

INTRODUCTION

The surface activation of carbon fibres by various oxidation methods is very effective in improving the adhesion of polymer matrices; the surface chemistry of the surface activated carbon fibres has been studied extensively [1]. This study is concerned with (1) some boundary conditions (drying, cleaning of the fibre surface, and modification of surface functional groups), which may significantly influence the experimental results on the surface chemistry, and (2) a comparison of experimental methods (contact angle measurements, X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD)) in view of their usefulness.

EXPERIMENTAL

The studies were performed with three HT fibres (HTU (uu) from Akzo = fibre (A), HTA (ou) from Akzo = fibre (B), HTU (uu)/ozone treated = fibre (C), (AS4 (ou) from Hercules = fibre (D)), an IM fibre (T800 (ou) from Toray = fibre (E)) and a HM fibre (M40 (ou) from Toray = fibre (F)); (uu) means unoxidized, unsized and (ou) means oxidized, unsized). The surface chemistry was analyzed by contact angle measurements with aqueous solutions of different pH value (Wilhelmy technique), XPS and TPD [2]. Drying of all as-received and all treated fibres was performed at 110°C with a vacuum of $1.97 \cdot 10^{-3}$ Pa and 4 h treatment time. For removing of adsorbed oxidation products from the fibre surface extraction with boiling water was found to be most effective and generally used. For modification of surface functional groups the following reactions were applied: (1) esterification of carboxyl groups with methanol/HCl, (2) selective reduction of surface functional groups with sodium

boron hydride, and (3) non-selective reduction of surface functional groups with lithium aluminium hydride. Details are given in reference [3].

RESULTS

Figs. 1 (a) to (c) show the work of adhesion in dependence of the pH-value for fibres (C), (E) and (F) after the following treatments: as received (---), dried as described above (—), and extracted with water (—). Fig. 1 (a) shows an impressive example of the removal of adsorbed oxidation products by extraction with water, Fig. 1 (b) the effect of careful drying of an as-received, not sufficiently dried fibre, and Fig. 1 (c) another effect of the extraction with water, namely an increase of the work of adhesion by hydrolysis of anhydrides. The fibre obviously was "overdried" by the producer, whereby carboxyl groups underwent condensation (results by XPS).

Detailed results of XPS studies will be presented elsewhere [3]. Fig. 2 shows a correlation between the work of adhesion, W_{SL} , and the O1s:C1s ratio determined with all extracted fibres. Neither $W_{SL,min}$ (pH = 2) nor $W_{SL,max}$ (pH = 13) correspond with the O1s:C1s ratio. The reason is as follows: the work of adhesion gives an image of the most outer surface, whereas XPS signals result from a surface volume. High O1s:C1s ratios indicate strong internal oxidation. The specific surface areas of fibre (C), (D) and (F) are as follows: $1.1 \text{ m}^2/\text{g}$ (C), $0.34 \text{ m}^2/\text{g}$ (D) and $0.52 \text{ m}^2/\text{g}$ (F). Internal oxidation can even better be analyzed by TPD, because decomposition products of all functional groups are detected. Fig. 3 shows a correlation between the amount of oxygen desorbed up to 1000°C by formation of CO₂ and CO in dependence of the O1s:C1s ratio.

These quantities correlate pretty well and thus confirm the previous conclusion. It will be shown in another paper of this conference [4] that W_{SL} is the only quantity which can be correlated with the shear failure of UD-composites produced with all fibres (A) to (F) and various HT-thermoplastics as matrix. Fibres with chemically modified surface functional groups were studied analogously. It was found that the reactions investigated were neither selective nor occurred complete [5].

SUMMARY

The results have shown that the real surface chemistry of a carbon fibre can only be determined (1) after careful cleaning of the surface by removal of adsorbed oxidation products which, according to FTIR-studies, are highly oxidized aromatics, (2) after careful drying or hydrolysis of anhydrides formed by a too severe drying treatment. Chemical modification

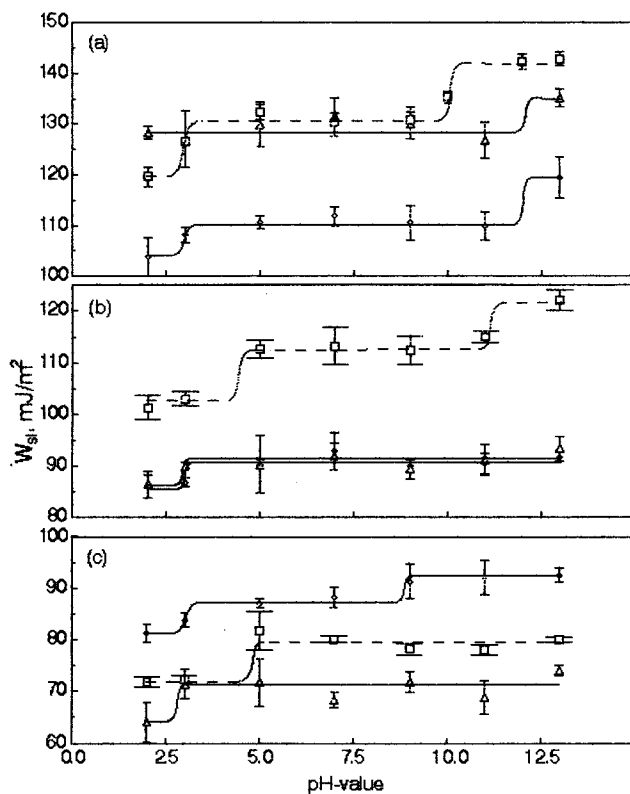


Fig. 1: W_{SL} in dependence of the pH-value for as-received, dried and extracted carbon fibres.

reactions should be handled very carefully, and XPS data may not necessarily be favourable correlation quantities for the surface functionality of a fibre.

ACKNOWLEDGEMENT

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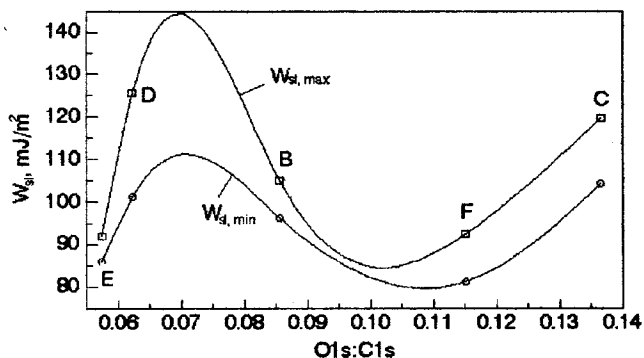


Fig. 2: W_{SL} of carbon fibres of different nature in dependence of the O1s:C1s ratio as determined by XPS.

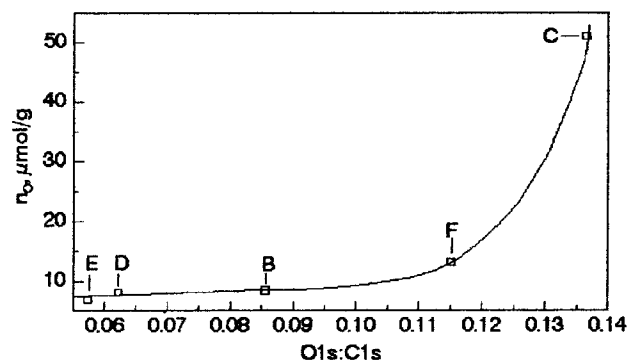


Fig. 3: Amount of oxygen desorbed in TPD experiments (CO_2 , CO) in dependence of the O1s:C1s-ratio.