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Stabilization of paper by nitrogen plasma assisted application of chitosan at atmospheric pressure

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Abstract

The acidic newsprint paper was covered by chitosan dissolved in water in accordance with nitrogen plasma treatment at atmospheric pressure. Plasma was applied before or after chitosan application. Aging stability of the modified paper was tested by artificial accelerated thermal aging. The mechanical, chemical and structural changes were characterized by mechanical double-bending and tear work, wetting and soaking and absorption FTIR spectroscopy (using 25 reflection ATR techniques). Correlations among aged paper parameters were considered, while the biggest changes were found in mechanical properties and in whiteness and soaking. Stabilization effect within aging is evident as mechanical strengthening, soaking reduction and pH stabilization; however the yellowness is deeper due to chitosan presence. Plasma treatment is more effective in the case of afterwards application at the relative chitosan content of 1% round.

Keywords: Plasma, paper, chitosan, stabilization, strengthening

Introduction

Many efforts have been focused to stabilize cellulose-based materials, like papers and books in order to preserve valuable archival documents and cultural heritage all over the world. Aging processes cause mainly mechanical and colour degradation of documents which become brittle with a considerable lost of fastness and strength. The key processes of deterioration are 1) microbial degradation, 2) acidic hydrolysis forced by moisture and residual chemicals present in paper as a result of paper production technology used or coming from the air pollutants, and 3) oxidative degradation accelerated by temperature and light (Browning 1977, Vohrer et al. 2001).

Several highvolume processes for paper or book treatment have been proposed namely based on deacidification of paper by inorganic compounds; however current strengthening processes including coating the paper are not suitable for strengthening brittle paper (Havermans 1996). Marginally the environmentally friendly organic or native compounds/polymers were used to stabilize the paper, also in combination with plasma treatment (Vaswani 2005, Černák et al. 2005).

Plasma treatment is a well-established technique in a number of processes, such as plasma cleaning, etching and coating. Concerning cellulosic materials and paper, special after-glow plasma was used to remove microbial contamination and to increase the paper strength (Vohrer et al. 2001). Implantation of $-Si(CH_3)_x$ groups into the surface layers of the paper substrates was performed by fluorosilane plasma, where the functional groups were chemically linked mainly to the rest lignin component in the paper (Navarro et al. 2003). Teflon-like protective layers on a filter paper substrate were prepared by mixture of nitrogen with C_4F_8 in surface discharge at atmospheric pressure (Kloc et al. 2006). Hydrophobic coatings were deposited on a stack of different porous filter papers using four types of plasma from several fluorine-containing monomers. This study indicates that a very thin coating (average thickness smaller than 1-2 nm) is needed for hydrophobic behavior. However, plasma-induced coatings can modify surface properties of high-porosity materials and the extent of plasma permeation can be controlled. (Mukhopadhyay et al. 2002).

Dielectric barrier discharge, particularly coplanar one, is referred as the most suitable for plasma treatment of paper (Černák et al. 2005, Mikula et al. 2003). Thin films with desired surface properties e.g. permeability and wear resistance were successfully deposited on paper by means of atmospheric pressure surface barrier discharge using organosilicon monomers and octafluorocyclobutane (Sťahel et al. 2005).

Chitosan is native polymer containing amino-groups in basic polysaccharidic skelet with some biostabilizing effect. There is a chance to use it in environmentally-friendly process of stabilization of paper. In assistance with oxygen-plasma polypropylene surfaces was pre-treated and coated by immobilized chitosan covalently bonded to the plasma pre-treated surface in order to improve wetability, dyeing behavior and reactivity of the surface (Bratskaya et al. 2004).

There is a chance to use alkaline plasma (nitrogen, ammonia) for sterilization and slight deacidifying of aged papers and strengthening them by following chitosan application.

The aim of this work is to evaluate the extent of stabilization of acidic paper by chitosan application supported by nitrogen discharge plasma.

Experimental

Special acidic groundwood calandered nonsized newsprint paper (as the simulation model of the major paper production in 19-20th century, 45 g/m^2,Vetrni Czech. Rep.) was used as the model paper for modification and aging. Activation of paper and/or chitosan was performed by standard (volume) dielectric barrier discharge (DBD) nitrogen plasma (5 kHz, 10 kV) at atmospheric pressure in the configuration via Fig. 1.

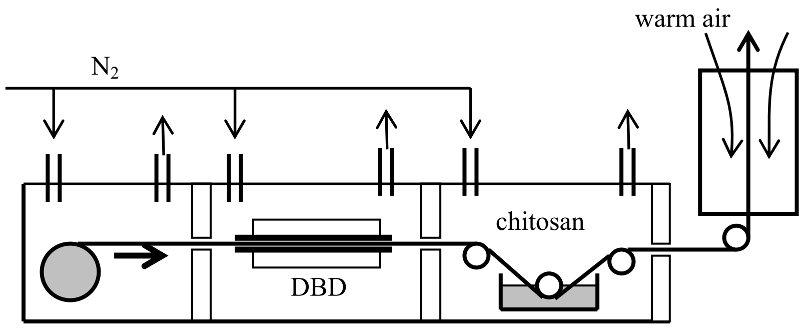

Fig. 1 Experimental arrangement of DBD plasma treatment of the roll of paper

Plasma treatment was applied in two manners:

A: Plasma before chitosan application. The treatment chamber was first flowed 5 minutes by nitrogen at the flow rate of 5 l/min and then the flow was stated to the actual treatment value. The drive motor started to move the paper and high voltage was applied to the electrodes to start the discharge. At the paper drive velocity of 0.4 cm/s the treatment time of paper between 2 electrodes was 10 s that corresponded with the exposition of 2 J/cm^2. After plasma treatment the paper is drawn to the chitosan bath and then to the drying chamber with a warm air flow.

B: Plasma after chitosan application. Considering that the wet paper cannot be exposed by plasma, in this case the paper was drawn through the chamber 2 times in the same direction as in the A case: First, without discharge plasma, just to apply the chitosan solution and drying in the air conditions. Second, just to apply the N_2 plasma onto the dried NP with chitosan without repeated chitosan application and drying.

Native polysaccharide chitosan (low molecular weight, dissolvable in water at pH < 6.5, Aldrich) was used as the strengthening and stabilizing agent in the form of water solutions at 4 different concentrations: 0.22, 0.4, 0.65 and 1 g/100 ml in 0.1 M CH_3COOH water solution. At the used paper drive velocity (0.4 cm/s) through the chitosan bath (Fig. 1), 4 different resulting (dry) coatings of paper were achieved: 0.5, 1, 2, and 4 wt%, respectively.

Original and modified papers were aged artificially by the new accelerated aging method by Begin and Kaminska 2002: 9 g of treated paper was pre-conditioned at relative humidity RH = 50% (at 23°C), afterwards enclosed into 300 ml glass bottle, covered by Viton® (DuPontDow) sealing and heated to 100°C for 5 days. Fold endurance were measured by double bending technique by Schopper instrument (DFP, VEB, Germany) at draw force 3.5 N. Several tear parameters (maximal strength, breaking length, tensile strain and Young modulus) were measured and calculated by INSTRON 1122. However, tear work was the most sensitive to applied modifications. Wetting and water soaking properties were characterized by contact angle measurement of sessile drop and by 3 µl water drop imbibition using CCD camera (SEE software 6.1, MU Brno, Czech.Rep.,). Surface functional groups were monitored by attenuated total reflection (ATR) technique of FTIR spectroscopy (Excalibur, FTS 3000 MX, Digilab, USA, resolution 4 cm^{-1}, 25 reflections KRS-5 crystal, 45°).

Results and Discussion

Generally, chitosan layers had strengthening effect on paper before aging, as was expected for any polymer application onto paper. Moreover, mechanical tensile tests and double bending showed that in several cases the papers covered by chitosan were reinforced not only after chitosan application, but also after artificial aging (Fig. 2). (All mechanical data in Fig. 2 belong to aged samples, except the P_{init}. P/Pl/Chit belongs to the A case and P/Chit/Pl to the B case of paper modification). The significant embrittlement of papers with aging was reduced namely in case of 0.5 and 1 wt% of chitosan content, especially in the case B, when the plasma was applied after chitosan application. Maybe it is caused by protective effect of the layer of chitosan against the degradation effect of plasma to paper substrate. However, when the chitosan layer is thicker, plasma has no effect on the chitosan-paper bonding, because of its surface impact. So, there is no strengthening effect after aging for 2 and 4 wt% of chitosan content in the case B. It is important to realize the big experimental error of mechanical tests that achieves here the values up to 30%. (Each mechanical test was performed on 10 parallel samples and the results are the average values).

Aging of papers generally leads to yellowing (or browning) of papers, while the yellowing is little deeper at the presence of chitosan layer.

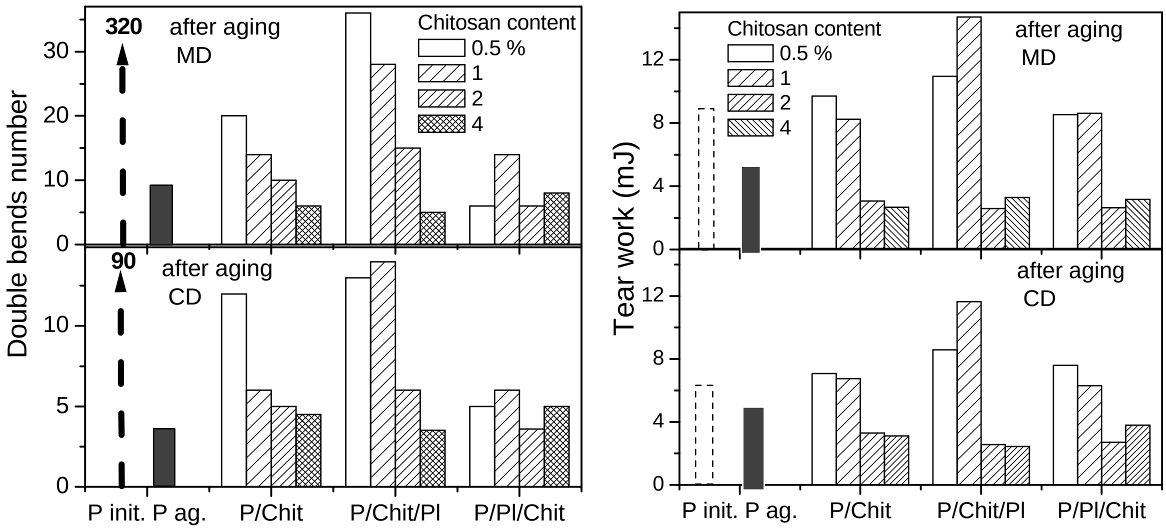

Fig. 2 Mechanical properties of different treated papers after aging (MD – machine direction, CD - cross direction), P indicates paper, Pl plasma and Chit chitosan application, P_{init} an P_{ag} initial and aged paper, respectively.

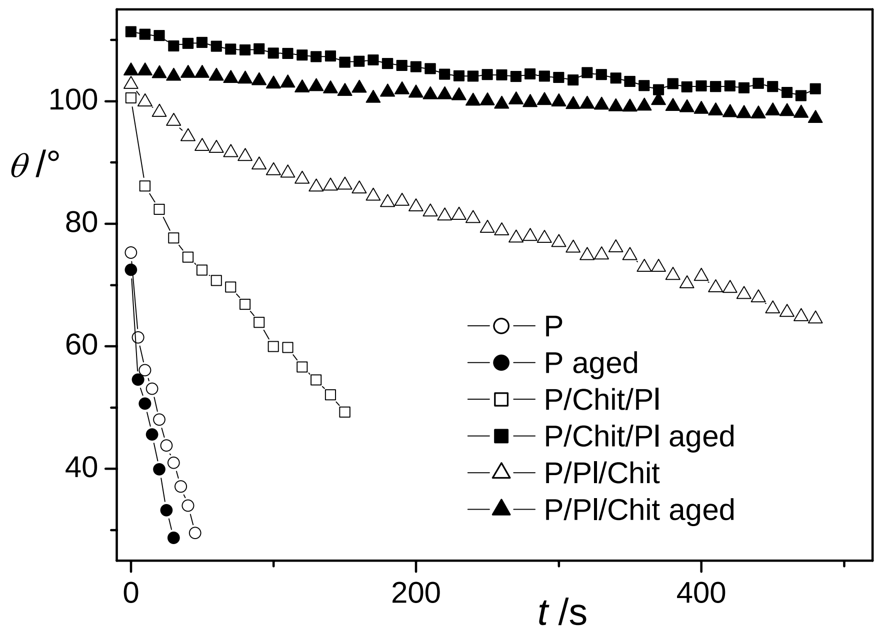

Fig. 3 Wetting contact angle as a function of the water drop imbibition time for differently modified paper (P).

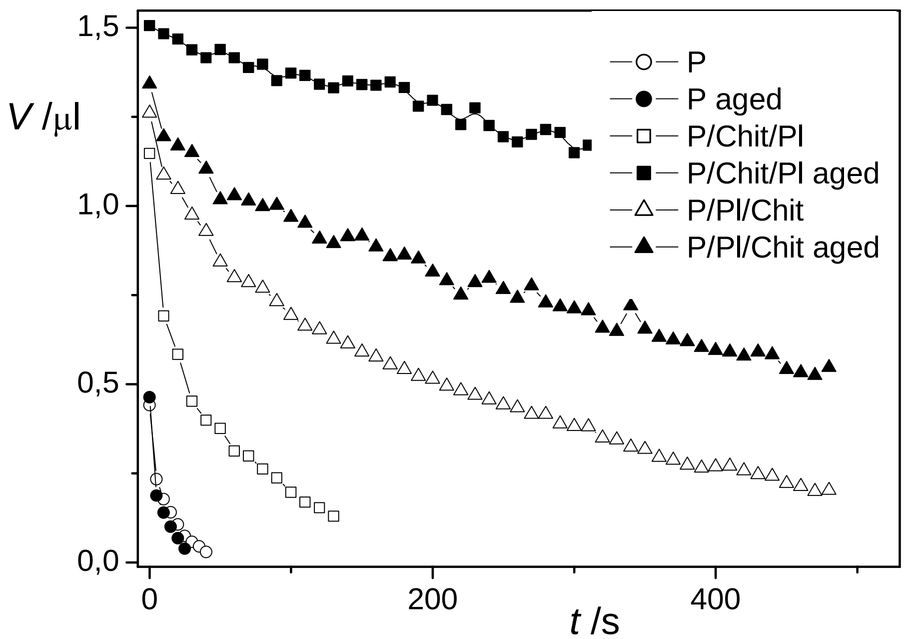

Fig. 4 Time dependence of the sessile drop volume V during the water drop imbibition for differently modified paper (P).

As was expected, the wetting contact angles were increased and water imbibition (soaking) times were prolonged after chitosan application because of fill up the pores and a slightly hydrophobic nature of chitosan alone. However, it is interesting that contact angles as well as imbibition times were increased also after aging in both cases (A and B) of chitosan application (Fig. 3 and 4). It indicates some synergetic stabilization effect of chitosan on paper and maybe chemical bonding between chitosan and paper substrate.

IR absorption spectra in transmission mode showed some small changes with aging of papers covered and noncovered by chitosan, mostly in the region of carbonyl and carboxyl groups (1520 – 1750 cm^{-1}), Fig. 5. However, in spite of using the most sensitive IR surface technique, ATR with 25 reflections, no considerable and reproducible spectral changes were found between plasma treated and nontreated aged samples, (Fig. 6). It means, the IR spectra did not confirm the stabilization effect of plasma treatment. Probably, the IR technique is not sensitive enough to judge if there is some chemical bonding caused by plasma at the interface, or there is not.

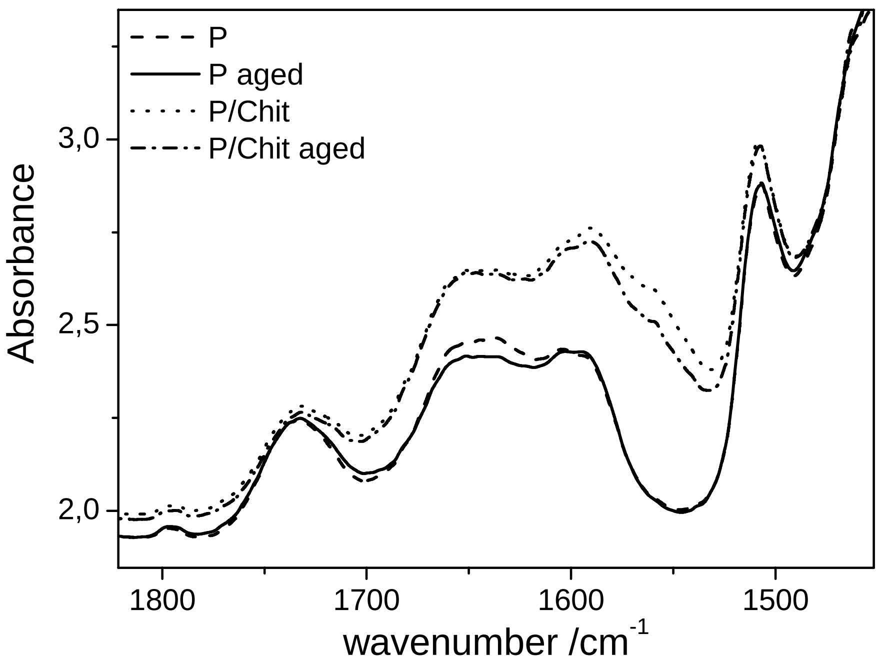

Fig. 5 Transmission IR spectra of initial and aged papers with (P/Chit) and without (P) chitosan (1%)

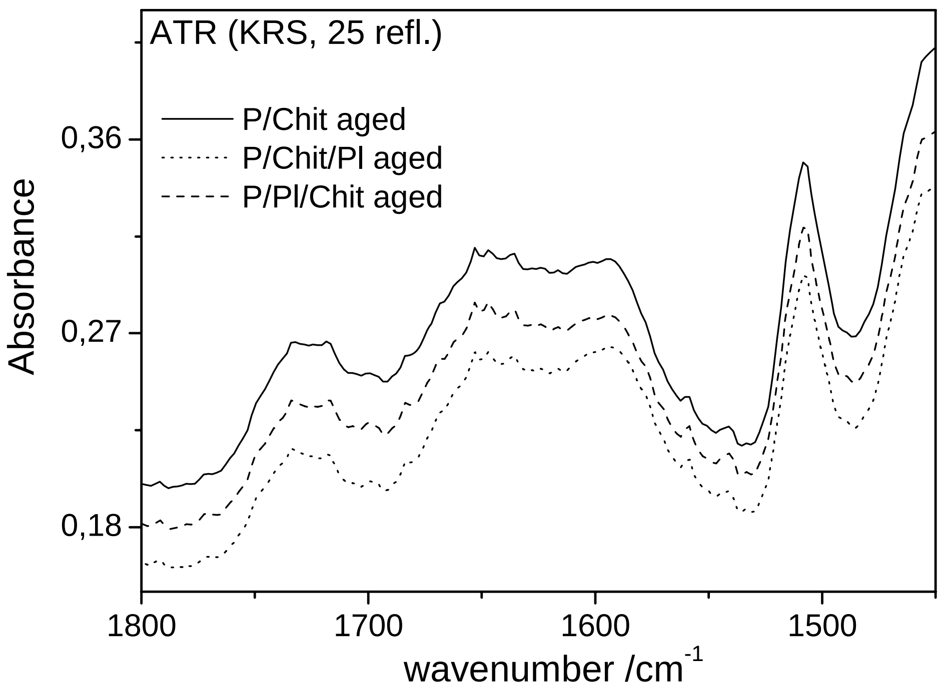

Fig. 6 Absorption IR spectra (ATR technique) of aged paper (P) with chitosan (Chit, 1%), with and without plasma (Pl) treatment

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