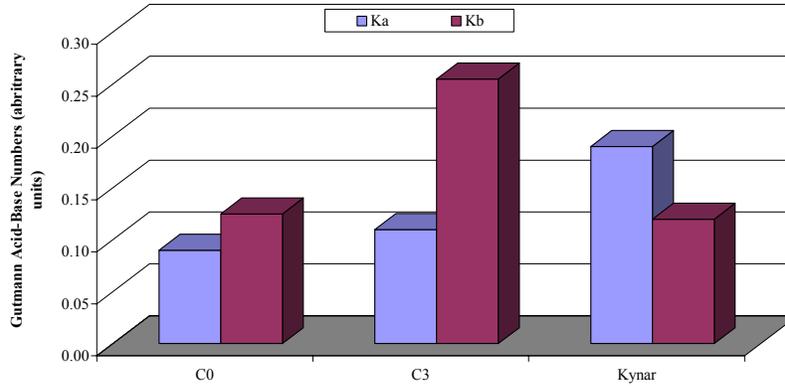


Fig. 3. Acid-Base numbers calculated from the Gutmann concept.

The van Oss concept has been applied to obtain the total surface energy and subsequently the work of adhesion. The numbers are shown in Table 1 together with the apparent interfacial shear strength.

Table 1: Total surface energy, γ_S^{total} and work of adhesion, W_{adh} . (fibre-polymer) in comparison with apparent interfacial shear strength T_{IFSS} (fibre-polymer).

Sample	γ_S^{total} (mJ/m ²)	W_{adh} . (mJ/m ²)	T_{IFSS} (MPa)
C0	124.0	353.7	27.7
C3	176.7	428.3	28.0
Kynar (PVDF)	270.5	-	-

The interfacial shear strength increases with increasing work of adhesion as expected. However, the increase in T_{IFSS} is relatively small. It was suggested that fluorination has a positive impact on the measurable adhesive strength. The data show that the practical adhesion is only slightly improved. This could be due to the existence of an optimum F/C ratio (related to the highest adhesion) with improved physical compatibility between the fluorinated fibres and the surrounding PVDF matrix. This ratio corresponds to the surface F/C ratio of PVDF of around 0.8 [9]. This means that the degree of fluorination in the sample investigated is too high for an optimized adhesion which would explain the limited improvement in strength.

Further experiments with different F/C ratios below 1.8 need to be conducted to prove these assumptions.

4. CONCLUSIONS

Surface energy and acid-base measurements have been carried out on fluorinated carbon fibres and PVDF polymer using inverse gas chromatography. Results were used to calculate

the work of adhesion between fibres and polymers. A comparison with apparent interfacial shear strength numbers shows that the practical adhesion increases less significantly due to fluorination than expected from energy measurements. This is most likely due to an existence of an optimum F/C ratio which is lower than the one for the samples investigated.

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