Anodic oxidation of high modulus carbon fibres in sulphuric acid

E. FITZER, H. JÄGER*

Institut für Chemische Technik, Universität Karlsruhe, FRG

N. POPOVSKA

Higher Institute of Chemical Technology, Burgas, Bulgaria

F. VON STURM

SIGRI GmbH, Meitingen, FRG

The continuous anodic oxidation of high modulus (HM) carbon fibres in sulphuric acid electrolyte, with varied concentrations as a possible surface treatment method, is presented. It can be shown that within the applied potential ranges and the resulting current densities no loss of mechanical fibre properties or increase in BET surfaces is observable. The formed surface oxides are detected by a thermal fibre decomposition treatment up to 1000° C and thus give an explanation for the increase in ILSS (interlaminar shear strength) caused by the different applied current densities. It is also shown that the specific electric charge (current density × pretreatment time) of a particular electrolyte concentration can be taken as a parameter to describe the surface activation by anodic oxidation and its consequent influence on the ILSS of composites fabricated from treated carbon fibres in epoxy polymer. However, this fibre activation is predominantly affected by the concentration of the electrolyte.

1. Introduction

To achieve a good adhesion between HM carbon fibres and polymeric matrix systems, a surface treatment is necessary. In most cases this surface treatment consists of an oxidation process. Various surface treatment methods for carbon fibres are described in the literature, but little information is available about industrially applied methods. However it can be assumed from the patent literature [1–3] that electrochemical oxidation is preferably used for commercial products instead of thermal [4–6] and wet oxidation [7–9] because of the shorter oxidation times and the superior processing control possibilities. Only limited literature exists on the electrochemical oxidation of carbon fibres.

Weinberg et al. [10] have shown that the amount of surface oxides formed during electrochemical oxidation of cellulose-based carbon fibres in sulphuric acid (15 wt%) is independent of the working potential. Donnet et al. [11, 12] performed electrochemical oxidation experiments on carbon fibres in alkaline and oxidizing electrolytes and an improvement in polymer reinforcement behaviour resulted. All the above experiments were operated under conditions where fibre degradation caused by the applied oxidation potentials occurred. Fitzer et al. however [13–17] have

shown that electrochemical carbon fibre surface activation is possible without fibre damage by degradation.

The present paper is concerned with the anodic oxidation of HM carbon fibres in sulphuric acid electrolyte. The effect of the electrolyte concentration at different current densities on the fibre properties, as well as the surface oxides and the resulting ILSS values are described. The specific electric charge as the parameter to characterize the carbon fibre surface activation by anodic oxidation and thus ILSS increase of CFR-epoxies will be discussed in detail with respect to the various sulphuric acid concentrations used.

2. Experimental details

Sigrafil UHM-3 HM (modulus 430 GPa) carbon fibres (untreated, 0.1 p.c. polymer sizing) with 3000 mono-filaments were used. As electrolyte aqueous solutions of sulphuric acid (0.2 M – 3.8 M) were selected.

CY 209 (CIBA GEIGY), a liquid epoxy resin, and HT 972 (CIBA GEIGY), a powdered aromatic diamine hardener component, were used as precursors for the polymer matrix (CY 209 : HT 972 = 100 : 30). The continuous potentiostatic C-fibre surface treatments (residence time: 1–10 min) (Fig. 1) were performed using a Wenking Potentioscan (Model POS 73). The electrochemical cell itself (see dashed box in Fig. 1)

CONTINUOUS OXIDATION PLANT

1. Furnace
2. Electrolytic Cell
3. Post Washing
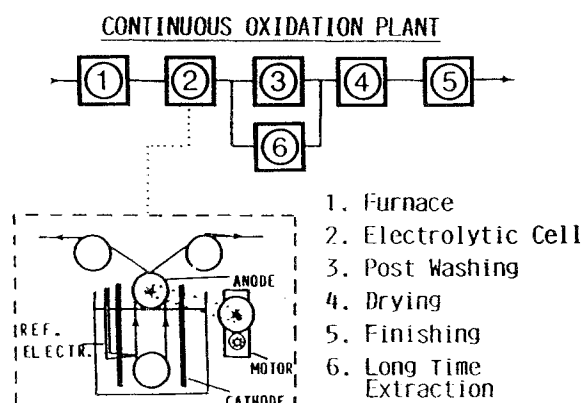4. Drying
5. Finishing
6. Long Time Extraction

Fig. 1. Plant for the continuous anodic oxidation of multifilament carbon fibres.

was equipped with a working electrode existing of a carbon fibre bundle, continuously pulled through the electrolyte solution and contacted by graphite rollers. Two graphite plates (distance to the fibre bundle 15 cm) acted as counter electrodes. A standard calomel electrode was used as a reference electrode.

The electrochemical oxidation line (Fig. 1) consisted of the carbon fibre unwinding equipment followed by a furnace (1) for the thermal removal of the carbon-fibre finish ($700°C/N_2$); the electrochemical cell (2); a counter current washing bath (3) with a length of 0.5 m (21 H_2O min^{-1}); a subsequent drying tube (4); a finish ('sizing') bath (5) (acetone with 0.2–1% of epoxy resin); further drying equipment and finally a winding up facility. For anodic oxidation treatments exceeding 1 min in 3.8 M sulphuric acid, the carbon fibres were directly wound on glass tubes and extracted in hot water for several days (6). The fibre strength (about 2350 MPa) was increased by this extraction process to virgin values of about 2700 MPa. We assume therefore an intercalation of some sulphuric acid into the high oriented graphitic layers of the HM carbon fibre.

The possible effect of fibre damage caused by anodic surface treatment was assessed by monofilament tensile strength measurements (gauge length: 30 mm, 70–100

test samples) and by N_2-adsorption (one point method) with a Ströhlein-Areameter (reproducibility 20 p.c.).

The surface oxides formed during anodic oxidation of the carbon fibres were determined by their thermal decomposition products ($CO_2/CO/CH_4$) using IR-gas analysers (Leybold Heraeus (Binos)). The heating rate up to the final temperature of 1000°C was 10°C min^{-1}.

UD (unidirectional) composites were prepared by a dry winding technique and subsequent resin impregnation. The composites with a fibre volume fraction of 60% were cured under pressure for 6 h at 60°C, 3 h at 80°C and 12 h at 110°C.

The adhesion between fibre and matrix was estimated by ILSS measurements (s:d = 5) with the short beam test according to ASTM-D-2344-76 T. All the tested composites showed interlaminar shear failure. With those fibres transverse fracture can only be observed at ILSS values exceeding 60 MPa.

3. Results and discussion

The influence of the sulphuric acid concentration as well as the specific electric charge on the BET surface area and mechanical fibre properties is shown in Table 1. Over the wide range of applied electrolyte concentrations and specific electrical charges, no significant change either in the BET surface areas or in mechanical fibre properties, Young's modulus and tensile strength, could be recognized. BET surface areas between 0.32 m^2 g^{-1} and 0.45 m^2 g^{-1} were measured.

In the following studies with the anodically oxidized fibres the increase in ILSS of epoxy composites can therefore only be caused by the chemical surface modification, i.e. increase in oxygen complexes on the fibre surface. The thermal decomposition of such surface-treated HM carbon fibres, the subsequent identification of the volatile products and their quantitative determination enables us to compare the influence of the different process variations on the fibre activation.

In Fig. 2 the nature of the decomposition products

Table 1. Carbon fibre properties after anodic oxidation in sulphuric acid solutions

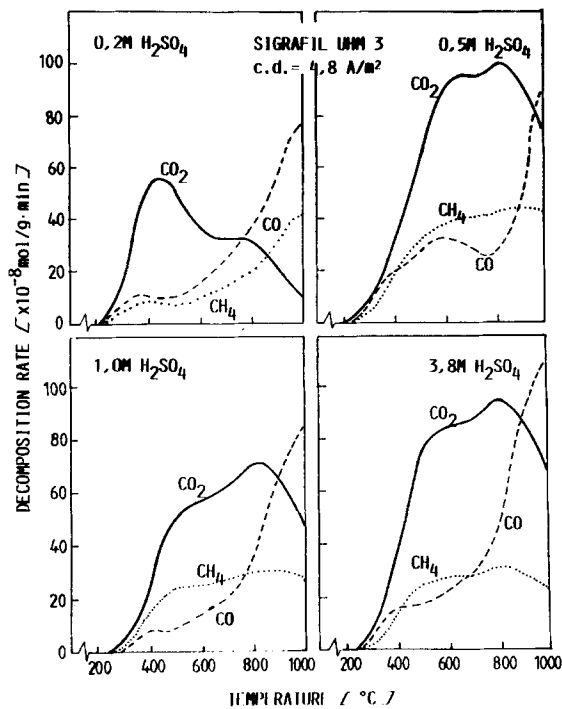| H_2SO_4 [mol/l]	Spec.El.Charge [C/m²]	Bet [m²/g]	Tensile Strength [MPa]	Young's Modulus [GPa]
–	–	0.32	2750	430
0.2	16.2	0.37	2800	430
	277.8	0.45	2550	420
0.5	15.4	0.36	2770	430
	279.5	0.43	2630	425
1.0	15.2	0.36	2700	430
	300.6	0.40	2760	420
	16.3	0.35	2790	430
	26.4	0.32	2800	420
	70.8	0.39	2710	440
3.8	276.0	0.42	2700	430
	300.9	0.38	2800	430
	663.2	0.39	2720	430
	708.0	0.41	2660	430
	1326.0	0.38	2600	430

Fig. 2. Variation in the amount of thermal decomposition products CO, CO_2 and CH_4 with increasing electrolyte concentrations.

$(CO_2$, CO, $CH_4)$ analysed during heat treatment of anodically oxidized carbon fibres up to 1000°C is plotted. In accordance with the literature [18–20] CO_2 is mainly formed between 400°C and 550°C and between 700°C and 850°C. These temperature ranges during thermal decomposition experiments were confirmed for all anodically treated carbon fibres. It seems that these two detectable decomposition maxima can be related to two oxygen surface complexes of different thermal stability.

For CO a main decomposition maximum area around 850°C and an additional maximum at 400°C–450°C in the range of the first maximum of the CO_2 formation was found. The strong increase in CO formation above 950°C cannot be explained by the thermal decomposition of oxygen containing carbon fibre surface groups but by a secondary reaction between the carbon fibres and the silica of the sample support.
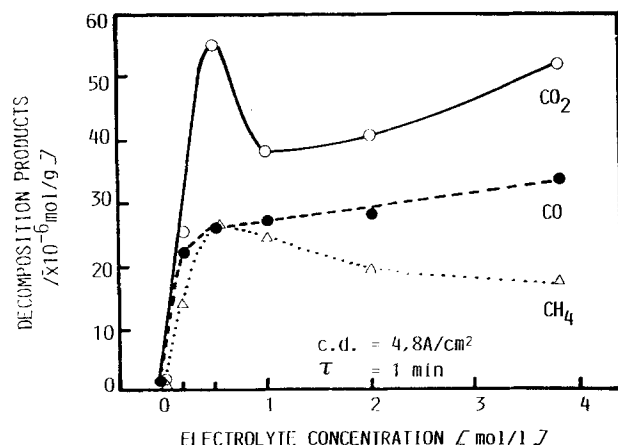

Fig. 3. Variation of the concentration of thermal decomposition products CO, CO_2 and CH_4 with change in electrolyte concentration.
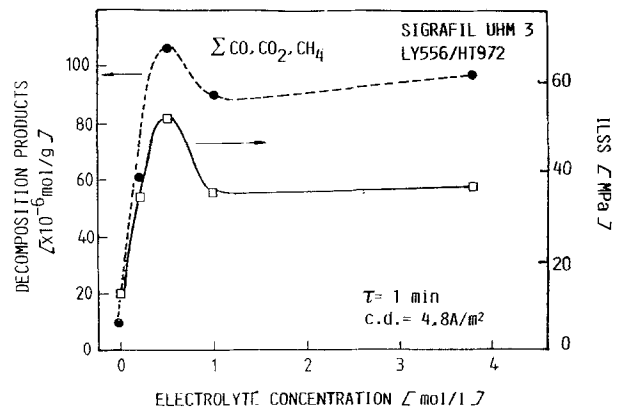

Fig. 4. ILSS values of composites with anodically oxidized carbon fibres compared to the total amount of the thermal decomposed products CO, CO_2 and CH_4.

This explanation was experimentally confirmed by a long thermal post heat treatment of the fibres at 1200°C up to 12 h [21]. A steady CO formation was observed during this heating period. Because of the limited oxygen content of the untreated HM carbon fibres used for these experiments, this CO formation cannot be explained by the thermal decomposition of oxygen surface complexes only. Studies are in progress which involve the inductive heating of carbon fibres in pure graphite crucibles followed by the analysis of the decomposition products of the oxides. This should eliminate side reactions between carbon and glass compounds. CH_4, as a further main product of the thermal decomposition studies, is formed in the temperature range between 350°C and 450°C where CO_2 and CO maxima could be detected. A second maximum at 800°C is observable. This CH_4 formation seems to be a secondary reaction with the decomposition products CO_2, CO, H_2O and H_2 in the temperature regions investigated.

In Fig. 3, the amount of decomposition products, CO_2, CO and CH_4 formed from anodically treated fibre surfaces is plotted against electrolyte concentrations. At a constant current density and residence time (in the electrolyte) a maximum CO_2 and CH_4 formation as well as a strong increase on CO formation is analysed at an electrolyte concentration of 0.5 M H_2SO_4. Sulphuric acid concentrations above 0.5 M result in a slow decrease in CH_4 formation but further increase in CO formation. After an initial strong decrease the CO_2 formation increases again.

In Fig. 4 the effect of the above analysed surface oxides on the resulting ILSS in epoxy is demonstrated. We recognize a similarity between the increase in ILSS and the total amount of surface oxides with a maximum adhesion for the treatment in 0.5 M sulphuric acid. Although for electrolytic concentrations above 1 M the total surface oxide concentration increases, the maximum ILSS value of 52 MPa for 0.5 M H_2SO_4 cannot be achieved within the experiments performed.

These results indicate the dominant contribution of the carboxylic surface oxides (mostly decomposed as CO_2) to the adhesion. The fibre with the highest amount of releasable CO_2 results in the best
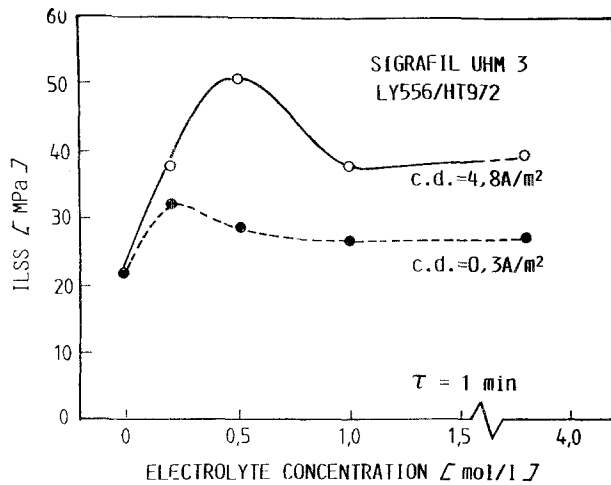
Fig. 5. Influence of current density during anodic oxidation in sulphuric acid solutions on the ILSS of composites.

Fig. 7. Composite ILSS versus specific electric charge for various concentrations of sulphuric acid electrolyte.

ILSS values of the composite. Though a steady increase in CO formation over a wide range of electrolyte concentrations can be observed, it does not appear to control the ILSS behaviour which parallels the CO_2 formation directly. As a consequence, the contribution of the surface oxides which decompose as CO to the resulting adhesion behaviour is only minor (compare [22]).

A further interesting effect concerning the anodic fibre oxidation is the influence of the current density on the reinforcement behaviour of the surface treated carbon fibres (Fig. 5). With lower applied current density, the maximum ILSS shifts to a lower electrolyte concentration. A second effect is also found: the higher the current density, and thus specific electric charge (constant residence time), the higher the resulting ILSS values.

With increasing electric charge the amount of surface oxides also increases. As shown in Fig. 4 these oxides formed during anodic oxidation are responsible for the resulting promotion of adhesion between the fibre and the polymer matrix. In the present study the highest ILSS value (32 MPa) at a specific electric

charge of $20 \, C/m^2$ is found for 0.2 M sulphuric acid, whereas 52 MPa at a specific electric charge of $280 \, C/m^2$ could be measured in 0.5 M solution. These experiments were performed with a residence time of 1 min. To compare the results with those of varied residence times the specific electric charge was selected as parameter. The anodic oxidation studies at differing specific electric charges were performed in 3.8 M H_2SO_4. As can clearly be recognized from Fig. 6, there exists a linear correlation between ILSS and specific electric charge. The same adhesion behaviour of the anodically treated carbon fibres from 1 to 10 min treatment time was found. This indicates the effect of the electric charge on the surface oxide formation and thus the carbon fibre surface activation. The general influence of the electric charge on the ILSS increase was proved by the application of different sulphuric acid concentrations of the anodic oxidation process. As is indicated in Fig. 7, an increase in ILSS with increasing specific electric charge is achieved for all sulphuric acid concentrations investigated. However the electrolyte concentration dominates the adhesion behaviour: the same specific electric charge results in different ILSS values while performing experiments with varied concentrations. The prediction of the effect of electrolyte concentrations on the adhesion (fibre surface activation) is not possible.

4. Conclusions

The experiments confirm the advantage of anodic oxidation in sulphuric acid as a surface activation method without fibre damage. It was shown that the increase in adhesion is caused by the formation of surface oxides during electrochemical treatment. This surface oxide formation is strongly influenced by the current density while maintaining a constant electrolyte concentration and residence time.

Furthermore it could be shown that the specific electric charge applied during the anodic oxidation can be generally taken as a criterium for the effectiveness of the carbon fibre surface activation. With increasing specific electric charge ILSS increases
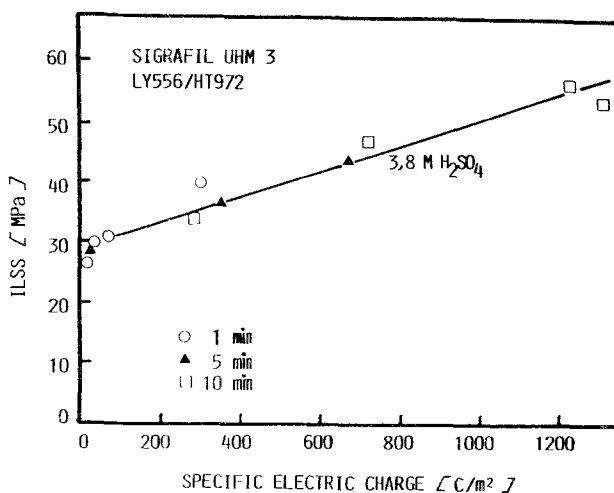

Fig. 6. Anodic oxidation of carbon fibres with varied specific electric charges (due to change in residence time and voltage) and resulting ILSS values of the composites.
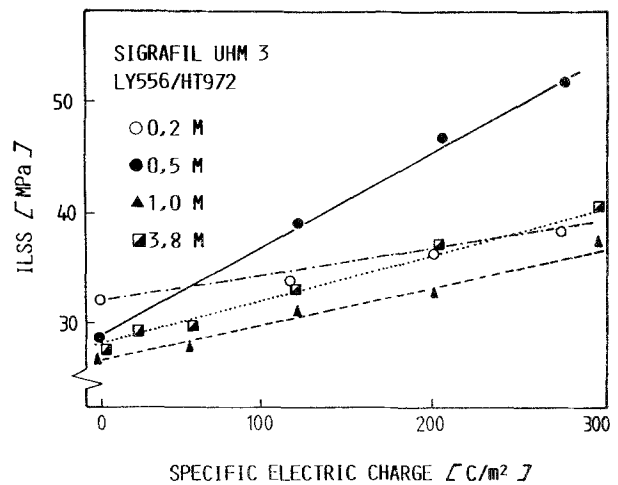
linearly up to about 70 MPa maximum (wet oxidation of the UHM 3 carbon fibres in concentrated nitric acid). With the short beam test, the transverse strength of the carbon fibres controls the fracture behaviour of the composites and the brittle transverse fracture of composites reinforced with HM carbon fibres limits the ILSS values. This is about 70 MPa with the applied fibre/matrix combination.

The effect of electrolyte concentration on the fibre surface activation however is dominant but not predictable. Using sulphuric acid as electrolyte, best adhesion (52 MPa) was found when the anodic oxidation was performed in 0.5 M solution.

Treatment times less than 1 min seem possible by application of increased current densities and thus the direct introduction of this anodic treatment for final surface activation in carbon fibre production plants can be recommended.

References

[1]   Morganite Ltd, British Patent 1 326 736 (1969).
[2]   Airforce, US Patent 3 671 411 (1972).
[3]   Courtaulds Ltd, British Patent 2 204 156 (1971).
[4]   Monsanto Research Corporation, St. Louis, US Patent 3 627 570.
[5]   J. Cziollek and E. Fitzer, International Carbon Conference, Bordeaux, France (1984) pp. 166, 242.
[6]   J. Cziollek, PhD thesis, Universität Karlsruhe, Institut für Chemische Technik, Karlsruhe-FRG (1983).
[7]   P. Ehrburger, J. Herques and J. B. Donnet, ACS-Symposium Series 21 (1976) p. 324.
[8]   E. Fitzer, K.-H. Geigl and L. M. Manocha, 5th International Conference on Carbon and Graphite, London (1978) p. 405.
[9]   E. Fitzer and R. Weiss, 16th Biennal Conference on Carbon, San Diego, USA (1983) p. 473.
[10] N. L. Weinberg and T. B. Reddy, J. Appl. Electrochem. 3 (1973) 73.
[11] J. B. Donnet and P. Ehrburger, Carbon 15 (1977) 143.
[12] P. Ehrburger, J. J. Herque and J. B. Donnet, 5th International Conference on Carbon and Graphite, London (1978) p. 398.
[13] E. Fitzer, F. V. Sturm and R. Weiss, 6th International Conference on Carbon and Graphite, London (1982) p. 259.
[14] Idem., 16th Biennal Conference on Carbon, San Diego, USA (1983) p. 494.
[15] E. Fitzer and R. Weiss, International Conference on Interface-Interphase, Liège, Belgium (1983).
[16] R. Weiss, PhD thesis, Universität Karlsruhe, Institut für Chemische Technik, Karlsruhe-FRG (1984).
[17] E. Fitzer and H. Jäger, Z. Werkstofftech. 16 (1985) 215; 16 (1985) 232.
[18] G. Tremblay, G. Vastola and P. L. Walker, Carbon 16 (1978) 35.
[19] M. P. Voll and H.-P. Boehm, Carbon 8 (1970) 741.
[20] J. Adler, PhD thesis, Universität Karlsruhe, Institut für Chemische Technik, Karlsruhe-FRG (1984).
[21] E. Fitzer and H. Jäger, 17th Biennal Conference on Carbon, Lexington, USA (1985) p. 317.
[22] Idem., DGM-Symposium, Haftung von Verbundwerkstoffen und Werkstoffverbunden 12–13 Juni 1986, Konstanz, FRG, in press.