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Polymerization of pyrrole on cellulose fibres using a $FeCl_3$ impregnation- pyrrole polymerization sequence

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Abstract

Polypyrrole was polymerized on the surface of cellulose fibres using a sequence of fibre impregnation in $FeCl_3$ solutions, thickening and re-dispersion in a pyrrole solution. ζ-Potential and adsorption isotherms of the $FeCl_3$-cellulose systems showed that the adsorption of iron III was associated with the formation of free Fe^{3+} cations in the impregnation liquor. Moreover, under the test conditions applied, the amount of adsorbed iron III was not sufficient to promote the polymerization of a adequate amount of pyrrole on the fibre surface. Optimization of the polymerization reaction required that the $FeCl_3$ concentration in the impregnation liquor be increased to approximately 1 mol/l with a subsequent decrease of pH to approximately1.8. Based on scanning electron (SEM) micrographs and the low cellulose polymerization degree measured after pyrrole polymerization, we concluded that the decrease in the electric resistance of bulky polypyrrole/cellulose compounds was associated with a not negligible degradation of the cellulose fibres due to acid hydrolysis and the subsequent impossibility to prepare hand sheets with modified fibres due to the insufficient strength of the wet fibre network. The results of this investigation bring into question the use of $FeCl_3$-pyrrole-cellulose systems for the elaboration of conducting paper sheets with good and stable mechanical properties.

Introduction

During the last decade, the focus on the use of intrinsic conducting polymers (ICP) in organic electronics devices has led to the development of a totally new class of smart materials. These have been applied practically to the manufacturing of organic transistors and light-emitting diodes (Carpi and De Rossi 2006), functional textiles (Dall'Acqua et al. 2004; Lin et al. 2005), organic electrodes (Otero and Cantero 1999; Schultze and Karabulut 2005), coatings for fuel cells and corrosion protection (Bouzek et al. 2001; Breslin et al. 2005) and biosensors (Gerard et al. 2002). Polypyrrole, one of the ICPs that has attracted the interest of researchers, is characterized by a good electrical conductivity and a relative ease of synthesis. Pyrrole can be polymerized by electrochemical oxidation on metallic substrates or by chemical oxidation (Diaz and Bargon 1986), and its conducting properties, in terms of conductivity and environmental stability, can be adjusted by doping the polymer with anionic surfactants (Omastova et al. 2003; Sik Jang et al. 2004; Song et al. 2004). Furthermore, some polypyrrole properties (and those of ICPs in general) i.e. volume, surface energy and ionic conductivity depend on the polymer redox state. The subsequent application of a bias current to a polymer film can induce both a hydrophobic to hydrophilic transition and a volume variation. This unique behaviour has recently been used to electrochemically induce fluid movement in polypyrrole-coated capillaries (Causley et al. 2005) and to develop artificial muscles (Careem et al. 2004; Otero et al. 2004).

In the wake the interest shown by the microelectronics industry for ICPs, that of the textile and paper industries for the wide range of new functionalities of ICPs has increased progressively during the past 5 years. Conductive fabrics from natural (wool and cellulose) (Dall'Acqua et al. 2004; Varesano et al. 2005) and synthetic (Lin et al. 2005) fibres have been elaborated by polymerizing in situ pyrrole using ferric compounds as oxidizing agents. Moreover, conducting cellulose fibres have been obtained by fibre encapsulation with a polypyrrole film (Huang et al. 2005; Johnston et al. 2005a, b), thus showing that conductive paper sheets can be prepared by the polymerization of pyrrole on the surface of cellulose fibres using ferric chloride as oxidizing agent (Huang et al. 2006). Most of fibre modification studies have been conducted by adding pyrrole and ferric chloride to a fibre suspension, with $FeCl_3$ concentrations up to 1 mol/l and a polymerization time of approximately 2–15 h. However, due to the presence of a strongly acid aqueous medium and the relatively long polymerization time, cellulose can be subjected to acid hydrolysis and fibre degradation. Nevertheless, in most of the cited studies, pyrrole is polymerized in the bulk solution, with a large fraction of the polymer remaining dispersed in the liquid phase and cellulose degradation by $FeCl_3$ rarely mentioned as a significant side-effect of the fibre modification reaction.

The aim of this work was (1) to elaborate conducting fibres by polymerizing pyrrole on papermaking fibres by a $FeCl_3$-pyrrole impregnation sequence in order to promote the selective polymerization of pyrrole on the fibre surface and (2) to evaluate the consequence of this treatment on fibre degradation and to determine if cellulose polypyrrole compounds can actually be used for the manufacturing of conducting paper sheets.

Experimental

Adsorption of ferric ions on cellulose

α-Cellulose (Sigma-Aldrich, St. Louis, Mo.) was washed with a pressurized jet of deionized water on a 115-mesh wire screen in order to remove most of fine elements. The fibre fraction was then collected and dried at 95°C overnight. Cellulose fibres were dispersed at 10 g/l in a 10^{-2} mol/l solution of NaCl and used to prepare a set of 10 g/l fibre suspensions. Iron chloride (Sigma-Aldrich, 99%) was added to the fibre suspension in order to obtain concentrations ranging between 10^{-6} and 5×10^{-3} mol/l. After 3 h under gentle stirring, 10 ml of the fibre/$FeCl_3$ solutions were sampled and centrifuged. A 2 mol/l KSCN solution (2 ml), HCl (1 ml at 30%), distilled water (1 ml) and a 50:50 acetone:methyl-ethylcetone solution (1 ml) were added to 5 ml of the supernatant, and the residual concentration of Fe^{3+} was dosed by colorimetric titration at 480 nm (Charlot 1961).

Fibre/$FeCl_3$ solutions were also filtrated through a 45-μm wire screen, and a ζ-potential analyzer (model 2000; Malvern Instruments, Malvern, UK) was used to measure the electrophoretic mobility of the cellulose fine elements in the filtrate. Three consecutive measurements were taken for each sample at room temperature; these were averaged and the ζ-potential calculated from electrophoretic mobility data using the Smoluchowski equation. ζ-Potential measurements were repeated on fibre/HCl solutions with HCl concentrations ranging between 2×10^{-6} and 5×10^{-3} mol/l in order to compare the contribution of surface protonation and Fe^{3+} adsorption to the ζ-potential of cellulose fines under acid conditions.

The total charge density of the fibres was determined by conductimetric titration. The ionizable groups on the cellulose were first converted to their Na form by treatment with 0.01 mol/l NaOH, following which the fibres were washed with deionized water until the water had a conductivity lower than 8 μS/cm. The fibre suspension (10 g/l) was then titrated with 10^{-3} mol/l HCl. The fibre charge was found to be 54×10^{-3} mol of equivalent/g.

Polymerization of pyrrole on cellulose

Cellulose fibres were re-dispersed at 10 g/l in $FeCl_3$ solutions ranging in concentration from 1×10^{-3} to 1.1 mol/l. After approximately 3 h under stirring the suspension was filtrated on a porosity-4 glass filter, and a 50% consistency fibre mat was recovered and dispersed in 45 ml of 1 g/l (0.016 mol/l) pyrrole (Sigma-Aldrich, 98%) solutions. After impregnation in a 0.53 mol/l $FeCl_3$ solution and filtration, cellulose fibres were also dispersed in 2, 4 and 8 g/l pyrrole solutions. Polymerizations were run under gentle stirring at room temperature for 20 h.

Cellulose fibres/polypyrrole suspensions were washed with a pressurized jet of deionized water on a 115-mesh wire screen and the washing water recovered and filtrated on a 0.22-µm Millipore membrane in order to recover bulk polypyrrole and cellulose fines. Both fibre and fine fractions were dried at 95°C overnight, weighed and characterized by Fourier transform infrared (FT-IR) (model Paragon 1000; Perkin-Elmer, Foster City, Calif.) scanning electron microscopy (SEM) (model FEI, Quanta 200) and DSC (TA, Q100) analysis. The viscosity of α-cellulose dissolved in cupriethylendiamine (TAPPI 1976) solutions before and after impregnation with $FeCl_3$, thickening and re-dispersion was measured using an Ubbelhode capillary viscometer in order to evaluate the effect of ferric chloride on cellulose hydrolysis. Hand sheets were also prepared using a Rapid-Köthen former in order to evaluate the mechanical properties of paper sheets obtained from modified fibres.

Electrical properties

The contribution of fibre modification on the electrical properties of the bulky cellulose/polypyrrole compound was evaluated on 1.3-cm-diameter, 200 ± 10-µm-thick pellets prepared by compacting 200 mg of the fibre/polypyrrole fraction at 0.74 GPa during 2 min. The electric resistance of the pellets was measured after a 1-week storage at room temperature (23°C, 50% RH) by applying an increasing pressure to steel electrodes in order to minimize the contribution of internal porosity and to optimize the electrode/pellet contact. The scheme of the experimental setup used for resistance measurements is shown in Figure 1.

Iron speciation in solution

The speciation of iron III in solution was calculated using the PHREEQ-2 code (Parkhurst 1999) on a personal computer. This code is made available at no charge by its author on the website: wwwbrr.cr.usgs.gov/projects/GWC_coupled. PHREEQ-2 includes Debye Hückel expressions to account for the non-ideality of aqueous solutions. We used the standard database of PHREEQ-2. pH calculations were straightforward with PHREEQ-2. The initial pH (i.e. before the introduction of $FeCl_3$) was set to 5.7 to account for the initial pH of the de-ionized water. At those concentrations where the calculation lead to a positive saturation index with regard to solid amorphous $Fe(OH)_3$, we made a second calculation

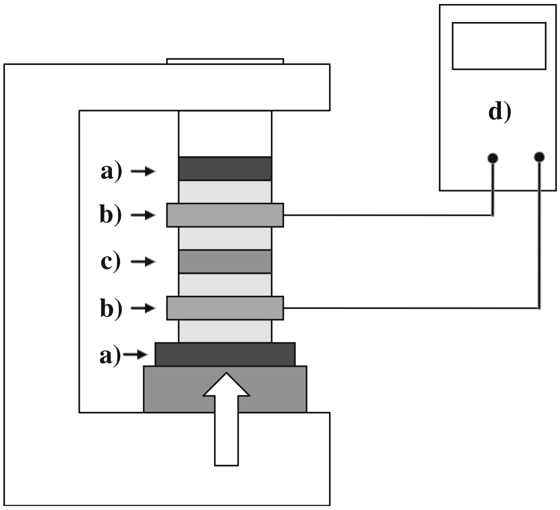

Figure 1. Scheme of the experimental set-up used to evaluate the resistance of bulky cellulose/polypyrrole compounds. The *arrow* indicates the force used to compress pellets during resistance measurements. (a) Polyethylene insulator spacers, (b) steel electrodes, (c) cellulose/polypyrrole pellet, (d) digital multimeter.

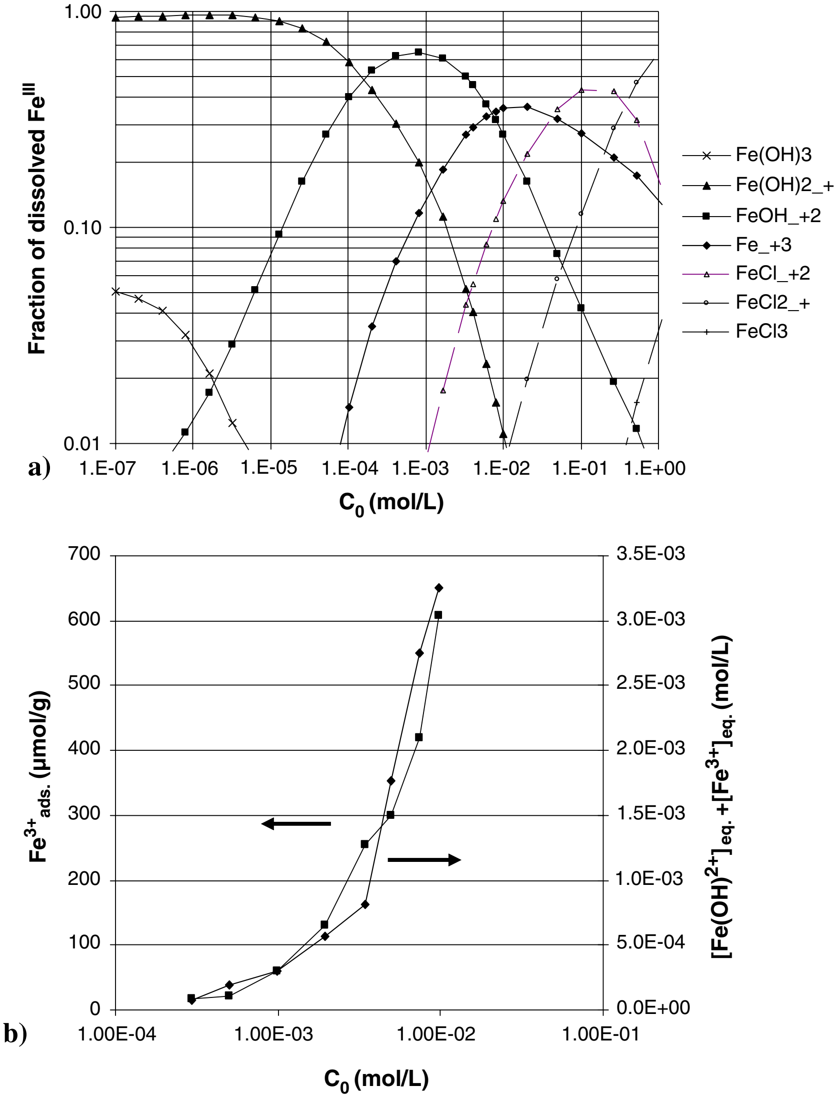

Figure 2. Adsorption of iron III on cellulose fibres. (**a**) Iron III speciation in $FeCl_3$ aqueous solutions plotted against equilibrium concentration, (**b**) adsorption of iron III on cellulose and the concentration of dissolved Fe^{3+} plotted as a function of the $FeCl_3$ concentration.

to include equilibrium with $Fe(OH)_3$. We verified that this did not significantly modify the pH. As the calculated pH was found to be in good agreement with the experimental one, we consider that the sorption of Fe(III) species on cellulose does not significantly modify the pH.

Fe(III) speciation calculations were performed considering the actual pH and Fe(III) concentration in solution. We verified that the supersaturation index is negative, so precipitation of $Fe(OH)_3$ has not to be considered.

Results and discussion

Adsorption of ferric ions on cellulose

Fe(III) forms aquo-hydroxo complexes in aqueous solutions (Baes and Mesmer 1986; Jolivet 2000), such as: $Fe(H_2O)_6^{3+}$ (Fe^{3+}), $Fe(H_2O)_5(OH)^{2+}$ ($Fe(OH)^{2+}$), $Fe(H_2O)_4(OH)_2^{+}$ ($Fe(OH)_2^{+}$), $Fe(H_2O)_3(OH)_3^{0}$ ($Fe(OH)_3^{0}$). In the presence of Cl^- ions, chloro complexes are also present (Högfeldt 1982).

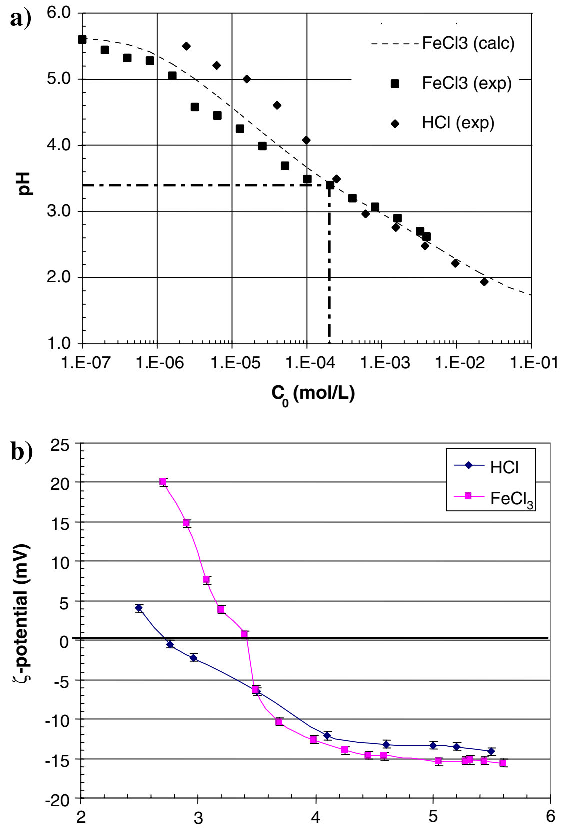

Figure 3. Comparison of fibre charge neutralization in the presence of $FeCl_3$ and HCl. (**a**) pH versus electrolyte concentration curves. The *dotted line* represents the pH values calculated at the equilibrium concentrations of Figure 2. (**b**) ζ-Potential versus pH plots of cellulose/$FeCl_3$ and cellulose/HCl systems.

Figure 2 shows that Fe^{3+} adsorption on α-cellulose starts at a total $FeCl_3$ concentration C_0 of approximately 3×10^{-4} mol/l (Figure 2a). Below this concentration, the concentration of free Fe^{3+} cations in $FeCl_3$/cellulose solutions is negligible compared to that of ferric tri- and di-hydroxides, and the increase in cellulose ζ-potential shown in Figure 3 can be associated with the weak adsorption of the ferric monohydroxo cation. For c_0 higher than approximately 3×10^{-4} mol/l, the concentration of Fe^{3+} both dissolved and adsorbed on cellulose fibres increases abruptly (Figure 2b), and the adsorption of Fe^{3+} cations on cellulose fibres is reflected by a slope increase in the ζ-potential versus $FeCl_3$ concentration curve and the neutralization/inversion of the cellulose surface charge. The adsorption closely follows the total concentration in highly charged species: $[Fe^{3+}]$ + $[Fe(OH)^{2+}]$ (Figure 2b). For $FeCl_3$ concentrations higher than 6×10^{-3} mol/l, first Fe^{3+} (up to 4×10^{-2} mol/l), then $FeCl^{2+}$ (up to 4×10^{-1} mol/l) become the most abundant dissolved cations. However, the excessive conductivity of cellulose/$FeCl_3$ solutions when the $FeCl_3$ concentration is above 4×10^{-3} mol/l does not enable reliable ζ-potential measurements to be obtained.

The comparison of fibre ζ-potential using $FeCl_3$ or HCl (Figure 3) shows a shift in the isoelectric point from pH 3.4 to 2.7, respectively, thereby showing the contribution of $Fe(OH)^{2+}$ and Fe^{3+} adsorption on fibre cationization compared to fibre protonation when in the presence of HCl (Stana-Kleinschek and Ribitsch 1998; Buschle-Diller et al. 2005). Although Figure 3 shows that α-cellulose does bear some negative charges above pH 2.7 (HCl) that emerge from the delignification process, the contribution of these negative charges to the adsorption process via electrostatic interaction is almost insignificant as their level (about 54×10^{-3} equivalent/g) is much lower than the iron III adsorption. With respect to the strong base behaviour of water compared to cellulose hydroxyls, iron interaction with cellulose surface hydroxyl groups is expected to occur via the adsorption of $Fe(OH)^{2+}$, Fe^{3+} or $FeCl^{2+}$ species formed in the bulk solution.

Figures 2 and 3 show that for sufficiently high $FeCl_3$ concentrations (for example, approximately 4×10^{-3} mol/l), ferric cations are adsorbed on cellulose fibres mainly as $Fe(OH)^{2+}$ and Fe^{3+}. Nevertheless, under the conditions tested the total amount of adsorbed ferric cations did not exceed approximately 600 μmol/g and, according to the stoichmetric polymerization reaction of pyrrole with Fe^{3+}, $2nFe^{3+} + n\mathrm{py} \rightarrow (\mathrm{py})_n$, only approximately 300 μmol/g (approx. 2% w/w) of pyrrole can actually polymerize on the fibre surface with adsorbed ferric ions. Cellulose fibres were therefore impregnated in $FeCl_3$ solutions of a concentration $>1\times10^{-3}$ mol/l (0.05, 0.27, 0.53, 1.1 mol/l) in order to have enough iron III adsorbed/retained on the thickened fibre mat to promote pyrrole polymerization.

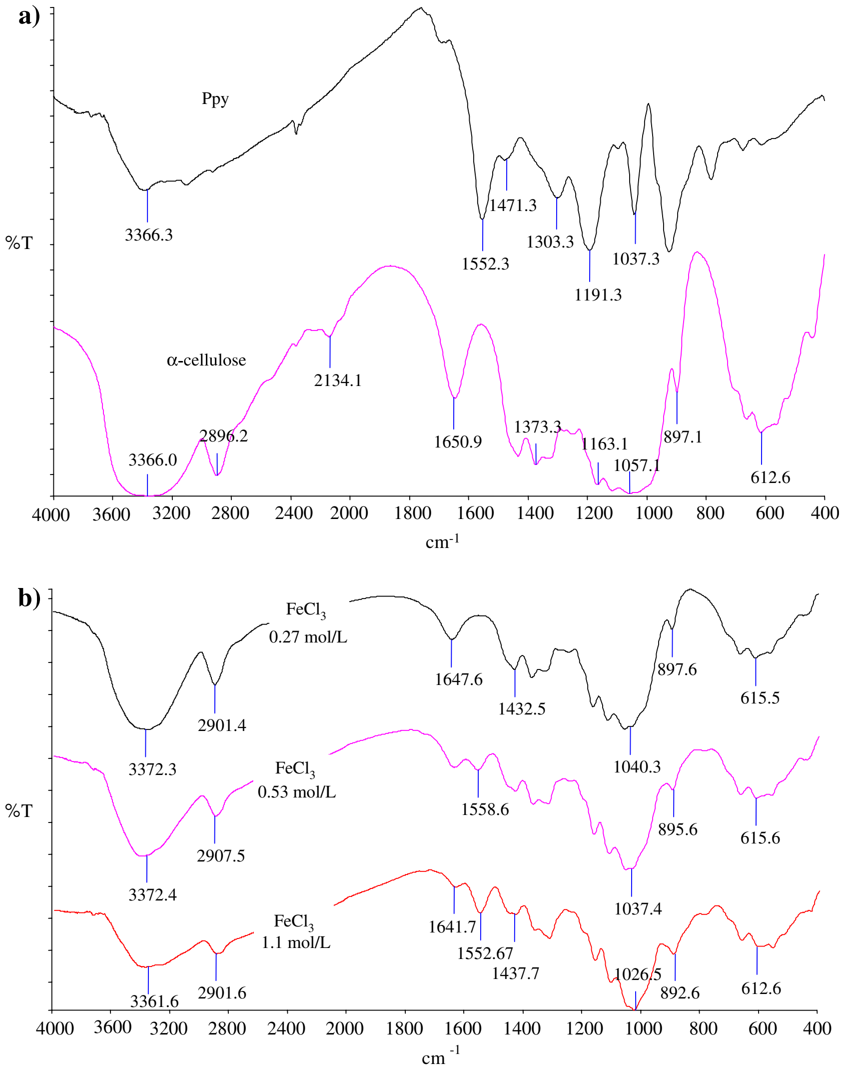

Figure 4. FT-IR transmission spectra of cellulose/polypyrrole systems. (**a**) Spectra of α-cellulose and polypyrrole, (**b**) Spectra of cellulose/polypyrrole compounds obtained for increasing concentrations of $FeCl_3$.

Polymerization of pyrrole on cellulose

FT-IR transmission spectra of polypyrrole and α-cellulose (Figure 4a) display similar absorption regions, except for the typical absorption due to the C=C ring stretching band of polypyrrole at 1552 cm^{-1} (Omastova et al. 2003). The transmittance intensity at 1552 cm^{-1} was therefore used to detect the presence of polypyrrole on cellulose fibres. For $FeCl_3$ concentrations ≤ 0.27 mol/l, cellulose fibres turned from white to grey within a few hours; however, there was no relevant detectable variation in light transmittance at 1552 cm^{-1}. Only when the $FeCl_3$ concentration was increased to 0.53 and 1.1 mol/l did an absorption peak that was proportional to ferric chloride dosage appear (Figure 4b).

Pyrrole polymerizations run at a fixed $FeCl_3$ dosage (0.53 mol/l) and with different pyrrole concentrations gave similar intensity bands at 1552 cm^{-1}, showing that the polymerization reaction was limited by the amount of oxidant adsorbed/retained in the fibre mat and not by the concentration of the monomer. Differential scanning calorimetry (DSC) analysis of modified cellulose supported the observations made from FT-IR spectra. An endothermic transition obtained for bulky polypyrrole at 255°C

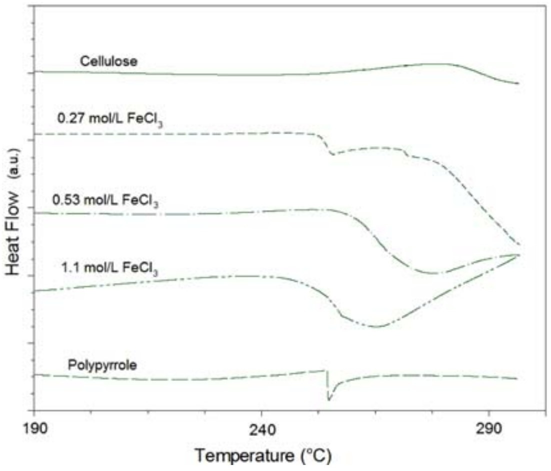

Figure 5. DSC analysis of α-cellulose and cellulose/polypyrrole compounds obtained with different $FeCl_3$ concentrations in the impregnation liquor.

(Dall'Acqua et al. 2004) was also observed for cellulose/polypyrrole compounds (Figure 5). The results of the FT-IR spectra analyses revealed that the increase in the $FeCl_3$ concentration was reflected by an increase in the peak area, while those of the FT-IR and DSC analyses of the cellulose/polypyrrole compound fine fraction (< 115 mesh) were in line with those of the fibre fraction, thus suggesting that pyrrole polymerization occurs mainly at the surface of cellulose fibres/fines without generation of bulky polypyrrole particles suspended in the polymerization liquor.

SEM images, in line with the FT-IR and DSC analyses (Figure 6), showed that pyrrole polymerization on the fibre surface is clearly detectable only for the highest $FeCl_3$ concentration. Indeed, for a $FeCl_3$ concentration of 0.53 mol/l, smooth polypyrrole films seldom appeared on the fibre surface (Figure 6c–d). For higher ferric chloride concentrations (1.1 mol/l), the fibre surface is homogeneously covered by spherical polymer particles (Figure 6e–f) with diameter of 0.64 μm (SD: 0.22).

The increase in polypyrrole amount on the cellulose fibres is also reflected by a decrease in the electric resistance of the compacted modified fibre pellets (Figure 7). The progressive formation of homogeneously distributed polypyrrole clusters on cellulose fibres when the $FeCl_3$ concentration is doubled (i.e. from 0.27 to 0.53 and 1.1 mol/l) induced a decrease in the electric resistance of the pellets by two orders of magnitude. The general drop in electrical resistance (approx. two orders of magnitude) obtained when the pressure applied on the electrodes was increased from approximately 0 to 0.15 GPa was associated with a decrease in the contact resistance of the electrode/pellets and with the internal porosity of the pellet. The modest resistance decrease (by a factor approx. three) observed when the applied pressure was increased from 0.15 to 0.37 GPa, however, was ascribed only to a decrease in the thickness of bulky pellets.

However, the resistance calculated (Omastova et al. 2003) for a polypyrrole 200 μm × 1.3-cm pellet (i.e. 9 mΨ) shows that modified cellulose prepared in this study still behaves as an insulator (Figure 7) and that both $FeCl_3$ and pyrrole dosage should be further increased to obtain conducting compounds.

Fibre degradation during pyrrole polymerization

Polypyrrole formation on the surface of cellulose fibres could only be obtained under extremely aggressive polymerization conditions: fibres were initially immersed for 30 min in concentrated $FeCl_3$ solutions where the pH ranged between 1.8 and 2 and during the subsequent 20-h polymerization the pH never exceeded 3. Figure 6 shows that this acid treatment degraded cellulose fibres and resembled that of enzymatic fibre degradation (Wang et al. 2006) in that the smooth and uniform surface of the untreated α-cellulose (Figure 6a, b) becomes rough and swollen and the fibres have a bent and twisted appearance (Figure 6c–f) after polymerization. When using $FeCl_3$ concentrations of 0.53 and 1.1 mol/l, the fibre fraction (>115 mesh) and fibre average diameter decreased from 83 to 53% and from 19 (SD: 7.4) to 15 μm (SD: 7), respectively. Figure 6b, f also shows that the 20% decrease in fibre thickness was associated with the presence of 0.4-μm diameter (SD: 0.1) fibrils parallel to the fibre axis. The efficient pyrrole polymerization was therefore supposed to be accompanied by the erosion of the fibre primary wall and presumably of the S1 layer in the secondary wall. Moreover, the relative viscosity, η/η_0, of cellulose/cupriethylendiamine solutions dropped from 3.8 to 1.9 (corresponding to a DP reduction from 475 to 190) and, when using polypyrrole-modified fibres to prepare hand

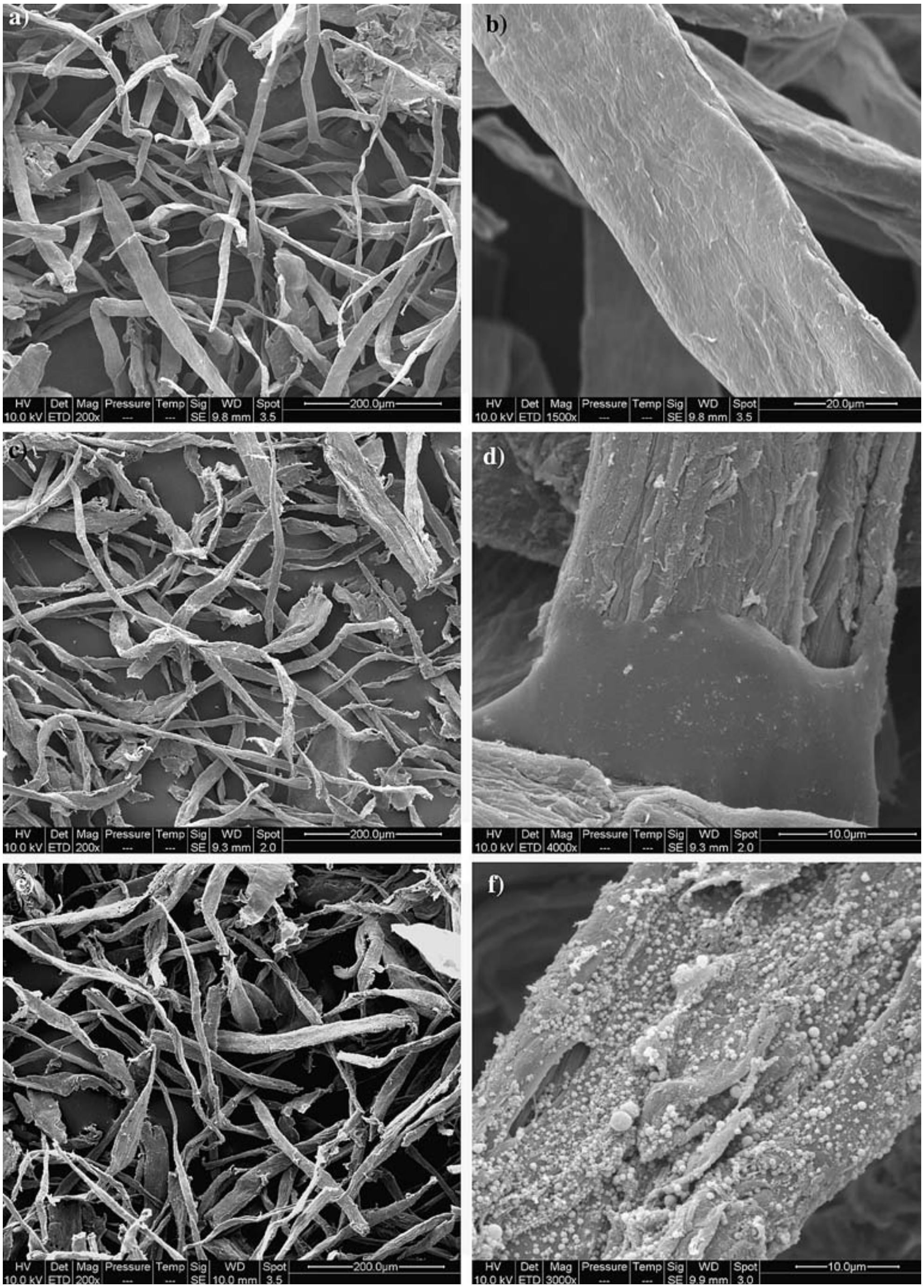

Figure 6. SEM images of cellulose fibres. (**a**) Not modified α-cellulose, 200×, (**b**) Not modified α-cellulose, 1500×, (**c**) α-cellulose modified using a $FeCl_3$ concentration of 0.53 mol/l during fibre impregnation, 200×, (**d**) α-cellulose modified using a $FeCl_3$ concentration of 0.53 mol/l during fibre impregnation, 4000×, (**e**) α-cellulose modified using a $FeCl_3$ concentration of 1.1 mol/l during fibre impregnation, 200×, (**f**) α-cellulose modified using a $FeCl_3$ concentration of 1.1 mol/l during fibre impregnation, 4000×.

sheets, the wet sheet did not display any mechanical resistance and it was not possible to transfer it from the absorbing paper to the dryer. This decrease in the wet fibre network resistance was ascribed to the high fines content in the modified fibre suspension and to a decrease in the inter-fibre

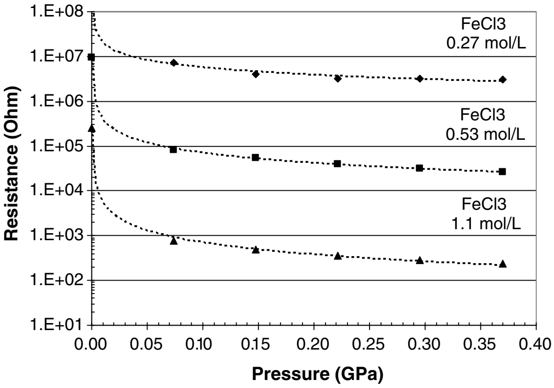

Figure 7. Resistance of 200-μm thickness cellulose/polypyrrole pellets plotted as a function of $FeCl_3$ concentration in the fibre impregnation solution and of the pressure applied on the electrodes.

hydrogen bonding due to the presence of polypyrrole clusters on the fibre surface.

Conclusion

The following general conclusions can be drawn from this investigation:

- Iron is adsorbed on cellulose fibres in $FeCl_3$ solutions as multivalent ferric compounds, thereby inducing fibre cationization; nevertheless, the amount of Fe^{3+} adsorbed/retained on fibres with ferric chloride concentrations lower than approximately 0.5 mol/l is not sufficient to promote pyrrole polymerization.
- Pyrrole polymerization on cellulose fibres when an impregnation/thickening procedure was applied was only possible when the $FeCl_3$ concentration in the impregnation solution was higher than 0.5 mol/l.
- A direct correlation was observed between $FeCl_3$ concentration in the impregnation solution, the generation of homogeneously dispersed polypyrrole clusters on the fibre surface and the electric resistance of modified cellulose pellets. Indeed, a low electric resistance was associated with the generation of 0.6-μm-diameter polypyrrole spheres on the fibre surface and with a high concentration of $FeCl_3$ in the impregnation solution.
- Cellulose fibres were exposed to a strongly acid medium during the impregnation and the polymerization sequence which induced the erosion of the fibre surface, the generation of fines elements and a drop in the polymerization degree of cellulose.

This investigation shows it is possible to use an impregnation/thickening sequence to promote pyrrole polymerization on cellulose fibres for the formation of a low-electric resistance cellulose/polypyrrole compound. Nevertheless, the strong degradation of cellulose fibres during fibre impregnation and pyrrole polymerization lead to the supposition that the application of this kind of treatment – and the use of $FeCl_3$ in general – for the polymerization of pyrrole and other conducting polymers, such as PEDOT, on cellulose does not allow elaboration of the cellulose fibre/polypyrrole compounds for the manufacture of conducting paper sheets with good mechanical properties and environmental stability.

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