

Surface Groups on HT-Carbon Fibers and Their Contribution to the Adhesion in CFRPs

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1. INTRODUCTION

Surface treatment of C-fibres is needed to guarantee good adhesion and stress transfer between fibers and polymer matrix [1,2]. Different oxidation methods are used for this purpose and acidic as well as alkaline surface oxides are formed on the fibres. It was tried to explain this improvement in adhesion by the presence of surface oxides [3,4].

DONNET et al [5] achieved partial reversibility of such improvement by removal of the oxygen surface complexes during post heat treatment in vacuum. In UD-composites, he measured ILSS values of 55 MPa for surface treated fibres and the partial reduction to 77 MPa by post heat treatment of the surface treated fibres. The author explained the residual improvement of the ILSS after the post heat treatment by the BET surface in his case increased during surface treatment.

A more specific proof of the contribution of the surface oxides to the adhesion was performed by FITZER et al [6,7]. The author blocked the acidic surface groups of various types of carbon fibres (wet oxidized in boiling HNO_3) as well as of commercially surface treated carbon fibres by means of the chemical reaction with CH_2N_2 . A complete inhibition of the adhesion improvement by acidic surface oxides was only found for HM-fibres. In case of HT-fibres, however, they found similar as DONNET a residual improvement of the adhesion after chemical blocking of the surface oxides.

The present paper describes experiments to explain this residual improvement in composites with HT-fibres. For this purpose, a carbon fibre was selected which does not show any difference in BET surface neither between non-surface treated and surface treated states nor after desorption treatment of the surface treated fibres.

2. EXPERIMENTAL

2.1 Fibre Materials

Commercially available PAN-based HT-carbon fibres without and with commercial surface treatment (TORAYCA T300U and T300S) were used. The commercial finish was removed by extraction in boiling acetone for several days and subsequent washing in boiling water. The drying process was carried out for 24 h at 130°C under N_2 and con-

tinued for 12 h under reduced pressure (10^{-5} bar) at room temperature for complete desorption of physically adsorbed rest-gases. The oxygen surface complexes were removed by post heat treatment between 500°C and 1400°C in separate runs (heating rate 10°C/min). The final heat treatment temperature of each run was selected from viewpoint of the temperature ranges in which the special surface oxides are decomposed. The amount of volatile products CO_2 , CO and CH_4 was measured by IR-analysis.

2.2 Composite Preparation and Testing

Matrix resin LY556 (CIBA GEIGY), a liquid epoxy resin and HT972 (CIBA GEIGY), a powdered aromatic diamine hardener were used as precursors for the polymer matrix.

UD model composites were prepared by dry winding and subsequent resin impregnation under N_2 . The composites with a fibre content of 60 vol-% were characterized by their interlaminar shear strength values (ILSS), using the short beam test.

3. RESULTS

Fig. 1 shows the amount of decomposition products formed during heat treatment within temperature ranges up to 1400°C. In accordance with literature, CO_2 is formed mainly between 300°C and 450°C and between 700°C and 850°C. These temperature ranges were confirmed for non-surface treated as well as surface treated carbon fibres.

For CO_2 a second maximum was found at 800°C, again for both fibre types. CO-formation shows an additional maximum in the low temperature region around 350°C and a further increase at temperatures above 1000°C. Both these effects cannot be explained by thermal decomposition of the oxygen surface complexes. The first CO-maximum at 350°C is explained by a secondary reaction of CO_2 with the carbon fibre surface according to the BOUDOUARD-equilibrium and is thus correlated with the amount of CO_2 formation

The amount of respective volatile products mentioned above, differs between surface treated and untreated fibres by the factor of 2 or 3 (see Tab. 1). On the contrary to this result, the increase of CO formation at temperatures above 1000°C is equal for fibres with and without surface treatment. This indicates a secondary reaction; for instance, between the carbon fibres

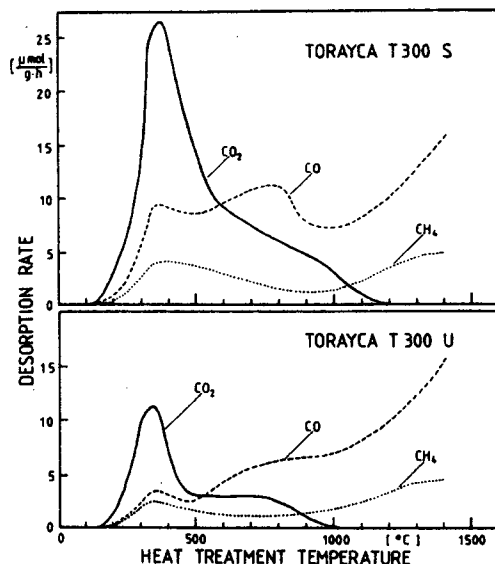


Fig. 1. Desorption products, CO_2 , CO and CH_4 of untreated (U) and surface treated (S) carbon fibre T300.

and glass compounds of the sample support. This explanation is experimentally confirmed by a long thermal post heat treatment of HM-fibres at 1200°C up to 12h. A steady CO -formation was observed during this long-time heating period. Also, this CO -formation cannot be explained by decomposition of oxygen compounds within the oxygen-free HM-fibres. A similar explanation can be considered for the CH_4 -formation, namely a secondary reaction with hydrogen.

The amount of volatile products CO_2 , CO and CH_4 is compiled in Table 1 together with the nitrogen content of the fibres before and after heat treatment as well as the ILSS data of UD composites with the respective fibres. One can recognize the improvement of adhesion by surface treatment of the fibres, but also the residual improvement after heat treatment of surface treated carbon fibres.

Fig. 2 shows in more detail the correlation between ILSS in composites and analytical results concerning the post heat treated fibres. These results can be summarized as follows:

- a) The improvement of ILSS by the commercial oxidation treatment can be reversed completely by heat treatment up to 1000°C . No residual

Table 1. Amount of Desorbed Gases CO_2 , CO and CH_4 During Heat Treatment of HT Carbon Fibre T300 Up to Final Temperature T, Fibre Nitrogen Content and Resulting ILSS.

FIBRE-TYPE	DESORPTION-TREATMENT T [°C]	DESORBED GASES (μmol/g)			FIBRE-ANALYSIS N (%)	ADHESION IN LY 556 ILSS (MPa)
T 300 U	1000	5.16	5.53	2.76	5.6	78.6
	—	—	—	—	—	78.7
T 300 S	530	11.01	5.12	1.97	—	91.9
	—	—	—	—	—	82.0
	1000	17.69	12.53	4.59	5.4	78.9
	1200	17.50	12.82	4.92	2.6	63.5
	1400	17.82	13.91	5.57	1.1	32.6

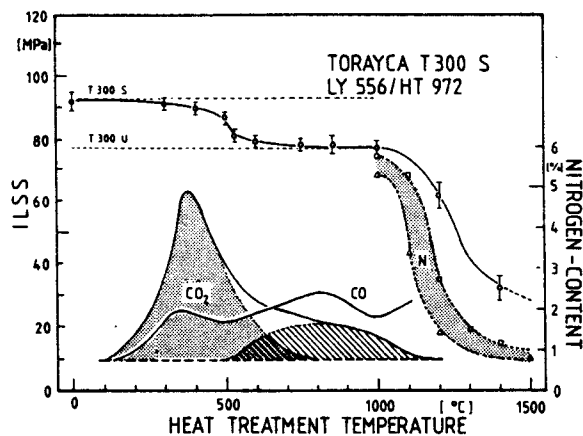


Fig. 2. Influence of desorbed CO_2 , CO and fibre nitrogen content on the residual ILSS.

improvement of adhesion is found.

- b) The decrease of ILSS improvement by surface treatment occurs in the post heat treatment temperature range between 300°C and 450°C . It can be directly correlated with the main CO_2 -formation as decomposition product.
- c) There is a minor further reduction of ILSS improvement above 500°C to 1000°C in the order of 4 MPa, indicating that the surface groups which decompose to CO have only a minor influence on adhesion improvement by surface treatment.
- d) There is a drastic decrease of ILSS by post heat treatment above 1000°C of surface treated as well as non-surface treated T300 fibres to residual ILSS around 30 MPa after heat treatment up to 1400°C .
- e) There is a surprising correlation between this drop in ILSS and nitrogen lost from the HT-carbon fibres.

4. DISCUSSION OF THE RESULTS

As mentioned in Chapter 2, BET surfaces of the untreated fibres as well as surface treated and post heat treated fibres have not changed and were measured with $0.32 \text{ m}^2/\text{g}$. Therefore, an effect of the BET surface on the changes in ILSS values can be excluded quantitatively. Only after long post heat treatment (some hours) above 1200°C an increase in BET surface was measured.

It is not yet described in literature, that the improvement of adhesion of HT-fibres can be completely reversed by post heat treatment. The experimental results shown above indicate that the improvement of adhesion by surface treatment is caused mostly by the surface groups which decompose below 500°C and form CO_2 as decomposition product. Although the formed decomposition products cannot describe the type of surface groups decomposed, this CO_2 -formation seems to be caused mainly by thermal decomposition of carboxylic groups. These findings confirm former discussion in literature, that the improvement of ILSS by surface treatment is dominated by acidic surface oxygen complexes.

In all literature data on the adhesion between carbon fibres and polymer matrix materials, the

measured ILSS can be split into two parts:

a) basic adhesion, which is measured after desorption treatment or blocking of the reactive surface groups.

b) the contribution to the ILSS caused by the surface treatment.

The basic adhesion in composited with HM-fibres is reported in the area of 20 MPa. The basic adhesion in HT-fibres is in the area of 60-80 MPa. It was shown previously /7/, that this basic adhesion in HT-fibres can be reduced to a lower limit in the order of 30 MPa. At that time, it was discussed that the basic adhesion of HT-fibres, if compared with HM-fibres, is caused by surface oxides, always present in HT-fibres. As it is shown here, untreated HT-fibres with ILSS of 78 MPa can be reduced to basically 30 MPa only by heat treatment above 1000°C.

This decrease can be correlated with the decrease in nitrogen content. It seems therefore probable that the residual nitrogen content in HT-fibres cause this residual adhesion in the range of 60 MPa to 80 MPa.

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