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Modification of cellulose with amino compounds: A fluorescence study

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Abstract

Celluloses treated with amino compounds such as polyethylenimines and ethylenediamine show a noticeable fluorescence which depends on the thermal history of the material. Samples of cellulose were treated with polyethylenimine and ethylenediamine in aqueous solutions and subjected to thermal treatments in order to study the fluorescence and obtained information about the chemical transformations that take place in the modified celluloses. To elucidate the nature of the fluorophores existing in the treated cellulose, the fluorescence of model compounds obtained in the reaction of polyethylenimine with acetaldehyde was also measured. The products of this reaction and the modified celluloses were characterized using FTIR and UV–vis spectroscopic techniques. The analysis of the results indicate that the amino groups react with carbonyl groups present in the modified celluloses to form conjugated imines, which are responsible for the observed fluorescence.

Keywords: Cellulose; Polyethylenimine; Fluorescence; UV–vis spectroscopy; FTIR

1. Introduction

Celluloses modified with amino compounds are materials of increasing importance in different application fields. For instance, aminosilicones are widely used as softening agents in textile treatments and show strong interaction with the cellulosic surfaces (Burrell, Butts, Derr, Genovese, & Perry, 2004). Celluloses treated with polyethylenimines are used in thin-layer chromatography for some separation processes (Kok, Evertsen, Velthorst, Brinkman, & Gooijer, 2000). Polyethylenimines (PEI), which are highly branched polymers with primary, secondary, and tertiary amine groups, are also used in the papermaking process, for improving the retention of small particles and the separation from the liquid phase (Poptoshev, 2001; Porubská, Alince, & van de Ven, 2002; Sutý & Luzáková, 1998). Blends of cellulose and chitosan, an amino-polysaccharide obtained from chitin, are very promising materials because fibres obtained from these blends can show the good mechanical properties of cellulose and the interesting chemical functionality of chitosan (Hasegawa, Isogai, Onabe, Usuda, & Atalla, 1992; Rogovina, Akopova, Vikhoreva, & Gorbacheva, 2001; Wu et al., 2004). Other amino compounds, such as aminosilanes (Maldas, Kokta, & Daneault, 1992; Martínez Urreaga, Matías, de la Orden, Lechuga Munguía, & González Sánchez, 2000), have been proposed as coupling agents in cellulose reinforced composites.

However, in spite of the wide use of cellulosic materials treated with amino compounds, the nature of the interactions between the cellulose surface and the amino compounds have been scarcely studied to the present. We have shown that celluloses can react, in the appropriate conditions, with several amino compounds, including aminosilanes (Martínez Urreaga et al., 2000; Matías, de la Orden, González Sánchez, & Martínez Urreaga, 2000), PEI (de la Orden, Matías, & Martínez Urreaga, 2004) and others (de la Orden & Martínez Urreaga, 2006). The main products of the reaction are Schiff bases produced in the condensation of amino and carbonyl groups. This reaction, which can be

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detected even in samples treated at room temperature, is responsible for the easy thermal yellowing of the treated celluloses (Martínez Urreaga et al., 2000; de la Orden & Martínez Urreaga, 2006).

Recently, we have observed that celluloses treated with the amino-polysaccharide chitosan show a weak but noticeable fluorescence (Martínez Urreaga & de la Orden, 2006). This emission, which does not appear in the starting materials before the treatments, can be assigned to fluorophores produced in a chemical reaction between cellulose and the amino compound. A similar fluorescence emission was observed by Kok et al. (2000) in PEI-cellulose sheets used in thin-layer chromatography. In the two cases, the emission intensity depends on the ageing state of the treated materials, and samples naturally aged, or subjected to thermal treatments, show more intense fluorescence. Thus, these results appear to indicate that the study of the fluorescence of the treated celluloses can reveal useful information about the nature of the chemical interactions between cellulose and amino compounds.

In this work we have studied the fluorescence of cellulose treated with PEI and ethylenediamine (EDA). Samples of cotton cellulose were treated with the amino compounds in aqueous solutions of different pH and subjected to different thermal treatments, in order to study the effect of pH and ageing conditions on the fluorescence. There was also studied the fluorescence of model compounds, obtained in the reaction of PEI with acetaldehyde. These model compounds, and the modified celluloses, were analyzed using FTIR and UV–vis spectroscopic techniques. The aims of this work were to gain information about the chemical reactions which take place in the surface of celluloses treated with amino compounds and describe the fluorescence of these materials.

2. Materials and methods

2.1. Materials

The cellulosic material used in this work was Whatman No. 41 filter paper, which contains more than 99% pure cotton cellulose. The only pretreatment was washing with distilled water and drying in air at 40 °C for 24 h. The polyethylenimine used (Lupasol® PR 8515, active matter >98%; M_w: 2000; CAS No.: 25987-06-8) was kindly supplied by BASF Española S.A. (Barcelona, Spain) and was used as received. The ratio of primary, secondary, and tertiary amines was 1:0.92:0.70. Acetaldehyde and EDA of high purity (Fluka), were used as received. The structures of PEI and EDA are shown in Fig. 1.

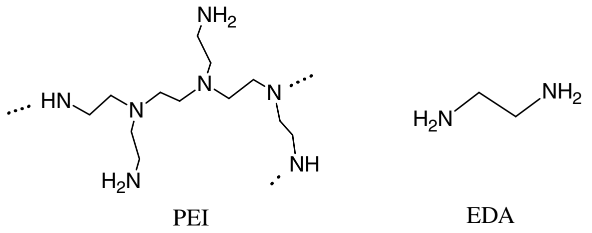

Fig. 1. Structures of polyethylenimine and ethylenediamine.

2.2. Treatments

One gram of cellulose was immersed in 20 ml of aqueous solutions of the amino compounds (5% by weight) for 5 min. The treatments with PEI were carried out at two different pH values: pH 11, the natural pH of PEI solutions and pH 6, obtained by adding HCl to the solution. After washing with the solvent, all treated celluloses were oven-dried in air at 40 °C for 24 h. Samples of the obtained materials were subjected to different thermal treatments in air.

The reaction between PEI and acetaldehyde was carried out in water or ethanol. In water, 1 mL of pure acetaldehyde was added to 5 mL of 5% PEI solution (at the natural pH of the PEI) in a vial at room temperature to give a colourless product. Samples of the reaction mixture were heated at 70 °C during different times to study the effects of the temperature. Yellow liquids were obtained during these thermal treatments. The reaction was also carried out in ethanol for the infrared study, in order to minimize the characteristic water absorption which appears at 1635 cm^{-1}, in the same spectral region where the characteristic absorptions of amines and imines are expected. In this case, PEI was treated with excess acetaldehyde in concentrated solution and yellow products were obtained at room temperature.

2.3. Spectroscopy

Attenuated total reflectance Fourier transform infrared (ATR–FTIR) spectra were recorded with a Mattson 3020 FTIR Spectrometer, using a Specac horizontal ATR accessory. Each spectrum was recorded at a resolution of 4 cm^{-1}, with a total of 30 scans. The diffuse reflectance Fourier transform infrared (DRIFT) spectra (90 scans at 4 cm^{-1}) were recorded with the same instrument, using a Specac diffuse reflectance accessory. The reflectance spectra were corrected according to the Kubelka–Munk function, using KBr as background. The UV–vis absorption spectra were obtained with a Shimadzu 2401 PC UV–vis spectrophotometer. The fluorescence spectra were measured at room temperature with a Perkin–Elmer LS-5 luminescence spectrometer. The fluorescence emission of the PEI–acetaldehyde reaction mixture was measured in aqueous solutions.

3. Results

Celluloses treated with amino compounds at room temperature, and dried at 40 °C during 24 h, show a noticeable fluorescence. This emission does not appear in the starting materials, before the treatments, and can, therefore, be assigned to the fluorophores produced in a chemical reaction between cellulose and the amino compounds. In order to investigate this fluorescence, which can provide useful information about the nature of the chemical reactions that take place in the treated celluloses, we have measured the emission spectra in samples subjected to different thermal treatments, using different excitation wavelengths (λ_{ex}). Two λ_{ex} were selected, 350 and 425 nm, taking into account the UV–vis spectra of the treated celluloses, which have been previously reported (de la Orden et al., 2004; de la Orden & Martínez Urreaga, 2006). Celluloses treated with PEI, EDA, and other amino compounds, show a characteristic absorption centred at 340–350 nm. $\lambda_{ex} = 425$ nm was chosen because of the weak absorptions that appear at wavelengths higher than 400 nm in the spectra of modified celluloses subjected to severe thermal treatments.

Fig. 2 gives the fluorescence emission spectra registered, with the two selected λ_{ex}, in PEI-treated celluloses. As can be seen in this figure, the spectra corresponding to samples treated at pH 11 and pH 6 are very similar. The two treated celluloses present a broad-band emission where at least four maxima, at ca. 420, 452, 488, and 525 nm, can be distinguished. This complex emission reveals the presence of different fluorophores produced in the interaction between cellulose and PEI. No different emission bands were detected in the spectra recorded with $\lambda_{ex} = 425$ nm (curve c), which present the known bands at 488 and 525 nm.

Fig. 3 shows the fluorescence emission spectra registered in samples of PEI-treated celluloses subjected to different thermal treatments (the spectrum of the unheated material is included for comparison). Again, samples treated in aqueous solutions of different pH show similar emission spectra, with the relative emission maxima appearing at similar wavelengths. The main result showed in Fig. 3 is the substantial changes produced by the thermal treatments in the fluorescence emission spectra of the modified celluloses. The emission of samples heated at 200 °C show the same relative maxima at ca. 420, 452, 488, and 525 nm; however, the relative intensities change and the emission bands at higher wavelengths become more important with the thermal treatment, revealing a change in the composition of the mixture of fluorophores.

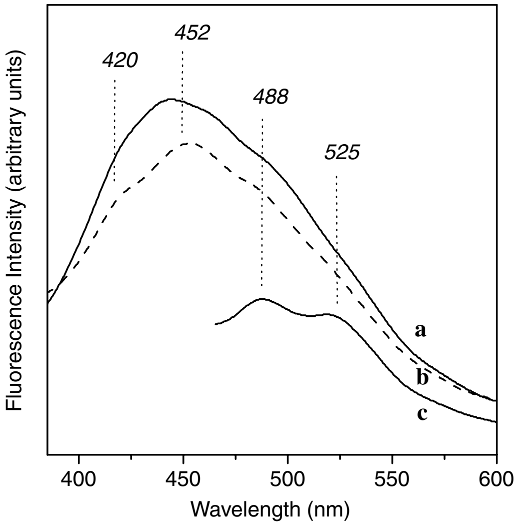

Fig. 2. Fluorescence emission spectra ($\lambda_{ex} = 350$ nm) of celluloses treated with polyethylenimine at pH 11 (curve a) and pH 6 (curve b, dash). Curve c: the emission spectrum of cellulose treated with polyethylenimine at pH 11, measured with $\lambda_{ex} = 425$ nm.

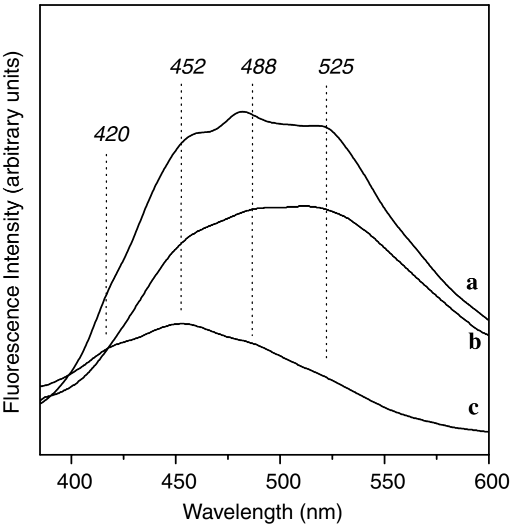

Fig. 3. Fluorescence emission spectra ($\lambda_{ex} = 350$ nm) of celluloses treated with polyethylenimine and heated at 200 °C in air. Curve a: cellulose treated at pH 11 and heated for 60 min. Curve b: cellulose treated at pH 6 and heated for 20 min. Curve c: the emission spectrum measured before the thermal treatment in cellulose treated with polyethylenimine at pH 11.

Very similar results were obtained in the analysis of the fluorescence of celluloses treated with EDA (Fig. 4). A broad emission band, with relative maxima at ca. 440, 486, and 525 nm in this case, appear in the spectrum of the unheated samples (curve a). Samples subjected to thermal treatment show more intense fluorescence. Again, the emissions at long wavelengths become more important in the heated materials, revealing the existence of chemical processes during the thermal treatment, which generates the corresponding fluorophores.

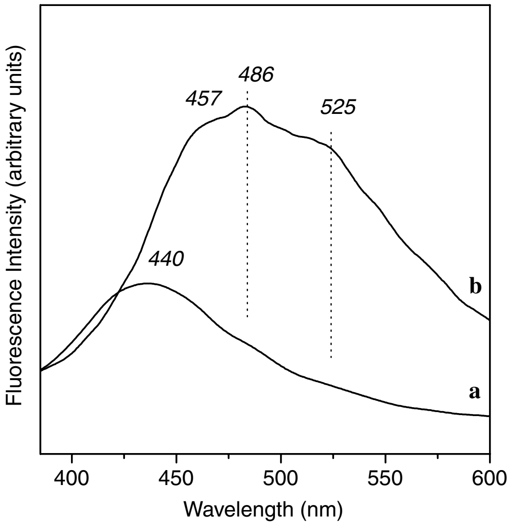

Fig. 4. Fluorescence emission spectra ($\lambda_{ex} = 350$ nm) of celluloses treated with ethylenediamine, measured before (curve a) and after (curve b) heating at 200 °C in air during 20 min.

4. Discussion

The above results show that the fluorescence of celluloses treated with PEI and EDA depend significantly on the thermal history of the materials, which suggests that compounds produced during the thermal treatments contribute to the fluorescence of the material. We have previously observed a similar behaviour in the fluorescence of celluloses treated with chitosan, a polysaccharide with pendant amino groups (Martínez Urreaga & de la Orden, 2006). A fluorescence emission was also described by Kok et al. (2000) in PEI-cellulose sheets used in thin-layer chromatography. These authors found that the fluorescence of the PEI-cellulose sheets was dependent on the ageing; however, the emission was assigned in this case to a PEI-cellulose complex and no covalent bonds between PEI and cellulose were observed.

We have previously studied the chemical interaction between cellulose and several amino compounds, including PEI, EDA, and chitosan, using diffuse reflectance spectroscopic techniques (de la Orden et al., 2004; de la Orden & Martínez Urreaga, 2006). In all cases, the spectroscopic results appear to indicate the formation of imines (Schiff bases) as a result of the reaction between amino groups and some carbonyl groups present in the cellulose. It is known that many Schiff bases are fluorescent compounds; for instance, Yi et al. (2003) reported a fluorescence emission in samples of chitosan-treated with glutaraldehyde, which was assigned to the Schiff bases produced in the reaction between glutaraldehyde an the amino groups of chitosan, because the emission decreased when $NaBH_4$ was added to reduce the imines. Taking into account these results, we have assigned the fluorescence observed in celluloses treated with PEI and EDA to Schiff bases produced in the amino–carbonyl condensation.

In order to evaluate this hypothesis, we have studied the fluorescence of model compounds obtained in the reaction of acetaldehyde (in excess) with PEI. It is well known that the reaction of aldehydes with primary amino groups produces Schiff bases with high yields. The products of the reaction were analyzed using UV–vis and FTIR spectroscopic techniques in order to compare the spectra with those corresponding to celluloses treated with PEI.

Fig. 5 shows the UV–vis absorption spectra corresponding to PEI–acetaldehyde reaction mixtures, measured before and after heating at 70 °C. There is also included the spectrum of the starting acetaldehyde. The spectrum of the reaction mixture at room temperature (curve a) shows some new bands that do not appear in the acetaldehyde spectrum, the most significant being the weak absorption at ca. 336 nm. After heating the room temperature reaction mixture at 70 °C for 10 min, the spectrum (curve b) shows the development of the band at 336 nm and the appearance of new absorptions with maxima centred at ca. 285 and 400 nm. A similar behaviour has been previously observed in celluloses treated with amino compounds; these materials show a characteristic absorption centred at 340–350 nm, which increases with the heating time during the thermal treatments, as well as weak bands at $\lambda > 400$ nm which appear in samples subjected to severe thermal treatments (de la Orden & Martínez Urreaga, 2006). These new bands which appear in both the reaction mixture and the celluloses treated with amino compounds can be assigned to the imines produced in each case in the reaction between amino and carbonyl groups (de la Orden et al., 2004).

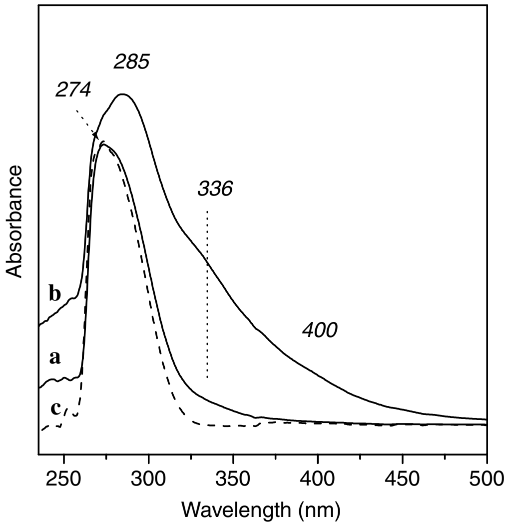

Fig. 5. UV–vis spectra measured in the polyethylenimine–acetaldehyde reaction mixture. Curve a: spectrum measured after 5 min of reaction at room temperature. Curve b: spectrum measured after heating the above reaction mixture during 10 min at 70 °C. Curve c: the spectrum of acetaldehyde.

Fig. 6 gives the ATR–FTIR spectrum of the PEI–acetaldehyde reaction mixture (curve a) and allows the comparison with the DRIFT spectra of cellulose treated with PEI and heated at 200 °C during 30 min (curve b) and pure cellulose

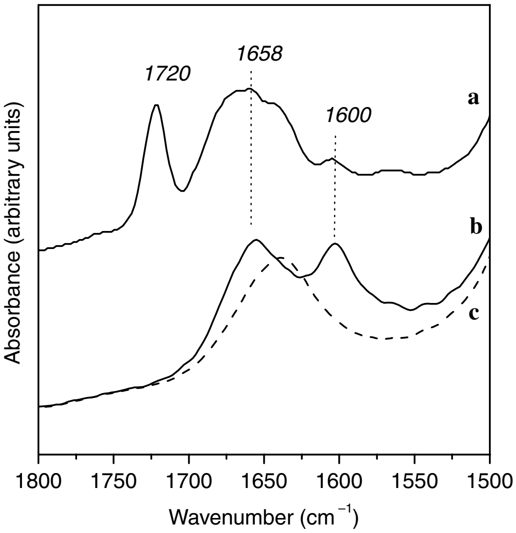

Fig. 6. FTIR spectra of PEI-treated cellulose and PEI reacted with acetaldehyde. Curve a: ATR–FTIR spectrum of the PEI–acetaldehyde reaction mixture (5 min in ethanol). Curves b, c: DRIFT spectra of the PEI-treated cellulose heated at 200 °C during 30 min (curve b) and the starting untreated cellulose.

(curve c). The spectrum of the reaction mixture shows characteristic absorptions at 1600, 1658, and 1720 cm^{-1}. The band at 1720 cm^{-1} must be assigned to the unreacted acetaldehyde (C=O stretching). The band at 1600 cm^{-1}, which appears also in the spectrum of PEI-treated celluloses, can be assigned to the primary amino groups of the unreacted PEI (N–H deformation band). The most significant absorptions are the bands centred at ca. 1658 cm^{-1} that appear in the two spectra. The appearance of these bands, which may be assigned to C=N stretching modes (de la Orden et al., 2004), confirms the formation of Schiff bases in both the PEI-treated cellulose and the PEI–acetaldehyde reaction mixture.

Fig. 7 shows the fluorescence emission spectra corresponding to PEI–acetaldehyde reaction mixture (aqueous solutions), measured before (curve a) and after (curve b) heating the reaction mixture during 10 min at 70 °C. These spectra are very similar to those recorded in celluloses treated with PEI and EDA, showed in Figs. 2–4. The fluorescence emission is a broad-band with at least four maxima, centred at ca. 440, 475, 500, and 538 nm in this case. When the reaction mixture is heated, the long wavelength emissions become more important and new emissions appear at longer wavelengths.

The close similarity between the fluorescence of the PEI–acetaldehyde reaction mixture and the emission observed in celluloses treated with amino compounds reveals that the fluorophores are the same in the two cases. As the spectroscopic analysis of the reaction mixture confirms that the main products of the PEI–acetaldehyde reaction are Schiff bases, we can conclude that the fluorescence of celluloses treated with amino compounds may be assigned to imines and reveals the existence of chemical interactions between cellulose and the amino compounds.

The evolution observed in the spectra during the thermal treatments, as well as the complexity of the fluorescence emission spectra, may be explained by the existence of different conjugated imines, produced in primary and secondary condensation processes, as those observed by Bandi, Mehta, and Schiraldi (2005) in the reaction between benzyl amine and acetaldehyde. In the primary condensation during the PEI–acetaldehyde reaction, a non-conjugated imine is obtained as a result of the reaction between acetaldehyde and primary amino groups. In the secondary condensation processes, which are accelerated during the thermal treatments, the produced Schiff base undergoes further condensation, with more acetaldehyde, to form conjugated imines. These conjugated imines are responsible for the yellow colour observed in samples subjected to thermal treatments. When celluloses treated with amino compounds are considered, the secondary condensation processes may be explained by the presence of acetaldehyde (and other carbonyl compounds) produced in the thermal degradation of cellulose. Indeed, it is known that significant amounts of carbonyl compounds, including acetaldehyde, are generated when celluloses and other polysaccharides are heated at temperatures as low as 200 °C (Baker, Coburn, Liu, & Tetteh, 2005; Liu, Lv, Yang, He, & Ling, 2005). The conjugated imines produced in these secondary condensation processes would be responsible for the fluorescence emissions at long wavelengths and the changes observed in the emission spectra during the thermal treatments.

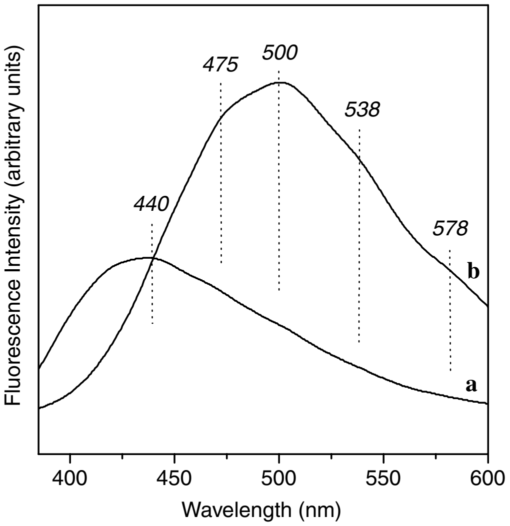

Fig. 7. Fluorescence emission spectra ($\lambda_{ex} = 350$ nm) of the polyethylenimine–acetaldehyde reaction mixture. Curve a: spectrum measured after 5 min of reaction at room temperature. Curve b: spectrum measured after heating the above reaction mixture during 10 min at 70 °C.

5. Conclusion

Celluloses treated with polyethylenimine and ethylenediamine show complex fluorescence emission spectra, which present several emission bands and change during the thermal treatments of the materials. The fluorescence emission increases and the long wavelength bands become more important when the treated celluloses are heated in air at moderate temperatures. A very similar fluorescence has been observed in model compounds obtained in the reaction between the amino compounds and acetaldehyde in excess, which have been identified as Schiff bases. These results indicate that the fluorescence of celluloses treated with amino compounds is due to the Schiff bases produced in the reaction between amino and carbonyl groups. The changes in the fluorescence spectra during the thermal treatments have been explained as a result of secondary condensation processes which produce conjugated imines.

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