

### Introduction

Although the surface properties of high performance carbon fibres are of technological importance, many aspects are still not fully understood (1), particularly the mechanism whereby the interlaminar shear strength (ILSS) of fibre/resin composites is enhanced by oxidative surface treatments (2,3). In an attempt to further elucidate the surface characteristics of PAN based fibres and their interactions with the type of functional groups which may be present in resin systems the investigations reported here were undertaken.

### Experimental

High modulus (HM), high strength (HT) and type A carbon fibres both untreated (u) and surface treated (s) by the manufacturer were investigated along with a series of HM fibres oxidised in 68% fuming nitric acid for periods of 9, 12, 25 and 50 hours followed by rigorous extraction in water.

Nitrogen adsorption measurements were carried out gravimetrically using a Beckman RIIC LM600 VM microbalance, buoyancy effects being reduced to a minimum. Adsorption-desorption measurements were made in the range 0.01-1.0 p/p<sub>0</sub> at 78K after degassing to < 10<sup>-5</sup> torr at temperatures up to 950°C.

Oxygen chemisorption was also performed gravimetrically at 340°C following the 950°C degassing. N<sub>2</sub> was gradually admitted to 90 torr and after equilibration O<sub>2</sub> was added to bring the total pressure to 110 torr. There was a rapid establishment of the buoyancy effect (previously assessed during the N<sub>2</sub> admissions) followed by a slower weight increase due to complex formation. Under these conditions weight increases of ±1.2 µg could be measured reproducibly.

The Microscal flow calorimeter was used to follow the adsorption of organic solutes; its mode of operation has been described in detail previously (4). Heat effects produced by adsorption of components from a carrier fluid which flows over a bed of adsorbent are detected by thermistors and displayed as peaks on a potentiometric recorder. Equal quantities of chopped fibres were carefully inserted into the calorimeter and compacted as nearly as possible to the same degree prior to measurement. Solvent was then flowed over the fibres at a precisely controlled rate and small quantities (usually 20 µl) of a solution of known concentration were injected into the stream. The areas of the exothermic and endothermic peaks produced by adsorption and desorption of species at the interface were measured by planimetry. n-butanol, n-butylamine, n-butyric acid and 1-2-epoxypropane dissolved in n-heptane (0.037 M) were the major adsorbates investigated.

### Results and Discussion

Degassing in vacuum at elevated temperatures brought about appreciable weight losses of all fibres, the amount increasing with increasing temperature. The vapours emitted were consistent with the removal

of trapped carbonization products as suggested previously (5). Nitrogen isotherms on these fibres were of type II, and were displaced to higher amounts adsorbed and exhibited sharper 'knees' after degassing at elevated temperatures. Figure 1 shows the amount adsorbed on the HM-u fibres degassed at various temperatures, plotted against the amounts adsorbed on the room temperature degassed sample at the same relative pressure (de Boer (6) type of analysis). The intercepts indicate the development of microporosity during heating. Similar results were obtained with all types of fibres and the microporosity created by heating at 950°C increased after surface oxidation.

Comparing the isotherms of the HM fibres oxidised in nitric acid with the untreated fibre in the same way, shows that oxidation produces no microporosity but increases the external surface area. The comparative plots show a decrease in slope at high amounts adsorbed suggesting some mesoporosity, but no hysteresis was apparent in the adsorption isotherms. The commercial surface treatments produced no significant change in the surface areas of all types of fibres. The active surface areas of the untreated fibres increased in the direction

type A > type HT > type HM ,  
were markedly increased by the manufacturer's surface treatment and to a much greater extent by nitric acid oxidation (HM fibres). It will be demonstrated that the fraction of the surface which is 'edge' surface also increases during this type of surface treatment. In this respect the effect resembles the change in active surface area of graphon during air oxidation observed by Walker and Janov (7).

Figure 2(a) shows a model trace obtained from the calorimeter following the injection of a reversibly adsorbed species into the solvent stream. The adsorption and desorption peaks are of equal area. Injections of n-butanol and 1-2-epoxypropane solutions into the n-heptane solvent stream produced effects approximating to this model, but with fibres of low active surface area the adsorption peak area was sometimes smaller than that of the desorption peak as a result of the endothermic heat of dilution becoming appreciable in comparison with the heat of adsorption. Adsorption of n-butyric acid could not be detected on any fibres, whilst n-butylamine was adsorbed very strongly and in part irreversibly. The trace obtained with this latter species was as shown in Figure 2(b); a large exothermic peak was followed by a tiny desorption peak. The second and subsequent adsorption peaks were smaller than the first, these being of reproducible area after the third injection. Injecting n-butanol after the n-butylamine adsorptions resulted in no change in the peak area, indicating that the irreversibly held butylamine is on different sites from those on which the alcohol adsorbs reversibly. However, when the n-butanol was injected into a flowing stream of n-butylamine solution no adsorption could be detected. This suggests the reversibly adsorbed amine and alcohol adsorb on the same sites, the amine being preferentially held there.

Whilst there is evidence of a very small increase in the n-butanol peak areas as the external areas of the HM nitric acid oxidised fibres increase, the areas of the first and the subsequent reversible exothermic butylamine peaks are magnified greatly by this treatment, Figure 3. There may also be a marginal decrease in the epoxypropane peak areas. On the commercially surface treated fibres the n-butylamine peak areas are also increased markedly but, as observed earlier, the external area is unaffected. In all cases the n-butylamine peak areas could be correlated with the active surface area measurements, a different relationship applying to each type of oxidation series.

n-Butylamine adsorption has previously been correlated with the amount of acidic surface complex on carbon surfaces (8) and it seems reasonable to assume that these are the sites for adsorption of this species. If this is so the results suggest that the fraction of the active surface which is covered by the acidic type of complex increases with oxidation time in nitric acid (HM-fibres) and is also greater for fibres treated by this method than those surface treated by the supplier.

The relevance of these results to the mechanism of enhancement of the ILSS of composites by surface treatment processes will be commented on at the meeting.

#### References

1. McKee, D.W. and Mimeault, V.J., "Chem. & Phys. Carbon", Vol.8, 151-245, (1973).
2. Herrick, J.W., 23rd Am. Tech. Conf. SPI Reinforced Plastics/Composites div., sect. 16-A, (1968).
3. Scola, D.A. and Brooks, C.S., 25th Soc. Plastics Ind. Meeting, Washington D.C., February 1970.
4. Grozcek, A.J., Lubric. Sci. Tech., 9, 67, (1966).
5. Mimeault, V.J. and McKee, D.W., Nature, 224, 793 (1969).
6. Lippens, B.C., Linsen, B.G. and de Boer, J.H., J. Catal., 3, 32 (1964).
7. Walker, P.L. Jr., and Janov, J., J. Colloid Interface Sci., 28, 449 (1968).
8. Puri, B.R., "Chem. Phys. Carbon", Vol.6, 191-282 (1970).

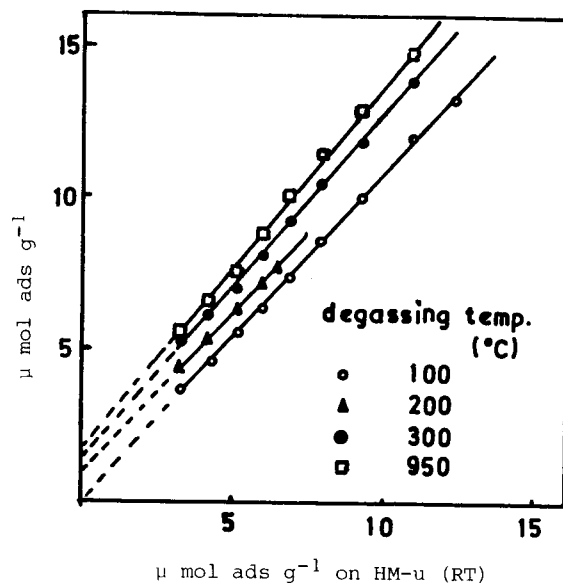


Fig.1 N<sub>2</sub> adsorption on HM-u fibres

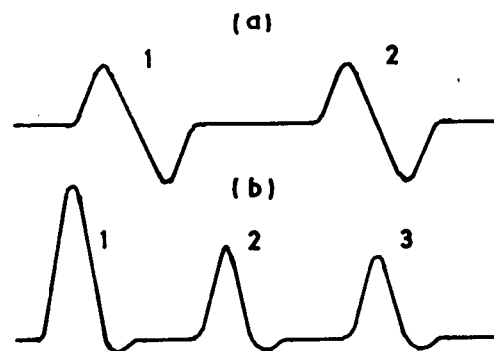


Fig.2 Typical calorimeter peak shapes  
- successive injections of  
adsorbate

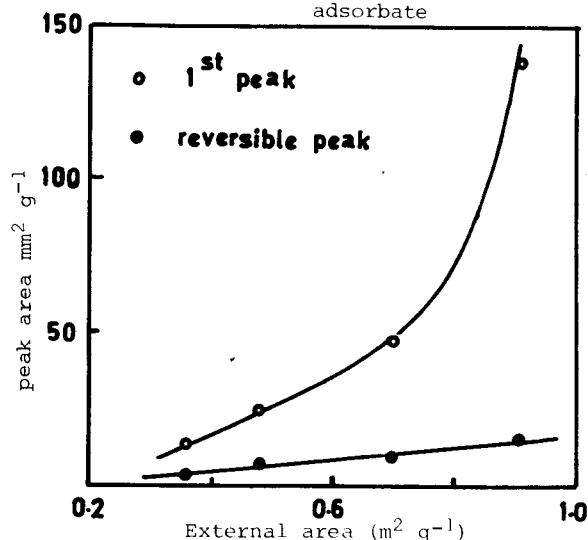


Fig.3 n-Butylamine peak areas for HM fibres oxidised in nitric acid