

Flame-Retardant Effect of Polyaniline Coating Deposited on Cellulose Fibers

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ABSTRACT: Filtration paper was coated with a thin polyaniline film. The content of conducting polymer was 8.2 and 6.3 wt % for polyaniline hydrochloride and polyaniline base, respectively. After burning, the coated material retains the original fibrillar morphology of cellulose. The polyaniline coating converts to solid carbonaceous products. The resulting structure prevents the formation of gaseous carbon oxides by restricting the access of oxygen to cellulose. While the ash from the uncoated paper after burning is 0.005 wt %, the microtubular residue of polyaniline-coated paper is 16–24 wt % of the original mass. The flame-retardant per-

formance of polyaniline and poly(1,4-phenylenediamine) coatings was comparable both for the protonated forms and the corresponding bases. The conversion of polyaniline-coated cellulose fibers to solid pyrolytic products was characterized by FTIR and Raman spectroscopies. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2347–2354, 2005

Key words: conducting polymer; polyaniline; poly(1,4-phenylenediamine); cellulose; paper; flame retardation; carbon microtubes

INTRODUCTION

Conducting polymers are a new class of materials. The coating of various substrates with a conducting-polymer overlayer has become a frequently-used way for the preparation of conducting composites. Polyaniline (PANI) and polypyrrole have been deposited on miscellaneous substrates, including organic and inorganic particles, fibers and textiles, polymer films and membranes, etc.^{1,2}

The preparation of composites based on cellulose and a conducting polymer has been reported early in the modern history of conducting polymers by Bjorklund and Lundström.³ These authors coated paper with polypyrrole during the in situ polymerization of pyrrole and demonstrated the conductivity changes as a response to the acidity variation. Yue et al.⁴ have also proposed polypyrrole-coated paper as a pH sensor, Dutta et al.⁵ coated filtration paper with PANI for the similar purpose. Dall'Acqua et al.⁶ have coated the textile prepared from regenerated cellulose fibers with

polypyrrole to obtain a conducting fabric; Bhat et al.⁷ covered cotton with PANI for a similar application. Other authors have deposited polypyrrole on cellulose nanowhiskers⁸ and natural cellulose fibers⁹ to prepare nonspherical conducting fillers. Sapurina et al.^{10,11} coated wood sawdust with PANI or polypyrrole, and tested the resulting composite materials in electromagnetic-radiation shielding.

The polymer overlayer deposited on the substrate during the in situ polymerization of aniline or pyrrole is thin, of the order of hundreds of nanometers.² Yet, it has been observed that a polyethylene membrane coated with polypyrrole does not lose its integrity even above the melting point of polyethylene.¹² This means that the framework provided by the conducting polymer can affect the properties of the whole composite by protection of the interior. This is also illustrated by the flame-retardation effect of PANI coating deposited on cotton⁷ and polyester¹³ fabrics.

Many cellulose-based materials, e.g., wood, paper, or natural and regenerated cellulose textiles, are currently met in everyday life. Their combustibility is a parameter of obvious importance and its reduction is a frequent goal. In the present study, we test the PANI¹⁴ coatings on cellulose fibers, a filtration paper, as a potential flame retardant. This is an illustration of the use of a conducting polymer outside the current field of electrical applications. The performances of PANI (Fig. 1) and of a related polymer, poly(1,4-phenylenediamine),¹⁵ have been compared.

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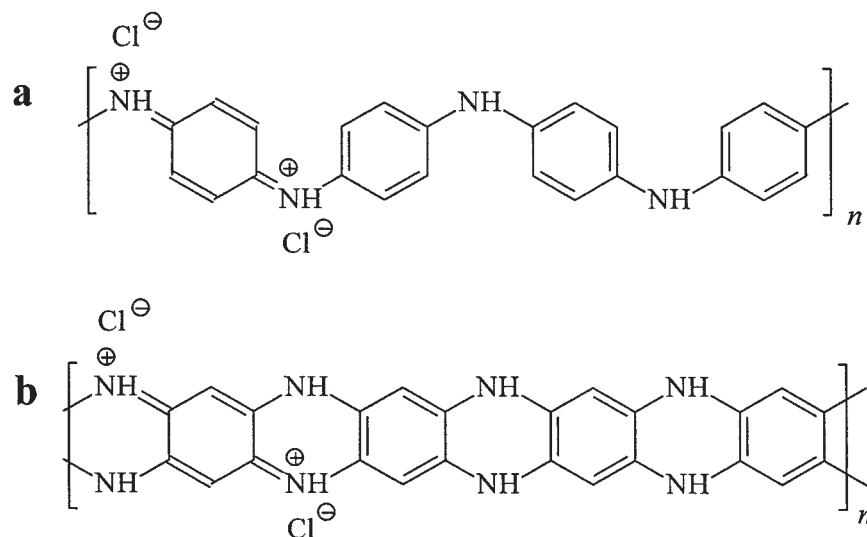


Figure 1 (a) Polyaniline hydrochloride¹⁴ and the proposed formula of poly(1,4-phenylenediamine) hydrochloride.¹⁵ The corresponding bases are obtained after the deprotonation, i.e., by the removal of hydrochloric acid with ammonium hydroxide.

EXPERIMENTAL

The coating of paper with a conducting polymer

Filtration paper (Filtrak, No. 389, circles of 70 mm diameter, Spezialpapier FILTRAK GmbH, Germany), used for the collection of fine inorganic precipitates in quantitative chemical analysis, was immersed in the aqueous reaction mixture used for the preparation of PANI. Polyaniline was prepared by the oxidation of 0.2M aniline hydrochloride with 0.25M ammonium peroxydisulfate in water.¹⁴ After about 1 h, the papers coated with PANI were rinsed with 0.2M hydrochloric acid, in acetone, and dried in air. Polyaniline hydrochloride deposited on several pieces of paper was deprotonated in 1M ammonium hydroxide to PANI base and, after rinsing with acetone, dried again in air. Polyaniline hydrochloride is green and the corresponding PANI base is blue in thin transparent films. The PANI-coated paper has a violet or golden metallic glance, respectively, corresponding to reflected wavelengths of visible light. The elemental composition was determined with a PerkinElmer 2400CHN Elemental Analyzer.

The filtration papers have similarly been coated with poly(1,4-phenylenediamine) hydrochloride. In that case, the aqueous reaction mixture contained 0.2M 1,4-phenylenediamine dihydrochloride and 0.5M ammonium peroxydisulfate. The corresponding base was obtained as mentioned earlier. The poly(1,4-phenylenediamine) coatings are brown.

The burning of the paper

A bent piece of filtration paper was placed on a Petri dish, ignited with a match, and left to burn. The origi-

nal sample and the residue were weighed. The experiment was repeated with at least five pieces of paper.

Infrared and Raman spectroscopies

Infrared spectra in the range of 400–4000 cm⁻¹ were recorded at 64 scans per spectrum at 2 cm⁻¹ resolution, using a fully computerized Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector. A Golden Gate[™] Heated Diamond ATR Top-Plate (Specac Ltd.) was used for measurements of spectra in the ATR mode. Spectra were corrected for the presence of moisture and carbon dioxide in the optical path.

Raman spectra excited in the visible range with a HeNe 633 nm laser were collected on a Renishaw inVia Reflex Raman microscope. The objective lens ×50 was used to focus the laser beam on the sample placed on a X–Y motorized sample stage. The scattered light was analyzed by the spectrograph with a holographic grating (1800 lines mm⁻¹). A Peltier-cooled CCD detector (578 × 385 pixels) registered the dispersed light. An acquisition time from 10 s to 60 s was optimized for each individual measurement. The positioning of a sample was controlled, and the data were processed with a Wire 2.2 software.

RESULTS AND DISCUSSION

The structural changes of PANI base exposed to temperatures up to 1000 °C has recently been studied.¹⁶ The mass of the polymer gradually reduced, but the morphology of PANI was preserved during the conversion to carbonaceous products. We anticipated that

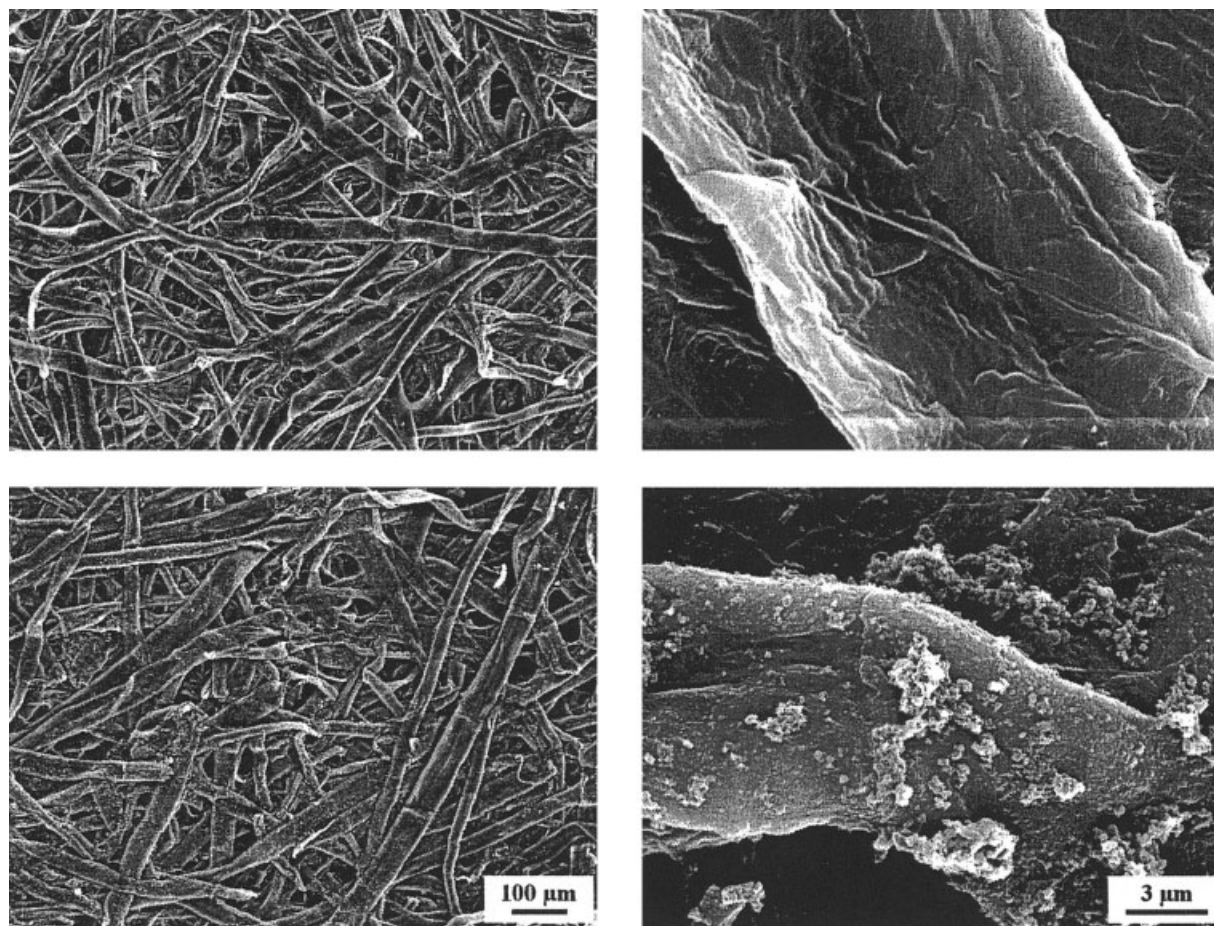


Figure 2 The micrograph of the filtration paper before (top) and after (bottom) the coating with polyaniline hydrochloride at lower (left) and larger (right) magnifications.

this finding might be potentially useful in the design of flame-resistant materials. Obviously, the PANI coating deposited on cellulose fibers, or later its carbonized version, may produce a barrier to oxygen diffusion into the burning material and, consequently, thus to reduce its combustion. The concept is discussed later.

The changes in morphology of paper after burning

The role of the PANI coating on cellulose fibers can be illustrated by the following experiment. If an uncoated filtration paper (Fig. 2, top) is ignited, it burns without leaving any visible residue (Table I). If a filtration paper is immersed in the reaction mixture used for the

TABLE I
The Conductivity, Polymer Content, and the Residue After Burning of Filtration Paper Coated with Polyaniline and Poly(1,4-phenylenediamine)

Material	Conductivity ^a (S cm ⁻¹)	Content of polymer ^b (wt %)	Residue (wt %)
Paper, uncoated	5×10^{-12}	0	0.005 ^c
+PANI hydrochloride ^d	8×10^{-4}	8.2	24.0
+PANI base	3×10^{-10}	6.3	20.0
+PPDA hydrochloride	3×10^{-10}	6.7	24.4
+PPDA base	2×10^{-12}	4.9	16.7

^a Determined by the two-point method.

^b Calculated from mass increase after the polymerization.

^c Manufacturer's information.

^d The conductivity of PANI hydrochloride¹⁴ is 4.4 S cm⁻¹.

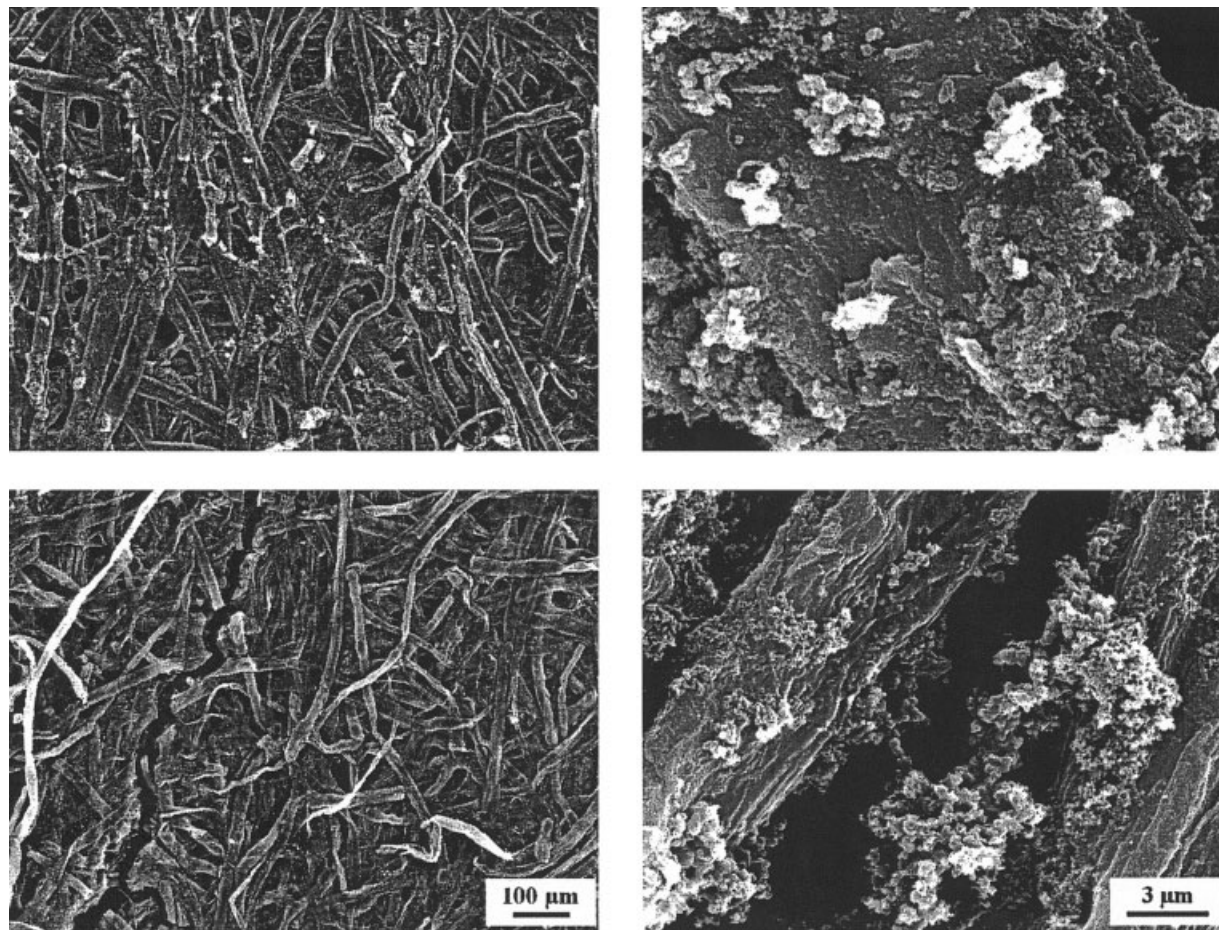


Figure 3 The filtration paper coated with polyaniline hydrochloride after burning (top) and after being kept in the flame to a red glow (bottom) at lower (left) and larger (right) magnifications.

oxidation of aniline,¹⁴ it becomes coated with a PANI (Fig. 2, bottom). The dry PANI-coated paper also burns, but the residue retains its integrity, although in a deformed shape. The PANI-coated, now mostly carbonized, paper preserves the original morphology of the cellulose fibers (Fig. 3, top), except that the fibers became thinner. When held in a luminous natural-gas flame for 10 s, a paper residue glows red, but the morphology does not change any more (Fig. 3, bottom).

The profile of the PANI-coated paper residue shows the presence of microtubes (Fig. 4, top). As expected, the structure does not change after an additional placement into the burner flame (Fig. 4, bottom). The success of the PANI ability to produce the microtubes consists in the completeness of the coating. When PANI film is produced on a flat support, its typical thickness is 100–200 nm. The thickness of the microtubular walls observed by electron microscopy is larger and is estimated to be close to 1 μm . The aqueous reaction mixture that produces PANI has obviously penetrated inside the surface region of fibers during the coating (Fig. 5). Consequently, PANI is

produced not only on the fiber surface but partly extends into the fiber interior.⁶ This fact is responsible for observed thicker walls of microtubes.

The mass of a residue

The residual mass after burning has been determined for papers coated with PANI hydrochloride or poly(1,4-phenylenediamine) hydrochloride, including the corresponding bases. From these polymers, only PANI hydrochloride is conducting (Table I). A non-conducting poly(1,4-phenylenediamine)¹⁵ is structurally related to PANI (Fig. 1), and its assumed chain structure can be regarded as being composed of two entwined PANI chains.

The content of PANI in the coated paper is 4–8 wt % (Table I). The residue left after the burning of uncoated paper is 0.005 wt %. If the coated paper burnt as easily, the residue should be constituted by a carbonized deposited polymer, and should be well below 8 wt %. We find the residue to be 16–24 wt % (Table I). There is only one explanation: the cellulose has partly been converted into carbon, rather than to carbon

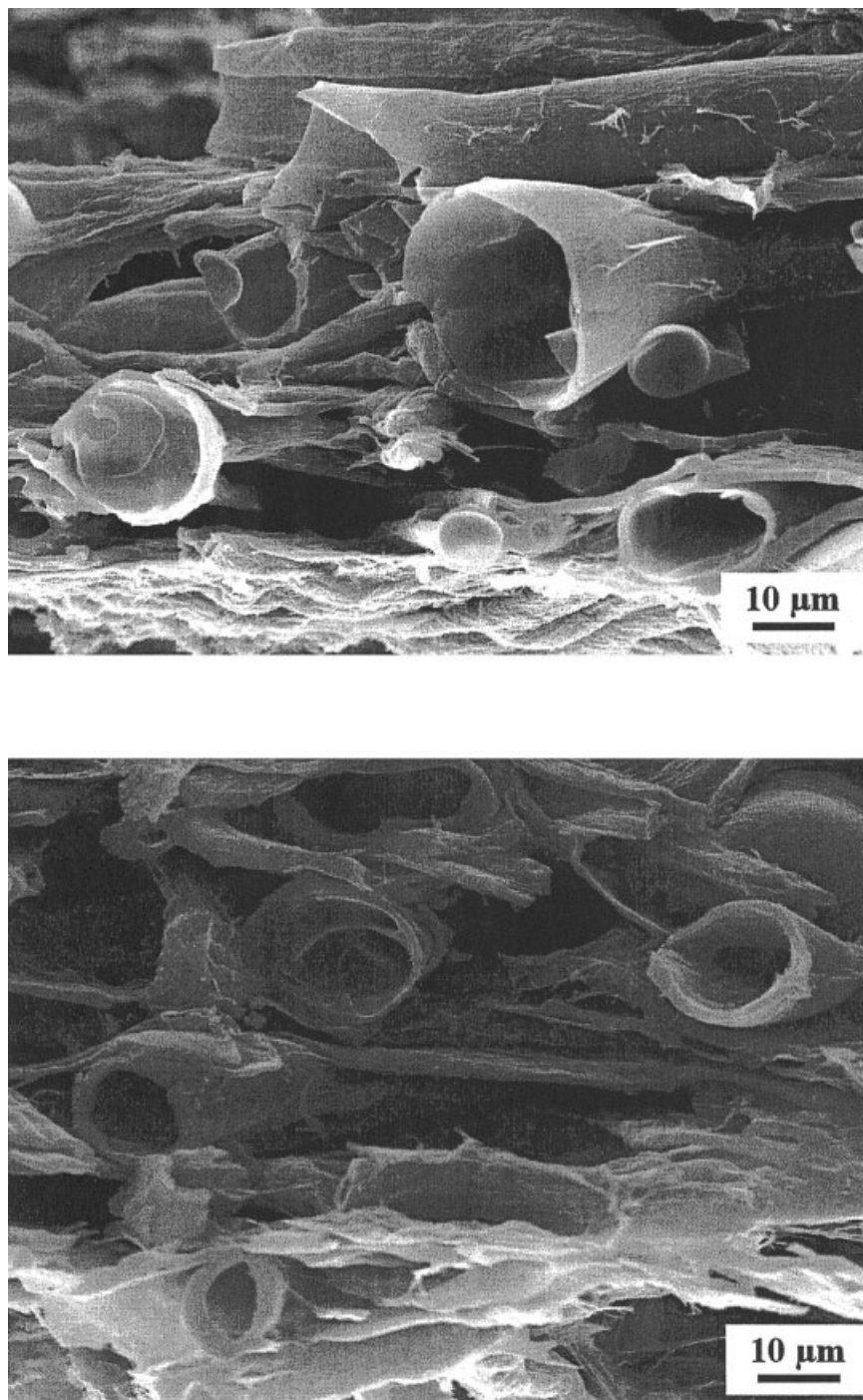


Figure 4 The profile of filtration paper coated with polyaniline hydrochloride after burning (top) and after being additionally kept in the flame to a red glow (bottom).

monoxide or dioxide. This concerns especially the surface part of the cellulose fibers penetrated by deposited polymer (Fig. 5). The increase in carbon content after burning is indeed marked (Table II), yet nitrogen is still present in the residue after burning. This confirms that the carbonaceous products of PANI pyrolysis partly constitute the residue. A nitrogen content of 14–17 wt % has been found in the samples of PANI

base¹⁶ exposed to temperatures up to 1000°C. On the basis of nitrogen content (Table II), we can roughly estimate that the pyrolytic PANI amounts to about one quarter to one half of the residue, the rest being created by the carbonaceous product achieved by cellulose decomposition. Yan et al.¹⁷ have similarly observed the incandescence of polypyrrole microtubes when they were carbonized by the heat produced by

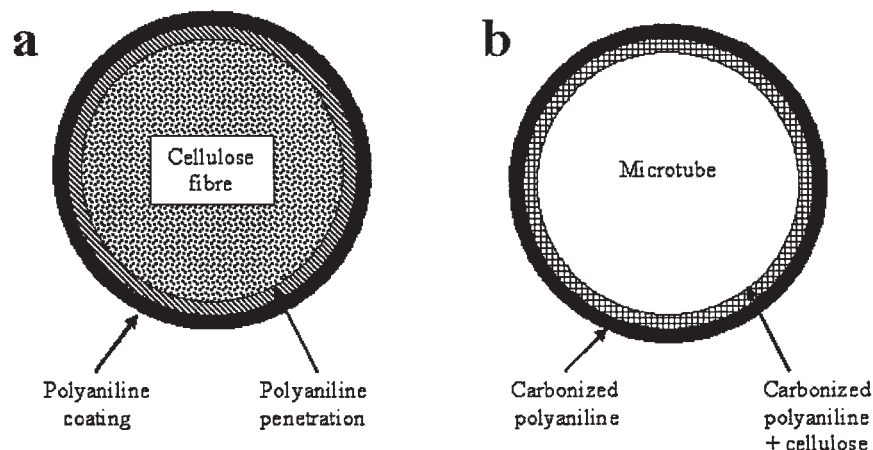


Figure 5 (a) The cellulose fiber becomes coated with polyaniline during the polymerization. The reaction mixture penetrates the surface regions of the fiber and polyaniline is also produced there. (b) After burning of cellulose, the walls of microtubes are composed of carbonized polyaniline and of the carbonized cellulose-polyaniline composite region.

passing an electric current. The content of both carbon and nitrogen increased during the continuing carbonization, similarly to the present case.

There is little difference between the performance of the protonated polymer forms and the corresponding bases when it comes to the reduction of the destruction of the material by flame, the bases leaving a slightly lower residue. The protonated forms liberate acids when heated, in the present case, hydrochloric acid. This may be a negative feature in the potential applications unless the acid has been well selected. We can speculate that the use of hydrobromic or phosphoric acids might improve the flame-retardant behavior. Nevertheless, coating with polymer bases might be preferred in practice.

Spectroscopic studies

The changes in both the conducting polymer and the cellulose are conveniently observed by FTIR and Raman spectroscopies. The ATR FTIR spectra of filtration paper before and after coating with PANI are compared in Figure 6. The spectrum of cellulose includes the bands of free or bonded OH vibrations, CH vibrations, and COO stretching vibrations.¹⁸ After coating

with PANI, the bands of cellulose are partly overlapped by the bands of PANI but they are still well distinguished (Fig. 6). This proves that the thickness of the coating of cellulose fibers with PANI is thinner than the penetration depth of IR radiation into the sample, a few μm . The spectrum has completely changed after burning the paper (Fig. 6). Two broad bands centered at 1578 and 1205 cm^{-1} then dominate the spectrum. Similar bands located at 1584 and 1226 cm^{-1} have been observed in the infrared spectrum of carbonized PANI base.¹⁶ Besides these two bands, a shoulder at 1703 cm^{-1} , a broad band with two maxima at 1504 and 1434 cm^{-1} , a shoulder at about 1030 cm^{-1} , and the peaks at 868, 806, and 753 cm^{-1} are present in the spectrum measured after the burning of PANI-coated paper. Additional exposure to a luminous flame has led to the reduction of the broad bands with maxima at 1504 and 1434 cm^{-1} (Fig. 6).

The changes in the structure of cellulose at 250 $^{\circ}\text{C}$ in air and argon have been studied using infrared spectroscopy by Cagniant et al.¹⁹ During the heating in air, the characteristic bands assigned to OH groups (a large band due to hydrogen bonding, 3600–3000 cm^{-1}), C—O—C (1150–900 cm^{-1}) and CH vibrations in CH—OH and CH₂—OH groups (3000–2800 cm^{-1})

TABLE II
Elemental Analysis of the Filtration Paper Before and After Burning

Material	Coated paper			Residue after burning		
	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)
Paper, uncoated	43.3	6.1	—	^a	^a	^a
+PANI hydrochloride	41.1	5.8	1.6	76.7	3.2	3.4
+PANI base	44.9	5.9	1.3	77.6	3.0	8.4
+PPDA hydrochloride	42.3	6.0	0.4	80.3	3.1	1.7
+PPDA base	42.2	6.2	0.5	78.1	3.1	2.4

^a The residue (an ash of inorganic nature) was too small for analysis.

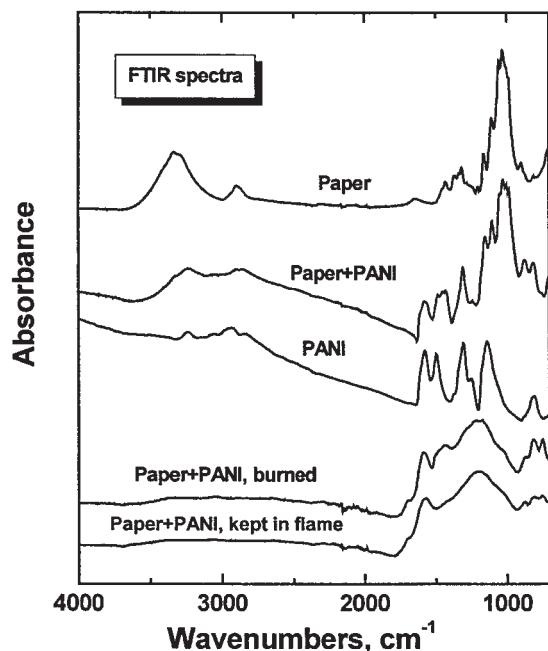


Figure 6 FTIR spectra of the filtration paper coated with polyaniline hydrochloride, its components, and the changes of the spectra after burning.

decreased. Two new bands emerged at 1712 and 1620 cm^{-1} corresponding to carboxyl and carbonyl groups and to unsaturated carbon-carbon stretching vibrations, respectively. The bands characteristic of several oxidized products, such as esters and carbonyl compounds, in the region 1770–1620 cm^{-1} are observed in the spectrum. During the heating in an argon atmosphere, a part of the cellulose structure was preserved for 4 h at 250 °C. The characteristic bands at 1712 and 1620 cm^{-1} were observed in the spectrum. The absence of the bands of oxidized products signified that the degradation of the products obtained by thermal depolymerization of the cellulose was limited under an inert atmosphere.

In the present case, the shape of the spectra of burnt paper corresponds to the superposition of the spectra of carbonized PANI base¹⁶ and thermally treated cellulose.¹⁹ The presence of nitrogen in the residues has been confirmed by elemental analysis (Table II). The absence of the bands of oxidation products in the region 1770–1620 cm^{-1} demonstrates that the conducting polymer prevents the complete oxidative destruction of cellulose during burning. We conclude that the layer of carbonized PANI prevents the access of oxygen to the neighboring cellulose regions. The band in the region of 1670–1550 cm^{-1} are typical of C=N stretching vibrations in oximes, imines, and amidines.²⁰

The filtration paper has been similarly coated with poly(1,4-phenylenediamine) hydrochloride, and the ATR FTIR spectra of the paper, before and after burn-

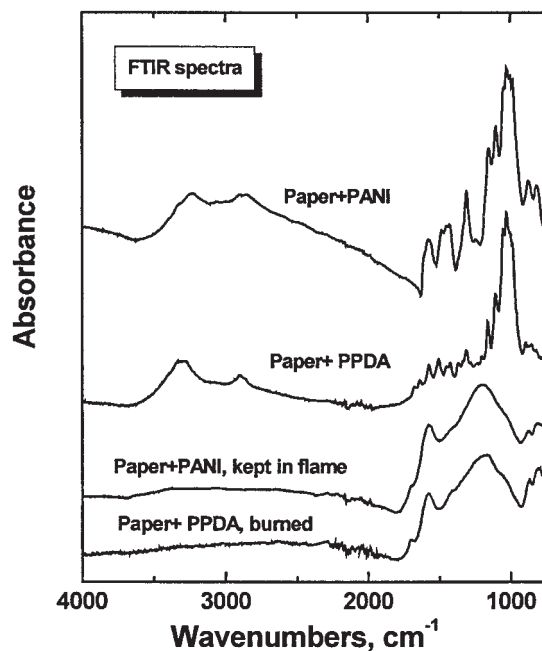


Figure 7 The comparison of the spectra of filtration paper coated with polyaniline or poly(1,4-phenylenediamine) before and after the burning.

ing, have been compared with those of paper coated with PANI (Fig. 7). The spectra of the well-burnt samples are identical. This means that the pyrolysis of both polymers yields the same carbonaceous products.

Raman spectra (Fig. 8) are even more useful to discuss the conversion of an organic material into a carbon-like one. The polymer coating dominates the spectra and the features of paper support are suppressed. Obviously, Raman scattering of the excitation radiation takes place only at the very surface of polymer coating, and the effective penetration depth is smaller compared with that of an ATR FTIR experiment. This confirms that the coating of cellulose with PANI has been complete. The Raman spectrum of the residue of the paper coated with PANI after spontaneous burning is composed of two broad bands with maxima at 1581 and 1349 cm^{-1} . After keeping the sample in the flame for 10 s, these maxima shift to 1586 and 1312 cm^{-1} . The shape of the spectra is typical of carbonaceous materials, which are characterized by so-called “G” (graphitic) and “D” (disordered) bands in their Raman spectra.²¹

Concluding remark

In the Middle Ages, the cathedrals in Europe were built with the help of a wooden scaffolding. After the construction has been completed, the scaffolding was set on fire, leaving the cathedral to be admired for many future centuries. On a micro-scale, if we deposit

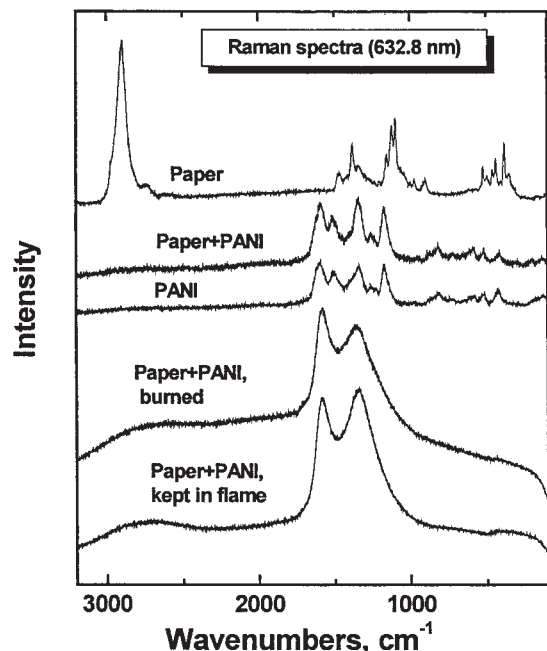


Figure 8 Raman spectra of the filtration paper coated with polyaniline hydrochloride, its components, and the changes of the spectra after burning.

a conducting polymer, e.g., PANI, onto a cellulose fiber, then, after burning off the cellulose scaffolding, we obtain a carbonized PANI structure strengthened with a cellulose residue incorporated into PANI-rich regions. This approach allows for the preparation of various carbonaceous morphologies. A suitable organic substrate, predetermining the future morphology, could be coated with a conducting polymer overlayer. After the exposure to elevated temperature, the substrate would burn and be carbonized in the limits set by conducting polymer coating and its penetration into the template material.

CONCLUSIONS

Cellulose fibers (filtration paper) have been coated with PANI when immersed in the reaction mixture used for the oxidation of aniline. The in situ coating of the material with a conducting polymer prevents the complete destruction of the paper during burning. The produced overlayer of carbonized PANI deposited on the cellulose fibers probably provides a barrier to oxygen. In the regions penetrated with a conducting polymer, the cellulose thus converts, in part, into solid

carbonaceous products instead of carbon oxide gases. In this way, the material integrity is better preserved and the residue after burning is much greater compared with that of an uncoated paper. Similar behavior has been observed after the deposition of poly(1,4-phenylenediamine). The coating of the flammable substrates with a conducting polymer overlayer may thus enhance their resistance to being destroyed by fire.

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