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Poly(carbazole-co-acrylamide) electrocoated carbon fibers and their adhesion behavior to an epoxy resin matrix

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The surface properties of original high strength and preoxidized high modulus carbon fibers were altered by electrocopolymerizing acryl amide and carbazole and therefore depositing a copolymer coating onto the fibers. Scanning electron microscopy and zeta-potential measurements confirmed the presence of a rough but dense and continuous electrocoating with a basic surface character. Therefore, 'good' adhesion behavior between the electrocoated carbon fibers and an epoxy resin matrix should be expected. The interfacial adhesion was measured using the single fiber pull-out and single fiber indentation test. It was shown that only 'intermediate' adhesion was present between the carbon fibers and the electrocoating, but superior adhesion between the coating and epoxy resin exists. The single fiber model composites always failed at the fiber/electrocoating interface. However, as shown by using the indentation test, the interfacial adhesion between fibers and electrocoating can be significantly improved if preoxidized fibers are used as substrate for electropolymerization. A very high tensile strength for the electrocoating can be expected as derived from the single fiber pull-out tests.

1. Introduction

The interest of the materials community in advanced fiber reinforced composite materials has increased during the last decades, however there is still a need for a better understanding of the physical and chemical mechanisms responsible for fiber-matrix adhesion as well as the role of fiber-matrix adhesion on composite properties. The use of fiber reinforced composite materials offers a number of advantages relative to conventional bulk materials, such as high strength and stiffness at generally low density, good thermal and chemical resistance, high fatigue and creep strength (which is often better than for metals) and control of the thermal and electrical conductivity [1]. It is also possible to produce required predetermined properties, which can meet individual needs [1]. However, there is still a need for the development of composite materials with improved fiber-matrix adhesion. The majority of such efforts were/are concentrated on increasing fiber-matrix adhesion through the use of surface treatments [2, 3]. Applied carbon fiber surface modifications are commonly performed by different wet (i.e. chemical and electrochemical) and dry (thermal oxidation, plasma treatments or fluorinations) oxidation procedures in order to change the surface chemistry of the fibers to enhance the possible formation of 'attractive' bonds (that can be polar interactions, hydrogen and of course covalent bonds) between the reinforcing fibers and the surrounding matrix polymer. Interfacial 'bonds' are desired to guarantee an optimal stress transfer from the matrix material into the reinforcing fibers. However, besides interfacial bond formation further factors can

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contribute to an improved adhesion behavior. This can be interdiffusion of polymer chains forming molecular entanglements, for instance, between a polymeric interphase applied to the fibers and the matrix as well as attractive electrostatic interactions and mechanical interlocking [4].

However, the major drawback of the most common oxidative carbon fiber surface modifications is the (sometimes significant) loss in fiber tensile strength even though the adhesive behavior is improved. Directly linked to the fiber/matrix adhesion is (generally) the impact performance of the resulting composite [5]. Good fiber/matrix adhesion is required for a high level of interlaminar shear strength, which will on the other hand lead to a reduced impact resistance. The application of a matrix-compatible (monomeric or flexible polymeric) 'interphase' acting as coupling agent will mostly not affect the fiber tensile strength, but it was found to improve the interfacial adhesion between reinforcing (carbon) fibers and a polymeric matrix [6–8]. It also improved the toughness by absorbing impact energy through deformation [9]. By changing the properties of the interlayer/coating it should be possible to adjust/control the fiber matrix adhesion [10], and therefore, tailor the interface/interphase to the 'individual' requirements.

There are several different possibilities for coating carbon fibers, however, if it is aimed to fix polymeric coatings covalently to the carbon fiber surfaces there are mainly three methods available: *in-situ* chemical grafting reactions [11–13], plasma polymer deposition [14, 15] and electropolymerization or -deposition. Such electropolymerization procedures offer the advantage of controlling the thickness, morphology and also functionality (the surface chemistry) of the coatings through selective processing parameters (i.e. the current density, monomer concentration, type of electrolyte, temperature etc.). The major advantage is that uniform coatings can be achieved in a continuous process [16, 17] at relatively low cost.

During electro(co-)polymerization the working electrode (i.e. the carbon fiber) is the source of active species that initiate the polymerization of electro-active monomers, such as pyrrole [18], 3-methylthiophene [19], aniline [20, 21] and 3-carboxyphenylmaleimide and styrene [22], or of monomers containing a variety of functional groups, like terminal vinyl-, carboxyl-, anhydride-, epoxy-, nitril- and acetylenic groups [6, 23]. Direct anodic or cathodic electrodeposition of functional polymers is possible too [6, 23].

Due to their electrical and photo-electrochemical properties, carbazole (Cz) based polymers have received much attention in the recent past [24, 25]. Chemical and electrochemical homo- and co-polymerization of Cz was investigated separately and in detail [26, 27]. Inclusion of acrylamide (AAm) into the polycarbazole (PCz) structure by electrocopolymerization resulted in improved thermal properties and a higher flexibility of the resulting copolymer [28].

Since it is hoped that during the electro(co)polymerization initialized by electrodic processes chemical bond formation (grafting) between the electrocoating and the fibers occurs, and the electrocoating remains reactive (because the copolymer still contains reactive amine functionalities [29]) a coupling agent (for epoxy resins) covalently bonded to carbon fiber surface should result. Furthermore, such coated carbon fibers (used as anodes) might have many potential applications due their good physical, chemical and electrochemical properties, and they could be even used for bioelectrochemical purposes, such as biosensors, and micron–sized reversible conductive polymer electrodes.

The aim of the present report was to gain some more information about the interfacial adhesion behavior of electrocoated carbon fibers to an epoxy resin matrix using micro-mechanical tests.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN) based unmodified and unsized high strength (HS) C320.00A (CA) and high modulus (HM) HM 48.00A carbon fibers (HMox) electrochemically oxidized continuously in a 1:1 mixture of 0.01 M KNO_3/KOH-solution were used for this study (both fiber types kindly supplied by SGL Sigri Carbon Group Meitingen, Germany). The experimental procedure used to oxidize the HM-carbon fibers continuously can be found in Ref. [30].

The HMox (F14) and CA (F15)-carbon fibers[§] were galvanostatically electrocoated in a single compartment electrolysis cell (as described in [31]) by keeping the current density ($i = I/A = 2\text{A/m}^2$) fixed [32]. The carbon fibers served as working electrode and two stainless steel plates as counter electrodes. The comonomers acryl amide (AAm) and carbazole (Cz) (both from Merck, synthesis grade) in a concentration ratio of [AAm]/[Cz] = 0.5 M/0.1 M and the supporting electrolyte tetra butylammonium hexafluorophosphate ($TBAPF_6$) ([$TBAPF_6$] = 0.10 M) (Fluka, puriss-electrochemical grade) were dissolved in acetonitrile (ACN) and continuously stirred during the electrolysis. The electropolymerization was performed in each case for a time, $t = 10$ min. After the electrolysis the carbon fibers were washed thoroughly with distilled water, and afterwards stored in distilled water for several days. After further washing procedures the fibers were dried overnight in a vacuum oven at 1 mbar at a temperature of 50°C. The electrocoating procedure, further experimental details and results of the fiber surface characterizations were reported earlier [32].

As matrix system we have chosen a hot-curing bisphenol-A-based epoxy resin Araldit LY 5052 (a novolac epoxy containing 1, 4-butanediol diglycidylether) and aromatic amine hardener HY 5052 (an aliphatic polyamine) (Ciba-Geigy, Basel, Switzerland). Resin and hardener of ratio 100 : 38 were used as recommended by the supplier. The resin was cured at 80°C for 3h and 140°C for 8h.

2.2. Surface morphology of fibers and single fiber composites

In order to evaluate the changes in the surface morphology, all the fibers and some of the investigated

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[§] The nomenclature used for the electrocoated fibers is the same as in [32].

single fiber composites (pull-out as well as indentation) were analyzed by scanning electron microscopy (SEM). The fibers and the 'model' fiber/epoxy composites were characterized after sputtering with gold using a SEM 515 (Philips, Eindhoven, Holland).

2.3. Adhesion tests between electrocoated carbon fibers and epoxy matrix

2.3.1. Single fiber pull-out test

The samples for the pull-out tests were prepared in a special embedding machine, which allows an orientation perpendicular to the matrix surface at a defined embedded length [33].

Pull-out experiments were performed with a home made apparatus with a very stiff frame to avoid energy storage in the free fiber length ($l_f = 30\ \mu$m) between the matrix surface and the clamping mechanism [34]. The fiber pull-out was performed at a constant speed of 0.2 μm/s from the matrix using a controlled load cell. Pull-out load against displacement was recorded using a computer controlled plotter.

The apparent shear strength τ_{IFSS} was calculated from the maximum load $F_{\max}$ and fiber embedded area in the matrix using the mathematical relation,

$$\tau_{\mathrm{IFSS}} = \frac{F_{\max}}{\pi d L}$$

where L is the embedded length and d is the diameter of the fiber.

2.3.2. Single fiber push-in test

A thin cross-sectional slice of the 'model' epoxy matrix composite (containing the separated single fibers) was polished perpendicular to the embedded fiber direction. In order to perform the test, a conical indenter needle of about the same size (5.6 μm) as the fiber with a flat top is positioned accurately above the fiber segment. Then an increasing loading force is applied to the fiber in the axial direction, which produces an increasing shear stress at the interface. Debonding starts beyond a certain load, it proceeds and finally the fiber is completely debonded and could be pushed through the slice.

Since the samples used for the indentation test were very thin (sample thickness $t \approx 100\ \mu$m), it can be assumed that the shear stress is constant along the embedded fibers [35]. The apparent interfacial shear strength than can be calculated using the following relation:

$$\tau_{\mathrm{IFSS}} = \frac{F_{\max}}{\pi d t}$$

2.3.3. Adhesion test between electrocoated brass and epoxy matrix

In order to obtain more information about the epoxy/electrocoating interface/interphase square (abutting face 6 × 6 mm) brass rods were electrocoated under the same conditions as described above for carbon fibers.

The abutting face pull-off tests were performed using a Minimat-tensile testing machine from Polymer Labs. As counter pistol we used an aluminum rod. Both, the electrocoated brass rod and the aluminum rod were spliced together using a the strain hardening epoxy resin LY 5052 and the hardener HY 5052 Ciba (24 h hardening time). The splicing was performed directly in the testing device, both rods were brought together (approx. 50 μm) and the resin system added. The tensile test was performed at a rate of 0.1 mm/min. The locus of the interfacial failure took always place at the brass electrocoating interface, never at the aluminum interface.

3. Results and discussion

3.1. Fiber and matrix surface characterization

3.1.1. Surface morphology

SEM-micrographs (always a small, randomly selected part of an investigated surface) taken of the electrografted carbon fibers clearly show that the fiber surfaces were electrocoated.

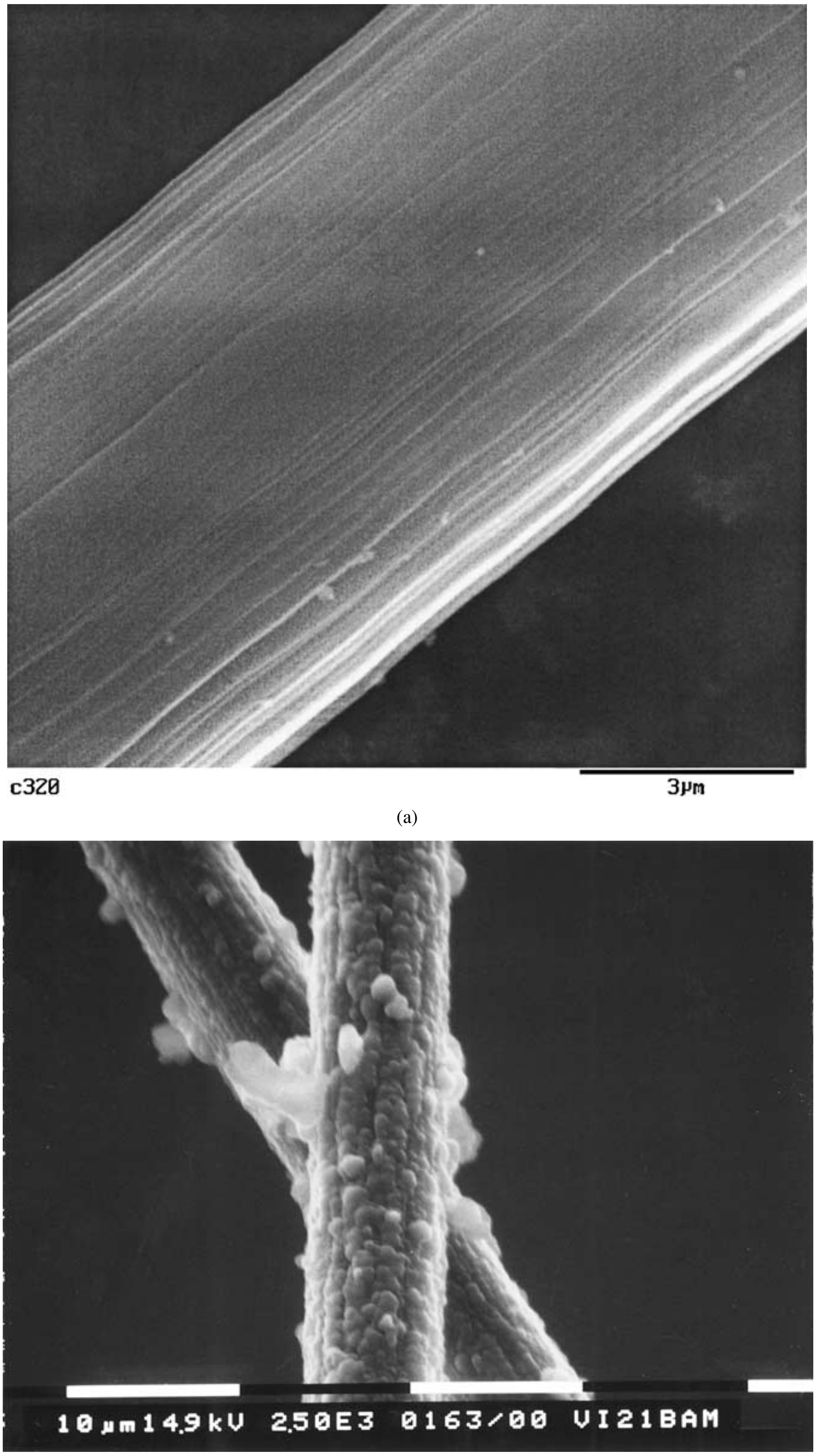
A continuous and thick electrocopolymer-coating could be observed after the applied experimental conditions on both fiber types; the 'original' CA-fibers (Fig. 1a) (F15) and the pre-oxidized HMox-fibers (Fig. 1c), resulting in the electrocoated fibers F15 (Fig. 1b) and F14 (Fig. 1d), respectively. In the case of the HMox-carbon fibers that contain a high concentration of surface functional groups [36], which probably resulted in better interactions to Cz and AAm via hydrogen bonds. Additionally, surface functional groups are capable of also forming free radical sites on the fiber surfaces, which then could initialize free radical polymerization (of AAm) or undergo termination reactions with growing polymer radicals resulting in polymer grafting [6].

The approximate thicknesses for P(Cz-co-AAm) electrocoatings obtained was in the region of around 0.4 μm for coated HMox-fiber F14 and 1.2 μm for the CA-fiber F15. The 'thick' electrocoating might be due to higher surface concentration of functional groups for the fiber F14. In the case of the CA-carbon fibers, however, this could be caused by a more homogenous 'grafting' probably due to a 'slower' electron transfer from the monomer to the carbon fibers due to the lower electrical conductivity caused by a different fiber structure (more amorphous) than HM-fibers, and therefore, enhanced grafting onto the surface. Since the electrocoating deposited onto the fibers exhibits a rough structured surface a positive contribution to the adhesion behavior between the electrocoated fibers and the epoxy matrix can be expected due to increased mechanical interlocking.

3.1.2. Zeta (ζ)-potential measurements

Measured ζ-potentials reflect the surface chemistry/nature of the investigated materials and, therefore, the acidic and basic surface character. The formation of the electrochemical double layer depends strongly on the surface character (hydrophilicity/hydrophobicity) and the adsorption of dissolved ions, which competes with water adsorption [37]. Thus, less adsorption of dissolved anions takes place at hydrophilic surfaces, consequently they exhibit a smaller ζ-potential compared to hydrophobic surfaces.

On the other hand, as reported in the literature [38, 39], ζ-potential measurements should also give indications about the trend in which adhesion will change,



(a)

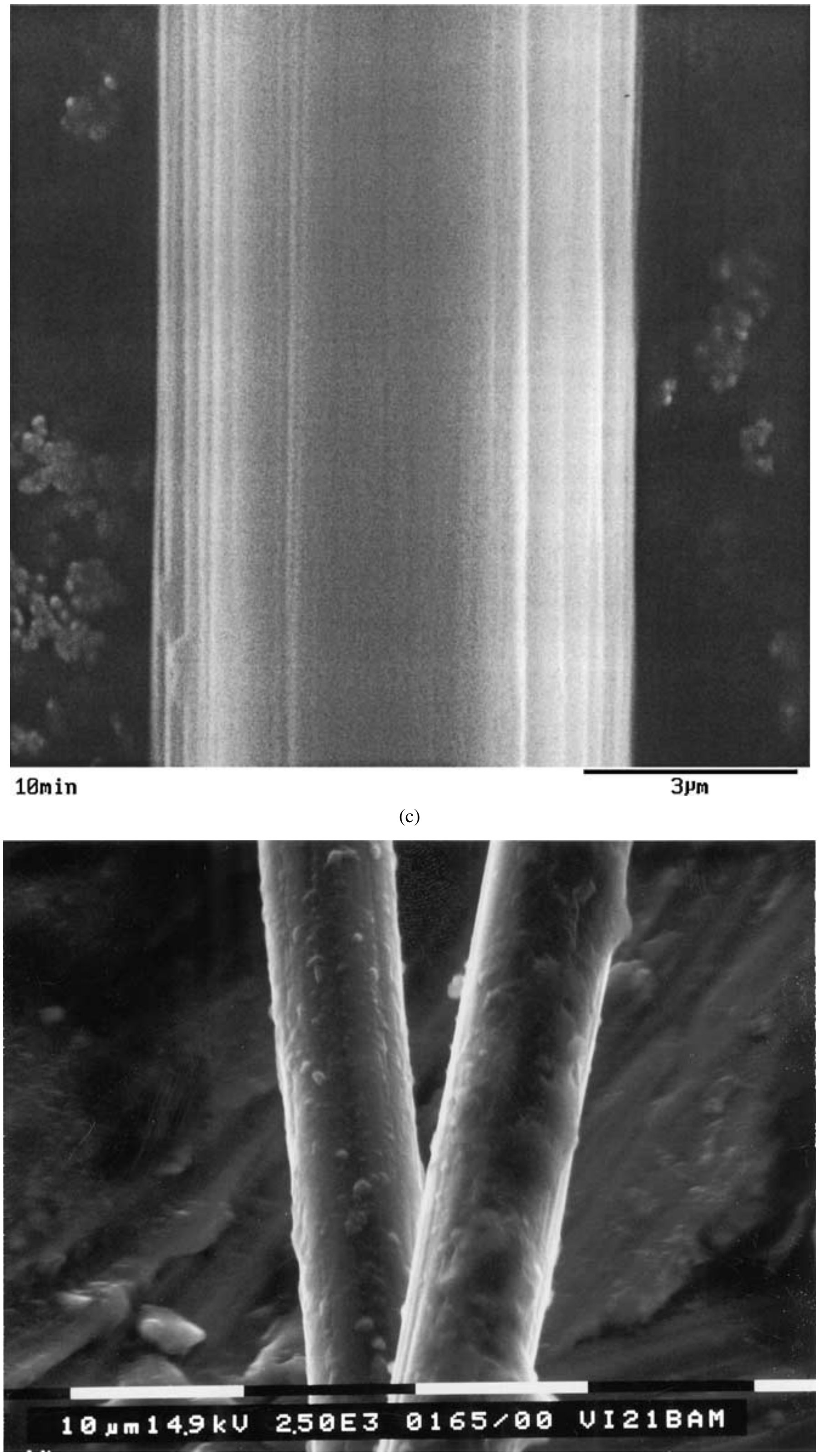
(b)

Figure 1 SEM-micrographs of the 'original' and non-coated as well as electrocoated carbon fibers. (a) 'Original' CA-fiber, (b) electrografted CA fiber F-15, (c) pre-oxidized HMox-fiber, (d) electrografted HMOx (pre-oxidized fiber) F14. (*Continued*.)

i.e. the larger the difference of the measured ζ-potentials for the matrix and the reinforcement the 'better' should be the adhesion behavior between them.

Electrografting of Cz/AAm onto carbon fiber surfaces in general changes the 'original' surface properties of the carbon fibers completely [32]. Here, we will focus the discussion only on the electrocoated CA-fiber example as compared to the matrix material.

Pronounced changes in the surface properties due to electrografting of P(Cz-co-AAm) could be detected for CA-fibers (Fig. 2). The acidic surface character of the original fibers was switched to basic after depositing the electrocoating; the ζ_{plateau}-values changed from -27 mV to $+12$ mV and the isoelectric point (i.e.p.), where the ζ-potential is zero, was shifted from pH 4.2 to pH 7.5. Comparing measured $\zeta = f(\text{pH})$ functions



(c)

(d)

Figure 1 (*Continued*).

of the untreated and electrocoated carbon fibers it can surely be stated (because of the ‘integral’ character of this measurement averaged over the surface properties of a fiber plug, $m_\mathrm{f} \approx 1.25$ g) that the carbon fiber surfaces are fully covered by a P(Cz-co-AAm) coating.

For the cured epoxy matrix system [30] a nearly linear, pH-dependent ζ-potential was measured. Such a ζ-potential curve is characteristic for solids, which contain almost no dissociable surface functional groups and is only determined by the adsorption of ions dissolved, these are protons and OH^- ions but also K^+ and Cl^-, in the supporting electrolyte. The low acidic i.e.p. of 3.9 is due to the preferential adsorption of OH^- competing with protons, but also indicates that protons are also preferentially adsorbed in competition to the Cl^- anions [40].

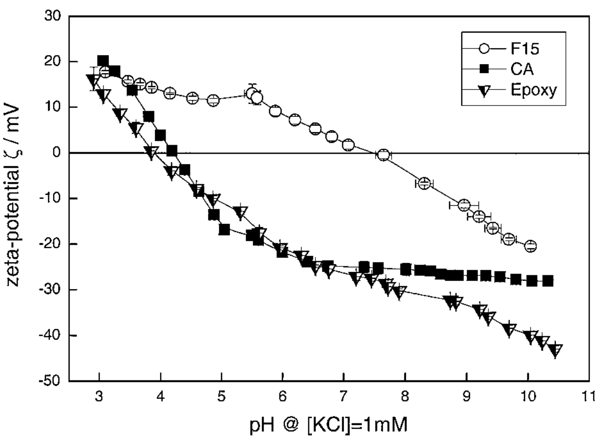


Figure 2 pH-dependent ζ-potential of 'original' and electrografted CA-carbon fibers and the cured epoxy resin matrix.

Considering the above results, we should expect a 'good' adhesion (i.e. a higher τ_{IFSS}) between the electrocoating deposited onto carbon fibers and the epoxy resin. It can be assumed that covalent bonds will be formed between the amide groups included in the electrocoating and the resin during the curing process. This and the increased surface roughness should have a positive influence on the fiber/matrix adhesion, but only if the coating is really covalently grafted to the fiber surface.

3.2. Adhesion behavior between the electrocoated carbon fibers and the epoxy matrix

The dependence of the apparent shear strength on the embedded fiber length allows one to distinguish between brittle and ductile fracture behavior. A relatively amorphous boundary layer would result in ductile failure, whereas crystalline polymer structures at the fiber/matrix interface cause increased bonding to the fiber, leading to brittle fracture during the single fiber pull-out test [41].

The straight line in the plot of the apparent shear strength as function of embedded fiber length L (Fig. 3) should be taken only as a trend indicator, and does not represent any data fitting. All measured values for both electrocoated fiber types follow one common trend, from which it is possible to characterize the fracture behavior. If the apparent shear strength shows no dependence on the embedded length this would indicate a ductile fracture behavior during the pull-out process according to a theoretical analysis [41]. On the other hand, a decreasing apparent shear strength with increasing embedded fiber length would represent a more brittle failure behavior, which was observed for both electrocoated fiber samples, irrespective of the 'underlying' fiber type. The observed force-displacement curves (Fig. 4) show that the pull-out force reaches a maximum value and drops-down sharply to a much lower level after the debonding is completed, which corresponds to the presumed frictional resistance from the common interface.

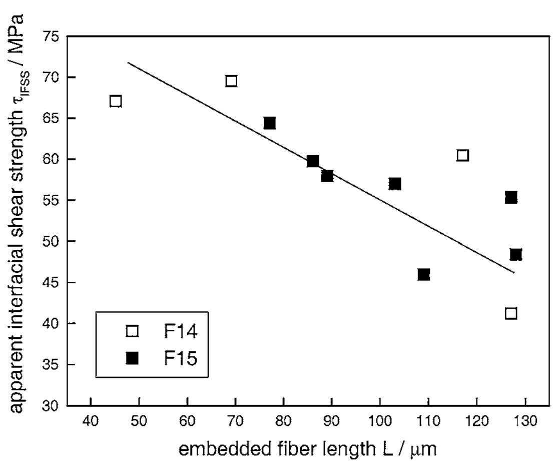


Figure 3 Apparent interfacial shear strength τ_{IFSS} as function of the embedded fiber length.

Fig. 5 presents the measured pull-out forces between the electrocoated fibers and the epoxy matrix as a function of the common fiber/matrix area A_{f}. As mentioned already above the two electrocoated fiber samples follow the same trend, and therefore all points were used to fit strength of adhesion, the interfacial shear strength τ_{IFSS}, which should correspond to the slope of the line [42]. The adhesion strength for the electrocoated carbon fibers was estimated to be $\tau_{\mathrm{IFSS}} = 38.8 \pm 6.7$ MPa. However, clearly the fiber/coating interface failed during the pull out process as can be seen from the SEM-micrograph taken of sample F15 after being pulled-out

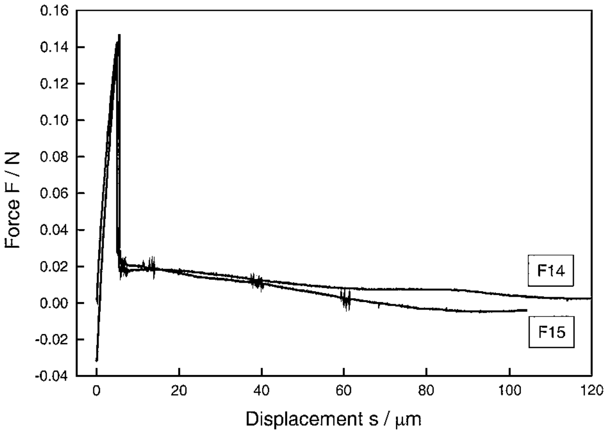


Figure 4 Fiber pull-out force-displacement curves of the electrocoated fibers F14 and F15 embedded in an epoxy resin matrix.

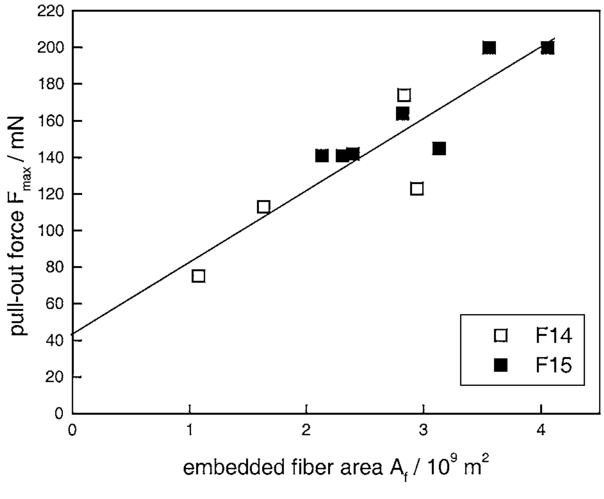


Figure 5 The maximum pull-out force as function of the embedded fiber area.

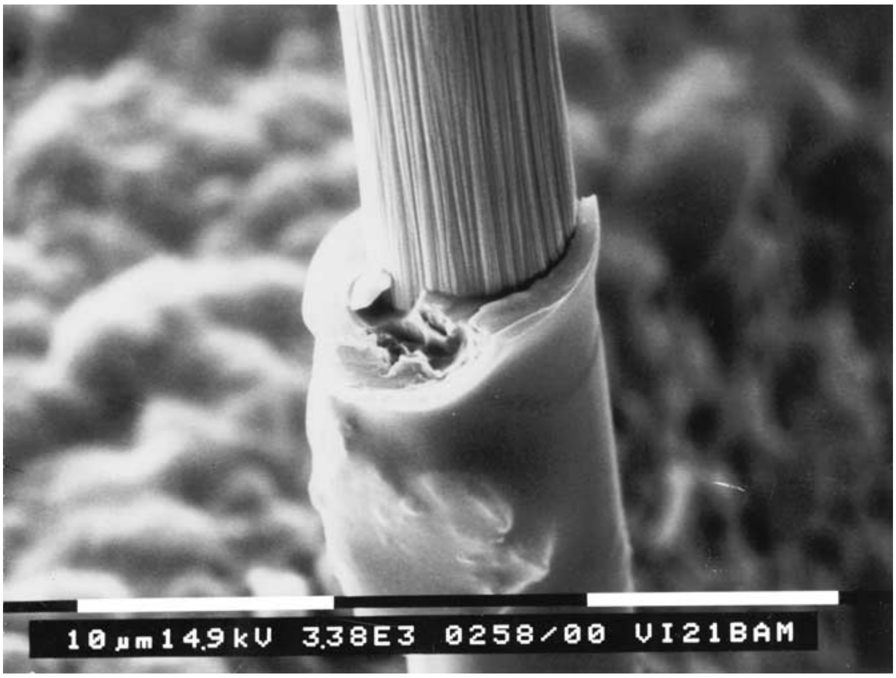


Figure 6 SEM-micrograph of a single electrocoated fiber F14 taken after the pull-out experiment showing the smoothly fractured coating and a clean pulled-out fiber.

from the resin matrix (Fig. 6); a clean fiber was pulled out of the 'grafted' electrocoating embedded in the matrix. The fractured coating displays nearly a smooth fracture area. Therefore, it can be assumed that the determined interfacial shear strength corresponds to the fiber/coating interfacial adhesion.

Additionally, it was found that the plot of the maximum force vs. embedded fiber area does not pass through the origin. Subramanian and coworkers [42] reported an analogous behavior, stating that the true relationship describing the graph is:

$$\sigma = \frac{F}{\pi d l} + C$$

assuming that C represents the force required to fracture the resin, which resulted in the formation of a matrix-cone adhering to the fiber. However, in the present case no 'cone' formation was detected, instead a clear coating failure occurred during the pull-out process approximately at half of the free fiber length. The value of C was estimated to be $C = 45 \pm 18$ mN. It should now be possible to obtain an estimate of the cohesive strength of the electrocoating from the force C to coating area A_c ratio $\sigma_c = C/A_c$ (since it is known from ζ-potential measurements that the coating is dense, compare with Fig. 2) making the following assumptions: the coating was deposited as nearly hollow cylinders surrounding the fibers (fiber diameter of the coated fibers, $d_{f,c} = 8.4 \pm 0.3\ \mu$m) and the 'original' fibers ($d_f = 7.5 \pm 0.5\ \mu$m) are cylindrical. From this simple calculation a value for the cohesive strength of the electrocoating in the order of magnitude $\sigma_c \approx 4 \pm 2$ GPa could be expected[¶].

Also, as can be seen from the SEM-micrograph (Fig. 7) obviously no failure of the coating/epoxy–matrix 'interphase' occurred. However, the single fiber pull-out experiments did not reveal any difference in the fiber/coating/matrix adhesion (similar trends were observed earlier [23]) between the two (HMox and CA) carbon fiber substrates used. Therefore, and in order to verify the above observation and to check if it is possible to detect differences in the fiber/electrocoating adhesion it was decided to perform fiber push-out (indentation) tests on the electrocoated fibers only.

However, comparing the obtained results on the interfacial adhesion between electrocoated fibers and epoxy matrix with the interfacial shear strength measured for the original fibers (CA and HMox) embedded in a slightly different epoxy matrix [36] a significant decrease in the interfacial adhesion is observed, which is probably due to the relatively 'weak' adhesion between the fiber and the electrocoating itself but not because of epoxy matrix/coating failure.

From the SEM-micrographs taken after the indentation tests of both electrocoated fibers (top- (Fig. 7a) and bottom view (Fig. 7b) for the 'model' composite prepared using F15 and after pushing the debonded fiber F14 back through the polished epoxy matrix slide (Fig. 7c)) it can be derived that covalent bonds between the electrocoating and the surrounding epoxy resin during the curing process must have formed, since only 'clean' fibers could be pushed out (nearly no coating or coating and matrix material adhering to the fiber can be seen; just at the fiber edges stick some but very few particles). Such covalent bond formation can be expected between the polymer incorporated acryl amide units and the epoxy functions during the curing process at elevated temperatures.

This again, clearly shows the failure of the fiber/coating interface whereas there is no indication that the matrix/coating 'interphase' fails. Furthermore, the indentation test also clearly reflects differences in the adhesion behavior (Table I) between the two different

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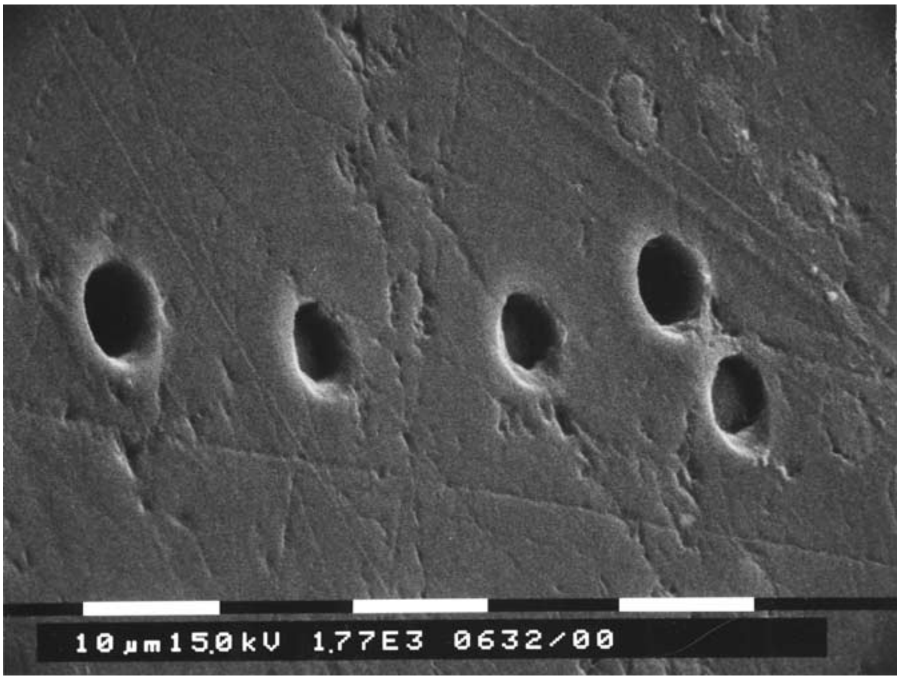
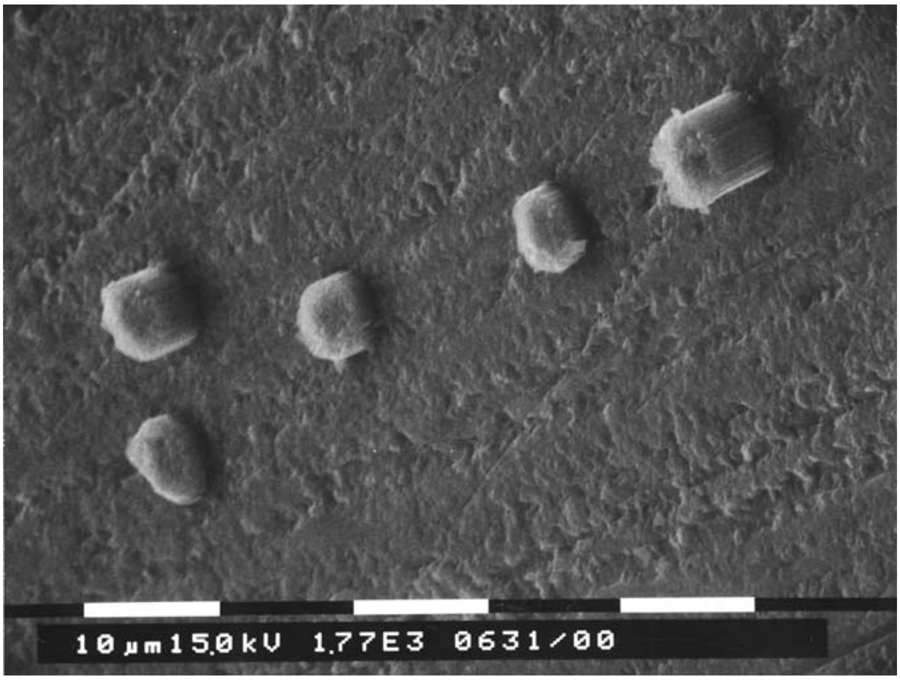
[¶] This value can be taken only as first approximation; further measurements have to confirm this expectation.



(a)

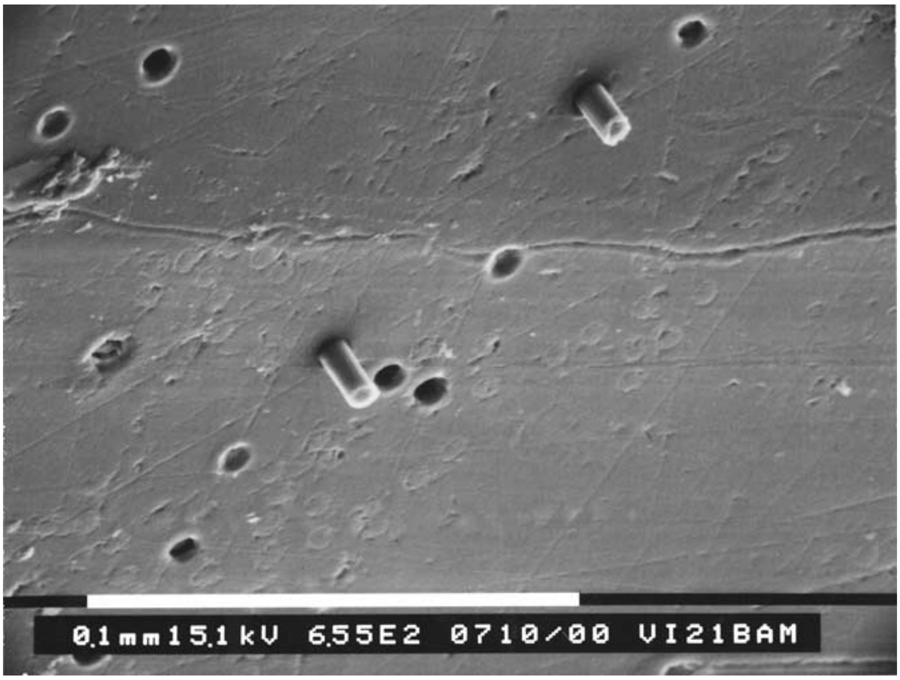


(b)

Figure 7 (a) SEM-micrograph of the model electrocoated fiber F15/resin composite after fiber push through (top-view). (b) SEM-micrograph of the model electrocoated fiber F15/resin composite after fiber push through (bottom-view), showing clean pushed-through fibers. (c) SEM-micrograph of the model electrocoated fiber F14/resin composite after pushing the fibers back through the epoxy matrix after fiber debonding (top-view), showing again clean pushed-through fibers. (*Continued*.)

fiber 'substrates', the pre-oxidized HMox-fibers and the original HS-fibers (CA), used to deposit the electrocoating. The interfacial shear strength τ_{IFSS} determined for both 'original' uncoated carbon fibers is significant lower as compared to the τ_{IFSS}-values determined using the single fiber pull-out test. Furthermore and unexpected the level of interfacial adhesion between the highly oxidized HMox-fiber and the CA-fiber are equal. A possible explanation for this behavior might be, that the surfaces of HMox-fibers are that much oxidized that highly oxidized graphitic fragments still stick to the fiber surface via van-der-Waals interactions and act partially as a 'weak-boundary layer' (compare also [43]). However, after depositing an electrocoating onto the fiber surfaces clear differences in the adhesion behavior to the epoxy can be distinguished.

In Fig. 8. characteristic load-displacement curves as obtained from the micro-indentation test are shown for both electrocoated fiber samples. The peaks observed in these curves should correspond for the studied case to the fiber/coating debonding, followed by a lower part that can be assigned to frictional load. The pre-oxidized HMox fibers F14 show a significantly higher level of interfacial adhesion (98% increment) than the



(c)

Figure 7 (*Continued.*)

TABLE I Interfacial shear strength τ_{IFSS} measured for the 'original' and non-coated as well as electrocoated carbon fibers using the single fiber pull-out and indentation test

Fiber	τ_{IFSS}[a] (MPa)	τ_{IFSS}[b] (MPa)
CA	61.4 ± 5.9 [36]	27.7 ± 3.6
F15	38.8 ± 6.7[c]	34.7 ± 3.1
HMox	84.4 ± 10.2 [36]	28.6 ± 5.5
F14	38.8 ± 6.7[c]	68.7 ± 9.0

[a] pull-out test.

[b] push-through, indention test.

[c] same value for the two electrocoated fibers from the single-fiber pull-out test, since they follow the same trend.

electrocoated CA-fibers F15. There are two possible explanations for such a behavior: (i) it could be simply caused by a non-dense coating. The of interfacial adhesion τ_{IFSS} (as measured using the single fiber pull-out test) of the uncoated, but preoxidized HMox-fibers is higher as compared to the electrocoated fibers F14, but which could not be confirmed using the indentation test. Secondly (ii), and more probable, the interfacial adhesion between the HMox-fibers and the electrocoating is much stronger, because of the higher concentration of oxygen-containing surface groups, which (as stated by Subramanian [23, 6]) can form surface free-radical sites and therefore induce polymer grafting. An increased number of interfacial bonds would of course lead to a higher level of adhesion.

After the debonding of the fiber/coating interface, the test specimen was reversed and reloaded in order to check (or better estimate) the frictional stress, since both chemical bonding across the interfaces and frictional stress (mechanical bonding) can contribute to the interfacial strength [3]. However, because of experimental difficulties, which arise from the small fiber- and indenter diameter, the fibers could not be totally pushed back. Therefore, it was just possible to roughly estimate the differences in the frictional stress (in mN/μm) between the two electrocoated fiber samples embedded in the epoxy matrix from the slope of the increasing push-back force-displacement graph. It turns out that the frictional stress between the fibers (HMox and CA) and the electrocoating (prepared under the same conditions) is about 4.1 times bigger for the HMox-fibers (F14) than for the CA-fibers (F15). Note that the locus of failure is situated in the fiber/coating interface. The higher frictional stress in case of the pre-oxidized HMox-fibers can be explained by the rougher surface of the fibers caused by the electrochemical oxidation (compare SEM-micrograph in Fig. 1c).

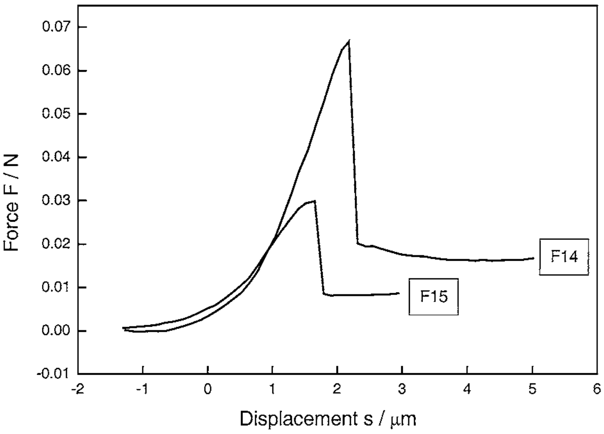


Figure 8 Indentation force-displacement curves of the electrocoated fibers F14 and F15 embedded in an epoxy resin matrix.

The observed values for the interfacial shear strength τ_{IFSS} of the embedded electrocoated F14 fibers as measured using the single fiber pull-out or the single fiber indentation test, however, agree quite well.

3.3. Adhesion behavior between the electrocoated brass and epoxy matrix

The performed microdebond tests on electrocoated and pure brass rods spliced together by the epoxy resin again showed that the splice between the metal rods that were electrocoated (10.8 ± 0.7 MPa) have a 10% higher tensile strength as compared to non-coated rods (9.6 ± 0.8 MPa). Since the interfacial failure always occurred at the brass/electrocoating (but never the electrocoating/epoxy interphase failed) or epoxy interface again no information about the electrocoating/epoxy interphase could obtained.

4. Conclusion

As shown in this study it is possible to deposit an electrocoating on carbon fibers, which has extremely good adhesion to a surrounding epoxy matrix but also a very high tensile strength for the coating can be expected. ζ-Potential measurements showed that the surface properties of the electrocoated carbon fibers were changed completely. The acidic surface character for the non-coated carbon fibers (original, untreated and unsized CA-fibers changed to basic caused by the presence of AAm-units in the polymeric coating, as revealed by the shift of the i.e.p. from the low pH (4.1) to a high pH (7.5)-range. These measurements support the fact that covalent bonds might have formed between the epoxy resin and the coating during the curing process. Additionally, attractive electrostatic interactions and mechanical interlocking (caused by the rough fiber surfaces) might also contribute to a better adhesion between coating and epoxy matrix. On the other hand however, as shown by the performed micro-mechanical tests the fiber/electrocoating interface is the plane of failure in the single fiber model composites and only an 'intermediate' fiber/electrocoating adhesion could be detected. The interfacial fiber/coating adhesion can be improved by performing the electropolymerization with pre-oxidized carbon fibers as substrate.

From the above mentioned, it should be expected to obtain composites having a sufficient level of interfacial adhesion but also high impact strength, since the impact energy can be easily dissipated by a debonding process occurring only in the fiber/coating interface without cracking the coating (because of its high tensile strength) or failure of the coating matrix interphase.

Additionally the superior thermal stability (even in air) [32] of the coating makes high temperature applications possible.

The flexibility and tensile strength but also the surface chemical composition and thereby the compatibility to different matrix materials are easily adjustable by a proper choice of co-monomers and the applied process parameters.

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