THE INFLUENCE OF MICROBICIDAL SUBSTANCES ON THE PROPERTIES OF CELLULOSIC AND LIGNOCELLULOSIC MATERIALS

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Abstract

An unsuitable storage of books can cause microbiological attack. The biological attack can be caused by bacteria or fungi. The next type of degradation reaction is hydrolysis, which is supported mainly by increased content of water in books. In this case is degraded the whole cellulose structure. This work is focused on the influence of three components of essential oils on strength and optical properties of lignocellulosic materials. These components, with their microbicidal effects and their hydrophobic character, could serve as protection of archive materials on cellulosic base. For testing were used cellulosic and lignocellulosic materials, common used in paper industry (coniferous sulphate pulp, deciduous sulphate pulp, sulphite pulp, groundwood, pulp for the production of handmade paper and sample of historical paper). It was proved no deteriorate effect of basic components composing of essential oils (EO) upon strength properties of paper matter.

Introduction

Essential oils are natural substances which protect the substrate (wood, plants) from the negative effects of mould. These compounds are synthetized in the plant to prevent the mould from attacking the plant body. The effect of essential oil had been observed by ancient civilisations. For instance the antimicrobial and beneficial action of essential oils has been verified a number of times[1].

The mixture of the compounds of essential oil evaporated at normal temperature forms a protective atmosphere while condensing in the paper matter.

At given relative humidity of air the wetness of paper is deceased through oil sorption into the paper. This physical phenomenon slows down the growth of mould. Due to the chemical action of the oil there is a sporicidal effect present[2].

The impact of the presence of essential oil on the mechanical and optical properties on the substrate was investigated. Simultaneously the said properties were investigated under the absence of essential oil.

The research resulted in showing an important action on the mould and fungi. The action of the oils on the substrate was mostly lower than the error variance of the properties investigated[3].

Materials and methods

Lignocellulose materials:

For testing mechanical properties were chosen conventionally used pulps for papermaking (Table 1). These cellulose and lignocellulose materials have been defibrillated in a laboratory hollander and then were beaten. Beating degree was determined according to Schopper-Riegler (SR). From the pulp were prepared sheets according to ISO standard 5269-2 on laboratory sheet former Rapid-Köthen. Basis weight of the specimens was about 400 g m^{-2} and 70 g m^{-2} of historical paper.

Table I
Lignocellulose materials

SaL	sulphate hardwood pulp from Ružomberok, the beating degree 25 °SR
SaJ	sulphate softwood pulp from Štětí, the beating degree 25 °SR
Si	sulphite pulp from Biocel Paskov, the beating degree 25 °SR
RP	the raw material for the production of handmade paper from the Velké Losiny, consisting of 60% cotton linters and 40% of pulp of flax, the beating degree 28 to 29 °SR
DS	groundwood with the addition of 10% of sulphite pulp, as described above
HP	historical paper 1909, consisting of 46% rag fibres, 23% sulphite pulp and 31% groundwood

Components of essential oils:

Three components of EO (eucalyptol, limonene, ocimene) with the highest microbicide effect have been chosen for testing. Bactericidal effectiveness was tested on microorganisms *Aspergillus brasiliensis*, *Penicillium aurantiogriseum exniger* and *Cladosporium cladosporioides*, which are the most frequently organisms attacking paper-based matters.

Description of the apparatus:

First all specimens were conditioned at a relative humidity of 50 ± 2% and temperature of 23 ± 1°C for two weeks. Then they were placed in a desiccator with saturated vapours of active substance and with relative humidity environment of 75%, which in a desiccator maintained saturated NaCl. Vapours of the active substance were evaporated from 2.5 ml of solution in petri dishes. One half of specimens were collected after 30 days of exposure for the purpose of testing properties. The other half was supplemented by a further 2.5 ml of solution and was exposed for 300 days.

Determination of strength properties

Sheets of paperboard with basis weight about 400 g m^{-2} were cut into test specimens of sizes 100 x 15 mm. Accurate basis weight was calculated and also thickness of the specimens was measured. To measure the strength properties after the application of vapour of essential oils was chosen parameter tensile index (TI).

The measurement was performed according to ISO 1924-2 on the machine TIRAtest 27025. There were used clamps no. 5044 with span 100 mm. Tensile index is calculated by the equation 1.

$$TI = F_{max} / BW \,.\, b \qquad (1)$$

Where F_{max} *(N) is the maximum force measured before the specimen was broken, BW (g* m^{-2}*) is the basis weight of the specimen and b (m) is the width.*

Determination of optical properties

Optical properties were measured by the spectrophotometer Elrepho Lorentzen & Wettre Company. The ISO brightness was measured at C illumination and L* a* b* coordinates were determined from which the colour difference ΔE* from the unexposed specimen has been calculated (Equation 2).

$$\Delta E = \sqrt{(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})} \qquad (2)$$

Discussion and result analysis

Measured mechanical properties of exposed samples were compared to blank samples, which were placed entirely in environment with a relative humidity of 75%. First part of reference specimens was measured before the exposure and the next parts were measured during exposition - after 30 and 300 days of exposition. As it is shown on FIG. 1 – there was no statistical significant decrease of tensile index in lignocellulosic material. Not even one of active ingredients had negative effect on mechanical properties of tested specimens, not even after 300 days of exposure.

However, there was a mistake which was made during measuring reference samples (from material, which is used for handmade paper, RP) after 30 days of exposure, and that is the reason why this value is not relevant. It is necessary to take account of reference specimens before exposition and after 300 days of exposition.

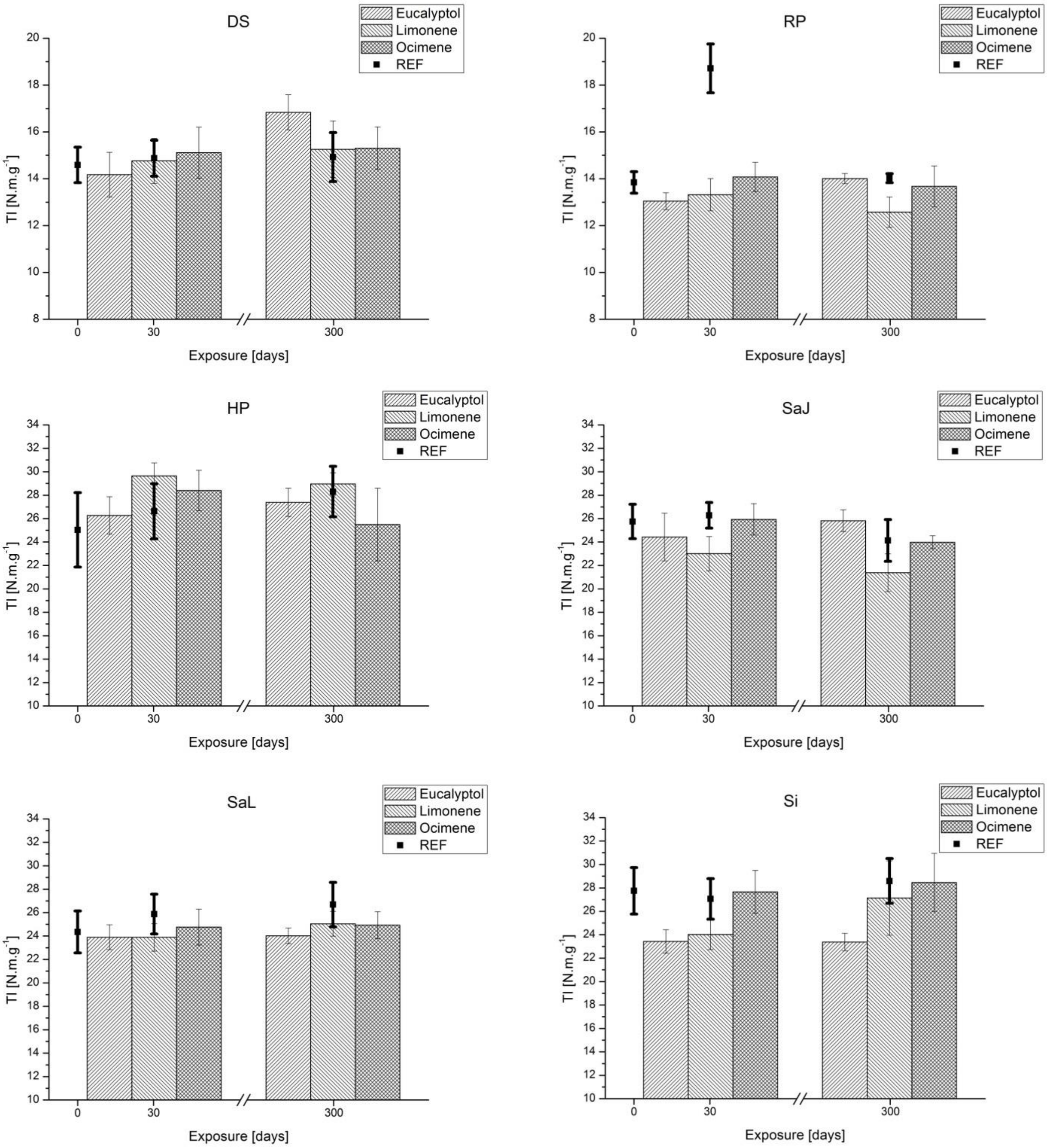

Figure 1. Dependence of tensile index on exposure time in the saturated vapours of microbicidal substances. Confidence Interval = 95%

Changes in the optical properties were monitored mainly by ΔE difference after exposure to the unexposed sample. Paper made from sulphate hardwood pulp showed stability after exposure to vapours eucalyptol and limonene. Saturated vapors of ocimene had significant effect on the colour change of the material (see Tab. 2). It seems that Ocimene had a significant effect on all materials both after 30 and even after 300 days of exposure. The smallest influence on the exposed materials had vapors of eucalyptol.

Table 2
Value of colour difference ΔE* after exposure 30 and 300 days in the saturated vapours of microbicidal substances

	SaL ΔE		SaJ ΔE		Si ΔE		RP ΔE		DS ΔE	
	30 days	300 days	30 days	300 days	30 days	300 days	30 days	300 days	30 days	300 days
eucalyptol	0,30	0,40	0,29	0,23	0,17	0,15	0,21	0,64	1,46	0,94
limonene	0,12	1,10	0,74	1,02	0,60	0,83	0,38	3,32	0,25	1,38
ocimene	4,18	3,88	2,08	1,66	2,61	3,28	3,75	4,23	0,80	2,49

Conclusion

The influence of components EOs on the behaviour and properties of the paper material is possible to indicate. There is a close connection between the influence and its absorption, possible interaction and reaction with the components on the pore wall surface of paper matter. Vapours and single components of EOs have an influence on surface-molecular properties of the porous structure of the paper matter. As especially reactive appear unsaturated aldehydes like citral or ocimene – having conjugated system of double bonds which is particularly subject to free-radical reactions. The effect of saturated vapours of eucalyptol, limonene and ocimene does not show statistically significant decrease of strength or mechanical properties of paper materials.

In case of application these vapours with active components of Essentials oils inside archive with books and archives, the vapours would have to be diluted many times. It is proved, that the absorbed vapours of chosen substances serve as retardant against microbiological attack in paper-based materials.

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