Spectroscopic Study of the Modification of Cellulose with Polyethylenimines

M. U. de la Orden,[1] M. C. Matías,[2] J. Martínez Urreaga[2]

[1]*Departamento de Química Orgánica I, E. U. Óptica, Universidad Complutense de Madrid, Arcos de Jalón, S/N 28037 Madrid, Spain*
[2]*Departamento de Ingeniería Química Industrial y del Medio Ambiente, E.T.S.I. Industriales, Universidad Politécnica de Madrid, José Gutiérrez Abascal 2, 28006 Madrid, Spain*

ABSTRACT: The reaction of cellulose with polyethylenimines (PEIs) was studied using diffuse reflectance ultraviolet–visible (UV–vis) spectroscopy, diffuse reflectance FTIR spectroscopy, and standard colorimetry. PEIs were applied from aqueous solutions at the natural pH (pH $\sim$ 11) and at pH = 6. The obtained materials were exposed to different thermal treatments in air. Celluloses treated at pH = 11 suffer the reversible formation of amine bicarbonate salts. This reaction was not observed in celluloses treated at pH = 6 because of the protonation of the amine groups. In all treated celluloses, the PEI amine groups reacted with cellulose carbonyl groups at moderate temperatures to form Schiff bases, which were responsible for the yellowing of the material. At higher temperatures other oxidation products were detected in the UV–vis and infrared spectra. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2196–2202, 2004

Key words: cellulose; polyethylenimine (PEI); UV–vis spectroscopy; FTIR; modification

INTRODUCTION

Polyethylenimines (PEIs) are highly branched polymers with primary, secondary, and tertiary amine groups. In acidic or neutral pH conditions the amine groups are partially protonated and PEIs behave as cationic polyelectrolytes that can be easily bonded to negatively charged surfaces. Because of this cationic character, polyethylenimines have been extensively used in the last decades for controlling colloidal stability and surface properties in many application fields.[1–8] Polyethylenimines can be found in the manufacturing of coatings, adhesives, food packaging films, textile fibers, and medical devices. Other applications of pure and modified PEIs are wastewater treatment,[9] heavy metal recovery,[10–12] and polymer modification.[13]

One of the most important applications of PEIs can be found in the papermaking process. Most papers are made from mixtures of fibers, fines, fillers, and additives. In water dispersion most of these components are negatively charged, thus preventing coagulation and reducing the retention of colloidal particles in the sheet-forming process. The addition of cationic polyethylenimines causes the neutralization of the anionic charges in the colloidal dispersion, thus promoting the coagulation and retention of the particles and improving the separation from the liquid phase.[2–4]

In spite of the wide use of polyethylenimines in the manufacturing of cellulosic materials, the chemical interaction of PEIs with cellulose has been scarcely studied to the present. However, it is known that celluloses can react, in the appropriate conditions, with several amino compounds.[14–16] Another related reaction between reducing sugars and amino compounds such as amino acids or proteins, usually referred to as the Maillard reaction, plays a fundamental role in medicine and food technology and has been extensively studied.[17–19] On the other hand, we must take into account that a chemical interaction between cellulose and PEI can (1) be a way to obtain cellulose derivatives and (2) determine some properties of the final cellulosic material, such as the ageing behavior. For example, we have shown in a previous work that the treatment of celluloses with aminosilanes increases the rate of cellulose darkening during thermal ageing.[20]

In this work we studied the treatment in different reaction conditions of pure cellulose with two polyethylenimines, using diffuse reflectance spectroscopic techniques [ultraviolet–visible (UV–vis) and infrared]. The darkening of PEI-treated celluloses was measured using standard colorimetry. The aims of this study were to characterize the treatment process and to investigate the nature of the chemical reaction between cellulose and PEIs.

METHODS

Materials

The cellulosic material used was Whatman no. 41 filter paper (Whatman, Maidstone, UK). It is an almost pure cellulose, consisting of >99% cellulose. The only pretreatment was washing with distilled water and drying in air at 45°C for 24 h. Two commercial polyethylenimines were used: PEI-2 (Lupasol® PR 8515, active matter > 98%; M_w: 2000; CAS No.: 25987-06-8) and PEI-25 (Lupasol® WF, active matter > 99%; M_w: 25,000; CAS No.: 25987-06-8). Ratios of primary, secondary, and tertiary amines were 1 : 0.92 : 0.70 and 1 : 1.2 : 0.76 for PEI-2 and PEI-25, respectively. The two polyethylenimines were kindly supplied by BASF Española S.A. (Barcelona, Spain) and were used as received.

Cellulose treatment

Samples (1 g) of Whatman paper were immersed in 20 mL of PEI solutions in distilled water for 5 min. PEI concentration varied from 1 to 5 wt %. The treatments were carried out at two different pH values. When the pH was around 11, the natural pH of PEI solutions, the sample codes of treated celluloses were PEI-2b and PEI-25b. Samples PEI-2a and PEI-25a were obtained by treatment of Whatman paper in solutions of PEI and HCl of pH around 6. After washing with the solvent, all treated celluloses were oven-dried in air at 45°C for 24 h. The thermal treatments of the obtained materials were made in air.
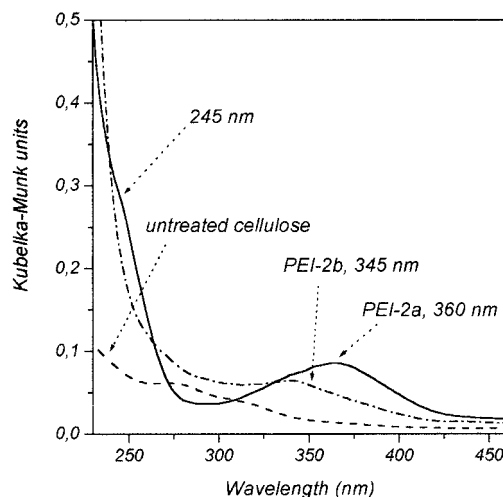
Spectroscopy

The diffuse reflectance Fourier transform infrared (DRIFT) spectra before and after treatments were recorded with a Mattson 3020 FTIR spectrometer (USA), using a Specac diffuse reflectance accessory. Each spectrum was recorded at a resolution of 4 cm^{-1}, with a total of 90 scans. The diffuse reflectance UV–vis spectra were obtained with a Shimadzu 2401 PC UV–vis spectrophotometer (Shimadzu, Kyoto, Japan), using a Shimadzu diffuse reflectance accessory, at 200 nm min^{-1}. All reflectance spectra were corrected according to the Kubelka–Munk function.

The color changes of treated celluloses were measured using a Minolta CM3600D spectrocolorimeter (Japan). Total color differences were calculated as

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \qquad (1)$$

where L^*, a^*, and b^* are the color coordinates in the CIE (Commission International d'Eclairage) 1976 color space. Each color difference reported in this article is the average of three measurements.

Figure 1 Diffuse reflectance UV–vis spectra of untreated cellulose and celluloses treated with 5% PEI-2, at pH = 6 (PEI-2a) and pH = 11 (PEI-2b).

RESULTS

UV–vis spectroscopy

Figure 1 shows the diffuse reflectance UV–vis spectra of the untreated Whatman paper and the celluloses treated with 5 wt % of PEI-2 at different pH conditions. All samples were dried at 45°C for 24 h. The two treated celluloses present strong absorptions below 240 nm, but the most characteristic absorption is a weak band that appears at about 345 nm in the PEI-2b spectrum and at about 360 nm in the PEI-2a spectrum. This last spectrum also presents a shoulder at about 245 nm. These bands, which do not appear in the original polyethylenimines, were also observed in the UV–vis spectra of celluloses treated with PEI-25.

The appearance of these new absorption bands reveals a chemical reaction between cellulose and polyethylenimines. To obtain additional information about the nature of this reaction, the PEI-treated cellulose samples were heated in air at different temperatures. Figure 2 shows the time evolution of the absorption spectra of PEI-2a samples subjected to heating at 120°C. The two absorption bands at 245 and 360 nm increase concomitantly with the heating time, revealing the progress of the reaction at this temperature, but no new absorptions could be detected. A similar result was obtained for PEI-2b samples. The yellow color detected in all PEI-treated samples after heating for 30 min at 120°C can be explained by the extension of the 345–360 nm band in the visible region of the spectrum.

A somewhat different result was obtained when the treated samples were heated at higher temperatures. Figures 3 and 4 give the UV–vis spectra of PEI-2a and PEI-2b, respectively, heated at 200°C for different times. Intense brown materials were obtained by this
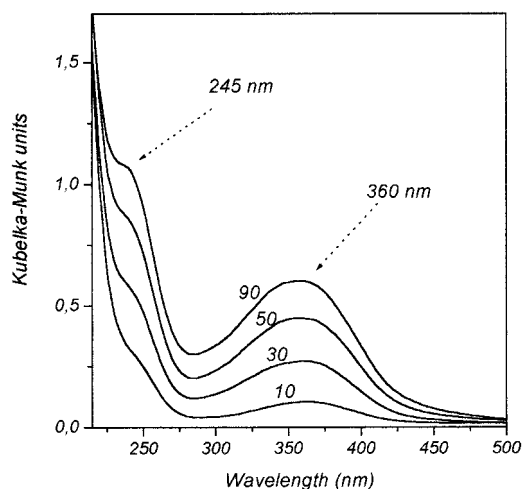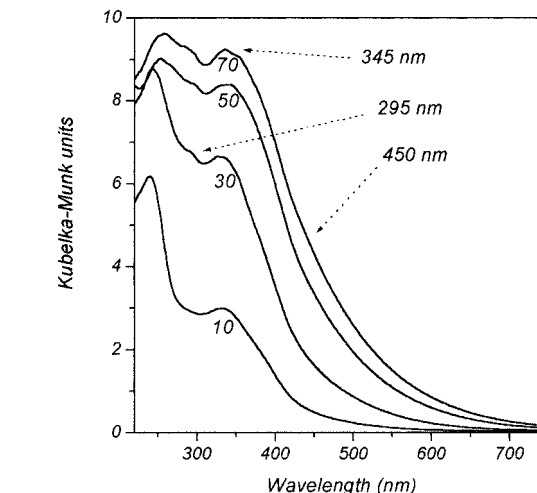
Figure 2 Diffuse reflectance UV–vis spectra of PEI-2a cellulose samples heated in air at 120°C for different times (in min).

Figure 4 Diffuse reflectance UV–vis spectra of PEI-2b cellulose samples heated in air at 200°C for different times (in min).

thermal treatment. Besides the two intense absorptions centered at 245 and 345–360 nm, the spectra of materials heated at 200°C for at least 30 min present two new absorption bands: a weak absorption at 295 nm, and a shoulder at about 450 nm, which contributes to the color of the heated materials. These bands reveal a new chemical reaction that occurs only when the PEI-treated samples are heated in air at high temperatures.
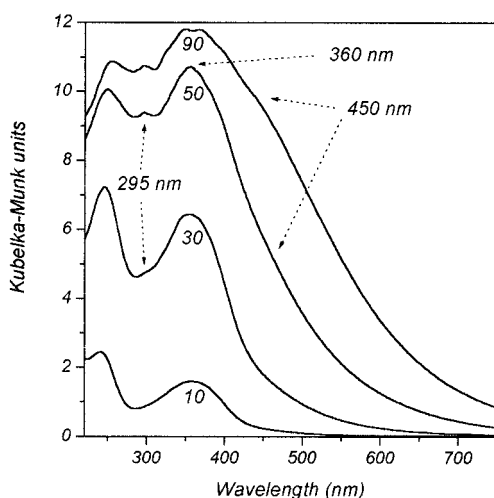
Infrared spectroscopy

The 1800–1400 cm^{-1} spectral region was chosen for monitoring the reaction process by DRIFT spectroscopy because of several advantages:

Figure 3 Diffuse reflectance UV–vis spectra of PEI-2a cellulose samples heated in air at 200°C for different times (in min).

- The disappearance of the PEI amine groups in the course of the reaction may be followed using the amine deformation modes that appear in this region.
- The cellulose matrix does not present strong interfering absorptions.
- Several possible reaction products, including imines, amine salts, amides, and other oxidized compounds, present characteristic absorption bands in this region.

Figure 5 shows the DRIFT spectra of untreated cellulose samples and samples treated with PEI-2 at natural pH, as well as the difference spectrum obtained by digital subtraction. The spectrum of PEI-2, included for comparison, presents two characteristic absorptions at 1465 (CH$_2$ bending) and 1600 cm^{-1} (δ_{N-H} corresponding to free primary amine groups). The weak N—H deformation mode, corresponding to secondary amines, was not detected. The shoulder at about 1650 cm^{-1} can be attributed to absorbed water. The difference spectrum, with three characteristic absorptions at 1490, 1570, and 1660 cm^{-1}, is clearly different from the spectrum of pure PEI-2. This difference reveals a chemical reaction that will be discussed later. Very similar spectra were obtained for pure PEI-25– and PEI-25–treated celluloses.
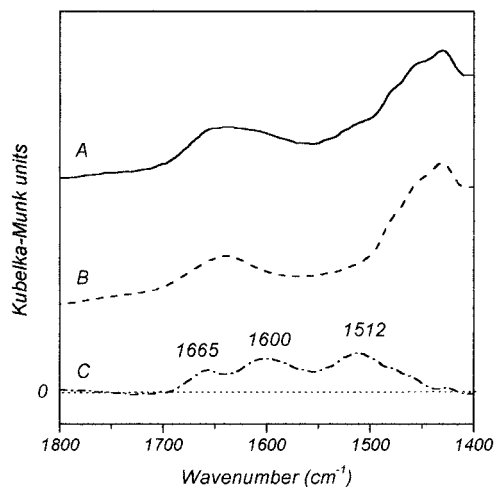
The above reaction was not detected in samples treated with PEIs at pH = 6 (Fig. 6). In this case the difference spectrum shows the two expected absorptions [i.e., two bands at 1600 (δ_{N-H}) and 1512 cm^{-1}]. The band at 1512 cm^{-1}, which was assigned to –NH$_3^+$ groups,[21] reveals that most of the primary amine groups are protonated when celluloses are treated in acid aqueous solutions of PEI.
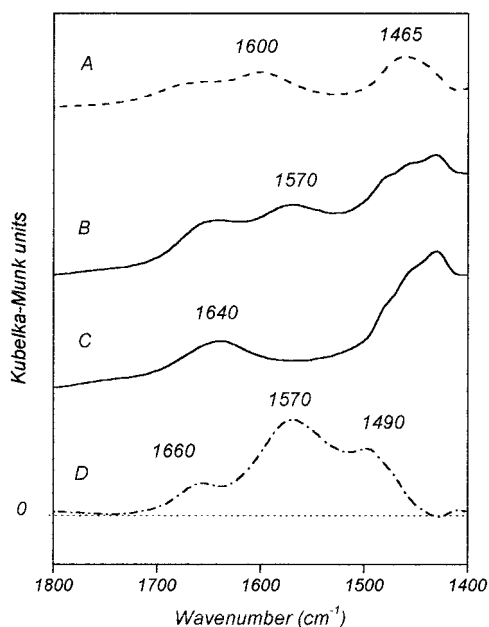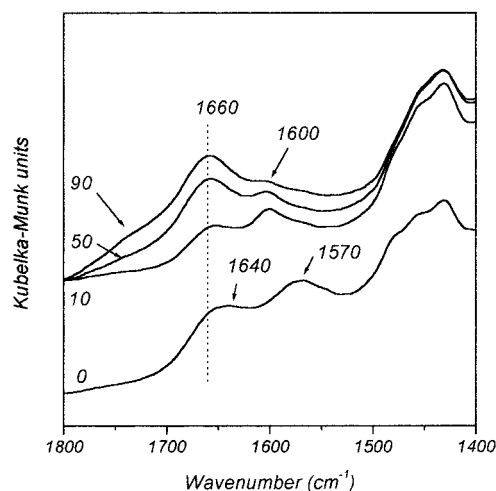
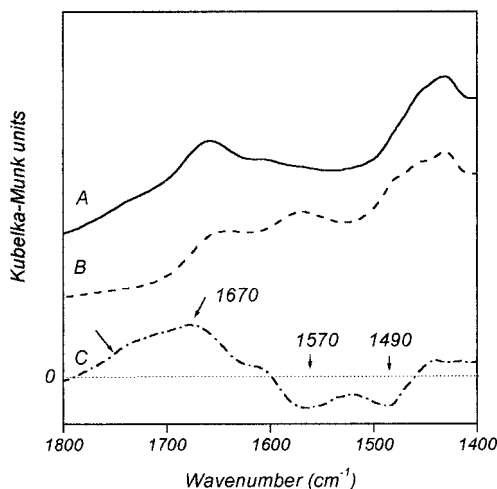**Figure 5** DRIFT spectra of: (A) PEI-2; (B) PEI-2b cellulose; (C) untreated cellulose. Curve D is the difference spectrum B − C.

Figure 7 DRIFT spectra of PEI-2b cellulose samples heated in air at 200°C for different times (in min).

The DRIFT spectra of PEI-treated samples heated in air at different temperatures were analyzed to investigate the chemical reactions between cellulose and PEI. Figure 7 depicts the DRIFT spectra collected after heating the PEI-2b samples at 200°C for different times.

In the first stage of the process, the 1570 cm^{-1} band decreases as the amine characteristic band at 1600 cm^{-1} increases. The two bands coexist after heating for 10 min [Fig. 7(B)], but the transformation is complete after heating for 20 min at 200°C. At lower temperatures this process is much slower; for example, at

160°C the transformation is complete only after heating the cellulose samples for 60 min.

The amine groups disappear in turn in a second stage of the heating process, as revealed by the gradual disappearance of the amine band at 1600 cm^{-1}. After heating for 90 min, most of the amine groups have been consumed in this irreversible way. At the same time, the 1640 cm^{-1} band of the unheated material shifts to 1660 cm^{-1}, revealing the development of a new absorption. Very similar results were obtained for celluloses treated at pH = 6.

This new band can be easily seen in Figure 8. The difference spectrum (Fig. 8, curve C) shows the disappearance of the original functionality of the PEI-treated cellulose (negative bands at 1570 and 1490 cm^{-1}) and the development of a new band a 1670

Figure 6 DRIFT spectra of: (A) PEI-2a cellulose; (B) untreated cellulose. Curve C is the difference spectrum A − B.

Figure 8 DRIFT spectra of: (A) PEI-2b cellulose heated in air at 200°C for 90 min; (B) PEI-2b cellulose. Curve C is the difference spectrum A − B.
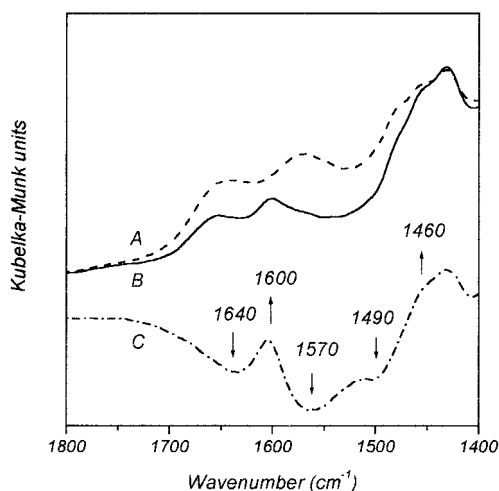
Figure 9 DRIFT spectra of: (A) PEI-2b cellulose; (B) PEI-2b cellulose heated in air at 200°C for 10 min. Curve C is the difference spectrum B − A.

cm^{-1}. Other new bands in the 1700–1800 cm^{-1} region could be detected only after heating for long times at high temperatures. For instance, they cannot be observed in PEI-treated celluloses heated at 120°C for 90 min (not shown).

DISCUSSION

The above spectroscopic results reveal that several chemical interactions take place between celluloses and PEIs during the drying and heating processes of PEI-treated materials.

The first transformation occurs in the drying of samples treated at natural pH. As can be seen in Figure 5, the difference spectrum attributed to the cellulose modification does not match the spectrum of pure PEIs. To explain this somewhat unexpected difference spectrum we must take into account that celluloses treated with basic PEIs will absorb carbon dioxide during the drying process in air, with formation of amine bicarbonates. Some years ago, Culler et al.[21] demonstrated that glass fibers treated with aminosilanes absorb CO_2 when the fibers are dried in air. When the silane was 3-aminopropyltriethoxysilane, it was found that 54% of the amine groups were converted to bicarbonate during the drying process in air. The percentage of salt formation was even higher when a diaminosilane (*N*-2-aminoethyl-3-aminopropyltrimethoxysilane) was used. The most characteristic infrared absorptions assigned by Culler et al. to the amine bicarbonate salts were the bands at 1488 and 1575 cm^{-1}. Thus the bands at 1490 and 1570 cm^{-1}, observed in the spectrum of celluloses treated with PEIs at natural pH (Fig. 5), indicate the formation of amine bicarbonate salts in the drying process. Culler et al. also reported that the salt formation is strongly

dependent on the pH of the silane solution. At low pH values no amine bicarbonate was detected because most of the amine groups are protonated. This is also in good agreement with our results: no evidence of salt formation was observed in the infrared spectra of celluloses treated at pH = 6 (Fig. 6).

Another evidence supporting the above hypothesis could be obtained from the infrared spectra of modified celluloses subjected to thermal treatments. It is well known that amine bicarbonate salts decompose under heating, with loss of CO_2 and H_2O, and regenerate the original amine groups. This is exactly the behavior observed when PEI-treated celluloses were subjected to heating, as can be seen in Figure 9. In Figure 9, spectrum A is the unheated sample, spectrum B is the PEI-2b sample heated for 10 min at 200°C, and spectrum C is the difference spectrum (A − B). This spectrum shows that the heating produces the loss of water (negative band at 1640 cm^{-1}), the disappearance of the amine bicarbonate salt (negative bands at 1570 and 1490 cm^{-1}), and the regeneration of the original amine groups (positive bands at 1600 and 1460 cm^{-1}).

The above reversible reaction cannot be responsible for the irreversible discoloration of PEI-modified celluloses caused by the thermal treatments. However, the infrared analyses (Figs. 7 and 8) of the process reveal other chemical transformations such as the disappearance of the amine groups during the thermal treatment (decrease of the 1600 cm^{-1} absorption).

To investigate the role of this reaction in the color formation, the variations during the thermal treatment of the amine content (measured as the area of the 1600 cm^{-1} band) and the color of PEI-treated samples (measured as total color difference, ΔE^*) were compared.
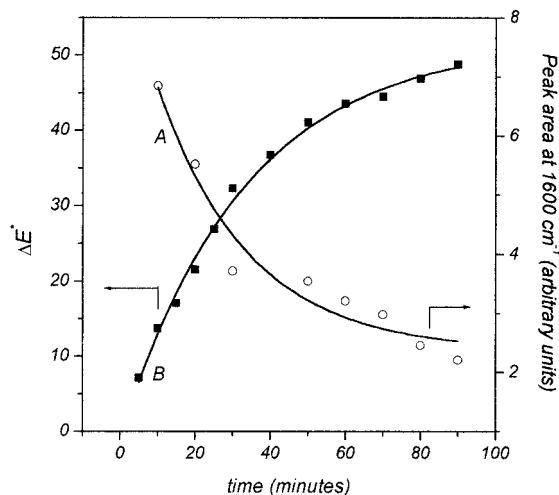
Figure 10 Time evolution of the peak area at 1600 cm^{-1} (curve A) and the total color difference (curve B) during the thermal treatment of PEI-2b cellulose samples at 200°C in air.
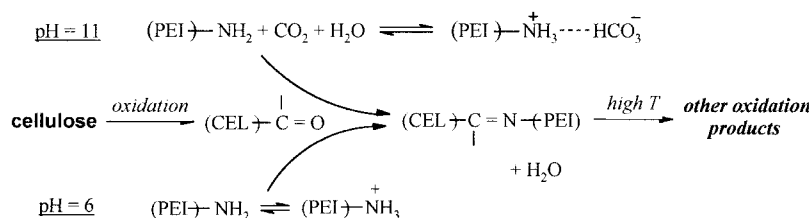
Scheme 1

The obtained result is shown in Figure 10. The good correlation observed reveals that the yellowing of PEI-treated samples during the thermal treatment is mainly attributed to a reaction involving the amine groups of PEIs.

Previously we showed that aminosilanes react with cellulosic materials with formation of imines.[15,16] In this case we also propose that imines (or Schiff bases), formed in the easy reaction of PEI amine groups with cellulose carbonyl groups, are responsible for the UV absorption bands (and the yellowing) detected in the PEI-treated celluloses. Taking into account that the carbonyl content in unheated celluloses is minimal, as can be deduced from the lack of noticeable absorption at 1730 cm^{-1} in the cellulose infrared spectrum [Fig. 5(A)], the carbonyl groups for this reaction must be produced during the cellulose oxidation.

There are several reasons that support the main role of imines in the yellowing of PEI-treated celluloses:

- It is well known that imines present UV–vis absorption bands corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. Many of these imines absorb in the 300- to 450-nm interval and are yellow compounds.[22,23] Moreover, several authors have shown that protonation of the imine groups causes a shift to the red in the corresponding UV–vis absorptions.[23,24] In our case the yellowing observed after moderate heating is attributed to absorption bands centered at 345 and 360 nm, for materials treated at pH values of 11 and 6, respectively.
- The infrared analysis of the reaction process reveals that one of the reaction products presents a characteristic IR absorption at 1665–1670 cm^{-1} (Figs. 6 and 8). This weak band may be assigned to imines (st. C=N).[23,24]
- The formation of imines has been observed in other reactions of cellulosic materials, such as the treatment of wood with liquid ammonia,[25] the ammoxidation of cellulose,[14] and the reaction of dialdehyde cellulose with nitrogen compounds.[26]
- Another similar process is the Maillard reaction. In the first stages of this complex reaction, reducing sugars having carbonyl groups react with compounds having amine groups, such as amino

acids and proteins, to form Schiff bases. At the same time, an absorption band appears in the 300- to 400-nm interval.[27,28]

When the Maillard reaction is carried out at high temperatures, the imines undergo a complex set of reactions. Usually these reactions cause an intense browning because of the appearance of new absorption bands at $\lambda > 400$ nm.[27,28] We have observed a similar behavior in the reaction of cellulose with PEIs. At high temperatures and long heating times a new absorption appears at 450 nm, and new IR bands develop in the 1700–1800 cm^{-1} interval, revealing the existence of a complex mixture of oxidation products.

The reactions deduced from the spectroscopic study are summarized in Scheme 1. These reactions produce colored compounds that can play a role in the ageing of those cellulosic materials that contain polyethylenimines as additives. On the other hand, these reactions can be useful as a way to modify celluloses and obtain new materials.

CONCLUSIONS

Several reactions between celluloses and polyethylenimines were detected using diffuse reflectance spectroscopic techniques. The spectroscopic results reveal that the PEI amine groups react with cellulose carbonyl groups, produced in the cellulose oxidation, to form Schiff bases. The good correlation observed between the rates of amine disappearance and color development indicates that this reaction produces most of the cellulose darkening. At high temperatures other oxidation products were detected that contribute to the cellulose browning. The formation of amine bicarbonate salts was observed in celluloses treated at pH = 11, but this reversible process does not contribute to the cellulose darkening. This reaction was not observed in celluloses treated at pH = 6 because of the protonation of the amine groups.

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