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FT-NIR SPECTROPHOTOMETRIC ANALYSIS OF PAPER, MADE OF CELLULOSE SULFATE BLEACHED DECIDUOUS PULP, WITH STARCH AND RESINOUS GLUE ADDITIVES, SUBJECTED TO MYCOLOGICAL BIODEGRADIATION

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Abstract. In the work, an attempt was made to evaluate quickness of mycological biodegradation of paper products, with various percentage content of cationized starch and resinous glue, with help of FT-NIR spectrophotometric analysis. As a biotic factor – *Ch. globosum* axenic culture and mixture of microfungi: *A. niger*, *T. viride*, *P. funiculosum* were used. As a criterion of biodegradation, one assumed resistance to overgrowth of samples' surface by test mycelium, and determined self-breaking, having completed mycological test on the 2nd, 4th, 7th, 10th and 14th day of observation. For the needs of research, one selected cellulose sulfate bleached deciduous pulp from which, together with the above listed pulp additives, sheets of paper were created, everything in laboratory conditions. Starch and resinous glue additives as packing of deciduous pulp caused an increase of susceptibility to overgrowth by test fungi, in comparison to samples without any additives. Paper products infected by *Ch. globosum* microfungus, generally showed bigger tendency towards biodegradation. Usage of FT-NIR spectroscopy allowed to analyse the complex process of degradation of ligno-cellulose material. Changes in the case of peak intensity of degraded waste paper pulps, were mainly noticed in the case of functional groups of cellulose C-H (4280 cm^{-1}), $C\text{-}H_2$ (4404 cm^{-1}), and O-H groups (range 4620-4890 cm^{-1}). Simultaneous usage of several independent methods of degradation degree evaluation, enabled objective interpretation of results, and the carried analyses mutually support the obtained research results.

Key words: paper samples, microfungi, biodegradation, FT-NIR spectrophotometry

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INTRODUCTION

Modern methods of paper production, based on sulfate method of wood pulping use mainly two kinds of pulps: cellulose and wastepaper/recycled paper. Due to ecological matters, recyclable pulps are the basis of paper production. However, as a result of multiple usage and mechanical processing, they may not fulfill requirements of assumed endurance and hygienic properties. In order to ensure required quality – it is necessary to add fresh primeval fibers – cellulose pulps [Przybysz 1997]. Examination concerning susceptibility to biological biodegradation of products of paper pulp (cellulose deciduous pulp) showed their resistance to mould attacks. Production of paper with usage of different pulp additives enables estimation of how these substances influence its endurance properties and resistance to biotic factors.

Traditional analysis of chemical composition of ligno-cellulose materials are time – consuming and expensive. Besides, they belong to destructive methods what makes them considerably limited. Alternative method is spectroscopy of near infrared radiation (FT-NIR), which is non-destructive, relatively quick and not expensive. It does not require complicated procedures of sample preparation but enables simultaneous detection of many components, and its accuracy is high [Sandak 2008, Sandak et al. 2010]. In paper industry, the method of spectrophotometric analysis is used first and foremost for quick evaluation of resources/raw materials' quality [Alves et al. 2006], paper products manufacturing, humidity estimation during paper production directly at paper machine and during evaluation of gsm and thickness of paper [Antti 1999]. Application of this method for the analysis of paper products, subjected to the activity of test fungi, was motivated by measurable results, obtained in the former marking of paper from recycled paper pulp with cereal bran additives.

The present article reports fragment of research over broad issue of determination of pulp additives' influence upon quickness and degree of biodegradation of paper products.

The aim of the work was to examine how starch and resinous glue additives influence quickness of overgrowth of samples by selected microfungi, using spectrophotometry of near infrared radiation (FT-NIR) and comparing it with two independent methods (standard method – using indexation for the description of samples' overgrowth degree, and evaluation on the basis of measurement of resistance towards self-breaking of the examined paper products.)

MATERIAL AND METHODS

During examination, one created seven paper products of cellulose sulfate bleached deciduous pulp, in laboratory conditions, using Rapid-Kötchen apparatus (PN-EN ISO 5269-2:2007), with gsm of 100 ±3 g/m^2 in the following configurations:

– deciduous pulp without additives – L1
– deciduous pulp + starch 2% – L2
– deciduous pulp + starch 3% – L3
– deciduous pulp + starch 5% – L4
– deciduous pulp + resinous glue 2% – L5
– deciduous pulp + resinous glue 3% – L6
– deciduous pulp + resinous glue 5% – L7.

Mycological test was carried out according to methodology proposed by Cofta and others [2006]. Research, concerning susceptibility of paper products to mould should be carried with the use of microorganisms, specific for the given product which we want to protect. In order to obtain utilitarian results, it is necessary to carry out research using fungi which cause the biggest destruction of the given material. According to laboratory practice, it follows that it is good to work with microorganisms of different susceptibility to fungicide and which do not show significant deviation in successive examinations. Due to this reason, *Ch. globusom* was applied since it develops/grows very well on the clean cellulose and is often isolated in various archives and libraries [Zyska 1993, 2000]. Indication/evaluation of resistance to overgrowth by microfungi was held with the usage of standard method using indexation to describe degree of overgrowth of samples. During marking, the following test fungi were used: *Chaetomium globosum*, *Aspergillus niger*, *Penicillium funiculosum*, *Trichoderma viride*, where the last three were used in the form of mixture [Fassatiova 1983]. The observation period lasted 14 days, where on the 2nd, 4th, 7th, 10th and 14th day – reading of the degree of samples' overgrowth, according to 4-degree scale, took place. Indication of self-breaking of paper samples was carried out according to the PN-EN ISO 1924-2:2009 norm. Before putting samples in the handles of the tearing machine, pieces of paper were taken out of Petrie's vessel, cleaned and dried.

Apparatus used for FT-NIR measurement was Vektor 22-N spectrophotometer. The measured spectral range in the case of all the conducted measurements was between 4000 and 12 000 cm^{-1}. In order to decrease the number of measuring errors/mistakes, each spectrum was an average of 32 consecutive inner measurements (scans). Each of the control samples was represented by five strips of paper which were measured

Table 1. Interpretation of molecular vibration FT-NIR
Tabela 1. Interpretacja wibracji molekularnych FT-NIR

Code Kod	Wavenumber Liczba falowa cm^{-1}	Interpretation of molecular vibration / relations to functional groups Interpretacja wibracji molekularnych / powiązania do grup funkcyjnych
1	4 198	Deforming vibration of C-H holocellulose groups Drgania deformujące grup C-H holocelulozy
2	4 280	Stretching vibration of C-H groups + deforming vibration of C-H cellulose groups Drgania rozciągające grup C-H + drgania deformujące grup C-H celulozy
3	4 404	Stretching vibration of C-H_2 groups + deforming vibration of C-H_2 cellulose groups Drgania rozciągające grup C-H_2 + drgania deformujące grup C-H_2 celulozy
4	4 620	Stretching vibration of O-H groups + deforming vibration of C-H cellulose groups Drgania rozciągające grup O-H + drgania deformujące grup C-H celulozy
5	4 890	Stretching vibration of O-H groups + deforming vibration of C-H cellulose groups Drgania rozciągające grup O-H + drgania deformujące grup C-H celulozy
6	5 219	Stretching vibration of O-H groups + deforming vibration of O-H water groups Drgania rozciągające grup O-H + drgania deformujące grup O-H wody
7	5 464	Stretching vibration of O-H groups + C-H crystalline and semi-crystalline region of cellulose Drgania rozciągające grup O-H + C-H krystalicznego i półkrystalicznego regionu celulozy

at three places. For each checkup 15 spectra were obtained which were recorded on a computer disk and placed in reference database.

Averaged out spectra (so called model ones) served for the data analysis. In order to decrease the effect of changeable/variable temperature of the examined samples, measurements were carried out in an air-conditioned room with air temperature of ~20 ±2°C and relative air humidity of 65 ±2%. Interpretation of molecular vibration FT-NIR (Table 1) was prepared on the basis of the research carried out by Tsuchikawa et al. [2005].

RESULTS AND DISCUSSION

During mycological research, in proportion to time passage – there was an increase of test mycelium. The nature of overgrowth of paper products by fungi and degree of their discolor were dependant on the species of a given test fungus. Paper products made of sulfate deciduous cellulose pulp showed various susceptibility to overgrowth by molds, considering different percentage content of pulp additives. Evaluation of degradation degree was carried out with the help of self-breaking research of selected paper products. This value decreased with time when samples underwent process of biodegradation. It follows that paper endurance decreased evenly as a result of cellulose pulp loss, in the consecutive days of observation (Table 2).

Table 2. Results of determination of overgrowth degree of analysed paper products by test fungi and their resistance to self-breaking.
Tabela 2. Wyniki oznaczeń stopnia porośnięcia badanych wytworów papierniczych przez grzyby testowe oraz ich odporność na samozerwalność

Resistance to overgrowth by test fungus Ch – *Ch. globosum* and M – mixture of fungi (*A. niger, P. funiculosum, T. viride*) of research paper Odporność na porastanie przez grzyb testowy *Ch. globosum* – Ch i mieszaninę grzybów (*A. niger*, *P. funiculosum*, *T. viride* – M) papierów celulozowych						Type of pulp Rodzaj masy	pH	Self-breaking of samples subjected to biodegradation, km Samozerwalność próbek poddanych biodegradacji, km					
day – dzień 2		day – dzień 7		day – dzień 14				day – dzień 2		day – dzień 7		day – dzień 14	
Ch	M	Ch	M	Ch	M			Ch	M	Ch	M	Ch	M
3	3	1.9	1.7	1.6	1.1	L1	7.03	14.60	15.57	4.06	4.19	1.74	2.33
3	3	1.6	1.7	0.2	0.6	L2	6.54	8.52	8.79	4.16	4.49	0.09	1.10
3	3	0.9	2.5	0	0.9	L3	6.15	8.19	8.59	4.57	5.25	0.00	2.00
3	3	1.3	1.5	0.1	0.6	L4	6.39	7.86	8.39	3.28	3.46	0.70	1.23
3	3	1.7	1.9	0.2	0.6	L5	5.61	8.46	9.19	3.30	4.00	0.86	0.91
3	3	1.6	1.7	0.3	0.6	L6	6.66	8.59	9.26	2.68	3.62	0.85	1.54
3	3	1.7	1.2	0.5	0.8	L7	6.46	8.92	9.92	1.60	2.82	0.28	1.51

Since the number of the obtained results is big, in order to represent possibilities of spectrophotometric analysis usage, only some exemplary paper products with 3% starch additive (L3) and 2% resinous glue (L5) were selected.

Presented charts (Figs 1 and 2) show interaction of microfungi to paper products with 3% starch additive (L3). Infected samples with *Ch. globosum* are more susceptible to biological biodegradation. Changes concern chemical structure of functional O-H and C-H cellulose and O-H water groups (Fig. 1). Looking at Table 2, one may also conclude that paper infected by mixture of fungi is more resistant to overgrowth and has better self-breaking parameters in comparison with the one infected by *Ch. globosum.* In this case FT-NIR spectra of individual control readings have more uniform course (Fig. 2).

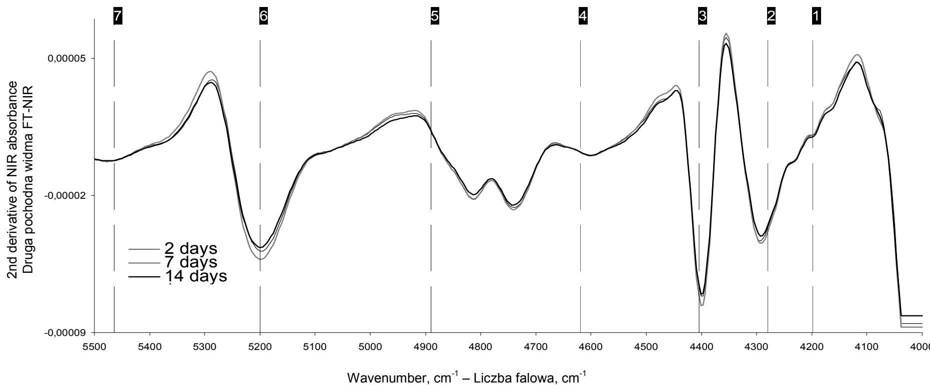

Fig. 1. FT-NIR spectra of deciduous pulp with 3% starch additive infected by test fungus *Ch. globusom*

Rys. 1. Spektra FT-NIR masy liściastej z 3-procentowym dodatkiem skrobi zainfekowanej przez grzyb testowy *Ch. globusom*

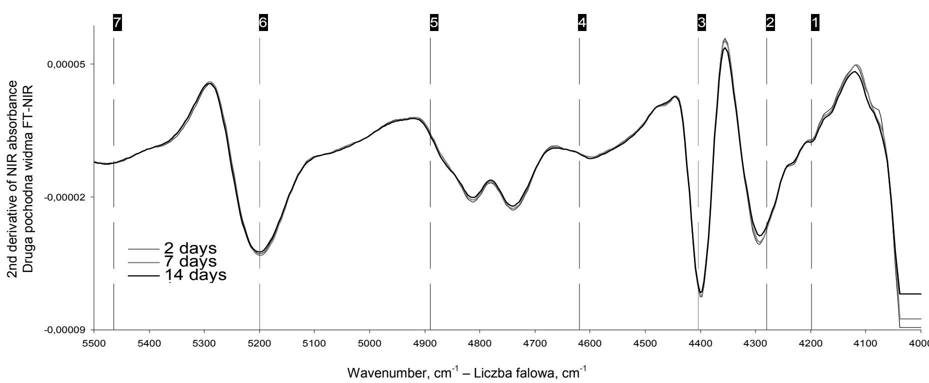

Fig. 2. FT-NIR spectra of deciduous pulp with 3% starch additive infected by the mixture of test fungi

Rys. 2. Spektra FT-NIR masy liściastej z 3-procentowym dodatkiem skrobi zainfekowanej mieszaniną grzybów testowych

Paper products with 2% of resinous glue (L5) infected by *Ch. globosum* show gradual tendency towards degradation. Visible in Figure 3 – values of second derivative of spectra in region 2, 3 and 4, 5 undergo gradual change. Whereas, in the case of paper infected by the mixture of fungi, readings of 2nd and 7th day, in the above listed regions, overlap (Figs 3 and 4).

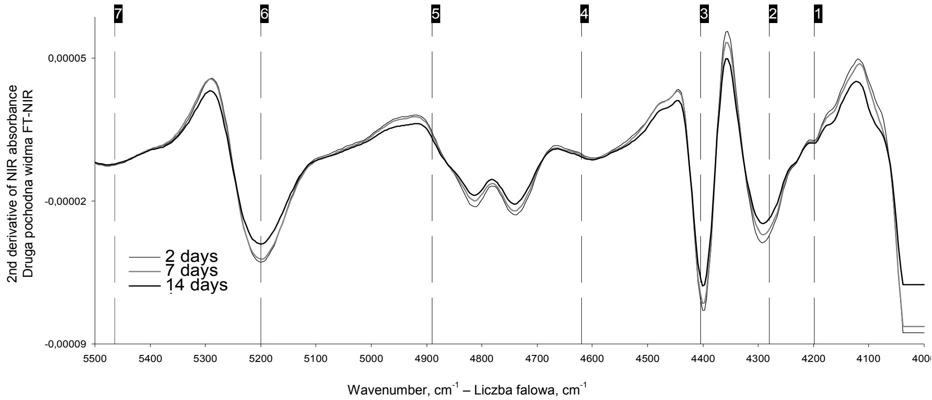

Fig. 3. FT-NIR spectra of deciduous pulp with 2% resinous glue infected by test fungus *Ch. globusom*
Rys. 3. Spektra FT-NIR masy liściastej z 2-procentowym dodatkiem kleju żywicznego zainfekowanej przez grzyb testowy *Ch. globusom*

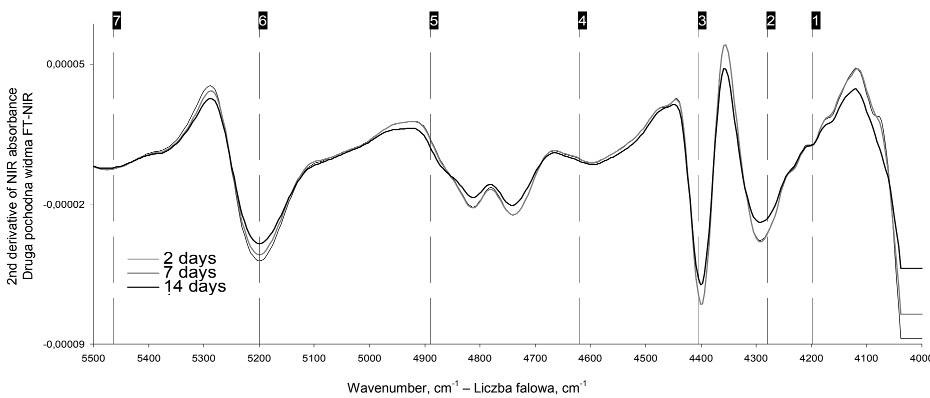

Fig. 4. FT-NIR spectra FT-NIR of deciduous pulp with 2% resinous glue infected by the mixture of test fungi
Rys. 4. Spektra FT-NIR masy liściastej z 2-procentowym dodatkiem kleju żywicznego zainfekowanej mieszaniną grzybów testowych

It proves that degradation was less intensive, especially at the first stages of infection. However, reading of 14th day, which course differs from others, indicates an increase of degradation and change in the chemical structure of examined material, as time goes by.

Analysing both resistance to overgrowth by test fungus and test results concerning self-breaking, one may notice that paper samples of deciduous pulp without additives show bigger values in both tests. Additives of both starch and resinous glue – significantly decrease self-breaking parameters and are conducive to overgrowth of samples. Degradation in the case of 2, 3 and 5% starch additive develops in comparable pace, however for *Chaetomium* degradation is more advanced after 14 days. Similar situation may be observed in the case of pulps with resinous glue. Samples infected by *Chaetomium* undergo more intensive biodegradation, while the biggest intensity of changes for the self-breaking parameters was observed in the case of samples of the indicated paper products with 5% additive.

CONCLUSIONS

Analysing obtained results one may arrive at the following conclusion:

During the carried research, applied spectrophotometry of near infrared radiation, FT-NIR, for the evaluation of dynamics and degree of biodegradation of selected paper products with different percentage content of pulp additives, turned out to be effective.

Usage of three independent methods simultaneously, enabled objective interpretation of results – performed analyses (standard method, FT-NIR, self-breaking evaluation) mutually confirm the obtained during research results.

Due to spectra analysis, one gained information: which of the functional groups of cellulose undergo the fastest degradation; changes at the intensity of peaks were mainly noted for the C-H (4280 cm^{-1}) and $C\text{-}H_2$ (4404 cm^{-1}) groups (stretching and deforming vibrations), and O-H groups (stretching vibrations) (region 4620-4890 cm^{-1}).

In the all examined configurations of paper, fungus *Ch. globosum* caused significantly bigger changes than the mixture of applied test fungi.

Realised research showed that pulp additives in form of starch and resinous glue have significant negative influence on resistance of paper products, made of cellulose sulfate deciduous pulp.

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ANALIZA SPEKTROFOTOMETRYCZNA FT-NIR PAPIERU Z MASY CELULOZOWEJ SIARCZANOWEJ BIELONEJ LIŚCISTEJ Z DODATKIEM SKROBI I KLEJU ŻYWICZNEGO PODDANEGO BIODEGRADACJI MYKOLOGICZNEJ

Streszczenie. W pracy podjęto próbę oceny szybkości biodegradacji mykologicznej wytworów papierniczych z różnym procentowym dodatkiem skrobi kationizowanej oraz kleju żywicznego za pomocą analizy spektrofotometrycznej FT-NIR. Jako czynnik biotyczny użyto kulturę akseniczną *Ch. globosum* oraz mieszaninę mikrogrzybów: *A. niger, T. viride, P. funiculosum*. Za kryterium biodegradacji przyjęto odporność na porastanie powierzchni próbek przez grzybnie testowe oraz oznaczono samozerwalność po teście mykologicznym w 2, 4, 7, 10 i 14 dniu obserwacji. Do badań wytypowano masę celulozową siarczanową bieloną liściastą, z której wraz z dodatkiem w.w. dodatków masowych sformowano w warunkach laboratoryjnych arkusiki papieru. Dodatek skrobi oraz kleju żywicznego jako wypełnienia do masy liściastej wywołał wzrost podatności na porastanie przez grzybnie testowe, w porównaniu z próbkami bez dodatków. Wytwory papiernicze zainfekowane mikrogrzybem *Ch. globulosum* generalnie wykazywały większą tendencję do biodegradacji. Zastosowanie spektroskopii FT-NIR pozwoliło na przeanalizowanie złożonego procesu degradacji materiału ligno-celulozowego. Zmiany w intensywności pików degradowanych mas makulaturowych odnotowano głównie dla grup funkcyjnych celulozy C-H (4280 cm^{-1}), C-H_2 (4404 cm^{-1}), oraz grup O-H (region 4620-4890 cm^{-1}). Wykorzystanie jednocześnie kilku niezależnych metod oceny stopnia degradacji umożliwiło obiektywną interpretację wyników, a wykonane analizy potwierdzają wzajemnie uzyskane rezultaty badań.

Słowa kluczowe: próbki papieru, mikrogrzyby, biodegradacja, spektrofotometria FT-NIR

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