



Determination of Carbon Fibre-Polymer Interactions by Inverse Gas Chromatography

Dan Burnett | Surface Measurement Systems Ltd.

The interaction between carbon fibres with different surface treatments and thermoplastic polymer matrices were investigated through thermodynamic, work of adhesion calculations and mechanical, practical adhesion measurements. The work of adhesion between the various carbon fibres and polymers were determined by measuring the dispersive and specific surface energetics of the individual components using Inverse Gas Chromatography (IGC SEA). The mechanical adhesion measurements were performed by measuring the interfacial shear stress of the carbon fibre embedded in the polymer through single fibre pull-out testing. Oxidation of the PAN-based carbon fibres investigated caused an increase in the dispersive surface energy and a decrease in basicity. Work of adhesion values calculated from the surface energetics correlated well with the interfacial shear strength values of the composites. For all types of polymers used in this study there was an increase in both the work of adhesion and shear strength values on oxidation of the carbon fibre. Sizing does not significantly increase the shear strength despite a higher work of adhesion value, which may be caused by incompatibility of the polymers and epoxy-based sizing agent.

Introduction

The quality and performance of carbon fibre 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, sizing agent and polymer have to be 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 materials which is commonly expressed by the surface energy.

In this study surface energies of three different carbon fibres and three different thermoplastic polymers have been determined by Inverse Gas

Chromatography (IGC SEA). Carbon fibre-polymer interactions have been calculated by means of the work of adhesion. Work of adhesion numbers were correlated with interfacial shear strengths as a measure for practical adhesion.

Method

IGC SEA is a well-known tool for the characterisation of particulates [1], fibres [2] and films [3]. IGC SEA involves the sorption of a known vapour (probe molecule) onto an adsorbent stationary phase (solid sample) with unknown physico-chemical properties. This approach inverts the conventional relationship between mobile and stationary phase found in analytical chromatography. The stronger the interaction, the more energetic the surface and





the longer the retention time. For this reason a range of thermodynamic parameters can be derived from the retention behaviour. A detailed explanation of the theory is given in Ref. [1].

One of the most commonly used 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 analogous to the surface tension of a liquid. In practical terms, 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 directly calculated from the retention times of a series of n-alkanes [4] that is injected. The specific contribution of the surface energy is obtained indirectly via the specific free energy which can be obtained by injecting a range of polar probe molecules.

By applying an appropriate concept the acid-base numbers can be calculated from the specific free energies. The study of acid-base properties by IGC SEA 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 SEA is the Gutmann concept [6]. Equation 1 gives an approximation:

$$\Delta G_{SP} = K_a \cdot DN + K_b \cdot AN^* \quad (1)$$

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. ΔG_{SP} is the specific free energy of an individual polar probe interacting with the solid surface. 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 comparisons.

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

$$\Delta G_{sp} = N_A \cdot a_m \cdot 2 \cdot ((\gamma_L^+ \cdot \gamma_S^-)^{1/2} + (\gamma_L^- \cdot \gamma_S^+)^{1/2}) \quad (2)$$

In this equation γ_S^+ and γ_S^- are the acid and base 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]. Despite this, however, it is a useful concept for the determination of the specific surface energy. The specific surface energy can be obtained from the acid and base parameters according to Equation 3:

$$\gamma_s^{SP} = 2 \cdot \sqrt{\gamma_s^+ \cdot \gamma_s^-} \quad (3).$$

Once the individual surface energies for the polymers and the carbon fibres are determined the work of adhesion between the individual solids can be calculated according to Equation 4:

$$W_{total}^A = 2(\gamma_1^d \cdot \gamma_2^d)^{1/2} + 2((\gamma_1^+ \cdot \gamma_2^-)^{1/2} + (\gamma_1^- \cdot \gamma_2^+)^{1/2}) \quad (4).$$

A higher work of adhesion would predict a strong a strong fibre-polymer interaction and a high interfacial shear strength.

Materials

The carbon fibres used in this study were PAN based high tensile strength materials. Two AS4 carbon fibres were investigated: AS4-12K and AS4-GP-3K. They were kindly supplied by Hexcel, Salt Lake City, USA. Both types of fibres were oxidized and AS4-GP was also sized with an epoxy based agent. A third fibre C320.00A, Sigri SGL Carbon, Germany, unoxidized and unsized was studied for comparison. The three samples will be referred to as AS4 unsized, AS4 sized and CA for the remainder of this paper. The polymers, polysulfone, polycarbonate and polyetherimide, were commercial thermoplastic materials and all supplied by Aldrich in the form of beads.

Results

The dispersive contribution of the surface energy, reflecting the graphitic nature of the fibres [9] is shown for each individual carbon fibre in Figure 1.

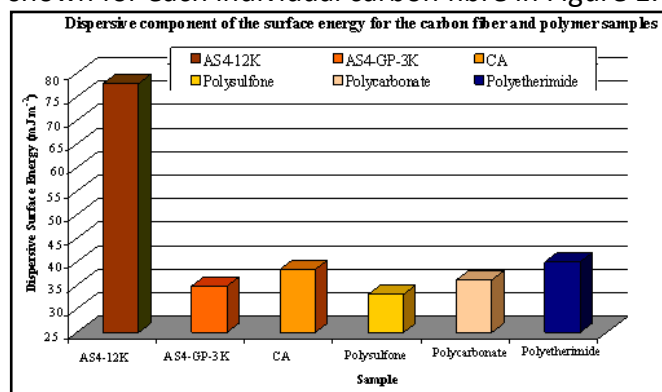


Figure 1. Dispersive surface energies of different fibres and polymers measured at 303 K.

The AS4 unsized fibre has a much higher dispersive surface energy than the unsized and unoxidized (CA) fibre. Oxidation obviously generates a more active surface. The sized fibre shows a much lower dispersive surface energy. In fact, it gives the lowest value of all three fibres. This suggests that sizing makes the surface less active (as far as the dispersive forces are concerned) due to a formation of an epoxy layer. That the value is even lower than for the untreated CA fibre is therefore not surprising since the oxidized layer on the fibre is covered by the sizing agent.

The specific interactions, expressed by the specific free energy, are shown in Figure 2.

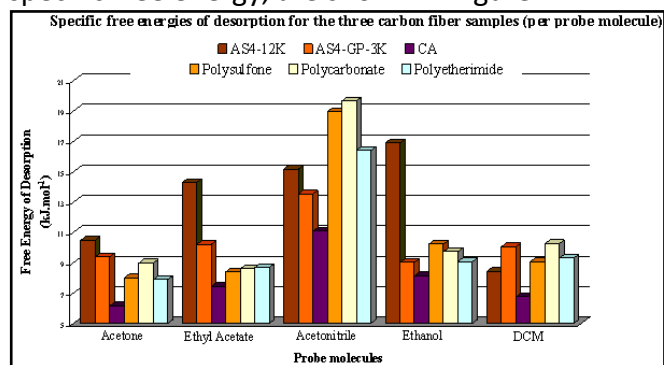


Figure 2. Specific free energies of different fibres and polymers measured at 303 K.

As shown in the Figure, trends in the specific free energies are different compared to those in the dispersive surface energy. As before most probes interact strongest with the AS4 unsized sample. However, the AS4 sized sample interacts stronger than the untreated CA fibre. This suggests that polar probes interact significantly with the epoxy layer.

From the specific free energies acid-base numbers have been calculated using the Gutmann concept. These numbers are displayed in Figure 3 for the carbon fibres.

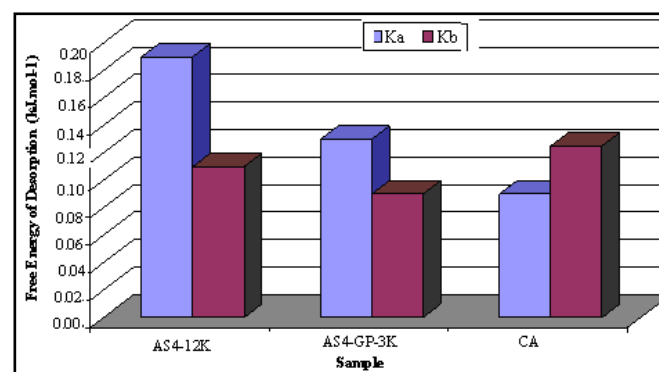


Figure 3. Acid (Ka) and base (Kb) numbers for different carbon fibres calculated from specific free energies.

All samples appear amphoteric. The untreated CA fibre seems to be predominately basic while oxidation causes a shift towards a dominating acidity. When the Ka numbers are compared directly the trend AS4 unsized > AS4 sized > CA can be observed. This can be explained by the fact that oxidation increases the amount of oxygen functionalities, so AS4 unsized shows the highest acidity. A comparison of the Kb numbers shows the following trend: CA > AS4 unsized > AS4 sized. The change in basicity from the untreated CA to the AS4 unsized sample can be explained by the decrease in the graphitic nature of the fibre due to the oxidation. Sizing seems to decrease the basicity even further.

In order to calculate adhesion parameters from surface energy values the specific free energies need to be converted into specific surface energies as shown in Equation 4.



The results for the specific and total surface energies are displayed graphically in Figure 4.

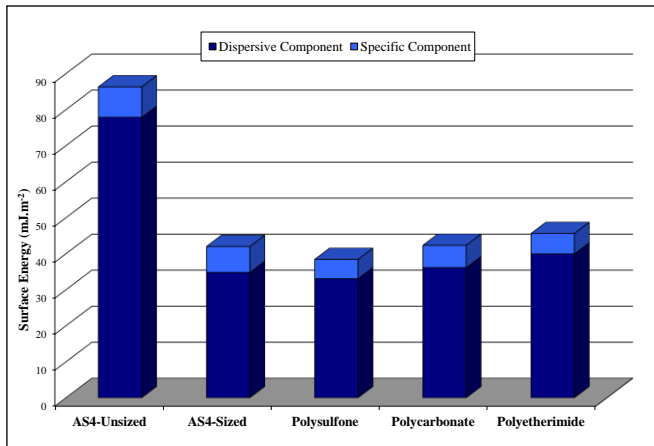


Figure 4. Dispersive, specific and total surface energies for carbon fibres and polymers.

Although it is well known that the van Oss concept overestimates the basic contribution, so the Della Volpe scale was used for these calculations. Figure 5 shows a correlation between the work of adhesion numbers obtained for the different carbon fibre – polymer composites (based on the surface energies obtained by IGC SEA) and interfacial shear strength numbers (from fibre pull-out tests).

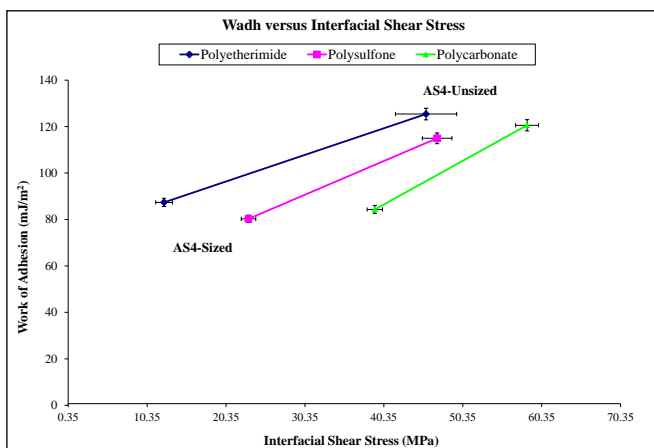


Figure 5. Correlation between work of adhesion numbers calculated for the different carbon fibre – polymer composites (based on the surface energies obtained by IGC SEA) and interfacial shear strength numbers (obtained from fibre pull-out tests).

For all three polymers predicted adhesion (y-axis) increases with shear strength (x-axis) when fibres are unsized. Additional sizing does not seem to increase the shear strength although predicted adhesion values are higher (in comparison to the untreated sample). Higher adhesion values suggest stronger carbon fibre–polymer interactions due to the higher total surface energy of the sized sample in comparison to the untreated fibre. This is due to the higher specific contribution of the sized sample. This higher specific interaction seems to be caused by the higher acidity. Since the practical adhesion (interfacial shear strength) does not change considerably due to the sizing despite oxidation) in comparison to the untreated CA sample and even decreases in comparison to AS4 unsized it can be concluded that the interaction at the interface is not dominating the stress behaviour of the sized composite. This is most likely due to an incompatibility between polymer and sizing.



Conclusion

Three carbon fibres, an untreated CA, an oxidized AS4 and an oxidized and epoxy-sized AS4 have been investigated by IGC SEA. The unsized AS4 has a much higher dispersive surface energy than the CA sample suggesting that oxidation generates a more active surface. The sized fibre shows the lowest dispersive contribution due to a formation of a less active epoxy layer. Acid-base numbers calculated from specific interactions with polar probes show a decrease in basicity from the untreated to the oxidized samples while the acidity is increasing. This is due to a decrease in the electron donor capacity of the oxidized fibres.

Adhesion values were calculated based on IGC SEA surface energy data and correlated with the apparent shear strength of the carbon fibre-polymer composites. 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.

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References

- [1]Thielmann, F., J. Chrom. A 1037 (2004), 115.
- [2]van Astem, A. et al, J. Chrom. A 888 (2000), 175.
- [3]Pawlisch, C., Macris, A. and Laurence, R., Macromolecules 20 (1987), 1564.
- [4]Schultz, J. et al., J. Adhesion 23 (1987), 45.
- [5]Buckton, G. et al, Intern. J. Pharm. 72 (1991), 157.
- [6]Gutmann, V., Coord. Chem. Rev. 2 (1967), 239.
- [7]Oss, C., Good, R. and Chaudhury, M., Langmuir 4 (1988), 884.
- [8]Della Volpe, C, Sibioni, S., J. Coll. Interf. Sci. 195 (1997), 121.
- [9]Bolvari, A.E., Ward, T.C. in Inverse Gas Chromatography, editors: Lloyd, D. et al, ACS Symp. Series 391 (1989), 217.
- [10]Hampe, A. and Marotzke, C., Polym. Intern. 28 (1992), 313.
- [11]Meretz S., Linke, T., Schulz, E., Hampe, A. and Hentschel, M., J. Mater. Sci. Letters 11 (1992), 1471.
- [12]Hampe, A., Klinka, G., Meretz, S., Schulz, E., Composites 26 (1995), 40.
- [13]Meretz, S., Auersch, W., Marotzke, C., Schulz, E., Hampe, A., Composite Sci. Technol. 48 (1993), 285.

Head Office:
Surface Measurement Systems, Ltd
5 Wharfside, Rosemont Road
London HA0 4PE, UK
Tel: +44 (0)20 8795 9400
Fax: +44 (0)20 8795 9401
Email: science@surfacemeasurementsystems.com

United States Office:
Surface Measurement Systems, Ltd, NA
2125 28th Street SW, Suite I
Allentown PA, 18103, USA
Tel: +1 610 798 8299
Fax: +1 610 798 0334

