CELLULOSE CHEMISTRY AND TECHNOLOGY

BEHAVIOUR OF LIGNOCELLULOSIC MATERIALS DURING WET AGING IN THE PRESENCE OF ESSENTIAL OILS

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The pH of water extracts of lignocellulosic materials usually indicates a deep chemical change in their structure and composition during aging. The process of aging is connected with the hydrolysis of lignocellulosic materials during their storage under different conditions. Therefore, the dependences of mechanical, optical properties and pH of water extracts upon relative air humidity are not simple functions, but are strongly influenced by the presence of essential oils. An explanation of this behaviour is based on the condensation of water vapours in the porous structures of lignocellulosic materials depending upon both the structure of the pores and the surface-molecular properties of pore interfaces. The submicropores are especially important, because the pH of the water condensed in these pores is strongly influenced by the presence and character of acidic surface groups. Also, the presence of essential oil vapours has been found to distinctly decrease the amount of condensed water.

Keywords: aging, cellulose, humidification, pH of water extract, essential oils, optical and mechanical properties

INTRODUCTION

The aging of paper may be caused by mechanical, physical (temperature, relative air humidity), chemical and photochemical, biochemical and radiochemical factors.[1] Unfortunately, a lot of attention has been devoted to the influence of physical factors upon cellulosic fibres during aging, while the influence of chemical factors has received only little attention.

It is known that aging alters: the hypermolecular properties of paper (hornification)[2] – a partly reversible process, stimulated by beating, and the chemical composition of lignin and cellulose by fully irreversible deteriorative processes with a fatal impact on cellulosic matter.[1]

Cellulose aging may be induced by

- acid and enzymatic hydrolysis;[3]
- chemical and photochemical oxidation;
- a combination of both reactions.

Typically, due to the reactions mentioned above, cellulose and lignocellulosic materials get fragile and yellow.

Typically, paper and similar lignocellulosic materials have a porous non-oriented hypermolecular structure. Due to this structure and the hydrophilic character of the pore interface, this type of materials are typically prone to absorbing humidity with characteristic water vapour absorption kinetics.[4-5] Additionally, the water condensation process is accompanied by a decrease of the pH of the water extract, because the presence of the anion-active acid groups further induces acid hydrolysis of the lignocellulosic matter. During this process, strong acids such as acetic and glucuronic[6-7] acids evolve, followed by acid cleavage of the glycosidic linkages of polysaccharides. First of all, the acid hydrolysis of polysaccharides, predominantly cellulose skeletal matter, has a fatal irreversible impact on the mechanical properties of lignocellulosic matter.

Obviously, a low pH induces deep changes in the lignocellulosic material during its aging.

With an increase of relative air humidity (RH), a decrease in the pH of the water extract of lignocellulosic materials should be observed, accompanied by appropriate changes of the optical and mechanical properties.

The aim of this study was to assess the influence of RH upon the mechanical and optical properties of lignocellulosic materials during accelerated aging, in the context of their water extracts pH, and to attempt to find any possibilities to alter them. We sought to find out the effect of the pH of the water extracts during the aging of lignocellulosic materials.

An environment was modelled varying the RH and including different essential oil vapours with antimicrobial activity (bactericidal, fungicidal and sporicidal effects)[8-10] to reduce the wettability of lignocellulosic materials.[11] Accelerated aging was induced by the conditions applied during 14 days of curing the samples in different environments (temperature equal to 80 °C). The pH values of the water and salt solution (0.1 M solution of KCl) extracts were assessed.

THEORETICAL BACKGROUND

A theoretical tool describing the pH of the aqueous supernatant in pore systems is needed to better understand this process.

To explain the dependency of pH of aqueous extracts of paperboard samples subjected to accelerated aging vs. RH, knowledge on the humidification process of paper and other cellulose and lignocellulose materials is essential.[4] During humidification of these materials and other micro- and, in particular, submicro-porous materials, water vapour is absorbed (condensation in the pores) depending on the tension in the pores, from the smallest ones to the maximal effective pore size given by a real RH, φ_{rel}. At low water vapour tension, i.e. at low RH of the atmosphere, water vapour condenses only in the smallest pores etc. This means that at the RH of the atmosphere of about 50%, steam in liquid form is contained only in a small part of the pores, but, due to the high specific surface of the predominantly small pores, it is in terms of acid hydrolysis highly reactive, i.e. it is bound to accelerate the aging process. This enables a considerable increase in the acidity degree and therefore a low pH of the micro- and submicropores moisture content. This water is, however, in a relatively small amount, thereby after its dilution, due to the methodology used to determine the pH of the water extracts, may not actually significantly affect the final pH of the extract. As the local pH is not examined exactly, but its cumulative value is measured only, the dependence of pH vs. relative humidity has then a complex character. The resulting pH is given not only by hydrolysis and the concentration of released acidic ingredients due to the presence of other waste substances in the pores, but also by the structure and porosity of the porous materials.

Provided that the composition of all pore interfaces in pore matter is qualitatively and quantitatively constant and the pH of water condensed in the pores is a product of negative decadic logarithmus of hydrogen ion concentration [H^+], the resulting pH is a product of the surface concentrations of the [H^+] ions around the microwalls of the pores filled with water, Γ_H (mol/dm^2), and their specific surfaces, φ_s (surface of the pore walls in dm^2 divided by the pore volume in dm^3, i.e. dm^{-1}), according to the following relationship (1):

$$pH = -\log\left[H^+\right] = -\log\left[\Gamma_H \cdot \varphi_s\right] \tag{1}$$

This means that if the surface concentration of hydrogen ions, Γ_H is constant, then pH depends only on a specific surface of the pores, i.e. on the pore sizes. The higher the specific surface and the lower the pore size, the lower the pH of the water located in the pore. In other words, the reactivity of water increases with the φ_s of the pores where it is contained. When diluting this water with a constant amount of dilution water during determination of the extract pH, the concentration of [H^+] ions decreases and the pH of the extract is therefore always higher. Indeed, the pH of the aqueous extract of the pores with a volume of pores (V_r) is determined by the following formula:

$$pH = -\log\left\{\frac{(\left[H^+\right]_r \cdot V_r + \left[H^+\right]_o \cdot V_o)}{(V_r + V_o)}\right\} = -\log\left\{\frac{(\left[\Gamma_H \cdot \varphi_s\right]_r \cdot V_r + \left[H^+\right]_o \cdot V_o)}{(V_r + V_o)}\right\}$$

More precisely, by Equation (2), supposing all of the pores from the smallest ones to the pore volume, V_r with a size of the effective pore, $r(\varphi_{rel})$ (see also Eq. 3) are filled with condensed water at a given RH, φ_{rel}: The values $\left[H^+\right]_o$ and V_o specify the pH with respect to the concentration of hydrogen ions in water and a volume used to perform the aqueous extract, respectively.

$$pH = -\log\left\{\frac{(V_s \cdot \varepsilon \cdot \int_{V_{r\min}}^{V_r} [H^+]_r \cdot f(V_r) \cdot dV_r + [H^+]_o \cdot V_o)}{(V_s \cdot \varepsilon \cdot \int_{V_{r\min}}^{V_r} f(V_r) \cdot dV_r + V_o)}\right\} = \tag{2}$$

$$= -\log\left\{\frac{(V_s \cdot \varepsilon \cdot \int_{V_{r\min}}^{V_r} \Gamma_H \cdot \varphi_s(V_r) \cdot f(V_r) \cdot dV_r + [H^+]_o \cdot V_o)}{(V_s \cdot \varepsilon \cdot \int_{V_{r\min}}^{V_r} f(V_r) \cdot dV_r + V_o)}\right\}$$

The V_s corresponds to the total volume of the sample used for extraction (V_s = m_S/OH, where m_S and OH are the weight and apparent density of the paper sample, respectively); ε is porosity and $f(V_r)$ is the relative fraction of pore size in the volume interval V_r to V_r+dV_r, respectively, a probability pore distribution function of the sample ranging in the value interval from 0 to 1.

Therefore, under comparable conditions (i.e. temperature, RH of air in which the paper has been air-conditioned and the maximal pore size in which the water steam is condensed are the same), the pH of the aqueous extract depends upon its quality (parameter Γ_H) and porosity (ε) mainly upon $\varphi_s(V_r)$ and $f(V_r)$, especially on the product of these functions whose shape is depicted in Fig. 1. As the specific surface of a pore decreases with an increase in pore size ($\varphi_s(V_r)$ = 4/r(φ_{rel})) and the pore distribution function is not a monotonic function, the dependence of the pH of the water extract of the paper material vs. relative air humidity has a tendency to go through a maximum. The shape and nature of this dependence thus rely on both the shape and location of the function $\varphi_s(V_r)$ and a probability function, $f(V_r)$, i.e. on the structure of the porous material.

It is supposed that the location and shape of the pH – RH curves are strongly influenced by both the pulp sort and partly by the condensed components of essential oils (EO), because the EO applications strongly have a great impact on the absorption of water in porous lignocellulosic materials (see Fig. 2).[11] It is possible to establish the effective maximal pore diameter (μm), including small pores, filled with condensed water at RH 49%, 75% and 97% by the following Equation (3):

$$r(\varphi_{rel}) \equiv i(\varphi_{irel}), j(\varphi_{jrel}), k(\varphi_{krel}) = \frac{4M\,\sigma_T(1+\sin\theta)}{\rho_l\,RT\ln(1/\varphi_{irel},\varphi_{jrel},\varphi_{krel})} \tag{3}$$

where

$i(\varphi_{irel}), j(\varphi_{jrel}), k(\varphi_{krel})$ – effective maximal pore diameter (μm), including smaller pores, filled with condensed water at RH 49%, 75% and 97%, respectively;

M - molar mass of water (kg/mol);

T - temperature (K);

σ_T - adhesion tension of liquid to pore surface[12] (N/m); in capillary $\sigma_T = \gamma_{l,g}(1-\sin\theta)/\cos\theta$;

θ - contact angle between the surface of the capillary tube and liquids internal meniscus (this angle is usually equal to 0^o);

$\gamma_{l,g}$ - liquid surface tension (water, 72.2 10^{-3} N/m at T = 295 K);

ρ_l - liquid density (kg/m^3);

R - gas constant (8.314 J/(K.mol)).

EXPERIMENTAL

Applied essences and lignocellulosic materials

Paperboard handsheets with a basis weight of 400 ± 15 g m^{-2} were prepared with the following composition:

- DM mixture consisting of 90% of the groundwood (beating degree according to Schopper-Riegler (SR) equal to 60) and 10% of MgBi-sulphite spruce bleached pulp (SR 25);
- Sa J (bleached sulphate softwood pulp), SR 25;
- Si (MgBi-sulphite spruce bleached pulp), SR 25.

After beating in a laboratory beater, the sample sheets were formed according to ISO 5269-2 standard. A method of molecular groping of pores has been used to characterize the pore structure and surface-molecular properties of pore interface of the paperboard samples. The method is based upon controlled humidification and vapour absorption of selected organic substances (toluene and methyl ethyl ketone) in porous non-structuralised flat material.[12-13] All samples were acclimatised before starting the experiment for 10 days in a desiccator filled with dry silica gel at room temperature (23 ± 1 ^{o}C). At least three measured values were averaged to give a mean value reported in this paper.

The received results are summarised in Table 1 and Table 2. The results are an average of duplicates with less than 8% deviation between samples.

Selected essential oils (EO) showing the best microbicide effects were assessed:

- *Lavender* (*Lavandula species*);
- *Lime* (*Citrus aurantifolia*);
- *Myrtle* (*Myrtus communis*);
- *Cinnamon* (*Cinnamomum zeylancium*).

The concentrated oils purchased from a dealer were not added into the medium, but dripped on open Petri dishes in amounts of 2 ml of EO per desiccator.

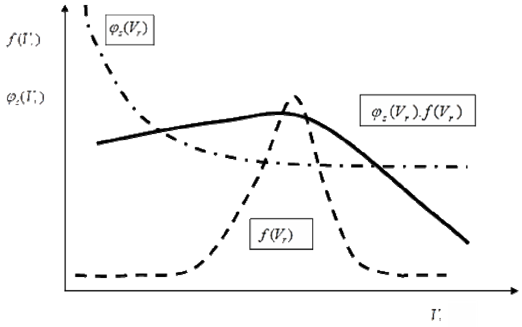

Figure 1: Schematic representation of theoretical dependence between the pH and volume of pores filled with condensed water

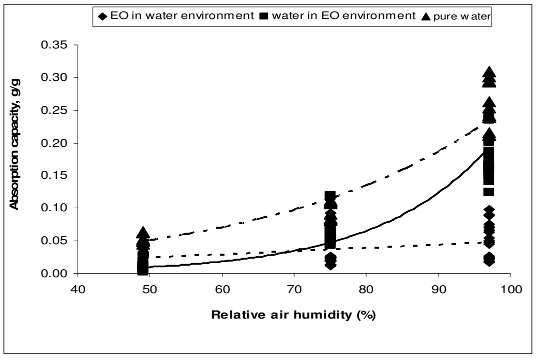

Figure 2: Absorption capacity (at 49%, 75% and 97% RH) of EO and water (g/g of dried pulp substance) vs. relative air humidity (the presented data refer to 3 types of lignocellulosic materials and 4 types of EO vapours)

Used methods

The mechanical properties of the paperboard specimens were measured on a TIRAtest 26005 device, by the 3-point method. All measurements were carried out in a constant climate room at a temperature of 23 ± 1 °C and RH of 50 ± 2% after 5 days of acclimatisation. Strips with a constant width of 15 mm were cut from the handsheets. For every paperboard strip, a typical dependence between specimen deflection and acting force was recorded.[14-15] The dependence between the acting force and deflection was determined at least 10 times for every paper sheet. All measurements are an average of duplicate samples with less than 10% deviation. However, to better characterize cellulose skeletal matter damage, the irreversible part of the stress–strain curve is more useful, because this non-linear part of strip deflection is more sensitive than the linear part characterizing bending stiffness. Due to this fact, a paperboard sheet-yielding was determined by using the following parameters:[16]

FH_{15} - touch force to sample at its deflection of 15 mm, N;

dFH - difference between the supreme force FH and FH_{15}, N;

δFH - relative difference $100*(FH-FH_{15})/FH$, %.

All of these parameters characterize the paper matter persistence – its ability to crumble. With increasing of dFH or δFH, the friability of paperboard sheet grows as well, and vice versa. The lower dFH or δFH, the higher is the flexibility of the paperboard sheet. For a better comparison, a factor of aging was introduced: $Fs = \delta F(H=1)/ \delta F(H=1)_{blank}$, i.e. the ratio of inner tension relaxation of aged and non-aged sample strips of 1 mm width.

If Fs > 1 – a negative influence of aging upon the mechanical properties of lignocellulosic matter is observed, i.e. a higher friability and the ability of material to crumble during its strain exposition; if Fs < 1 – a positive influence of aging upon the mechanical properties of paper matter is found.

Table 1
Porous structure and pore interface properties of paperboard samples

Paper parameters	DM (groundwood)	Sa J (bleached sulphate softwood pulp)	Si (MgBi-sulphite spruce bleached pulp)
Apparent density, kg·m^{-3}	442.73	643.26	708.55
Porosity ε, %	71.6	59.29	55.2
*Effective mean pore, μm	2.3	6.8	4.7
*Dispersion of pore distribution, μm	3.4	26	12
**σ_T, mN/m	2.6	7.5	5.7
**γs, mN/m	33.2	33.7	33.5
**γd, mN/m	30.1	30.1	30.1
**γ+, mN/m	0.28	0.28	0.28
**γ-, mN/m	8.6	11.6	10.5

**γp, mN/m	3.1	3.6	3.4
**d	0.91	0.89	0.90
**p	0.09	0.11	0.10
**p+	0.01	0.01	0.01
**p-	0.26	0.34	0.31
***Ye (97%), (g/g)	0.29	0.22	0.24
***Ye (75%), (g/g)	0.11	0.08	0.08
***Ye (49%), (g/g)	0.06	0.05	0.05

Remarks:

* Effective mean pore diameter and pore size dispersion provided that pore size distribution function is controlled by theoretical Gauss distribution

** (σT, γs, γd, γp, γ+, γ-, d, p, p+, p-) Surface-molecular pore interface parameters are characterized by adhesion tension of pore interface to water, surface tension of pore interface with air, dispersion (nonpolar) part of surface tension of pore interface with air, polar part of surface tension of pore interface with air, cation-active polar part of surface tension of pore interface with air, anion-active polar part of surface tension of pore interface with air, relative dispersion (nonpolar) part of surface tension, relative polar part of surface tension, relative cation-active and anion-active polar part of surface tension of pore interface with air, respectively

*** (Ye(97%), Ye(75%), Ye(49%)) Equilibrium humidity of paper (g of water per g of dry bone of paper) at air RH 97%, 75% and 49%, respectively

Table 2
Wet porous structure characteristics of paperboard samples

Paper parameters	DM (groundwood)	Sa J (bleached sulphate softwood pulp)	Si (MgBi-sulphite spruce bleached pulp)
Apparent density, kg·m^{-3}	442.73	643.26	708.55
Porosity ε, %	71.6	59.29	55.2
*ε_i (49%), %	2.76	3.34	3.67
*ε_j (75%), %	4.80	5.21	5.88
*ε_k (97%), %	12.78	13.73	16.57
**i (μm)	0.2	0.6	0.5
**j (μm)	0.5	1.5	1.2
**k (μm)	5.1	14.3	11.0

Remarks:

*(ε_i(49%), ε_j(75%), ε_k(97%)) Wet sample porosity, i.e. the porosity of samples filled with condensed water at RH 49%, 75% and 97%, respectively

**(i, j, k) Effective maximal pore diameter, smaller pores inclusive, filled with condensed water at RH 49%, 75% and 97%, respectively

Optical measurements were carried out using an ELREPHO spectrophotometer from Lorentzen & Wettre. Before all measurements, the paper samples were cured for 5 days at a temperature of 23 ± 1 °C and RH of 50 ± 2%. All optical parameters were tested, including brightness. All the brightness results in Figures 3-5 are averages of at least 10 measurements for every paperboard sheet with less than 4% of standard deviation.

The pH of the water and salt solution (0.1 M solution of KCl) extracts was measured in accordance with ISO 6588-1 and ISO 29681, respectively, using a pocket pH meter "Handylab pH 11" from Schott Instruments. All the results presented are an average of triplicate measurements with less than 8% deviation among them.

Accelerated aging of the tested 3 types of paperboards was realised by the method of wet aging, and the influence of EO upon this process was assessed. The samples were exposed to the wet aging process for 14 days in an oven at a temperature of 80 °C and different air RH (49%, 75% and 97%). At the bottom of the glass desiccator, an evaporating dish with 2 ml of EO and a container with salt solution corresponding to the desired relative humidity were placed. The relative humidity in the desiccator (49%, 75% and 97%) was achieved by means of KNO_2, NaCl and K_2SO_4 saturated solutions, respectively. The initial pH values of the paperboard extracts (pH blank) were 7.14, 6.96 and 7.43 for groundwood (DM), bleached sulphate (Sa J) and sulphite (Si) softwood paperboards in the case of water extracts, and 7.50 (DM), 7.64 (Sa

J) and 7.83 (Si) in the case of KCl solution extracts, respectively. In order to achieve a better visual comparison, the results obtained were then recalculated as relative pH = pH/pH blank.

RESULTS AND DISCUSSION

As follows from Table 1, paperboard prepared from groundwood (DM), representing high yield wood pulp, has distinctly the highest porosity, with a hydrophobic character of the pore interface, compared with the low yield bleached pulps under study. This determined the lower wettability of DM, as demonstrated by the lower values of its adhesion tension (σ_T), surface tension (γs) and the highest value of the relative dispersion component of surface tension (d). Moreover, the paperboard containing groundwood (DM) is distinguished by the highest saturated humidity (Ye) achieved at all RH values, because of the highest porosity and lowest size of its pores. Differences among bleached sulphate and sulphite paperboards from long-fibre pulps are small. Higher hydrophilicity is typical of these bleached pulps.

However, all tested pulps shared an anion-active character of the polar hydrophilic part of the surface tension – higher in the case of bleached pulps (compare parameters γ- and p-). Additionally, the data on the wet porosity structure of the paperboards used (see Table 2) support very well these observations. Due to the higher hydrophilicity of the bleached pulps, water vapours condensed in the bigger pores, compared to those of the groundwood paperboard samples (see Fig. 3).

Optical and mechanical properties

As expected, chemical reactions taking place during accelerated aging of porous lignocellulosic materials are indicated through changes of their optical (brightness – see Figures 4-6) and mechanical (see Figures 7-9) properties. It seems that an increased RH has a great influence upon the brightness of paperboard samples made of high yield pulp (see Fig. 4, groundwood), compared with that of low yield bleached pulps (see Figures 5-6). In comparison with bleached pulps, an application of some essential oils even improves the brightness of groundwood.

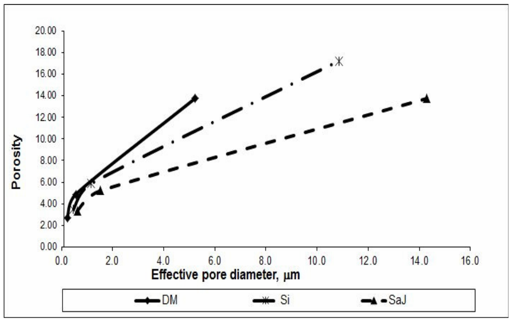

Figure 3: Porosity vs. maximal effective pore diameter of paperboards filled with condensed water

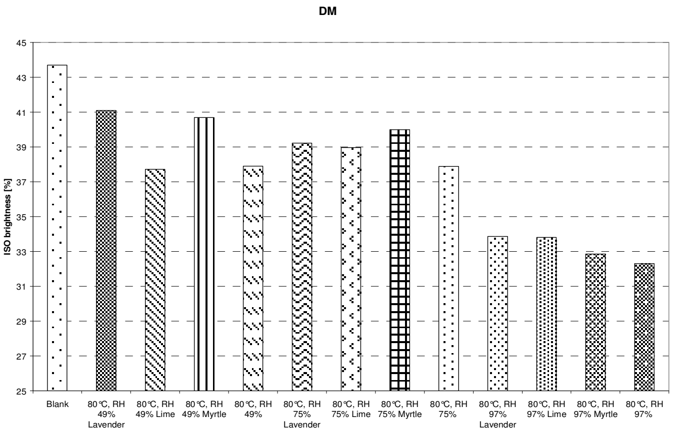

Figure 4: Brightness of groundwood paperboard subjected to accelerated aging at different RH levels and with different EO types

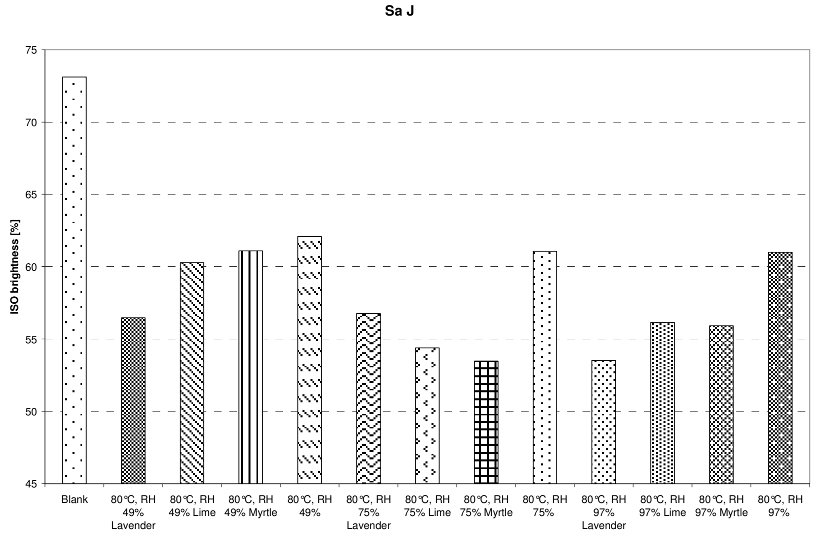

Figure 5: Brightness of bleached sulphate softwood paperboard subjected to accelerated aging at different RH levels and with different EO types

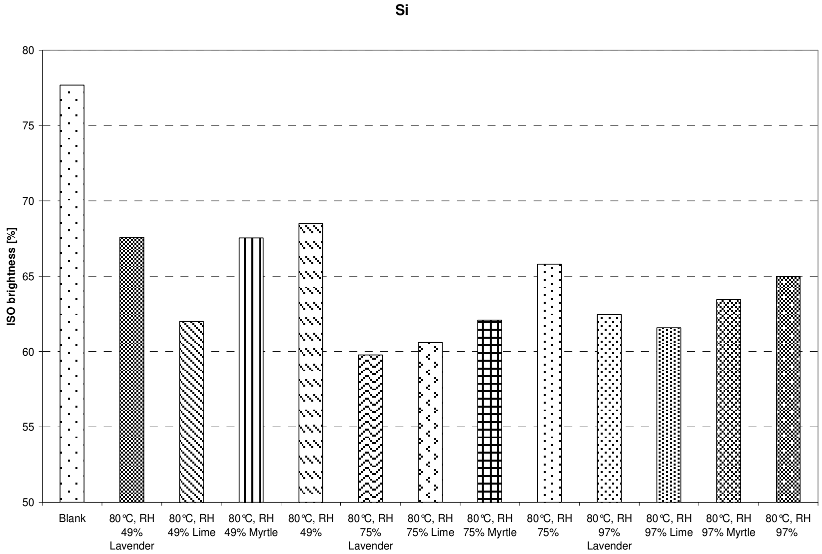

Figure 6: Brightness of bleached sulphite softwood paperboard subjected to accelerated aging at different RH levels and with different EO types

Increased relative air humidity had a worsening effect upon the mechanical properties of paperboard samples of all fibre types, without marked differences however between the effects of RH 49% and RH 97%, except in the case of groundwood (see Fig. 7). However, this deteriorating influence is slightly suppressed by the application of EO in the case of groundwood, while in the case of chemical pulps, a slight improvement has been observed (the values of relative parameter $F_S < 1$, see Fig. 8). This indicates the protective influence of EO application to lignocellulosic porous materials during aging, increasing at higher RH. The minimum relative Fs, i.e. the maximum protective influence of EO upon lignocellulosic materials during aging, has been shown at 75% RH (see Fig. 9). Obviously, this behaviour is connected with the depressing influence of EO application upon water vapour absorption (see Fig. 2). Even at room temperature, the humidification measurements in EO atmosphere indicate an affirmative influence of EO molecules upon depression of water vapour absorption in these paperboards.

Aqueous and KCl solution extracts – pH values

Obviously, acid hydrolysis reactions, mainly evoked due to the presence of NO_x in polluted atmosphere, explain the changes produced by the presence of other components, e.g. by essential oils. The acid hydrolysis of porous heterogeneous cellulosic materials is distinguished by a characteristic depolymerisation reaction taking place by the peeling-off cellulose degradation mechanism, well described by the so-called DP-peeling off model.[6] During depolymerisation, monosaccharides, mainly glucose and partly strongly acidic glucuronic acid are evolved, initiating a further destruction process followed by the formation of nascent organic acids, such as are formic, acetic, oxalic etc. acids.[1,17]

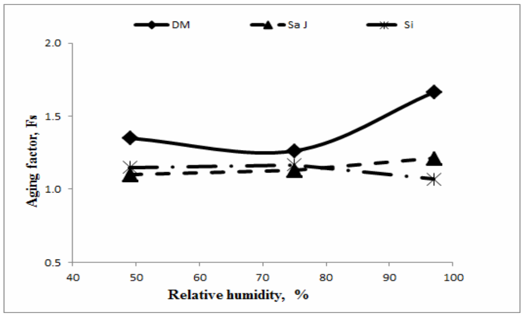

Figure 7: Mechanical properties of paperboards; accelerated aging without EO

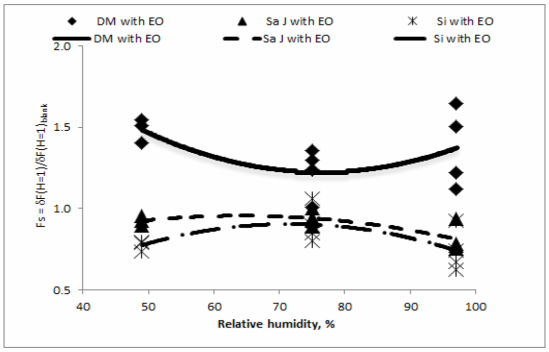

Figure 8: Mechanical properties of paperboards; accelerated aging with EO (Lavender, Lime, Myrtle, Cinnamon)

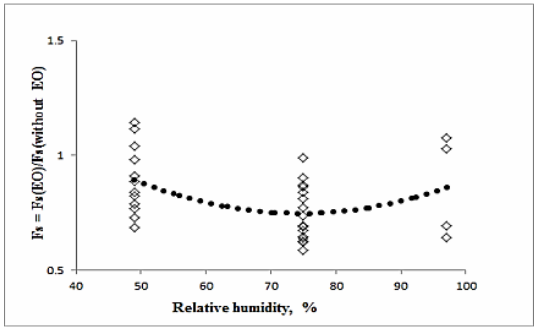

Figure 9: Cumulative comparative influence of EO upon relative mechanical properties of paperboards during accelerated paper aging

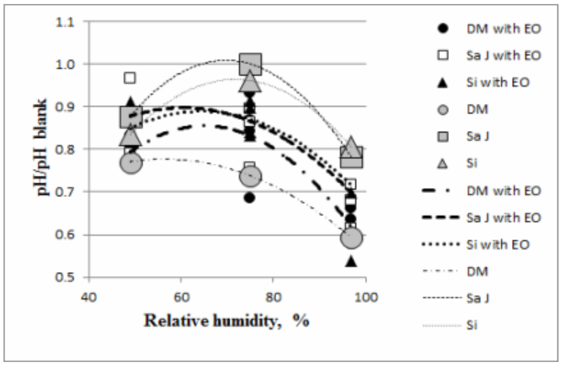

Figure 10: Relative pH of water extract of paperboard strips. Influence of accelerated aging (i.e. 14 days, 80 °C) and EO vapours

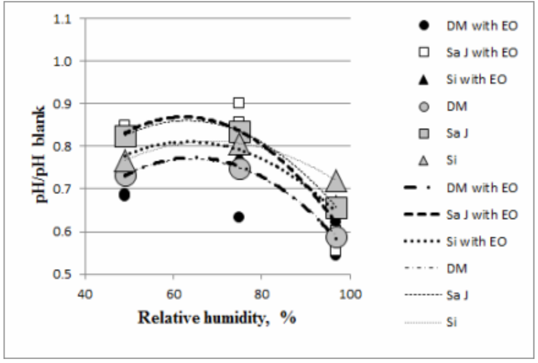

Figure 11: Relative pH of KCl solution extract of paperboard strips. Influence of accelerated aging (i.e. 14 days, 80 °C) and EO vapours

A typical feature of these processes is a pH decrease of water supernatants. With an increase in the relative air humidity of the environment, the amount of condensed water in the porous cellulosic materials increased (see Fig. 2),

In accordance with the above-mentioned theory (see Fig. 1), the pH–RH dependences do not have a monotonous descending trend, instead, they are complex functions reaching a maximum at approximately 75% RH for both water (Fig. 10) and KCl solution (Fig. 11) extracts.

The pH value of groundwood paperboard extracts was found to be lower than that of paperboard extracts prepared from bleached pulps. The observation is in full accordance with the data on wet porosity structure and absorption capacity presented in Table 2 and Fig. 2, respectively. That is to say, due to higher porosity of groundwood fibre matter with smaller pores and their less dispersive character, but with higher hydrophobicity, condensed water is contained predominantly in small, but more active pores. More precisely, this behaviour can be described by the help of Equation (3).

However, a tendency has been remarked upon EO application: the pH values of the water extracts of groundwood increased, while they decreased for bleached chemical pulps. This trend is depressed in KCl solution extracts (compare Figs. 10 and 11). Logically, the absorption of water vapour is suppressed by EO application in the simply shaped pores of the groundwood paperboard, because of the hydrophobic influences accompanied by an increase of pH. Obviously, in the case of the deeply eroded bleached pulps forming SaJ and Si paperboards, considering the complex shapes of the micropores, the pH vs. RH relation takes a different turn.

It seems further that due to absorption of the EO vapours, the pore distribution function (see Eq. 2) accessible to molecules of water vapour also changes, shifting the characteristic maximum to smaller micropores, respectively microholes, resulting in a decrease of the extract pH. Additionally, the methodology of aqueous extraction is based upon stirring of the fibre suspensions, i.e. electrokinetic phenomena also have a role to play. Compared with clear water, diffuse parts of electric double layers around pore interfaces filled with KCl solution are closer and more stabilised, with low sensitivity to liquid movement during extraction processes, predominantly to its penetration. With increasing accompanied by the above-mentioned acid hydrolysis processes, i.e. by a proportional decrease of pH. However, as demonstrated in Figures 10 and 11, this dependence is not so simple.

ionic strength of the extract agent, a tendency appears towards lower pH of the extracts and suppression of the EO influences, since the increase of the ionic strength leads to a decrease of width of the diffusion layer and vice versa. Due to this, the method of using water extracts for determining the pH is more sensitive than that of using KCl solution extracts.

CONCLUSION

The results presented herein indicate that usual storage conditions of lignocellulosic materials, i.e. relative air humidity around 50% or lower and temperature of about 20 °C, are not a solution to eliminate the chemical aging of these materials. This is certainly true particularly in the case of biochemical aging. By comparing the results of accelerated aging (biochemical aging does not apply) at different relative air humidity levels, it is clear that, though the lowest pH of an aqueous extract after ageing is found at 97% relative air humidity, an opposite phenomenon actually occurs. This is due to the different local acidity and pH at low and high relative environmental humidity. High acidity and low pH are formed at low relative environment humidity in the micro- and submicro-pores filled with condensed water. On the contrary, lower average acidity and higher pH of water condensed in virtually all the pores of the porous material, including large pores, occur at high relative environment humidity.

The presence of substances released from natural bio-products, as the essential oils are, certainly has an effect on the aging of lignocellulosic materials, since these substances at least depress their moistness. Generally, it was found that substances released from essential oils have a minimum negative impact and, in some cases, a positive effect on the aging of lignocellulosic materials as paper and other paper products.

Certainly, the pH of aqueous extracts is a simple and useful tool providing the possibility to monitor the aging process of lignocellulosic materials. However, the interpretation of the data obtained is complex and intricate, requiring adequate knowledge about the porosity and surface-molecular properties of the porous material under study.

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REFERENCES

[1] M. Milichovský, B. Češek, M. Filipi and J. Gojný, *Przeglad Papierniczy*, **69**, 291 (2013).

[2] Št. Šutý, K. Petriláková, Sv. Katuščák, S. Kirschnerová, M. Jablonský *et al.*, *Cellulose Chem. Technol.*, **46**, 631 (2012).

[3] M. Jablonský, J. Kazíková, M. Botková and S. Holúbková, *Cellulose Chem. Technol.*, **46**, 625 (2012).

[4] B. Češek, M. Milichovský, and Fr. Potůček, *ISRN Materials Science*, **2011**, 1 (2011) doi:10.5402/2011/794306.

[5] B. Češek, M. Milichovský, Fr. Potůček and J. Gojný, in *Procs. The 9th International Symposium "Selected Processes in Wood Processing"*, Štúrovo, Slovakia, September 7-9, 2011.

[6] M. Milichovský, T. Sopuch and J. Richter, *J. Appl. Pol. Sci.*, **106**, 3641 (2007).

[7] M. Milichovský, Bř. Češek and Sv. Milichovska, in *Procs. The 8th International Symposium "Selected Processes in Wood Processing"*, Štúrovo, Slovakia, September 9-11, 2009 p. 40-41.

[8] K. A. Hammer, C. F. Carson and T. V. Riley, *J. Appl. Microbiol.*, **86**, 985 (1999).

[9] E. Survilienė, A. Valiuškaitė, V. Snieškienė and A. Stankevičienė, *Scientific Works of the Lithuanian Institute of Horticulture and Lithuanian Universityo of Agriculture. Sodininkystė Ir Daržininkystė*, **28**, 227 (2009).

[10] M. S. Rakotonirainy and B. Lavédrine, *Inter. Biodeter. Biodegrad.*, **55**, 141 (2005).

[11] B. Češek, M. Milichovský and J. Gojný, *J. Biomater. Nanobiotechnol.*, **5**, 66 (2014).

[12] B. Češek, M. Milichovský and G. Adámková, *Cellulose Chem. Technol.*, **39**, 277 (2005).

[13] B. Češek, M. Milichovský and Fr. Potůček, *Cellulose Chem. Technol.*, **40**, 705 (2006).

[14] Fr. Potůček, Bř. Češek, P. Domin and M. Milichovský, *Cellulose Chem. Technol.*, **41**, 277 (2007).

[15] Fr. Potůček, Bř. Češek and M. Milichovský, *Cellulose Chem. Technol.*, **42**, 413 (2008).

[16] P. Domin, I. Nesládek, M. Milichovský, Bř. Češek and Fr. Potůček, in *Procs. EUCEPA Supported International Symposium "Challenges of Pulp and Papermaking Technology"*, Bratislava, Slovakia, November 8-10, 2006.

[17] M. Milichovsky, S. Milichovská, *J. Appl. Pol. Sci.*, **107**, 2045 (2008).