

IMPACT OF NITROGEN OXIDES ON THE CHANGES OF SELECTED PROPERTIES OF PULP

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Abstract

The aim of this study was to evaluate the effect of the atmosphere of nitrogen oxides on the selected properties of various cellulose and lignocellulose materials. Selected samples were hand-made paper from Velké Losiny (RP) and wood sulphite wrapping paper from Větrní (DSBP). In cooperation with the National Archive in Prague, selected samples were subjected to three cycles of exposure to nitrogen oxides (120, 240, and 360 hours.). After each exposure were measured hypermolecular selected properties. Measurements have shown that the influence of nitrogen oxides changes occur in structural and surface-molecular properties of lignocellulose materials.

Introduce

Nitrogen oxides are one of the important industrial pollutants at present time. Their share increases in the atmosphere and it is necessary to monitor their influence for the protection of historical and contemporary artefacts. The structure of the paper is porous and it is able to allow the input of water molecules between disordered macromolecular chains. It causes swelling, stress-relieved paper and dimensions change. Paper is a natural fibrous material upon cellulose and lignocellulose basis which belongs to the hygroscopic substance. These substances are able to humidify in a wet environment and in a dry environment moisture deprived.

The aim of this work was to study the influence of atmospheric nitrogen oxides upon aging of paper. Two paper sorts which have been exposed to an atmosphere of nitrogen oxides were selected for the experiments. They were monitored for changes in selected properties and the measured values were compared with the original samples that were not exposed to the influence of nitrogen oxides^{1, 2}.

Practical importance has the structural and surface-molecular characteristics of the cellulose material. Moistening and speed capability of the porous material to absorb water vapour is affect by many factors. The main factors influencing this process are temperature, pressure, and relative humidity of the environment. Moistening process is very well described by followed the mathematical model:

$$Y = \frac{a \cdot b + c \cdot x^d}{b + x^d} \quad (1)$$

where Y is the increase in the moisture concentration ($Y = Y_s - Y_0$; Y_s and Y_0 represent the actual and the initial moisture concentration of the sample, respectively) and x is the time. The parameters d and c characterize the rate alignment of equilibrium moisture and hygroscopicity of the material, respectively. Equilibrium moisture concentration of sample is then $Y_e = c + Y_0$. The ratio $100 \cdot c / (1 + b \cdot 100^d)$ characterises moistening velocity at beginning of the process³⁻⁶.

Experiment

As typical cellulose material was chosen handmade paper (RP) produced at the paper mill in Velké Losiny. The paper was made from following pulp composition: 60 % cotton linters (from USA) and 40 % flax pulp (from Olšany) both beaten at 28 to 29 SR. The paper was surface sized with 0.08% solution of the aluminium potassium sulphate dodecahydrate ($KAl(SO_4)_2 \cdot 12H_2O$), and 2% solution of technical gelatine in so-called a book (temperature of bath 45- 50 °C, time of impregnation approx. 5 minutes)). The basis weight of the paper was $120 \text{ g} \cdot \text{m}^{-2}$ ^{7, 8}.

As typical lignocellulose material used during experiments was groundwood sulphite wrapping paper from JIP Větrní (DSBP). This paper was made of unbleached sulphite pulp and groundwood containing 6% kaolin and further chemical aids as Hernostan (PAAE resin), Abimal (resinous size) and $Al_2(SO_4)_3$. The basis weight of the paper was about $60 \text{ g} \cdot \text{m}^{-2}$ ⁹.

These samples were subjected to accelerated aging in an atmosphere of nitrogen oxides¹⁰. They were exposed to three cycles of accelerated aging (120, 240, and 360 hours). The samples were measured hyper-molecular and mechanical properties after this exposure.

In determining moistening kinetics, samples were cut to the size of 5x1.5 cm with DSBP and 5x2 cm in RP. The thus treated samples were measured thickness (mm), basis weight ($\text{g}\cdot\text{m}^{-2}$) and calculated apparent density ($\text{kg}\cdot\text{m}^{-3}$)¹.

The samples were then placed in a desiccator with silicagel for 7 days in order to stabilize their initial moisture before the actual kinetics measurements. The samples were placed in pre-weighed glass bottles. Before the start of moistening process each weighing bottle with the sample was weighed, and thereby establish the initial weight of the sample. Weighing bottles with the samples were placed in a desiccator, which were filled with saturated solutions of inorganic salts controlling a relative humidity (KNO_2 – 49%, NaCl – 75% and K_2SO_4 – 97%) of experimental environment. It was subsequently observed gravimetrically kinetics of the moistening process. All measurements were performed in an air conditioned room at 23 ± 1 °C and relative humidity $50 \pm 2\%$.

The values of weight gain have been converted to the weight of absolutely dry fibres. With the help of these data we were generated graphics moisture concentration vs. the time of moistening. These curves were evaluated using a mathematical model of the MMF in the program OriginPro 9.0, by which the parameters a , b , c , d were received. By using these and other parameters (density of actual paper matter by use of inert gas pycnometer; apparent density of paper samples) we were able to calculate structural parameters (total porosity ϵ ; initially moistening velocity of the porous sample, the equilibrium moisture; wet porosity which characterize the porosity fulfilled with water at a given relative humidity etc.) of papers.

To determine the kinetics of absorption of the vapour of organic liquids the same specimens and their treatment before experiments were used as for the determination of moistening kinetics. Organic liquids were toluene and methylethylketone (MEK). Graphical curves were evaluated again by using the MMF model by which have been obtained parameters a_h , b_h , c_h , d_h . Moreover, we were calculated surface-molecular properties (adhesion tension of system sample-water, sample-toluene and sample-MEK, total surface tension, basic and acidic component polar portion of surface tension, relative representation of dispersive and polar component) by using these and other parameters. All the structural and surface-molecular parameters were calculated by use of own software in xlsx formate.

Results and discussions

Impact of nitrogen dioxide on the aging of paper according to ISO 187:1990 (23 ± 1 °C, $50 \pm 2\%$ RH), when samples were exposed to flowing atmosphere of nitrogen dioxide with volume concentration $0.005 \pm 0.00002\%$ ¹⁰.

If a characteristic quantity for the evaluation hygroscopicity of the materials is equilibrium moisture concentration in porous materials (Y_e) then this aging process evoked a reduction in hygroscopicity of paper, particularly at the high RH.

Paradoxically, however, the hydrophilicity of the pore walls, characterised e.g. by water adhesion tension, was significantly increased with time of aging. For cellulose samples RP but irregularly – after 240 hours occurred decrease and after 360 hours of aging a significant increase is occurred again. For lignocellulose samples DSBP the values of adhesion tension were slightly increased but only after a longer period of aging. Initially, i.e. after 120 hours aging, a decrease there was observed (see Figure 1).

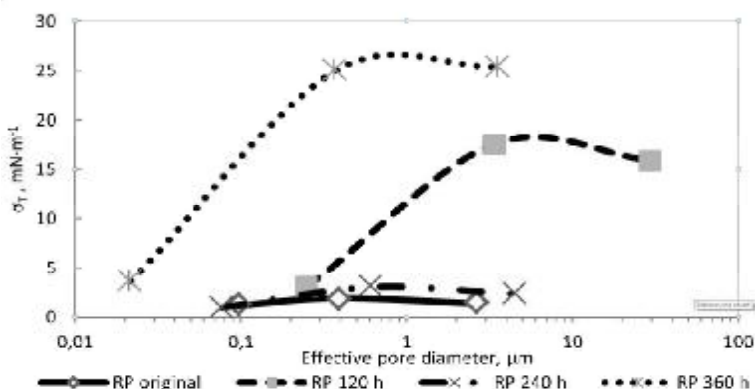


Figure 1. Mean value adhesion tension (σ_T) vs. maximal effective pore size fulfilled with water

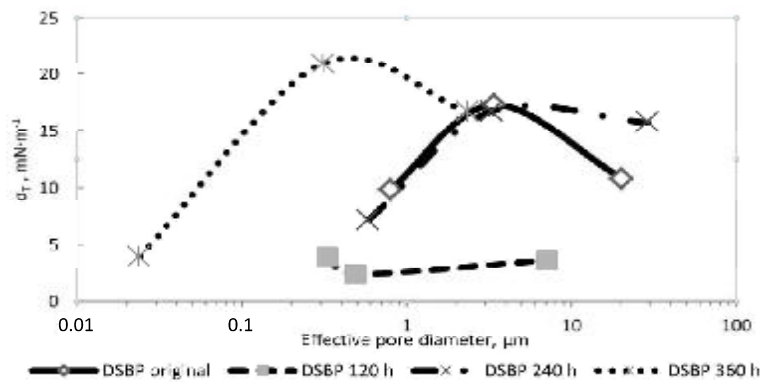


Figure 2. Mean value adhesion tension (σ_t) vs. maximal effective pore size fulfilled with water

Influence has also RH – with growth RH adhesion water tension (σ_t) rises, at high RH occurs again its decline, but compared with original samples RP its hydrophilicity were always a greater, particularly for paper aging of 360 hrs. This was reflected in the condensation of water vapour in bigger pores. For samples DSBP at high RH occurs again to its decline, expect aging of 120 hrs.

At first sight, it was caused by decrease total porosity of paper with prolonged time of aging, but the behaviour is a more complicated.

Probably, thanks to hydrophilisation of smaller pores at different stages of aging process (see Figure 3), this one leads to compaction of the internal structure of porous paper matter caused by the increase in the range of internal coupling of H-bonds and thus to its shrinking and cracking.

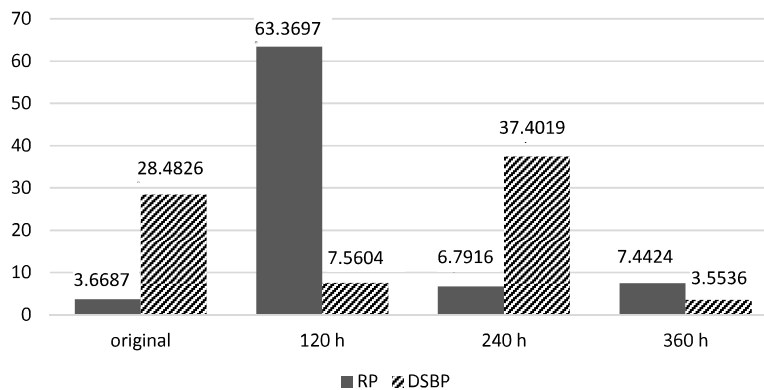


Figure 3. Approximated maximal effective pore diameter (d_{max}) fulfilled with condensed water at RH = 100%

This internal restructuring for cellulose samples RP was caused by hydrophilisation even large pores (see Figure 4) and it was reflected in filling of the larger pores with condensed water after a long time of aging (360 hrs.), but those were a less.

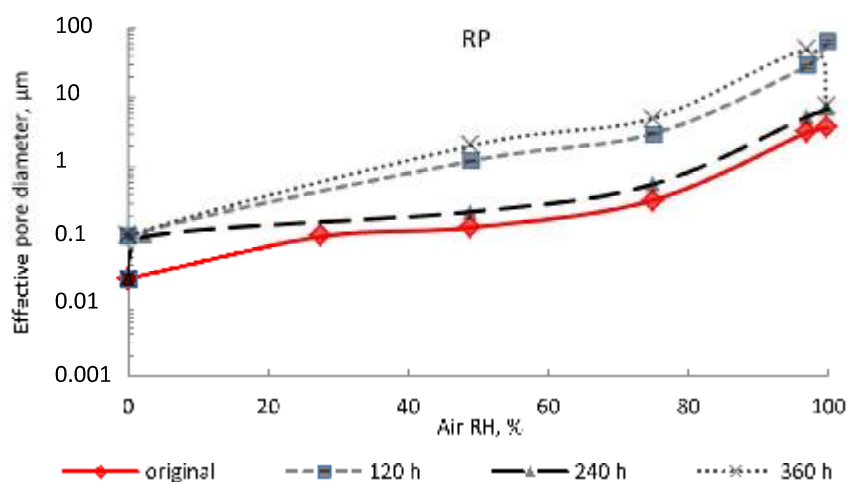


Figure 4. Maximal effective pore diameter fulfilled with condensed water vs. air RH

The internal restructuring for lignocellulose samples DSBP was caused by hydrophobisation of large pores (see Figure 5) and it was reflected in filling only smaller pores with condensed water after a long time of aging (360 hrs.).

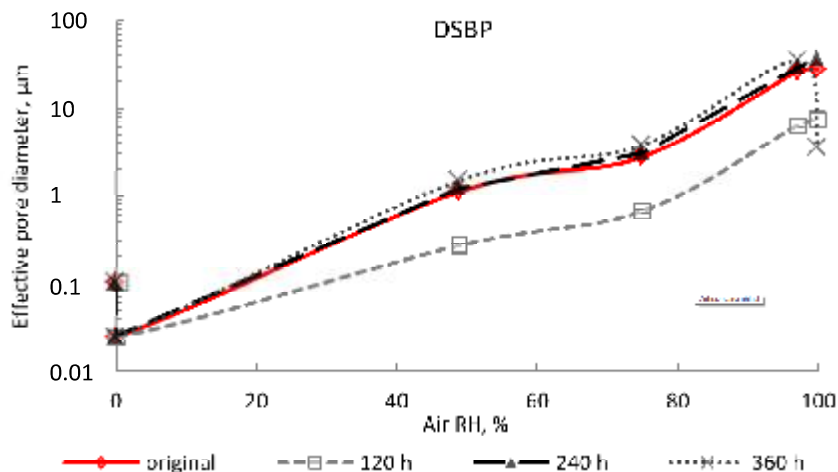


Figure 5. Maximal effective pore diameter fulfilled with condensed water vs. air RH

Comparing of both papers, a similar behaviour DSBP and wood-free paper RP during an aging was observed, but differences occur in relatively deeper hydrophilisation of the cellulose pore walls surfaces than of lignocellulose paper matter (see Figures 1 or 3).

In comparison of these papers, we have to also take into account a fact that DSBP in original condition was a more hydrophilic and a more porous than the surface sized paper RP. Obviously, the aging in an atmosphere of nitrogen oxides that occurred in the sized paper (RP) completely eliminates this sizing and its surface-molecular properties reached the level of the DSBP.

Conclusion

The effect of nitrogen oxides environment upon cellulose and lignocellulose materials was studied by monitoring of selected properties of the paper. The structural and surface-molecular changes were monitored during aging of these materials in this environment. To obtain structural and surface-molecular properties, kinetics of moistening and absorption kinetics of vapours of organic liquids were measured. We were able to calculate the monitored parameters as porosity, adhesion tension, etc. Received values indicate obvious effect of nitrogen oxides on monitored materials. There has been an increase in the hydrophilicity of the pore walls of samples. A significant increase was recorded in cellulose samples of RP and especially after 360 hours of aging. However, due to hydrophilisation of smaller pores at different stages of the aged paper, the reason have been occurred compacting the porous internal structure of paper matters caused by increase in the range of internal

H-bonds binding system and thus led to its shrinkage and cracking. For cellulose samples of RP, the reduction in the filling greater pores with condensed water after a long time of aging (360 hrs.) is caused by hydrophilisation even larger pores, but those were a less. For lignocellulose samples of DSBP, the filling only smaller pores with condensed water after a long time of aging (360 hrs.) is caused by hydrophobization of greater pores. Comparing both sort of these papers, the fact had to be also take into account that DSBP was in original state a more hydrophilic and a more porous than wood-free paper RP. A wood-free paper RP aging in an NO_x atmosphere evoked approximate alignment surface-molecular properties to the level of the groundwood paper DSBP.

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