

Flame Retardancy Afforded by Polyaniline Deposited on Wood

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ABSTRACT: Wood scantlings were coated with polyaniline (PANI) during the *in situ* polymerization of aniline with ammonium peroxydisulfate in an aqueous medium. The coating was made in hydrochloric or phosphoric acid solutions in both the absence and presence of stabilizers, poly(*N*-vinylpyrrolidone) or colloidal silica. The PANI-coated wood was placed in a flame or in a furnace operating at 400 or 600°C, and the decrease in the mass was determined. The wood coated with PANI was less reduced in its mass than uncoated samples and was converted to charcoal rather than to ashes. The deposition of related polymers, polypyrrole and poly(1,4-phenylenediamine), provided similar protection against heat exposure. Fourier transform infrared and Raman spectra of

the residues after the burning of PANI-coated wood were compared. The soaking of wood in PANI colloids did not result in similar protection of wood against fire; the coating of the cellulose fibers with PANI during the polymerization was needed for the enhanced stability of wood at elevated temperatures. The concept of carbonization processes at the surface layer of PANI-coated cellulose fibers leading to the formation of carbonaceous microtubes is offered to explain the improved stability of wood against flame and heat exposure. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 24–30, 2007

Key words: colloids; conducting polymers; fibers; polypyrroles; polyaniline; cellulose

INTRODUCTION

Polyaniline (PANI; Scheme 1) ranks among the most studied conducting polymers.¹ Besides its electrical properties, its optical, electrochemical, chemical (e.g., catalytic), and surface properties have come to the forefront. This study concerns the investigation of PANI coatings in a less common application of conducting polymers, the protection of materials against damage by fire.

Any surface in contact with the acidic aqueous reaction mixture used for the oxidation of aniline becomes coated with a thin PANI film typically 100–200 nm thick.^{2,3} In addition to forming the coating, PANI is also produced as an accompanying precipitate. The thickness of the film can be reduced below 100 nm when the polymerization proceeds in the dispersion mode,⁴ in the presence of a water-soluble polymer⁵ or a nanocolloidal silica.⁶ In such a case, a

colloidal PANI dispersion is produced instead of a precipitate.

Surfaces of various cellulose materials have recently been modified with conducting polymers for various purposes. Filtration paper coated with a conducting polymer was proposed for acidity sensing.^{7,8} Deshpande et al.⁹ used polypyrrole-coated paper as an actuator. Johnston et al.¹⁰ also demonstrated the feasibility of coating paper fibers with PANI. Attention has been paid to the preparation of cellulose-based conducting textiles.^{11,12} Flandin et al.¹³ and Omastová et al.¹⁴ coated cellulose fibers and used them as asymmetric fillers in conducting composites. Wood sawdust coated with PANI has been tested for electromagnetic-radiation shielding.¹⁵

It has recently been reported that PANI deposited on organic fibers has a flame-retardant property.^{12,16} Cellulose fibers coated with PANI yielded hollow, carbonaceous microtubes after burning.¹⁷ In this study, we develop this property to test the protection of wood against burning.

EXPERIMENTAL

Preparation of wood modified with PANI

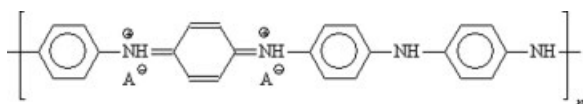
In situ deposition of PANI

Aniline hydrochloride (0.2 M; Fluka, Switzerland) was oxidized in an aqueous solution with ammonium

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Scheme 1 Conducting emeraldine form of PANI protonated with an arbitrary acid (HA; e.g., hydrochloric or phosphoric acid).

peroxydisulfate¹⁸ (0.25 M; Lachema, Brno, Czech Republic). Aniline hydrochloride (2.59 g) dissolved in water to a 50-mL solution was mixed at room temperature with a 50-mL aqueous solution containing 5.71 g of ammonium peroxydisulfate. Fir-wood scantlings ($1 \times 1 \times 5 \text{ cm}^3$) were immersed in a gently stirred reaction mixture and occasionally reversed to ensure homogeneous coating with PANI. After the polymerization was completed, in about 15 min, the wood was removed, rinsed with 0.2M hydrochloric acid, and left to dry in air for at least 1 week. The repeated deposition of PANI on the same sample was also tested. The accompanying PANI precipitates were collected on the filter and dried.

In one case, excess 1M hydrochloric acid was used as the reaction medium instead of water. In other polymerizations, 0.2M aniline was oxidized with 0.25M ammonium peroxydisulfate in 0.4 or 1.2M phosphoric acid.¹⁵

Dispersion polymerization of aniline

If the reaction mixture contains a stabilizer, colloidal PANI dispersions are obtained instead of a PANI precipitate.^{4,19} The immersed substrates become coated with PANI also in this case.^{5,6} The polymerization thus was performed in the presence of 2 wt % poly(*N*-vinylpyrrolidone) (PVP; Fluka; molecular weight = 360,000)^{3,19,20} or 5 wt % colloidal silica^{6,21,22} (Ludox AS-40; Aldrich, Prague, Czech Republic). Samples of wood were immersed in the reaction in the same fashion as the aforementioned examples. Colloidal dispersions produced in this way were used for the preparation of additional samples. Wood scantlings were dipped in PANI colloidal dispersions for 5 s or soaked for 1 h and then left to dry in air for 1 week.

Coating with other polymers

Besides aniline, also polypyrrole coatings were produced on wood by the oxidation of 0.2M pyrrole (Fluka) with ammonium peroxydisulfate in 0.2M HCl. Poly(1,4-phenylenediamine) hydrochloride was similarly deposited during the oxidation of 1,4-phenylenediamine dihydrochloride (Fluka) with 0.5M ammonium peroxydisulfate in water.²³

Wood sawdust

Fir-wood sawdust was coated with PANI phosphate in a reaction mixture containing 0.4 or 1.2M phos-

phoric acid.¹⁵ The composite thus prepared contained 20 wt % PANI. Both uncoated and coated sawdust was compressed with a hydraulic press into pellets 13 mm in diameter and 1 mm thick.

Thermal exposure of wood

Wood in flame

The behavior of fir wood (scantlings or pellets of compressed sawdust) in flame was tested with a laboratory Bunsen burner with a luminous flame of natural gas 20 cm high. A sample was placed on a stainless-steel mesh ($1 \times 1 \text{ mm}^2$) in the upper part of the flame for 2 min. Then, it was transferred to a Petri dish, extinguished by a stream of nitrogen if burning, weighed, and again exposed to the flame for another 2 min. This procedure was repeated once more. The pellets of compressed wood sawdust were exposed to the flame similarly to the wood scantlings. The test was repeated with three samples, and the results were averaged.

Wood in the furnace

The wood samples were placed into a porcelain crucible and exposed to an elevated temperature of 400 or 600°C for 2 h in the ambient atmosphere in a Classic (Revnice, Czech Republic) 3013R electric high-speed furnace. Then, the samples were left to cool in a desiccator, and their mass loss was determined.

Spectroscopic characterization

Infrared spectra in the range of 400–4000 cm^{-1} were recorded at 64 scans per spectrum at a 2- cm^{-1} resolution with a fully computerized Thermo Nicolet Nexus 870 Fourier transform infrared (FTIR) spectrometer (Madison, WI) with a DTGS TEC detector. A Golden Gate heated diamond attenuated total reflection (ATR) top plate (Specac, Ltd., Orpington, England) was used for the 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 with a He–Ne laser of a 633-nm wavelength were collected with a Renishaw InVia Reflex Raman microscope (Renishaw, Wotton-under-Edge, England). The objective lens (50 \times) was used to focus the laser beam on a sample placed on an X–Y motorized sample stage. The scattered light was analyzed by a spectrograph with a holographic grating (1800 lines/mm). A Peltier-cooled charge-coupled detector (578 pixels \times 385 pixels) registered the dispersed light. An acquisition time of 10 s was optimized for each individual measurement. The positioning of the sample was controlled, and the data were processed with Wire 2.2 software.

RESULTS AND DISCUSSION

Wood scantlings were surface-modified with PANI and related polymers in various ways. Their behavior in a flame or in a furnace at elevated temperatures was tested. The mass loss was taken as a primary criterion for the assessment of resistance to heat exposure (Table I). The lower the mass loss was, the better the performance was. The morphology of the residues after burning was taken as the second criterion. The samples that were converted to charcoal without losing their integrity were marked as better and more flame-resistant than the samples that burned to ashes.

Behavior of PANI-coated wood at elevated temperatures

In the first series of experiments, wood scantlings were coated with PANI in different ways. Any *in situ* deposited coating improved the stability of wood against fire exposure by reducing the mass loss (Table I). The coatings prepared in the presence of phosphoric acid performed best. In all cases, wood scantlings converted to charcoal pieces, whereas uncoated reference samples burned to ash under the same conditions. There was a slight difference if the samples were coated in precipitation or dispersion polymerizations of aniline. The PANI coating produced in dispersion polymerization performed slightly better, despite the thinner, albeit more uniform, coating of the substrate with PANI.⁶

This result was supported by the observation that the repeated coating of wood with PANI, providing a thicker coating,²⁴ did not lead to a marked improvement of the sample stability (Table I).

A similar deposition of related polymers, polypyrrole and poly(1,4-phenylenediamine), under corresponding reaction conditions performed similarly during flame or heat exposure. This leads us to conclude that the coating of cellulose fibers with a polymer film is of importance, whereas the details of its chemical nature play a secondary role.

The scantlings penetrated with a PANI colloidal dispersion briefly (dipping for 5 s) or for a longer time (soaking for 1 h) performed much worse than *in situ* deposited PANI. When placed in the flame, they were more stable than the untreated wood. After a longer exposure, however, they often burned to ashes. This especially applied to the soaked samples. The inferior protection of wood was even better illustrated by the samples exposed in the furnace to 600°C. The samples coated with PANI converted to charcoal, whereas those penetrated with colloidal forms of PANI ignited and burnt, practically without leaving any residue (Table I). The organic polymer used for the stabilization of colloids, PVP, was probably responsible for the easier ignition. The dispersions stabilized with colloidal silica also failed to enhance the wood resistance against fire. The latter experiments show that the coating of cellulose fibers is needed for the improved stability of wood in flame, whereas a mere penetration of

TABLE I
Effect of the Surface Modification of Wood Scantling on the Mass Loss After Exposure to a Flame or Elevated Temperature in the Furnace

Coating	Mass loss (wt %) ^a				
	In a flame			In a furnace for 2 h	
	2 min	4 min	6 min ^b	400°C	600°C ^b
Uncoated wood	78	91	97 A	90	95 A
<i>In situ</i> deposited PANI					
Standard ¹⁸	63	71	74 C ^c	72	87 C
Double coating	67	71	73 C	65	88 C
In 1.2M HCl	70	73	75 C	61	88 C
In 0.4M H ₃ PO ₄	45	64	67 C	61	81 C
In 1.2M H ₃ PO ₄	57	60	62 C^c	65	76 C
PVP-stabilized dispersion ³	70	73	76 C ^d	66	82 C
Silica-stabilized dispersion	59	66	70 C	67	85 C
Other <i>in situ</i> deposited polymers					
Polypyrrole	67	72	75 C	63	84 C
Poly(1,4-phenylenediamine)	63	67	69 C	72	87 C
Treatment with colloidal PANI dispersions					
PVP-stabilized, dipping	72	77	84 C	69	99 A
PVP-stabilized, soaking	65	69	71 A ^d	70	99 A
Silica-stabilized, dipping	68	72	78 C	74	88 A
Silica-stabilized, soaking	62	65	72 A	62	95 A

^a The lowest mass loss in the series is set in bold type; the highest is set in italics.

^b Wood burned to ashes (A) or converted to charcoal (C).

^c A micrograph of the residue is shown in Figure 5.

^d A micrograph of the residue is shown in Figure 6.

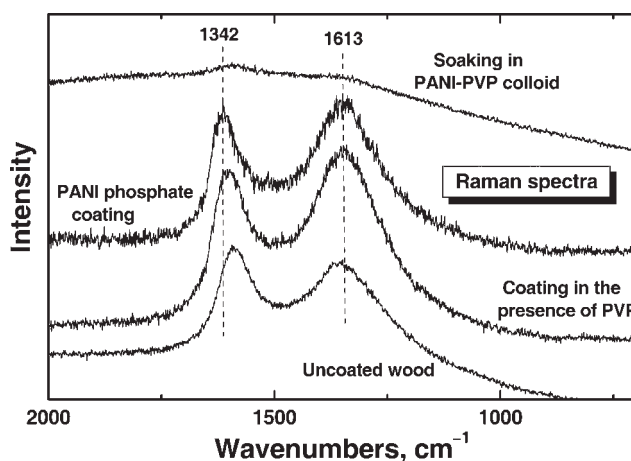


Figure 1 Raman spectra of the residues after 2 h at 600°C.

the space between fibers with PANI does not provide a desirable effect.

Spectroscopic characterization of residues

The residues after the burning of wood can be conveniently analyzed with the help of FTIR and Raman spectroscopy. Raman spectra are especially useful for discussing the conversion of an organic material into a carbon-like one. Raman scattering of the excitation radiation takes place only at the very surface of a polymer coating, and the effective penetration depth is smaller than that of an ATR-FTIR experiment. The Raman spectra of the residues after 2 h at 600°C of uncoated wood (Fig. 1) are dominated by two so-called G (graphitic) and D (disordered) bands,²⁵ which are typical of carbonaceous materials. The Raman spectrum of the residue of uncoated wood has two bands with maxima at 1588 and 1356 cm^{-1} with a relatively high radiation baseline. Their positions in the spectra of the PANI base treated at the same tem-

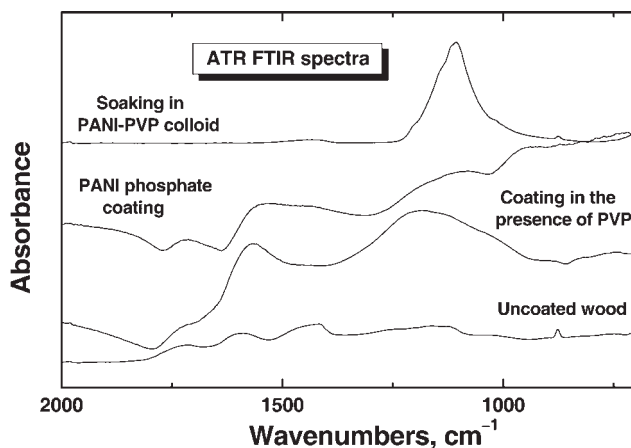
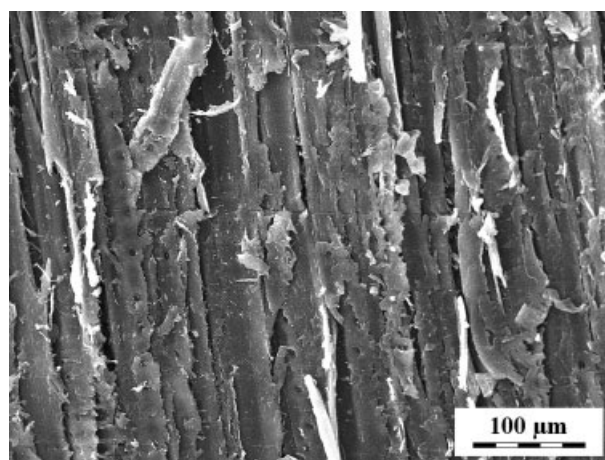


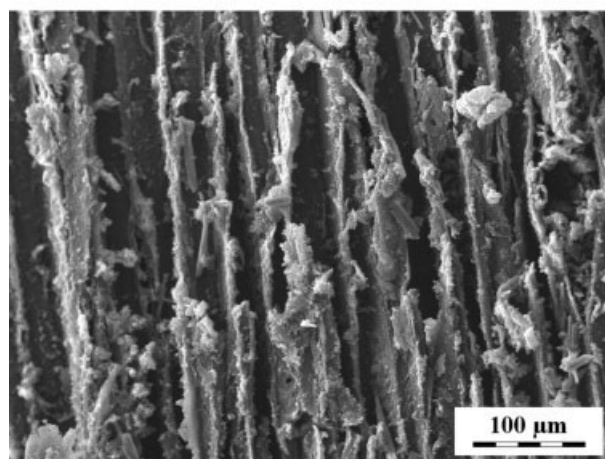
Figure 2 Infrared spectra of the residues after 2 h at 600°C.

perature are 1598 and 1366 cm^{-1} .²⁶ Wood coated with PANI during either precipitation or dispersion polymerization yielded a residue having a spectrum with the two peaks situated at 1613 and 1342 cm^{-1} . This means that the surface of the residue is not composed only of carbonized PANI but has a more complex, possibly composite nature. The absence of similar peaks in the spectra of the residue of wood soaked in a PANI colloidal dispersion confirms the absence of carbonaceous components and suggests that the ash is composed mainly of inorganic oxides.

As expected, the FTIR spectra of the residues are relatively featureless (Fig. 2). The presence of the bands at 1715, 1593, 1423, 1172, 1120, 1023, and 876 cm^{-1} in the spectrum of the residue of uncoated wood signifies that the structure of the wood has not been completely destroyed. These bands correspond to the spectrum of cellulose,²⁷ particularly to various COO stretching and CH₂ bending and wagging vibra-



(a)



(b)

Figure 3 Surface of wood (a) before and (b) after the coating with PANI. The wood was coated by immersion in a reaction mixture containing 0.2M aniline hydrochloride and 0.25M ammonium peroxydisulfate.

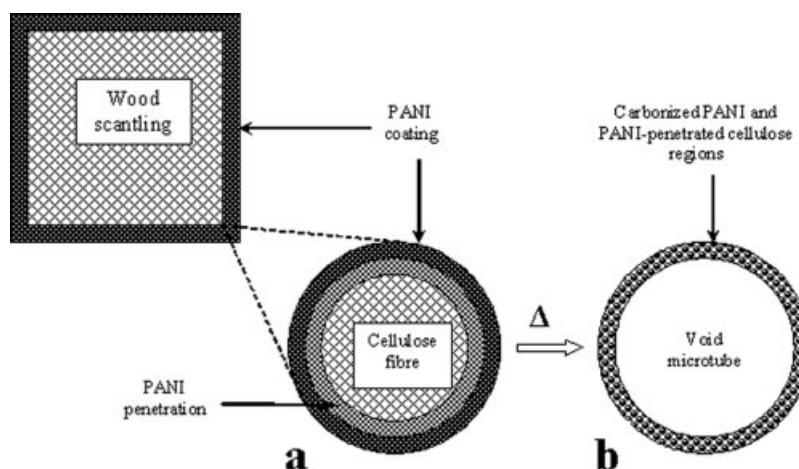
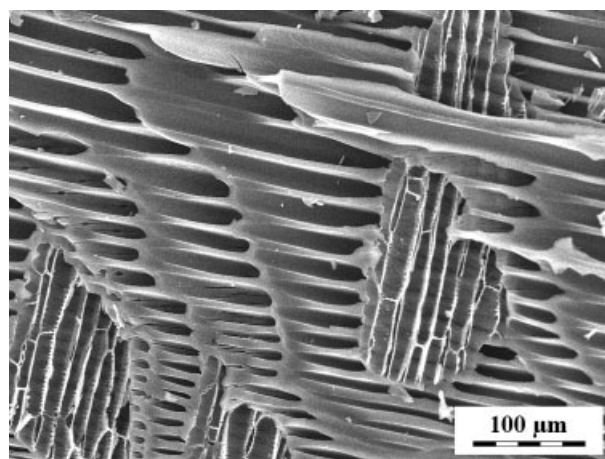


Figure 4 The surface layer of wood scantling, penetrated with an aqueous reaction mixture containing aniline and peroxydisulfate, contains PANI after the polymerization of aniline. (a) The cellulose fibers in this region are coated with a thin PANI film, and PANI also penetrates the interior of the fibers. (b) The PANI coating becomes carbonized at elevated temperatures, and the fiber interior converts to gases, leaving carbon microtubes as a result. The microtubular layer on the surface of the wood provides protection against burning.

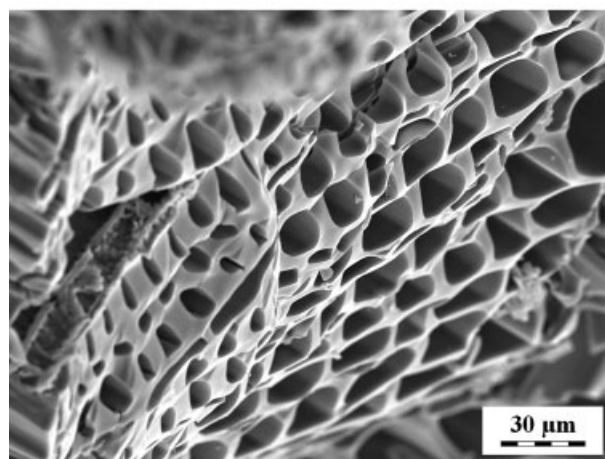
tions. The broad and intensive band with a maximum at 1025 cm^{-1} corresponds to C—O stretching vibrations. The peak at 876 cm^{-1} is most likely connected to the asymmetric out-of-phase ring-stretching vibration. The spectra of the residues of PANI-coated samples correspond to the superposition of the spectra of the carbonized PANI base²⁶ and thermally treated cellulose.²⁸ The spectrum of the residue of wood soaked in a PVP-stabilized PANI colloid displays a dominating peak at 1105 cm^{-1} , reflecting the presence of Si—O bonds or similar bonds in inorganic oxides.

Concept of flame-retardant performance

On the basis of the aforementioned results, we propose the following explanation for the role of PANI coatings. During the *in situ* deposition of PANI, the fibers constituting the wood structure become coated with a PANI film (Fig. 3). Macroscopically, the coating extends approximately 1 mm into the scantling body (Fig. 4). Microscopically, the fibers in this region are coated at the surface, but PANI partly also penetrates the fiber interior; the aqueous polymerization mixture is expected to diffuse easily into the hydrophilic cellulose fibers. When the sample is placed in a flame or exposed to an elevated temperature, the cellulose interior of the fibers disintegrates, and the PANI-containing surface becomes carbonized.^{17,26} Thus, carbonaceous microtubes are produced (Fig. 5). On the macroscopic level, the surface microtubular layer of carbonaceous material provides heat insulation by restricting heat convection and restricts the transport of oxygen to the sample interior. That is why a wood block converts to charcoal rather instead of burning to ashes. Coating the fibers is thus an essential prerequisite to obtaining the flame-



(a)



(b)

Figure 5 Residue of wood coated with (a) PANI hydrochloride and (b) PANI phosphate after burning in the flame.

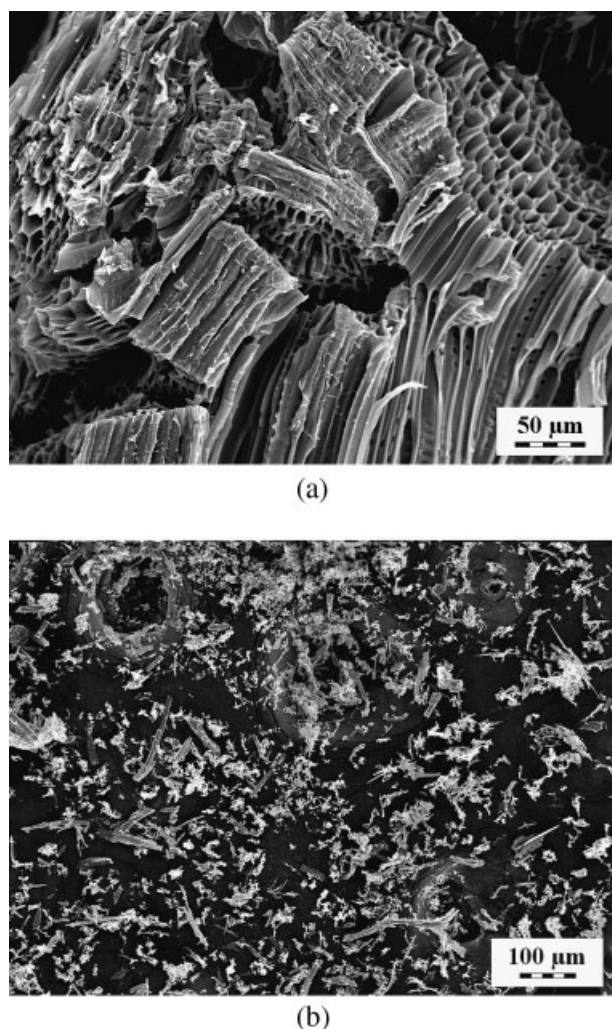


Figure 6 Residue of the wood (a) coated with PANI during the dispersion polymerization of aniline and (b) soaked in the PANI dispersion after polymerization for 1 h after exposure to 600°C for 2 h.

retardant effect. The thickness of the coating is of secondary importance.

Coating in dispersion polymerization and soaking in PANI colloids

Mere penetration with a PANI colloid does not provide a similar performance (Table I) because the cellulose fibers are still exposed to the external environment and are prone to oxidation and burning. This is illustrated by the following experiment. The wood scantling was placed in the reaction mixture used for the production of the colloidal PANI dispersion stabilized with PVP.³ During the polymerization, a thin PANI layer was deposited on the cellulose fibers in contact with the reaction medium. In the rest of the reaction mixture, a PANI colloid was produced and separated. After the exposure of dry PANI-coated wood to 600°C,

the sample converted to porous charcoal (Fig. 6) and had good stability in the flame (Table I). When the wood was just soaked in the colloidal PANI dispersion after the polymerization, the sample exposed to the same temperature burned completely (Fig. 6), practically without leaving ashes (Table I). Also in a flame, the mass loss was higher, although here the difference in the behavior of the two types of samples was less marked.

PANI-coated wood sawdust

The electric stability of PANI phosphate at elevated temperatures belongs to the best among PANIs protonated with various acids.²⁹ When pellets of compressed uncoated sawdust were placed in a flame for 1 min, as with the scantlings, the mass loss was 93 wt %. The samples were smoldering after their removal from the flame and, if left in air, completely converted to ash. The pellets of sawdust coated with PANI phosphate (20 wt %) lost much less mass under the same conditions (58 wt %) and self-extinguished after being removed from the flame. The pellets kept their integrity, but in a flame, blisters were formed on their surface, accompanied by cracking sounds and jumping. This experiment illustrates the improved stability of wood after PANI coating; if the wood burnt completely and the residue were formed by carbonized PANI, the mass loss would be well above 80 wt %.

The surface coating of cellulose materials with conducting polymers, such as PANI, thus may improve their resistance to being burned. When cellulose fibers coated with a conducting polymer are used as fillers in composites with various commodity polymers,¹⁴ the flame retardancy expected on the basis of these experiments can be regarded as a new value-added property of such materials.

CONCLUSIONS

Wood scantlings were coated with PANI during the *in situ* polymerization of aniline. The mass loss of PANI-coated wood exposed to a flame or an elevated temperature in a furnace was in all cases lower than that of the original uncoated samples. Moreover, the conversion of coated samples to charcoal was observed, whereas the original samples burned to ashes. The thicker PANI coatings produced during the precipitation polymerization and the thinner coatings obtained during the dispersion polymerization had comparable effects. The PANI phosphate coating performed better than an analogous hydrochloride overlayer. A similar flame-retardant effect after the wood was coated with related polymers, polypyrrole and poly(1,4-phenylenediamine), was also demonstrated. The improved heat stability of wood sawdust coated with PANI was reported. The soaking of wood

scantlings in colloidal PANI dispersions, however, had little effect or even a detrimental effect and was definitely inferior to the *in situ* deposition of PANI.

It is proposed that the burning of PANI-coated cellulose fibers yields a microtubular, carbonaceous structure at the surface layer of the wood and that this restricts the transfer of heat and oxygen to the sample interior; this reduces the flammability of the wood and improves the resistance to disintegration of the wood at elevated temperatures.

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