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Electrochemically polymer-coated carbon fibres: characterization and potential for composite applications

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Electrochemical polymerization is used to achieve carbon-fibre coatings with heteroaromatic conducting compounds, such as polypyrrole or polyindole. The coated-fibres surfaces are characterized by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The resulting chemical and mechanical properties are studied and this new material is tested as a reinforcement agent in an epoxy resin matrix.

1. Introduction

Carbon fibres constitute a material essentially characterized by a high specific strength and stiffness, in comparison with the other currently available engineering materials. Initially developed for the aerospace industry, they find nowadays a wide range of applications in fields such as road and marine transportation, sports goods, audioequipment, medical prostheses, etc. [1]. These fibres are mainly used as reinforcing agent in composites along with a light-weight matrix, commonly an epoxy resin. However, they also seem promised to a bright future as a reinforcement for light metals [2].

The fibre/matrix interface plays a critical role in transmitting the component's individual properties, to produce the outstanding mechanical behaviour of the whole material. However, a limiting factor to the applications just can be the nature of the bonding between fibres and matrix. Insufficient interaction can lead to shear failure of the composite. To overcome this difficulty, controlled surface modifications are commonly applied to carbon fibres [3].

In a first approach, various methods of fibre-surface oxidation have been developed [4–9]; the oxidation process increases the surface area of the fibres, but it is generally reported that the creation of chemical functionality constitutes the main factor really influencing the composite shear strength [6]. However, this treatment is not entirely satisfactory, since the fibre strength is decreased to some extent and the impact resistance of the composite is lowered.

A different method consists in using the conductivity of the carbon fibres to carry out polymer coatings (electrodeposition or electropolymerization) [10–14]. The introduction of a polymer interphase induces significant improvements in composite shear and impact strength. Moreover, the extent of modification can be controlled by the nature of the polymer.

Along the same line, this work deals with the synthesis and characterization of conducting polymers on the surfaces of carbon fibres. These polymers are heteroaromatic conjugated systems such as polypyrrole and polyindole (Fig. 1). Being totally insoluble and chemically stable [15], this kind of polymer has already been used as electrode coatings, in particular for protection purposes [16]. They are synthesized electrochemically from a monomer solution, directly onto the fibre surface.

The coatings have been characterized mainly by X-ray photoelectron spectroscopy (XPS) [17], a powerful surface investigation technique, and their growth and morphology has been followed by scanning electron microscopy (SEM). The mechanical and several chemical properties (such as stability or functionalization) of the coated fibres are briefly described and finally we tested a composite made of these fibres along with an epoxy resin (Araldite XD 893/HY 932 epoxy resin, Ciba-Geigy).

2. Experimental details

The electrochemical synthesis of the polymer is performed under potentiostatic conditions. The anode, which is the electrode where the polymerization takes place, is constituted by a carbon fibres wisp containing 6000 single filaments (Toray T300 carbon fibre). The cathode is a platinum or a gold plate and the reference electrode consists in a calomel or a silver/silver nitrate electrode, depending on the medium; indeed the synthesis can be carried out in aqueous or organic medium. The electrolytic solutions content 0.1M monomer (pyrrole or indole) and 0.1M electrolyte salt (generally Et_4NBF_4 or $LiClO_4$). In water, the pH is maintained around 7. The anodic potential is kept at +0.7 V in organic media or at +1.0 V in water for pyrrole polymerization. In the case of indole, the anodic potential is 0.3 V higher. The polymerization time is varied from 15 sec to 90 min and during the synthesis currents of 5 to 10 mA are observed.

To build up composite samples including these fibres, it is necessary to treat large amounts of fibres (10 to 20 m). The apparatus used for that purpose is schematically shown in Fig. 2. In these experiments,

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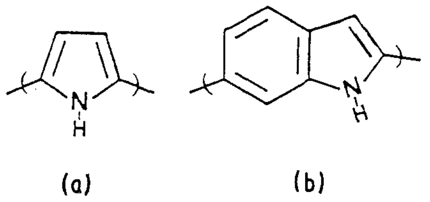

Figure 1 Molecular structures of (a) polypyrrole and (b) polyindole.

the rotor speed was chosen in such a way that the fibres were dipped for ≃ 20 min into the polymerization solution. The final composite material contained 60% fibres (in volume).

The XPS spectra were recorded on an HP 5950 A Spectrometer using the Al$K\alpha_{1,2}$ monochromatized radiation; the electron microscopic study was performed with JEOL JSM 35.

3. X-ray photoelectron spectroscopic results

The XPS spectra were calibrated by setting the anionic counter-ion F1s line at 686.4 eV or $Cl2p_{3/2}$ line at 208.7 eV, values known from absolute calibrations of Et_4NBF_4 and $LiClO_4$ salts.

Fig. 3a shows the spectrum of a carbon fibre as received from the manufacturer. The intense O 1s signal comes from the oxidative surface treatment which tends to increase the chemical reactivity of the fibre by creating hydroxyl, carbonyl and carboxyl groups. Before coatings, these fibres are placed for 10 min in a 400° C furnace under a nitrogen stream, in order to obtain the pristine material (Fig. 3b). After coating, we detect the C 1s and N 1s lines specific to the polymer along with a small oxygen contamination. The F 1s peak corresponds to the presence of the electrolyte anion (BF_4^- in this case) introduced into the film during the growth of the polymer (Fig. 3c).

The core level binding energies of polypyrrole and polyindole synthesized on carbon fibres are listed in Tables I and II where they are compared to the values obtained for "classical" polypyrrole and polyindole (prepared on metal electrodes and much better characterized) [18, 19]. The similarity of the XPS results for the two experiments suggests that the electronic structure of the two polymers is unaffected by the nature of the substrate. Moreover, the reaction medium has no influence in the final coating. However, in the case of the coated fibres, the full width at half maximum of the C 1s peak reaches 2.4 eV compared to 1.9 eV for the polymer on gold plate. This is probably due to a partial coating of the wisp allowing the detection of the carbon atoms of the fibre. The C 1s levels of the polymer and of the fibre are too close in binding energy to be well resolved; they just give rise to this observed broadening.

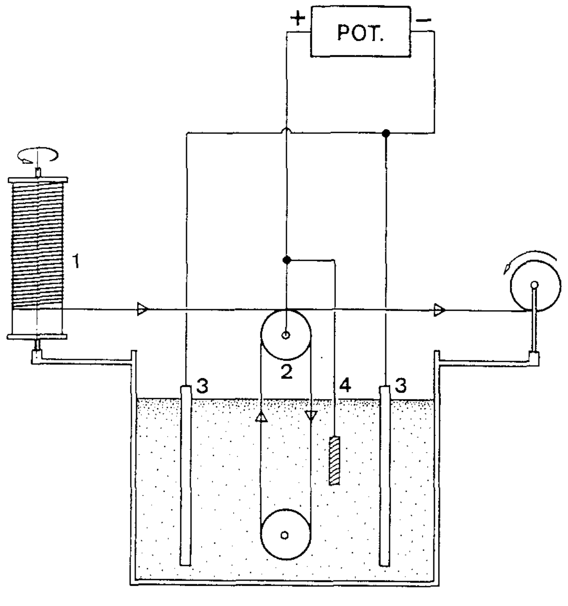

Figure 2 Electrochemical cell for the coating of large amounts of fibres: 1, fibre feeder; 2, anode; 3, cathodes; 4, reference electrode.

TABLE I XPS core levels binding energies of polypyrrole (eV)

	Solvent	Anion	C 1s	N 1s	F 1s or C l2p
Polypyrrole	CH_3CN	BF_4^-	285.6	400.6	686.4
	CH_3CN	ClO_4^-	285.7	400.8	208.7
	THF	ClO_4^-	285.7	400.8	208.7
	H_2O	ClO_4^-	285.7	400.8	208.7
Polypyrrole on fibres	CH_3CN	BF_4^-	285.6	400.6	686.4
	CH_3CN	ClO_4^-	285.7	400.8	208.7
	THF	ClO_4^-	285.8	400.8	208.7
	H_2O	ClO_4^-	285.7	400.8	208.7

The intensities, I_1 and I_2, of the XPS signals can provide the atomic ratio N_1/N_2, in an homogeneous sample by using the formula:

$$\frac{N_1}{N_2} = \frac{I_1}{I_2}\frac{\sigma_2}{\sigma_1}\left(\frac{E_{k1}}{E_{k2}}\right)^{1/2}\left[\frac{1+\beta_2/2(3/2\sin^2\phi-1)}{1+\beta_1/2(3/2\sin^2\phi-1)}\right]$$

where σ is the photoemission cross-section of the level, E_k is the kinetic energy of the photoelectron and β is the anisotropy factor. Therefore, the doping level of the polymers can be calculated from the N/F (BF_4^- doping) or N/Cl (ClO_4^- doping) ratios. For the polymers deposited on carbon fibres, we find a doping level around 25 to 30%, a value which is again very similar to that obtained after electro-polymerization on a metal electrode.

In the same way, the C/N atomic ratio yields the degree of fibre coating. Indeed, for pure polypyrrole, this ratio is equal to 4. If the coverage of the fibres is only made partially, the carbon atoms of the fibre are detected and contribute to the C 1s signal. The result is an increase of the C/N ratio which can be related to the percentage of coverage (Fig. 4), assuming the density of "emitting" atoms to be the same in the two materials (this assumption has been checked by comparing separate spectra of the two components). Table III gives the experimental results obtained with polypyrrole doped by BF_4^- or prepared in aqueous solutions. For polyindole, however, it must be noted that the fibres are totally covered after 20 min (in that case, the theoretical C/N value is 8).

TABLE II XPS core levels binding energies of polyindole (eV)

	Solvent	Anion	C 1s	N 1s	C l2p
Polyindole	CH_3CN	ClO_4^-	285.6	400.7	208.7
Polyindole on fibres	CH_3CN	ClO_4^-	284.8	400.8	208.7

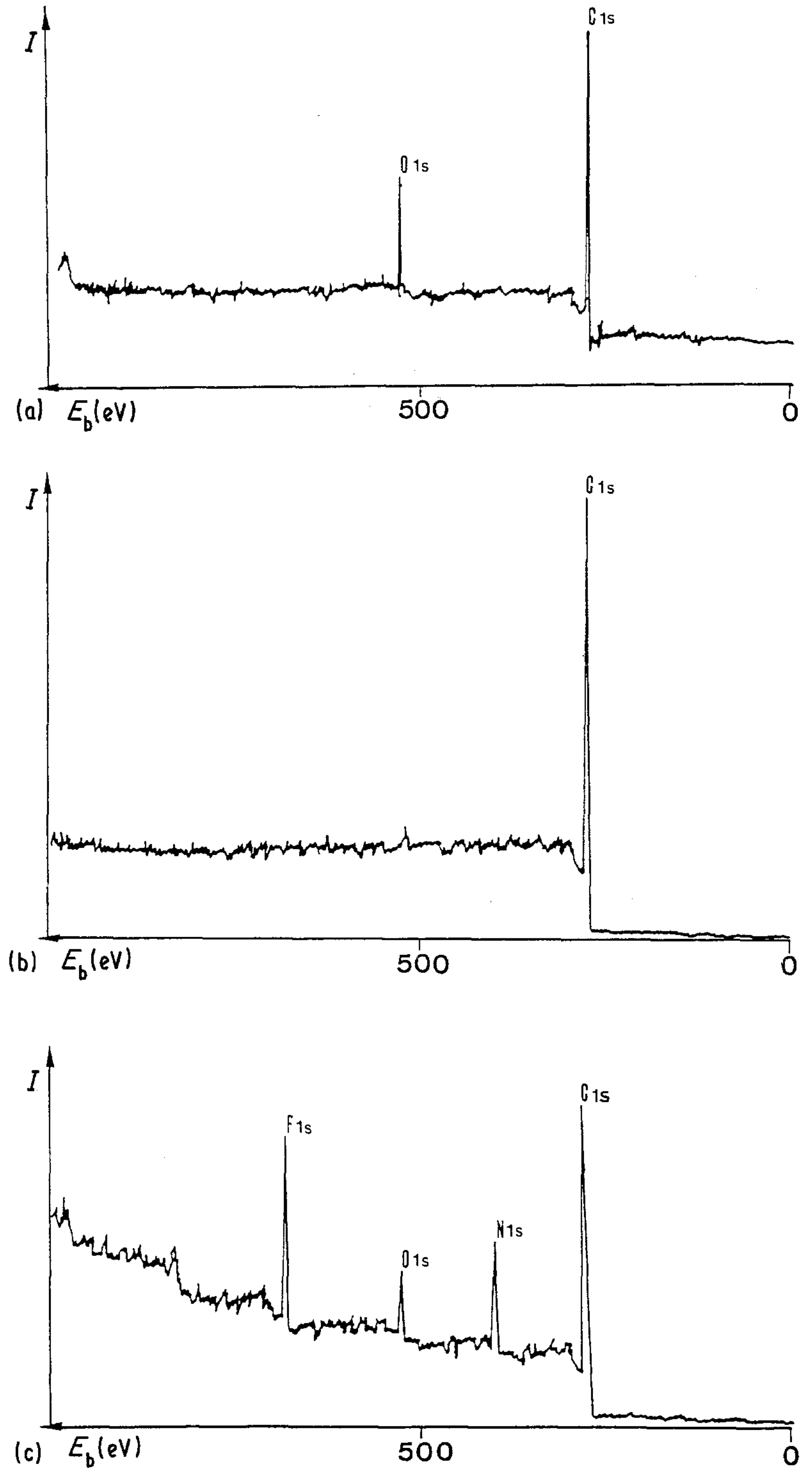

Figure 3 XPS spectra. (a) Commercial Toray T300 fibre, (b) thermally desized fibre, (c) polypyrrole-coated fibre.

4. SEM study of the coating morphology

4.1. Polypyrrole coating

Voltage application for 15 sec causes small polymer islands (0.1 μm or less) to appear on the fibre surface; the XPS spectra confirm that the islands actually are the growing polymer (Fig. 5a). After 5 to 10 min, a thin continuous film covers a part of the fibres. Its thickness, estimated from the electron micrographs, is approximately 0.5 μm (Fig. 5b).

If the polymerization time reaches 30 min, the polymer coating presents a very irregular aspect: large lumps (up to 5 μm) lying over the continuous film; for longer polymerization times (more than 60 min), polypyrrole totally covers the fibres (Fig. 5c).

TABLE III Degree of fibre coating after a 20 min polymerization

	Solvent	Anion	C/N	Coating (%)
Polypyrrole	CH_3CN	BF_4^-	5.0	80
	CH_3CN	ClO_4^-	6.0	67
	THF	ClO_4^-	6.5	63
	H_2O	ClO_4^-	4.5	89
Polyindole	CH_3CN	ClO_4^-	7.7	100

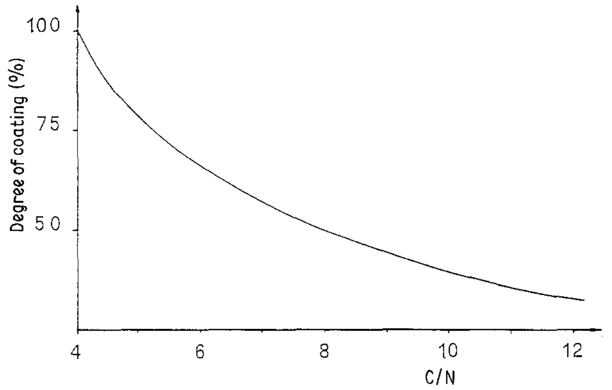

Figure 4 Fibre coating by polypyrrole from C 1s/N 1s intensities ratio.

4.2. Polyindole coating

A complete covering of the fibres is observed after 20 min in agreement with the XPS results. One should notice that the coating shows a cracked aspect, suggesting that this polymer could be rather brittle (Fig. 5d). However, we have no information concerning the intrinsic mechanical properties of polyindole.

5. Properties of polypyrrole-coated fibres

5.1. Stability

Generally, dipping carbon fibres into sulphuric acid solutions leads to a partial oxidation which creates hydroxyl, carbonyl and carboxyl groups at the surface [20]. If the polymer-coated fibres are treated in the same way, the oxidation process does not seem to occur, as seen on the XPS spectra, meaning that the coating somewhat protects the material against degradation.

5.2. Polymer functionalization

The modulation of the coating chemical reactivity is

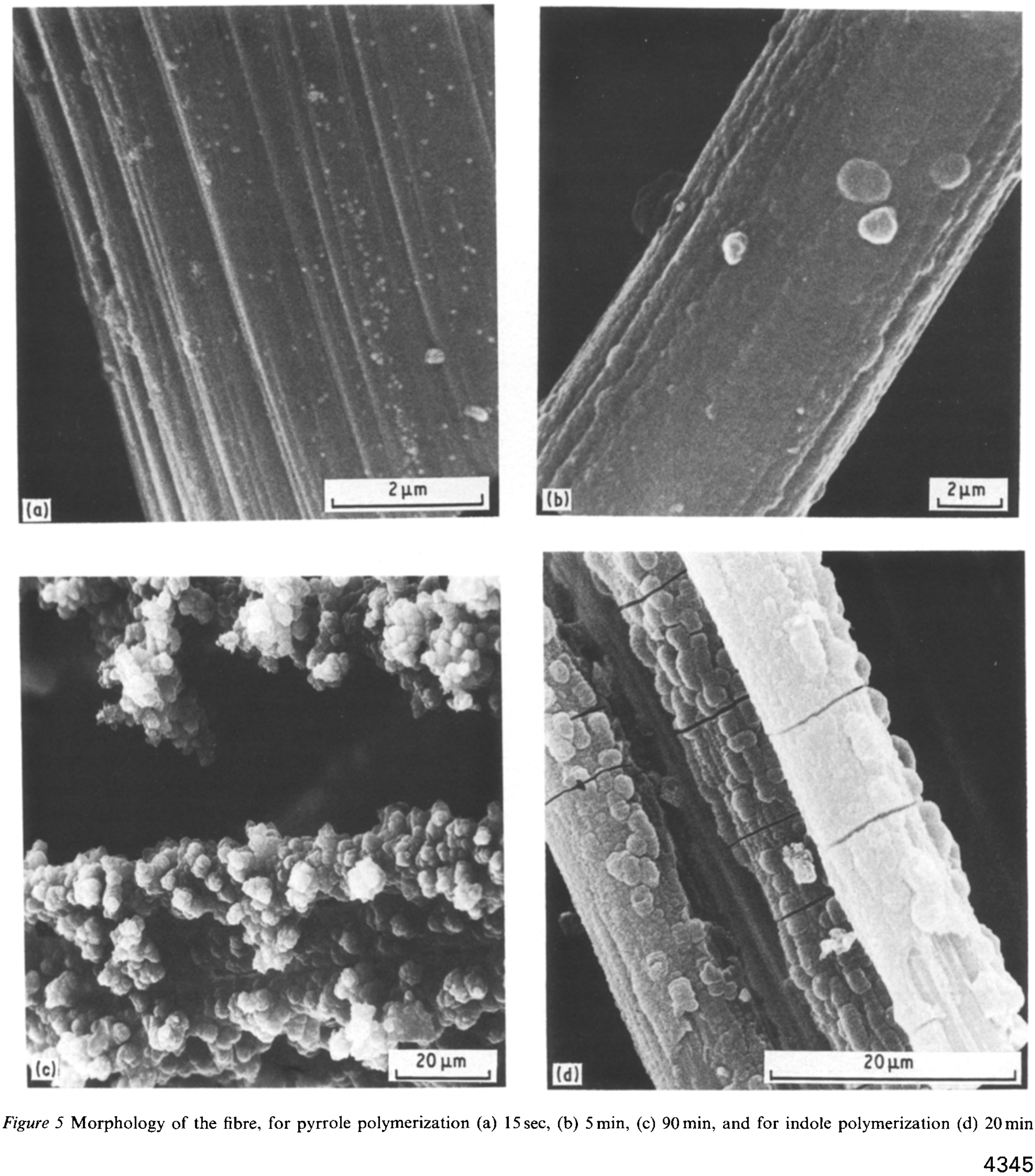

Figure 5 Morphology of the fibre, for pyrrole polymerization (a) 15 sec, (b) 5 min, (c) 90 min, and for indole polymerization (d) 20 min.

of first importance for an engineering material. To explore this possibility, we have as a first step, carried out the nitration of polypyrrole by putting the coated fibres into a concentrated nitric–sulphuric acid solution (40° C for 12 h). Such rough conditions are necessary, since the polymer is greatly chemically inert, as we have just described. The nitro groups are then reduced chemically (hydrazine, Ni Raney) into amine functions which are very interesting for future reactions with the epoxy resin.

5.3. Polymer–fibre adhesion

The adhesion of the polymer has been evaluated on a fibre after 20 min polymerization by the mean of two qualitative tests: 1-h sonication has been carried out both in water and organic solvents such as acetonitrile, which constitutes the polymerization medium, acetone and methanol; in some cases, solvent addition during the experiment was necessary to compensate for the evaporation due to the concomitant bath heating. These treatments do not modify the coating aspect. Furthermore, rubbing the fibres between two metallic plates again leaves the thin polymer film intact.

5.4. Mechanical properties

The mechanical properties of the coated fibres (rupture load, stress, strain) and related parameters, such as the radius, have been studied on 20 mm long single filaments with a Falegraph 4 dynamometer, equipped with an automatic recorder of the elongation–load curve, at a constant traction speed of 0.5 mm min^{-1}. The results presented in Table IV represent average values over 50 measurements.

A 5-min treatment does not modify the radius of the fibre, but the rupture load and so the stress value are markedly increased. For longer polymerization times, polypyrrole has grown and the fibre radius reaches 4.1 μm. The rupture load is a little higher, but the value per unit area falls. On the other hand, the polymer coating sensibly increases the strain values (1.15% to 1.36%). One possible explanation for these results is that, in the beginning of the polymerization, polypyrrole fills up the microdefects of the fibre surface, so increasing the stress. In the second stage, a thick film increases the rupture load, but without modifying the fibre itself.

Finally, we have tested the interlaminar shear strength of a composite in which the 20-min treated fibres constitute 60% in volume. These composite samples underwent a short-beam test on an Instrom 1121 apparatus, according to the ASTM D2344 standard. We observed a value of 64 MPa compared to 59 MPa in the case of uncoated fibres.

TABLE IV Mechanical properties evolution of the carbon fibres

	Radius (μm)	Rupture load (g)	Stress (kg mm^{-2})	Strain (%)
(a)*	3.6	10.10	248	1.15
(b)	3.6	11.56	284	1.31
(c)	4.1	12.40	228	1.36

*(a) uncoated; (b) after 5 min polypyrrole coating; (c) after 60 min of polypyrrole coating.

6. Conclusions

Coating of carbon fibres with electrochemically synthesized polymers leads to very adhesive films, which improve the mechanical properties of the system. It may also, to some extent, replace the sizing, and offer interesting perspectives for composites applications, in resistance to ageing because of the chemical stability of polypyrrole, and in increasing interlaminar shear strength. Finally, the possibilities of grafting the polymer coating with groups such as nitro or amine yield interfaces with enhanced reactivities.

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