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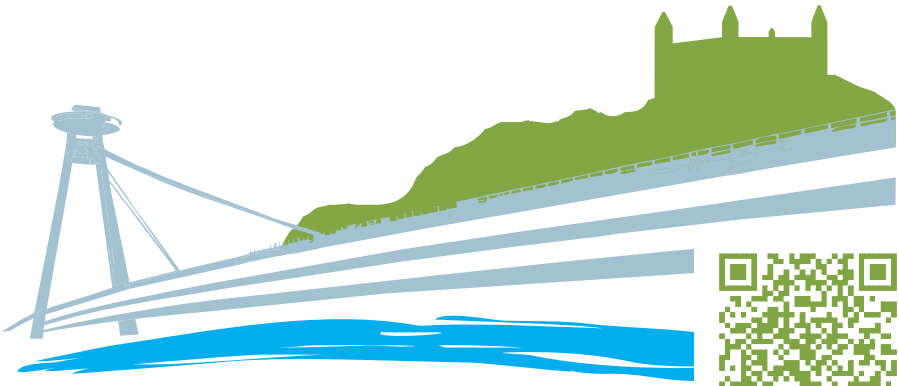

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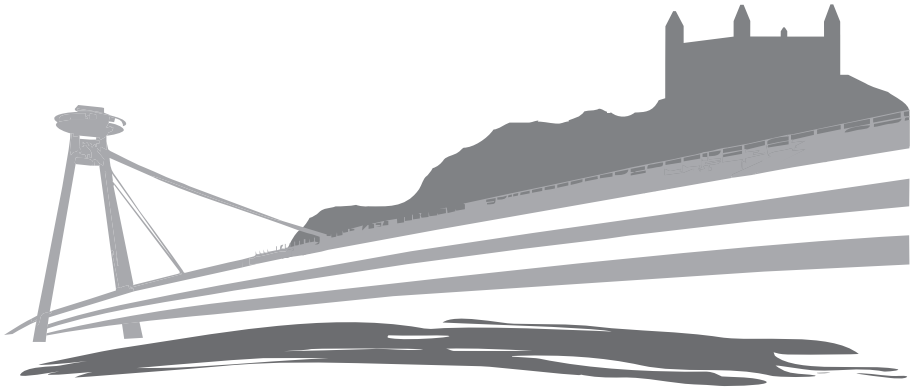

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WOOD, PULP AND PAPER 2025 POLYGRAFIA ACADEMICA 2025

19. a 20. marca 2025

Zborník recenzovaných vedeckých konferencií
Proceedings of reviewed joint conferences
Uzávierka všetkých príspevkov v zborníku: 14. februára 2025

Organizátori konferencie/Conference Organizers

Konferencia sa uskutoční pod záštitou prof. Ing. Antona Gatiala, DrSc. – dekana Fakulty chemickej a potravinárskej technológie STU v Bratislave. Na organizácii konferencie sa podieľajú: Ústav prírodných a syntetických polymérov FCHPT STU v Bratislave, Zväz polygrafi e na Slovensku, Výskumný ústav papiera a celulózy, Zväz celulózo-papierenského priemyslu SR, Zväz spracovateľov dreva SR, Společnost průmyslu papíru a celulózy, Slovenská chemická spoločnosť pri SAV, Slovenské centrum digitálnych inovácií (SCDI).

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Grafické spracovanie zborníka: Vladimír Dvonka, Lukáš Gál
Tlač zborníka: Slovenská Grafia, a. s.
Vydala Slovenská chemická knižnica FCHPT STU v Bratislave, 2025.
Náklad 135 ks.
ISBN 978-80-8208-154-4

Contents

Tento zborník podporili Agentúra na podporu výskumu a vývoja SR na základe zmlúv APVV-20-0410, APVV-22-0277, APVV-22-0388, APVV-22-0034, APVV-23-0066, Vedeckou grantovou agentúrou VEGA 1/0651/23, VEGA 1/0498/22, VEGA 1/0332/24, VEGA 2/0136/24, VEGA 1/0036/24, Slovenská technická univerzita v Bratislave grant 23-04-04-B a projekty 1387, 1332, 1612, 1609, 1333, 1388

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Plenárne a pozvané prednášky
Plenary and invited lectures

Technický rozvoj celulózo-papierenského priemyslu SR je základom udržania jeho konkurencieschopnosti

Miroslav Vajs[1], Štefan Boháček[2], Juraj Dlhopolček[1], Maroš Kováč[2]

Zväz celulózo-papierenského priemyslu SR[1]
Výskumný ústav papiera a celulózy a.s.[2]

Abstract: *The growing competitiveness of the cel-pap industry in Slovakia is demonstrated by its market position and the increase in production based on the implementation of the latest technological advancements and the resulting comparative advantages. Positive trends are evident in productivity development, the size of production capacities, and the consumption of basic raw materials, primarily wood, recovered paper, and water. Interesting trends are observed in the production of pulp and paper, as well as cardboard. The analysis will also cover the environmental sector, highlighting investment activities and positive results in technical development, reduction of emissions, pollution of surface waters, and reduction of energy intensity in production.*

Kľúčové slová: *konkurencieschopnosť, produktivita, technický rozvoj, papier, celulóza*

1. Úvod

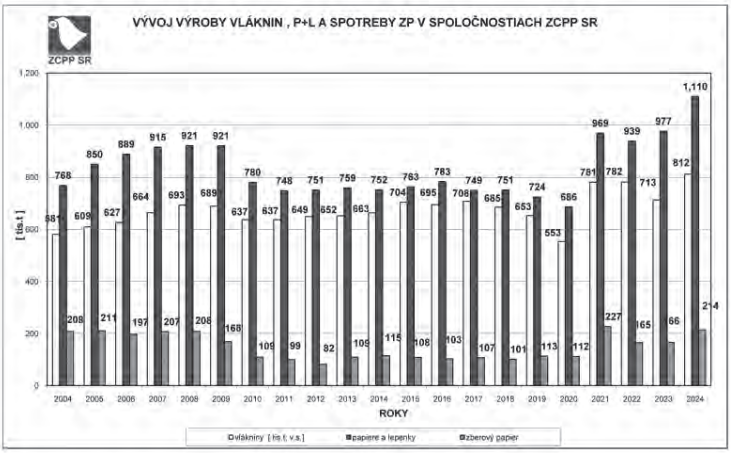
Celulózo papierenský priemysel je výnimočné priemyselné odvetvie, ktorého výrobný proces je technicky a technologicky zložitý. Je založený na využívaní a spracovaní domácej, obnoviteľnej surovinovej základne, drevnej hmoty nižších kvalitatívnych parametrov a zberového papiera. Patrí dlhodobo k významným hospodárskym pilierom ekonomiky. Podniky združené vo Zväze celulózo papierenského priemyslu SR (ZCPP-SR) dlhodobo pokrývajú 100 %-ný podiel výroby buničiny a papiera na Slovensku.

Strategické rozhodnutia o smerovaní, a z toho vyplývajúca investičná náročnosť, si za uplynulé roky vyžiadali investície vo výške viac ako 500 mil. EUR. Pri procesoch výroby papiera a výrobkov z neho, využíva najlepšie svetovo dostupné technológie, ktoré umožňujú dosahovať takú kvalitu výrobkov, že viac ako 90 % umiestňujeme na náročných zahraničných trhoch. Všetky výrobné procesy sú riadené tak, aby aj pri vysokej energetickej náročnosti, eliminovali nepriaznivé dopady na životné prostredie.

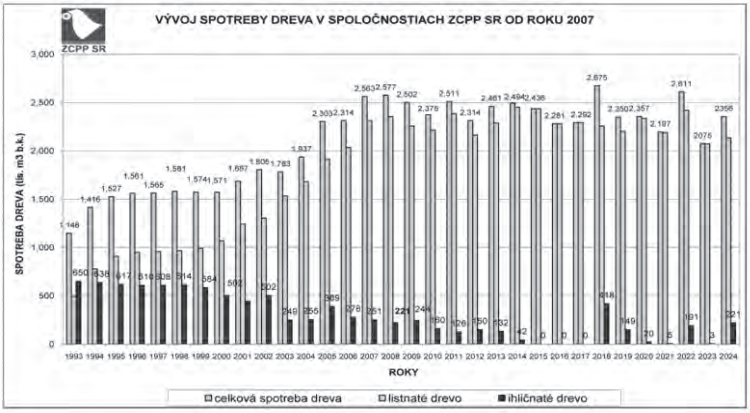
Uplynulý rok 2024 bol rokom prelomovým. Výroba papiera na Slovensku medziročne vzrástla o 15,3 % a dosiahla úroveň viac ako 1 mil. ton. Z celkovej výroby papiera v roku 2024 bola výroba grafických a obalových papierov na úrovni 90 %, pričom zvyšných 10 % tvorila produkcia hygienických papierov. Spoločnosti združené ZCPP-SR spotrebovali v histórií odvetvia najviac zberového papiera. Spotreba prekonala množstvo 214 tis. ton, čo predstavuje medziročný nárast o 29,7 %. Zberový papier

tvoril až 21,5 %-ný podiel na základných vstupných surovinách pre výrobu papiera.

Pokračujúci dynamický rozvoj celpap priemyslu na Slovensku v ďalších rokoch, bude vyžadovať inovatívne riešenia, ktorých potenciál zmení obalový priemysel a rispeje k ochrane životného prostredia. Predpokladom je, že v budúcnosti bude kladený ešte väčší dôraz na vývoj biologicky rozložiteľných obalov, využívanie obnoviteľných zdrojov a znižovanie uhlíkových emisií.



Obr. 1: Vývoj výroby vláknin, papierov a lepeniek v spločnostiach ZCPP



Obr. 2 Vývoj spotreby v spoločnostiach ZCPP SR

Výroba vláknin, papierov a lepeniek má za ostatné obdobie stúpajúcu tendenciu. Bol dosiahnutý rekord vo výrobe papiera, buničiny aj v spracovaní zberového papiera. Spotreba dreva sa zvýšil tiež o 13,55 %.

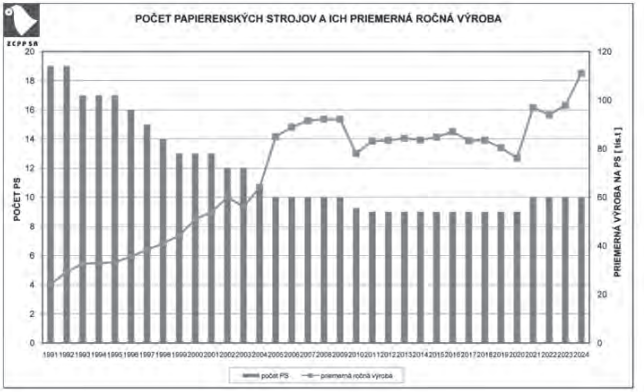
VÝVOJ ROZHODUJÚCICH UKAZOVATEĽOV V SPOLOČNOSTIACH ZCPP SR

Ukazovateľ	2023	2024	2024 / 2023
Výroba vláknin	712,935 t	812,101 t	113.91%
Výroba papiera a lepenky	873,762 t	1,110,213 t	127.06%
Spotreba dreva	2,075,252 m³	2,356,450 m³	113.55%
Spotreba zberového papiera	165,332 t	214,341 t	129.64%
Tržby	**1,007 mil.€**	**962 mil.€**	**95.57%**
Vývoz	**914 mil.€**	**859 mil.€**	**93.98%**
Podiel vývozu	**91%**	**89%**	
Počet zamestnancov	2,490 osôb	2,137 osôb	85.18%
Produktivita práce	406 tis.€	450 tis.€	110.89%
Priemerná mesačná mzda	1,794 €	2,240 €	124.84%
Investície	46.58 mil.€	28.64 mil.€	61.48%

ŠI ZCPP SR

Obr. 3: Vývoj rozhodujúcich ukazovateľov v spoločnostiach ZCPP SR

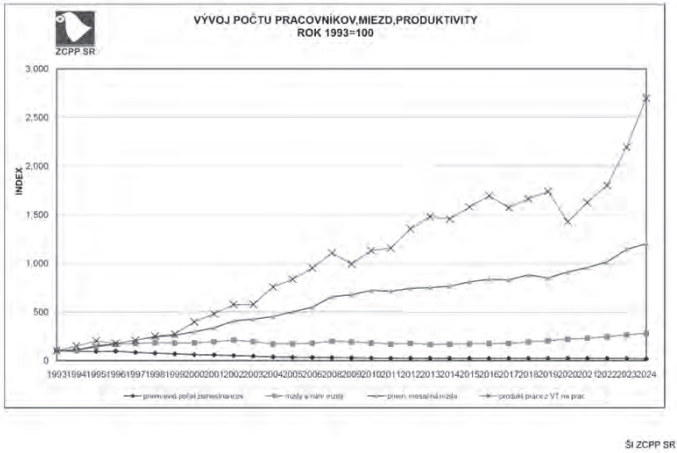
Produktivita práce zaznamenala tiež rekordnú úroveň, napriek miernemu poklesu tržieb.



ŠI ZCPP SR

Obr. 4 Počet papierenských strojov a ich priemerná ročná výroba

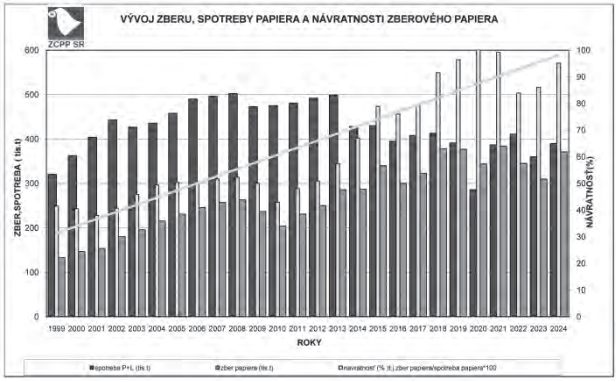
Počet papierenských strojov je 10, pričom vďaka rastu výroby priemerná výrobná kapacita zaznamenala tiež rekordnú výšku.



Obr. 5 Vývoj počtu pravovníkov, miezd a prodkuktivity

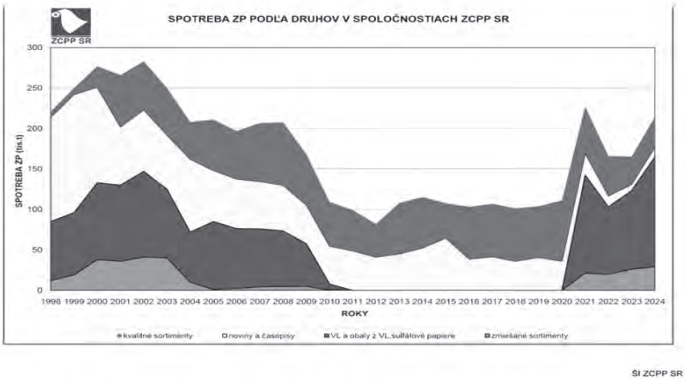
Počet zamestnancov dlhodobo klesá, v dôsledku automatizácie procesov a outsoursingu obslužných prác, zatiaľ čo produktivita práce na jedného pracovníka má za celé obdobie mimoriadneintenzívne stúpajúcu tendenciu.

Racionalizácia personálneho zloženia firiem a predvídavé investície do výroby vytvorili potenciál pre ďalšie investičné aktivity.



Obr. 6 Vývoj zberu, spotreby papiera a návratnosti zberového papiera

Potreba papiera, zber papiera ako aj návratnosť zberového papiera rástla.



Obr. 7 Spotreba ZP podľa druhov v spoločnostiach ZCPP SR

Z obrázku 7 je zrejmé, že spracovanie zmiešaných sortimentov zberového papiera a zberu vlnitých lepeniek a sulfátových papierov slovenským celulózo-papierenským priemyslom začala stúpať po nábehu nového papierenského stroja č.19 v Mondi SCP a.s. Ružomberok a neblahé trendy v týchto ukazovateľoch v rokoch predtým sa zmenily tiež na pozitívne.

Životné prostredie

Celulózo-papierenský priemysel je významným hráčom v prechode na cirkulárnu ekonomiku[2,10], kde sa materiály efektívne používajú, recyklujú a opätovne využívajú s minimálnym dopadom na prírodu. ZCPP aktívne sleduje a napomáha zosúladeniu politík štátov EU s cieľmi klimatickej neutrality do roku 2050 s dôrazom na udržateľnosť ekonomickej konkurencieschopnosti svojich členov.

Hlavné ciele papierenského priemyslu vo vzťahu k životnému prostrediu:

Udržateľné lesné hospodárstvo[8]: Papierenský priemysel podporuje obnovu lesov a certifikáciu dreva z udržateľných zdrojov, čo prispieva k ochrane biodiverzity a boju proti odlesňovaniu[7].

Znižovanie uhlíkovej stopy: Znižovanie emisií CO2 prostredníctvom stále zlepšujúcej sa energetickej účinnosti[9,11], používania obnoviteľnej energie a implementácie inovácií, ktoré minimalizujú environmentálne dopady výroby.

Zvyšovanie miery recyklácie: Hlavným cieľom je zvýšiť recykláciu papiera a kartónu, čím sa zníži tlak na nové zdroje dreva a minimalizujú sa environmentálne dopady[5,7].

Minimalizácia odpadu a znečistenia: Zníženie množstva odpadových produktov a toxických chemikálií[1,3] používaných vo výrobnom procese prispieva k čistejšiemu životnému prostrediu.

Ochrana vodných zdrojov: Znižovanie spotreby vody a zlepšenie technológií na čistenie odpadových vôd sú dôležité pre ochranu prírodných zdrojov.

Acknowledgement

The project leading to this application has received funding from the European Union's HORIZON EUROPE research and innovation programme under grant agreement No 101059552, Project name: Upgrade of the Centre of Excellence LignoSilva (Call: HORIZON-WIDERA-2022-ACCESS-01-two-stage).

Ďakujeme členským organizáciám Zväzu celulózo-papierenského priemyslu SR za poskytnutie informácií k prednáške.

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The future of pulping

Leo Arpa

Mondi, 1030 Vienna, Marxergasse 4A, leo.arpa@mondigroup.com

Abstract: *Kraft pulping is a widely used chemical process for converting wood into pulp, the raw material for paper production. Invented by Carl F. Dahl in 1879, the process uses sodium hydroxide (NaOH) and sodium sulphide (Na_2S) as cooking chemicals to break down the lignin that binds the cellulose fibres in wood. One of the key advantages of kraft pulping is that it is highly efficient and sustainable, particularly due to its closed-loop nature. In a kraft pulp mill, the chemicals used in the pulping process are recovered and reused, significantly reducing waste and environmental impact. Black liquor, a by-product of the pulping process, is processed in a recovery boiler to regenerate cooking chemicals and generate energy. This closed-loop system not only minimises the need for fresh chemicals, but also improves the overall energy efficiency of the mill. So why even think about changing such a superior process?*

There are at least 3 reasons why we should develop this excellent process:

1. Changing climate, challenged forests will change the availability of raw material and the raw material available. Recent research by forestry institutes, as well as our own research, shows that the European forest will change significantly in the coming decades. New species will require new cooking sequences to reach their full potential for pulp and paper products.
2. Increasing customer demand for sustainable packaging materials requires greener production of fibre-based packaging. Our MAP2030 action plan outlines our key commitments to improve environmental sustainability. In the area of climate change, this will include efforts to reduce greenhouse gas emissions, and in particular to reduce resource consumption, both in terms of raw materials and energy.
3. New applications for fibre-based solutions require new and improved fibre properties. To achieve such new and improved properties, not only new wood species may be investigated, but also new or adapted processes.

These reasons are guiding current and future research in chemical pulping. One such process is the use of deep eutectic solvents (DES). DES can dissolve lignin, hemicellulose and cellulose at low temperatures and atmospheric pressure, but have the disadvantage of complex recovery processes that don't yet match the efficiency of kraft pulping. Another approach is to develop kraft pulping processes to meet the requirements outlined above. This is why we have developed the laboratory and pilot facilities to work with academia on the future of kraft pulping.

Revolutionizing Material Printing: Cold Plasma-Enabled R2R Manufacturing of Optoelectronic and Photocatalytic Coatings

Tomáš Homola[1], Petr Dzik[2], František Zažímal[1], Jakub Kelar[1], Zlata Kelar Tučeková[1], Oleksandr Galmiz[1], Mirko Černák[1], Dušan Kováčik[1]

[1]Department of Plasma Physics and Technology, CEPLANT – R&D Centre for Plasma and Nanotechnology Surface Modifications, Faculty of Science, Masaryk University, Kotlářská 267/2, 602 00 Brno, Czech Republic
[2]Institute of Physical and Applied Chemistry Faculty of Chemistry, VUT in Brno, Purkyňova 464, Brno 612 00, Czech Republic
tomas.homola@mail.muni.cz

Cold plasma is a highly energetic, ionized, quasi-neutral gas that enables precise material transformations beyond conventional thermal and chemical processes. Composed of free electrons, ions, photons, and reactive species, it interacts dynamically with surfaces, making it valuable for advanced material printing. Plasma-driven processes enhance adhesion, material compatibility, and chemical control, making them ideal for surface activation, functional coatings, and nanostructure synthesis. In the wood and printing industries, atmospheric pressure plasma treatments improve adhesion, durability, and print quality by modifying surface energy. This allows materials to bond more effectively with coatings, adhesives, and inks–without the need for chemical primers or extensive surface preparation–offering an efficient and eco-friendly alternative to traditional methods.

In the wood industry, plasma treatment effectively enhances surface properties, improving adhesion, coating, and bonding performance. By introducing polar functional groups, it increases surface energy, making wood more receptive to water-based adhesives and coatings. It also reduces water droplet uptake time, enabling faster bonding and better coating penetration. Additionally, plasma shifts the surface pH to a more acidic level, enhancing adhesive interactions. Unlike traditional chemical treatments, it is a dry, solvent-free process, offering an eco-friendly alternative with minimal environmental impact [1].

In the paper industry, the flexibility and continuous nature of paper production demand efficient roll-to-roll (R2R) processing techniques for surface modifications. Plasma treatment offers a dry, solvent-free solution that enhances surface properties without affecting the bulk structure, making it ideal for high-speed R2R applications. This technology is particularly advantageous for coated and specialty papers, improving barrier properties for packaging and enabling high-quality printing on challenging substrates, all while maintaining production efficiency and environmental sustainability [2].

Integrating cold plasma technology into R2R manufacturing presents a transformative approach for producing high-performance coatings, surface modifica-

tions, and functionalized materials in the paper and printing industries. As the demand for flexible, lightweight, and sustainable materials grows, R2R-compatible plasma treatments provide an efficient, scalable, and eco-friendly alternative to traditional chemical and thermal processes.

Diffuse Coplanar Surface Barrier Discharge (DCSBD) (Figure 1) is a unique cold plasma technology adopted and advanced at the R&D Centre CEPLANT, Masaryk University and commercialized by Roplass s.r.o. It has been widely used for testing in various industrial and research applications, particularly in surface treatment, adhesion enhancement, and functional coating deposition. DCSBD generates high-power-density, thin-layer atmospheric plasma directly on a robust alumina ceramic surface, making it highly efficient for material processing. Unlike conventional plasma systems, DCSBD operates in open-air conditions, eliminating the need for vacuum chambers and enabling cost-effective, scalable integration into existing production lines. Its design allows for both flat and curved configurations, making it especially suitable for R2R manufacturing, where continuous surface treatment of flexible materials such as polymers, paper, and textiles is required.

This contribution presents a range of examples showcasing how DCSBD has been utilized to enhance printing technologies, spanning from low-TRL laboratory-scale applications to high-TRL industrial-scale implementations.

1. Optoelectronic coatings in solar cells: Plasma treatments can enhance the interface in heterojunction thin-film solar cells by modifying surface properties and improving charge carrier dynamics. Additionally, plasma can effectively passivate defects, reducing recombination losses and increasing overall efficiency. These advancements open new pathways for manufacturing flexible, large-area solar cells with improved optoelectronic coatings and long-term stability.
2. Photocatalytic coatings for water treatment: Plasma treatments can mineralize organic binders in large-area thin-film semiconductors, enhancing their structural stability and photocatalytic activity. This process enables the fabrication of high-performance photocatalytic coatings suitable for continuous flow wastewater treatment reactors. Such coatings improve pollutant degradation efficiency, offering a scalable and sustainable solution for advanced water purification.
3. Clay-coated paper: Plasma treatment effectively modifies the surface properties of clay-coated paper, enhancing its wettability, adhesion, and chemical composition without altering bulk characteristics. These modifications enhance ink absorption, barrier properties, and adhesion to polymers, making plasma-treated clay-coated paper more suitable for high-performance packaging, printing, and industrial coatings. Additionally, R2R plasma process ensures uniform, scalable, and cost-effective surface treatment for large-area application.
4. Digital printing: Plasma treatment using DCSBD enhances UV–digital printing adhesion by increasing surface free energy and introducing oxygen-rich functional groups. This results in better ink bonding, durability, and reduced ink shrinkage on polymer substrates like PMMA and PC.

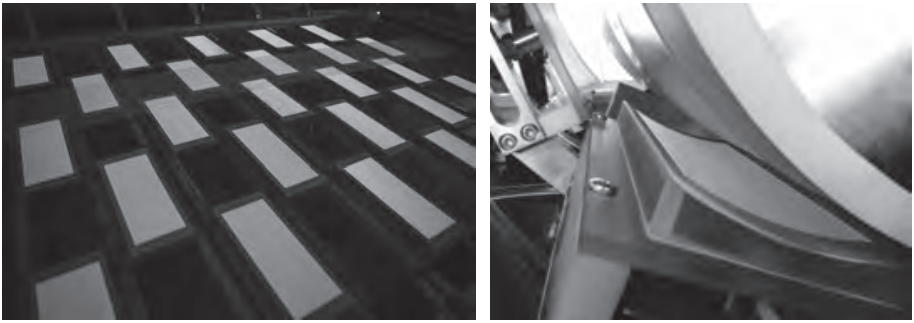

Figure 1: (left) Array of 25 flat DCSBD plasma panels (8 × 20 cm) used in roll-to-roll (R2R) treatment of nonwoven fabric; (right) Curved DCSBD plasma unit designed for the R2R treatment of polymer foil.

With its ability to deliver **uniform, high-intensity plasma over large areas**, **DCSBD has become a key enabling technology** for next-generation **printing, electronics, and coating industries**, offering **fast, precise, and environmentally friendly** surface modifications.

Acknowledgements

This work was supported by the project LM2023039 funded by the Ministry of Education, Youth and Sports of the Czech Republic.

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Vzdelávanie v polygrafii

Peter Blubla

Zväz polygrafie na Slovensku, Račianska 190, 831 06 Bratislava 3
email: office@zpns.sk

Zvyšujúce sa nároky na zručnosti a stále meniace sa profily pracovných miest na všetkých kvalifikačných úrovniach vyzývajú vzdelávací systém, aby pružne reagoval na nové potreby pracovného trhu, so zachovaním požadovanej kvalitatívnej úrovne. Príspevok je rozdelený na dve časti: 1. Situácia v polygrafickom vzdelávaní 2. Umelá inteligencia a polygrafia

V prvej časti pôjde o prezentáciu súčasného stavu v polygrafickom vzdelávaní predovšetkým na úrovní stredného odborného vzdelávania (aj keď sa konferencia odohráva na akademickej pôde). Zo štatistiky SR za desať rokov (2013-2022) vyplýva, že aj keď sa nám počet detí zvyšuje počet študentov stredných a vysokých škôl klesá.

materské školy	deti		učitelia	
rok 2022	rok 2013	rok 2022	rok 2013	rok 2022	rok 2013
3 137	2 870	178 830	153 059	17 811	14 841
základné školy	**deti**		**učitelia**	
rok 2022	rok 2013	rok 2022	rok 2013	rok 2022	rok 2013
1 493	1 462	461 090	405 309	35 766	32 336
konzervatóriá	**študenti** (denné štúdium)		**učitelia**	
rok 2022	rok 2013	rok 2022	rok 2013	rok 2022	rok 2013
17	15	2 993	2 940	881	1 070
gymnáziá	**študenti** (denné štúdium)		**učitelia**	
rok 2022	rok 2013	rok 2022	rok 2013	rok 2022	rok 2013
234	247	73 811	77 232	6 602	7 387
stredné odborné školy	**študenti** (denné štúdium)		**učitelia**	
rok 2022	rok 2013	rok 2022	rok 2013	rok 2022	rok 2013
424	462	132 812	158 122	12 474	14 464
vysoké školy	**študenti** (denné štúdium)		**učitelia**	
rok 2022	rok 2013	rok 2022	rok 2013	rok 2022	rok 2013
33	36	109 794	132 602	9 620	10 720

Zdroj: databáza ŠÚ SR/DATAcube

Aká je situácia v odbore 34 polygrafia a médiá? Momentálne sa odbor vyučuje v 30 školách na celom Slovensku s celkovým počtom 1777 žiakov vo všetkých ročníkoch. Najväčší záujem je o odbor 3447 K grafik digitálnych médií kde v prvom až štvrtom ročníku študuje 1368 žiakov! Pretrváva nedostatok operátorov tlače–tlačiarov a pracovníkov v dokončovacom spracovaní–knihárov.

Jedinou školou ktorá vychováva stredoškolských absolventov pre polygrafiu naprieč trom fázam výrobného procesu teda prípravy tlače, samotnej tlače a dokončujúceho spracovania je SOŠ polygrafická v Bratislave. Menovaná škola je aj centrom odborného vzdelávania a prípravy. Momentálne škola prešla významnou stavebnou modernizáciou a má zodpovedajúce materiálovo technické vybavenie a kvalifikovaný pedagogický zbor.

V druhej časti sa budeme venovať fenoménu poslednej doby a to je umelá inteligencia (AI) a jej uplatnenie v polygrafickom priemysle s dôrazom na potrebu vzdelávania. Umelá inteligencia pracuje na dvoch základných princípoch a to autonómia pri ktorej je schopná vykonávať komplexné úkony nezávislé od pomoci a zasahovania tretej osoby a princípu adaptability, kde sa AI učí na základe predošlých skúseností. Ako sa umelá inteligencia prejaví v polygrafickom priemysle? Podľa informácií z európskeho mediálneho priestoru elektronizácia a automatizácia dosiahla významné postavenie. Nástupom Industry 4.0 respektíve Industry 5.0 sa čoraz viac budú presadzovať prvky umelej inteligencie AI ako aj prvky ML (Machine learning), čo významne ovplyvní efektivitu výrobného procesu. Na jeseň roku 2023 sa uskutočnil prieskum a zo správy WhatTheyThink PRINT OUTLOOK pre rok 2024 sa publikovali trendy aký vplyv má AI na polygrafiu:

Výsledky tohto prieskumu naznačujú určitú nekonzistentnosť v nazeraní vplyvu AI a ML na polygrafický priemysel. Čas, možno najbližšia budúcnosť, ukáže ďalšie smerovanie. V roku 2023 sa spracoval národný projekt „Podpora kvality sociálneho dialógu". Bolo spracovaných viacero PESTLE a SWOT analýz nášho priemyslu.

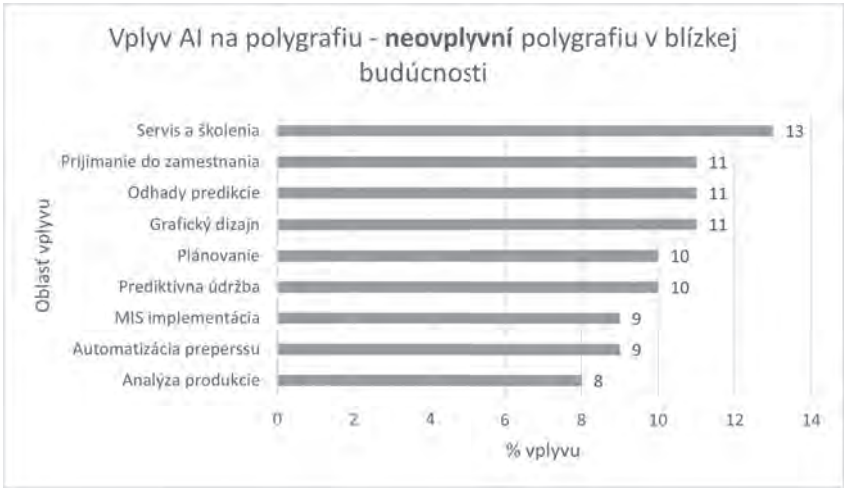
S narastajúcou digitalizáciou polygrafie a budúcim zapojením umelej inteligencie AI do procesov v polygrafickej výrobe sa otvárajú nové príležitosti a potreby z ľadiska „nových" zamestnaní a vzdelávania. Tu je niekoľko príkladov:

Špecialista na automatizáciu procesov (S nástupom umelej inteligencie a automatizovaných systémov v polygrafickom priemysle je dopyt po odborníkoch, ktorí sú schopní implementovať a spravovať tieto technológie.)

Expert na spracovanie veľkých dát v polygrafii (Digitalizácia polygrafických procesov prináša obrovské množstvo dát, ktoré je potrebné analyzovať a interpretovať.)

Manažér pre digitálnu transformáciu v polygrafii (S rastúcim vplyvom digitálnych technológií a umelej inteligencie je dôležité mať odborníkov, ktorí sú schopní riadiť proces digitálnej transformácie v polygrafickom priemysle.)

Sme svedkami, že rýchly nástup technického pokroku v posledných rokoch predbieha náš súčasný systém prípravy na povolanie v celom reťazci primárneho vzdelávania (základné školy / stredné školy / vysoké školy). To vytvára tlak na celoživotné vzdelávanie. Toto si musia uvedomiť nielen vzdelávacie inštitúcie ale aj zamestnávatelia.



Dovolím si bonmot na záver:

Verím, že AI z nás nakoniec nespraví IA!

Efektívna spolupráca medzi priemyslom a vzdelávacími inštitúciami: Cesta k inováciám a rozvoju talentov
Effective Cooperation Between Industry and Educational Institutions: A Path to Innovation and Talent Development

Ivana Keyzlarová

Riaditeľka Ľudských zdrojov Mondi SCP / Human Resources Director Mondi SCP
Mondi SCP, a.s., Tatranská cesta 3, 034 17 Ružomberok,
Ivana.Keyzlarova@mondigroup.com

Abstract: *The presentation focuses on effective cooperation between industry and educational institutions in the context of the pulp and paper industry. Our company actively cooperates with secondary schools and universities through plant tours, professional internships, support for diploma and bachelor's theses, and the "Summer Work" program, which provides students with hands-on experience through seasonal jobs. This partnership model not only contributes to the development of education but also allows us to systematically cultivate the next generation of professionals who may become part of our team.*

WPP PA

Polygrafia Academica
2025

Industrial inkjet printing as an integral part of future of print

Stanislav Vaníček

Koenig & Bauer (CEE), Pobřežní 249/46, 186 00 Praha 8
stanislav.vanicek@koenig-bauer.com

Přestože moderní technologie tisku, které pro zjednodušení nazýváme „digitální", stále oproti tradičním analogovým zařízením produkují jen několik procent objemu tištěné produkce, jejich význam průběžně roste. Mezi hlavní důvody patří především pokles průměrného tiskového nákladu na zakázku, způsobený snahou zadavatelů o častější změnu designu produktů, minimalizaci skladových zásob nebo přizpůsobení vzhledu různým cílovým skupinám konzumentů.

Tyto obecné trendy se následně propisují do poptávky výrobců tiskovin po technologiích, které by umožňovaly menší náklady tiskovin efektivněji vyrábět. Výrobci tiskových strojů a zařízení na to pochopitelně reagují investicemi do vývoje stále výkonnějších a sofistikovanějších řešení, která v některých oblastech dokáží tradičním tiskovým technologiím více než dobře konkurovat nebo je alespoň efektivně doplňovat.

Společnost Koenig & Bauer jako celosvětový tradiční výrobce tiskových strojů nezůstává v tomto snažení pozadu a ve svých R&D odděleních pracuje již mnoho let na vlastních „digitálních" řešeních pro různé oblasti tisku. Protože se koncern soustředí na výrobu vysoce výkonných průmyslových zařízení, nabízí v současné

době stroje využívající inkjetovou technologii s inkousty na bázi vody, která se pro toto využití ukázala jako nejvhodnější. Konkrétně se jedná o tři různé druhy strojů pro použití v odlišných tržních segmentech.

Prvním z nich je kotoučový stroj RotaJET na potisk papíru z role, který se v různých konfiguracích používá pro potisk knih, dekoru, nápojových obalů nebo třeba lineru na vlnitou lepenku. Využívá tisk čtyřmi barvami CMYK v rozlišení 1200x600 dpi nebo 1200x1200 dpi s využití osvědčené technologie piezoelektrických tiskových hlav FUJI Dimatix Samba umístěných ve dvou řadách pro každou barvu. Extrémně výkonné trysky a potisk materiálu v pásu dovoluje dosáhnout vysoké tiskové rychlosti 270 resp. 135 m/min. Tisku předchází konvenční primerovací jednotka s disperzním lakem a potištěný pás je možné také následně ještě lakovat nebo potiskovat v samostatné flexotiskové jednotce.

Protože se jedná o kotoučový tiskový stroj, je nedílnou součástí zařízení i rolový odvíječ a systém vedení pásu převzatý ze špičkových akcidenčních „rotaček" Koenig & Bauer. V nabídce je systém manipulace s rolemi Patras v několika verzích od manuální s ručním přelepením až po plně automatický s robotickými prvky a výměnou role za provozu vhodný pro velkoobjemovou produkci.

Každá oblast použití však klade velmi různé nároky na zpracování pásu. Tisk knih většinou vyžaduje především vysokou rychlost a možnost napojení snášecí jednotky a dalšího knihařského pracování. Výrobci plovoucích podlah a podobných dekorů zase trvají na excelentní kvalitě a tedy maximálním rozlišení. Výhodou je i možnost „nekonečného" pásu dekoru bez opakování designu, limitem je v tomto případě jen výkon počítače, který grafická data zpracovává. A například stroje pro nápojové kartony zase obvykle mají za tiskem několik flexotiskových jednotek pro tisk a lakování a jsou začleněny do komplexních linek. Totéž lze v podstatě říci o konfiguracích pro potisk obalů obecně.

Kotoučový stroj RotaJET v konfiguraci pro tisk obalů

Další oblastí, kde je Koenig & Bauer velmi aktivní, je potisk vlnité lepenky. Tento obor se v poslední dekádě také významně rozvinul a také do něho pronikají požadavky na vysokou kvalitu, častou změnu designu, vyšší množství verzí produktů a individualizaci, především krabic, displejů a stojanů. Protože je inkjet bezkontaktní tisková technologie, dokáže na specifickém povrchu vlnité lepenky dosáhnout excelentní kvality tisku, zároveň je ze své podstaty ideální pro malé a střední série,

včetně využití variabilních dat nebo stále více vyhledávaných bezpečnostních prvků.

Reakcí na tyto trendy je stroj Delta SPC 130 z dílny Koenig & Bauer Durst v několika různě výkonných provedeních. Využívá barvy Durst na bázi vody, v základní verzi CMYK s možností rozšíření o Orange a Violet, případně Green. Součástí může být i inkjetový primer. Rozlišení 600 x 600 dpi je pro lepenku velmi dobrý, pro speciální aplikace lze zvýšit až na 800 x 600 dpi a na dalším navýšení se pracuje. Lepenka se potiskuje v arších velikosti až 1300 x 2800 mm a strojem prochází úzkou stranou napřed, což snižuje potřebný počet tiskových hlav a tudíž i finanční náročnost investice.

Další oblastí, kde je Koenig & Bauer velmi aktivní, je potisk vlnité lepenky. Tento obor se v poslední dekádě také významně rozvinul a také do něho pronikají požadavky na vysokou kvalitu, častou změnu designu, vyšší množství verzí produktů a individualizaci, především krabic, displejů a stojanů. Protože je inkjet bezkontaktní tisková technologie, dokáže na specifickém povrchu vlnité lepenky dosáhnout excelentní kvality tisku, zároveň je ze své podstaty ideální pro malé a střední série, včetně využití variabilních dat nebo stále více vyhledávaných bezpečnostních prvků.

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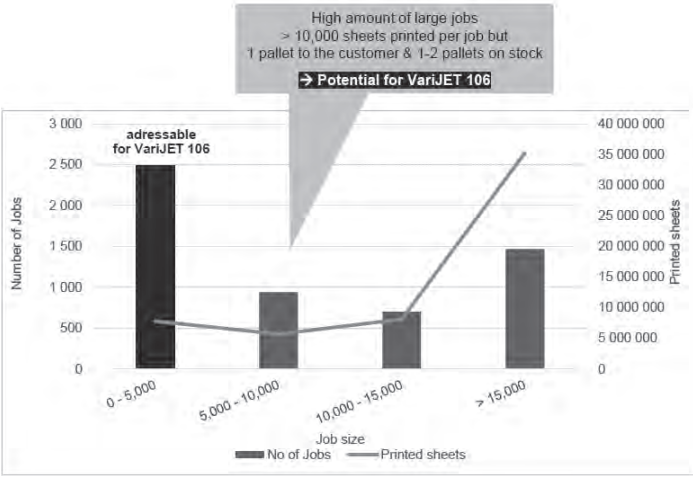
Inkjetový single-pass Delta SPC 130 pro potisk vlnité lepenky

Všechny komponenty stroje jsou přizpůsobeny specifikám manipulace s rozměrnými archy vlnité lepenky o velké tloušťce. Stohy materiálu jsou proto v provozech na výrobu a zpracování vlnité lepenky typicky transportovány bez palety na transportních pásech a výrobní zařízení jsou do tohoto systému oběhu palet

začleněny. To platí i o stroji Delta SPC 130, který je vybaven non-stop výměnou stohů v nakladači i vykladači. Je to více než nutné, protože tisková rychlost stroje se pohybuje mezi 60 a 120 m/min. a výměna stohu tak probíhá v řádu jednotek minut.

Nejmladším členem rodiny „digitálních" tiskových strojů, také z dílny Koenig & Bauer Durst, je archový inkjetový stroj VariJET 106 určený pro potisk kartonu tloušťky 0,2 – 0,8 mm ve formátu B1 (1060 x 740 mm). Stejně jako předchozí inkjetové stroje používá inkousty na vodní bázi a tiskové hlavy Samba G3L. Na rozdíl od nich však využívá sedmibarvovou technologii, tedy CMYKOVG, a jedno rozlišení 1200 x 1200 dpi při tiskové rychlosti 5500 archů/h.

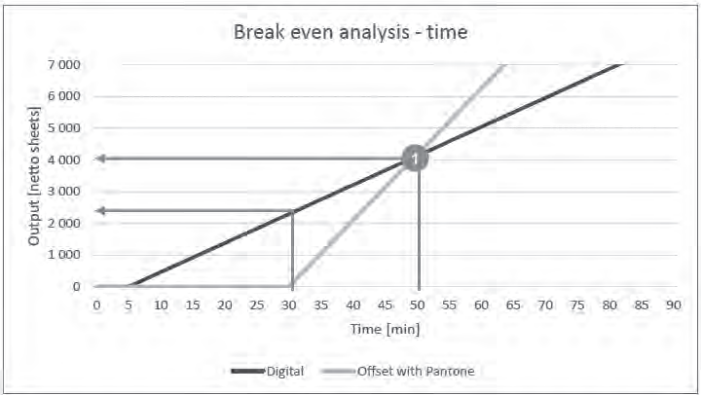
Jeho konstrukce a výbava reaguje na změny na trhu výroby skládaných krabiček z hladké lepenky, tedy již zmíněné klesající náklady, větší pestrost verzí, častější vzorkování a snahu o minimalizaci skladových zásob. Vzhledem k excelentní kvalitě tisku a rozšířenému gamutu srovnatelnými s ofsetovým tiskem je VariJET 106 ideálním doplňkem k archovému ofsetovému stroji stejného formátu. To je i základní filosofie technologie VariJET, tedy převzít z ofsetového stroje, který je v tomto segmentu z podstaty technologie ekonomicky výhodný pro nižší střední až vysoké náklady, všechny nízké a ultra nízké série krabiček a vyrábět je rychleji, levněji a s menším množstvím odpadu. K tomu využívá kromě stejného formátu i shodnou konstrukci s ofsetovým strojem Koenig & Bauer Rapida 106 – nakladač, lakovací jednotku pro primer, sušicí sekce, lakovací jednotky pro zušlechtění nebo vykladač.



Dobře se myšlenka vzájemného doplňování ofsetové a inkjetové technologie dá demonstrovat na výše uvedené zakázkové náplni. V této tiskárně zhruba 40 % zakázek reprezentuje jen asi 12 % objemu výroby, asi 6,5 mil. z celkového objemu 53 mil. archů za rok. Jejich náklad se pohybuje pod 5000 archů a jsou proto velmi vhodné pro inkjetovou technologii VariJET. Tiskárna má navíc velmi specifický vztah s hlavními klienty, kteří požadují dodávky zboží „na vyžádání", proto se kvůli efektivní výrobě na ofsetovém stroji zakázka předtiskuje a obvykle jedna paleta

materiálu (ca 2500 archů/paleta) putuje k zákazníkovi a 1-2 palety do interního nebo externího meziskladu tiskárny. Proto i nezanedbatelné množství zakázek o objemu 5000-10000 archů tvoří potenciál pro inkjetovou technologii.

Protože až 80 % zakázek v našem příkladu obsahuje přímé „pantone" barvy, příprava tisku na ofsetovém stroji se pohybuje průměrně na 30 minutách a pro tyto zakázky je třeba přibližně 250 archů makulatury, 5-6 tiskových desek (plus samozřejmě i osvitová jednotka) a také například nezanedbatelné množství ofsetových gum. Inkjetový stroj nic takového nemá, pro jeho rozjezd a kalibraci je třeba jen několik archů a produkci lze zahájit během 5 minut. Po třiceti minutách, kdy ofsetový stroj prováděl přípravu a rozjezd zakázky, má inkjetový stroj vytištěno zhruba 2500 archů. Výkonnostní bod zlomu pak nastává podle dosažené tiskové rychlosti ofsetové technologie mezi 3000 a 4000 archů (40-50 minut).



Započítáme-li u vybraných zakázek všechny náklady obou technologií (desky, gumy, makulaturu, barvy, energie), měl by v našem vzorovém případu tisk na inkjetu vyjít znatelně levněji. Ten bude zmíněnými 6,5 miliony archů vytížen zhruba na 1 směnu a nabízí tak dodatečnou kapacitu pro rozšíření výroby v tomto segmentu, případně tištění dalších zakázek na vyžádání a snížení skladových zásob. Ofsetový stroj navíc získá volnou kapacitu pro zakázky vyšších nákladů, které je na něm možné vyrábět efektivněji.

Jak se investice do stroje VariJET 106 projeví na vzorovém příkladu:

- Spousta malých úloh, které lze přesunout na VariJET 106
- Malé zakázky (≤ 5 000) na VariJET 106 zvyšují efektivitu výroby
- Další kapacita přes 20 mil. archů pro všechny typy zakázek (ofset + inkjet)
- Výroba „na vyžádání" s VariJET 106 a snížení nákladů na zásoby
- Snížení CO_2 stopy: méně odpadu, energie, dopravy

Další možné benefity:

- Rozvoj nových oblastí podnikání s inkjetovou technologií tisku
- Vytvoření unikátní prodejní nabídky („USP")
- Odlišení se od konkurence
- Dvojitý lak na inkjetovém stroji pro nové trhy (opce)

Archový single-pass inkjet VariJET 106-7+LTL pro potisk kartonu

Na závěr bych ještě jako zajímavost zmínil další novinku z oblasti inkjetového tisku. Jedná se o inkjetovou linku Met ONE na potisk plechu, kterou s využitím prověřené technologie multipass systému společnosti Durst vyvinula dceřiná v obru dekorování plechu etablovaná společnost Koenig & Bauer Metalprint.

Je více než evidentní, že inkjetová technologie již není jen záležitostí omezenou na malonákladovou akcidenční výrobu a formulářový tisk. Proniká do většiny oblastí polygrafické výroby a investice do jejího vývoje generují množství funkčních zařízení, která nacházejí své místo na trhu s tištěnými produkty. Do budoucnosti lze očekávat její další rozšiřování do tiskárenských provozů a vývoj směřující k vyššímu výkonu a pravděpodobně i nižším provozním nákladům, protože technologie ještě stále nenaráží na své limity.

Zdroj Koenig & Bauer

Material Printing of Antimicrobial Layers and Indicators not only for Smart Packaging

Michal Veselý, Vojtěch Dobiáš, Petr Dzik

Brno University of Technology, Faculty of Chemistry, Purkynova 118, 612 00 Brno, Czech Republic, michal.vesely@fch.vut.cz

Abstract: *Preparation and properties of functional liquids deposited by material printing to prepare gas indicators for smart food packaging. Their calibration and testing for quality, shelf life and lightfastness. Antimicrobial thin films, their material printing, production scale-up, operational efficacy tests.*

Keywords: *Material printing, Lotus foil, oxygen indicator, ozone indicator, flame retardant coatings.*

1. Introduction

Material printing is a process in which a functional liquid is delivered to the printed substrate. For this, conventional printing techniques or digital printing techniques are used. However, because one of the dimensions of the resulting patterns is typically 0.5-2 μm in size, the term 2.5 D printing is sometimes used for material printing. This produces both flat and height-structured patterns. The simplest example of material printing is coating techniques, the most used printing techniques are screen printing, flexo printing, gravure printing, pad printing and inkjet printing.

These printing techniques have several advantages. These include high reproducibility of functional liquid deposition, accurate multiple layer printing, high productivity, easy up scaling and last but not least, low consumption of expensive functional liquids compared to other liquid thin film techniques. In the following sections, examples of printing of sensors, indicators and layers with antimicrobial function at the authors' workplace are given.

2. Brief Overview of Printed Sensors and Indicators

At the authors' workplace, material printing techniques have been developped for 20 years. Recent examples include a conductivity sensor on glass, sintered alumina and polyimide foil printed with gold and silver ink followed by a burn-in (Fig. 1), a printed electrochemical UV sensor developed from a semiconductor formulation deposited on carbon electrodes (Fig. 2). A polymer gel electrolyte was deposited over the electrodes and semiconducting layer and fixed by random UV-initiated crosslinking of the reactive polymer. The sensor exhibited a linear photocurrent

response for irradiance of 0.5-8 mW.cm^{-2} and 0.05-0.5 mW.cm^{-2} for UVA. The next printed active element was an electrophotocatalytic cell, where a titanium dioxide layer in an organosilicon binder forming the anode was inkjet printed, an alumina insulator was screen printed, and then either a carbon cathode was screen printed or gold inkjet printed. The electrophotocatalytic cell has been successfully used to disinfect water at extremely low *E. coli* counts (Fig. 3).

A disposable radiation dose indicator, i.e. a chemical dosimeter for UVA+UVB radiation, was prepared, indicating by colour change the required erythemal effective radiation dose of 100, 200, 300 and 400 J.m^{-2}. At the Faculty of Chemistry, Brno University of Technology, it was prepared under semi-operational conditions on a roll-to-roll material printer Coatema Smart Coater. The UV dosimeter is primarily used for the control of sunbathing (Fig. 4).

Photocatalytically active layers were prepared from a mixture of nanocrystalline titanium dioxide and synthesized organosilicon binder. More than 1000 bm of photocatalytically active film was prepared using a Smart Coater printer for use in photocatalytic reactors for pool water purification (Fig. 5).

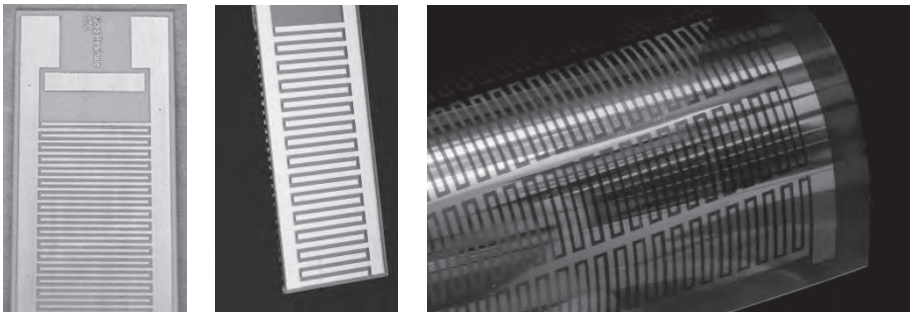


Fig. 1: Printed conductivity sensors.

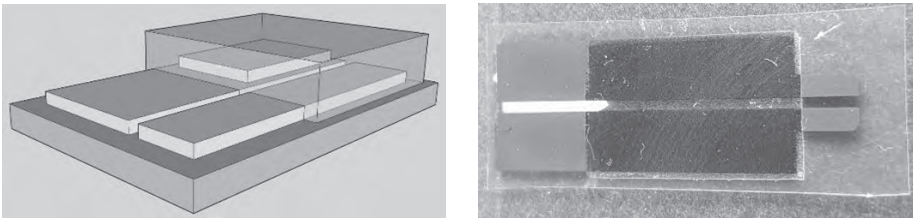


Fig. 2: Printed electrochemical UV sensor.

Fig. 3: Printed electrophotocatalytic cell.

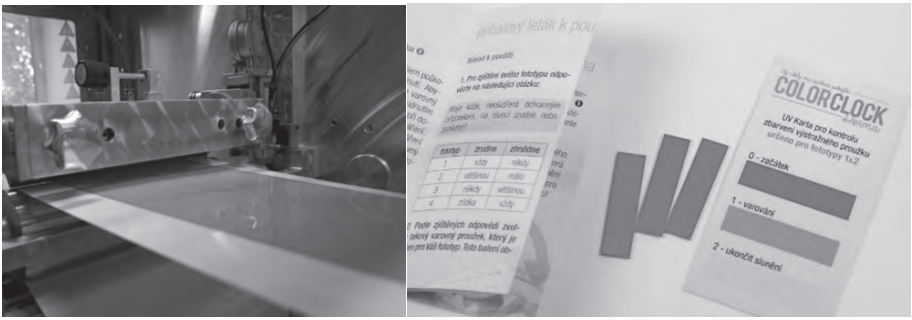


Fig. 4: Printed chemical dosimeter for UVA+UVB radiation.

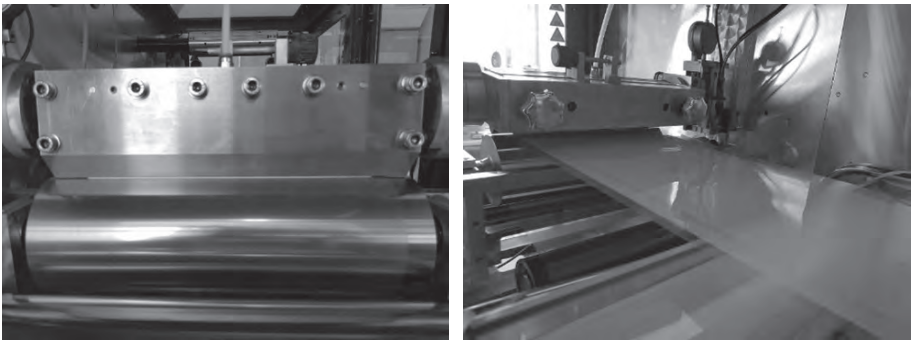


Fig. 5: Printed photocatalytically active layer.

3. Printed Antimicrobial Layers

Touchscreens are the new phenomenon of our time. In the covid period and even afterwards, people hesitate to touch screens or displays in shops. The solution is a protective film with an antimicrobial function on touchscreens, which would ensure a significant reduction in the population of micro-organisms on their surface.

One possibility for obtaining anti-adhesive (antifouling) or antimicrobial properties on various materials is surface functionalization. This approach has several advantages over disinfection techniques. Surfaces formed in this way are constantly active, unlike radiation or conventional cleaning. Another huge advantage of such functionalized materials is the fact that they exhibit biocidal properties without containing conventional biocide. They can therefore be placed in direct contact with humans without fear of harm, as they do not cause any harm to higher organisms.

The essence of the technical solution is that the multi-layered self-adhesive transparent covering film further comprises an antimicrobial layer arranged on the upper contact side of the carrier polymer layer, which is formed by a water-borne lacquer based on an inorganic-organic polymer, namely a silicone acrylate copolymer with at least one antimicrobial additive. The first antimicrobial additive is a photocatalyst covalently bonded to the silicone acrylate copolymer. The multi-layered self-adhesive transparent cover film provides protection against drift of microbial and organic pollutants. The material thus constructed is primarily designed for long-term broad-spectrum protection against the adherence, subsequent multiplication and unwanted transmission of bacteria, viruses and/or yeasts.

In an advantageous embodiment, the second antimicrobial additive is a biocidal substance, thus the antimicrobial layer uses the synergistic action of the first antimicrobial additive in combination with the second antimicrobial additive at a minimum effective concentration that meets the legislative requirements.

Preferably, the photocatalyst is an organic photoactive material based on a phthalocyanine derivative of zinc bound to the silicone acrylate copolymer by a covalent bond, thus not released into the environment. The absorption maximum of the zinc phthalocyanine derivatives lies in a suitable wavelength region of 600 to 700 nm, which corresponds to the spectrum of conventional light sources such as incandescent, LED or fluorescent lamps. This makes it possible to successfully apply these multi-layer self-adhesive transparent cover films indoors. Phthalocyanine derivatives are incorporated into the protective antimicrobial coating in the form of a substituted derivative that provides reactive fixation in the carrier polymer layer.

Thin films were prepared on a Coatema SmartCoater using a 2-roll technique as well as a slot-die technique (Fig. 6). The prepared layers on self-adhesive film (PET, PVC, PE) were tested for their ability to produce singlet oxygen based on the change in concentration of diphenyl isobenzofurane, antibacterial (ISO 27447 and ISO 22196) and antiviral activity (ISO 21702) and of course also for mechanical properties such as scratch resistance (ISO 15184) and adhesion by the grid method according to ISO 2409:2007.

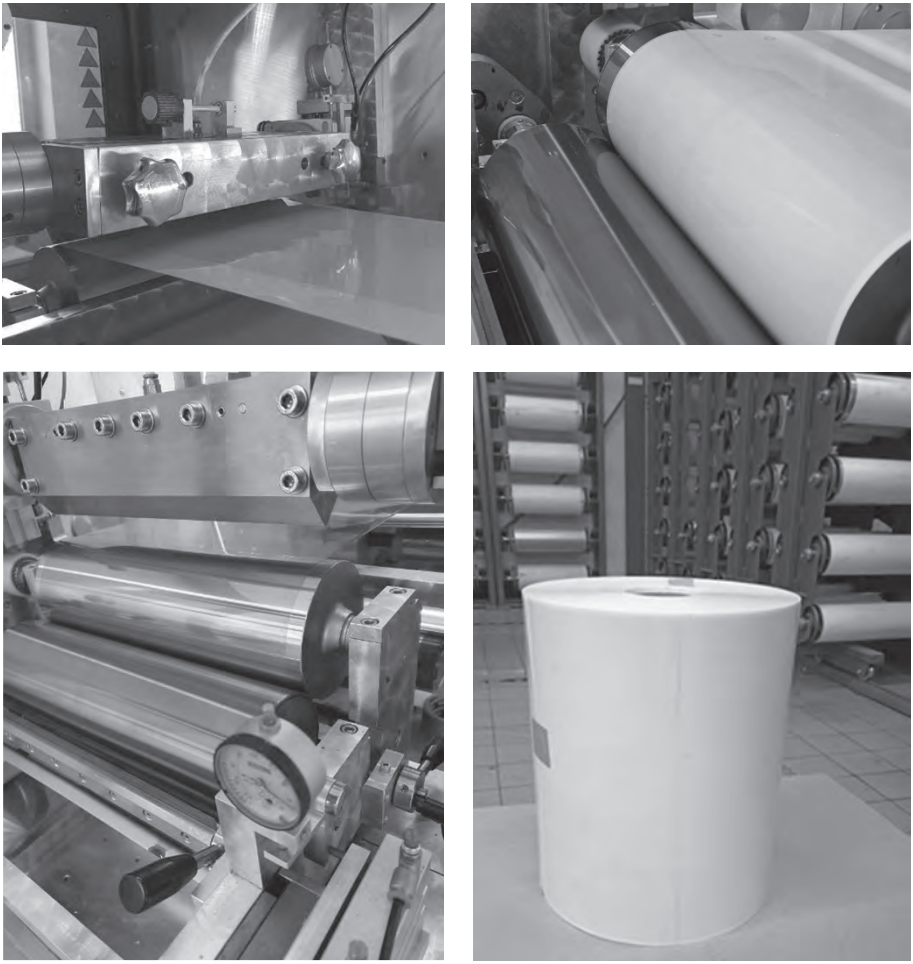


Fig. 6: Printed antimicrobial layer. A Lotus foil. See more information at https://www.forte-sinteractive.com/product/lotus-foil.

4. Disposable Printed Ozone Indicator

A printed sensor for ground-level ozone detection and dose determination has been developed in which the carrier polymer system consists of an alkyd polymer, a reactive dye and a component that controls the contact of ozone molecules with the dye. When the ozone molecules contact the dye, the dye is degraded and the polymer layer fades. The sensitivity of the printed sensor to ozone is calibrated by the addition of a calibration reagent. The printed sensor is adjusted to a sticker with

a printed standard–a colour scale for comparison with the sensor colour. The entire ozone sensor sticker is adhered to the object in the vicinity of which the ozone dose is to be determined. The discoloration of the printed ozone sensor is irreversible. When areas are disinfected with ozone generators, the concentration in ozone is not constant over time, so the sensor responds cumulatively to the total ozone dose given by the product of time and concentration. Thus, it is possible to determine the mean ozone concentration when a printed sensor is exposed to ozone for a known period.

The ozone sensor formulation was prepared under laboratory conditions by mixing screen printing varnish, dye solution in propylene glycol monomethyl ether, regulator suspension and calibration reagent. The viscous solution was then screen-printed onto polyester films. A 36-92W screen and a Roku Print05 semi-automatic screen printing machine with a 75 Sh screen was used for printing. The printed sensor was dried for 5 min at 100 °C in an oven.

The printed sensor samples were tested in an ozone chamber with known ozone concentration. The reciprocal properties of the printed ozone sensor were confirmed by testing at two different ozone concentrations.

The preparation of the ozone indicator was further scaled up to the level parameters on a Gallus RCS340 flexographic press. It was printed from 8 flexographic units with direct inks dipped to match the colour standard, UV curable, and the last unit was rotary screen-printed with an active indicator layer with infrared drying. The sticker with the indicator and colour standard was printed on Avery Dennison PET23 TOP CLEAR material/adhesive S692N/substrate BG40BR AI788, screen printed with Gallus Screen Digital DWD 40.

Fig. 7: Printed ozone indicator.

5. Printed Food Packaging Oxygen Indicator

The indicators are comprised of TiO_2, Remazol Brilliant Blue R, glycerol, and polymer. Two different polymer matrices, poly(vinyl acetate) (PVAC) or (carboxy)methyl cellulose (CMC) were used. The indicators were printed on a plastic foil and covered with a UV curable coating. Data for the kinetic study of photocatalytic reduction and oxidation were gathered with reflectance spectrophotometer and the kinetic analysis was based on the change of the indicator's optical density. Both indicators were successfully activated with UVA and both detected oxygen. The rate of oxidation depended on percentual oxygen concentration, increasing with increasing oxygen concentration.

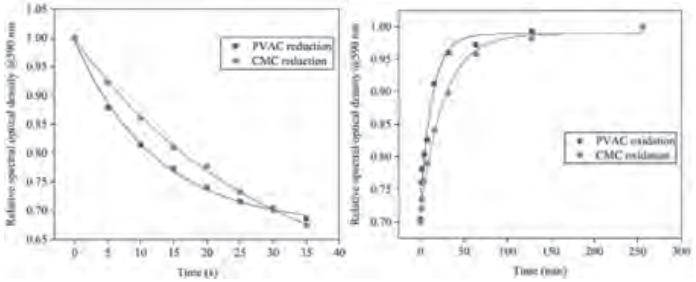


Fig. 8: Printed oxygen indicator.

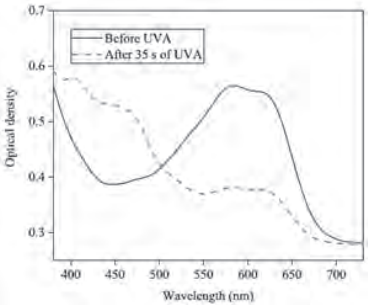


Fig. 9: Printed oxygen indicator.

6. Flame Reatardant Coating

A set of samples was prepared by screen printing–the theoretical thickness of one wet layer was approximately 65, 104 and 146 µm (one or two layers). However, the viscosity of the flame retardant was too high. After one set of samples, the av-

erage degree of polymerization of the binder was therefore reduced from 6000 to 1000 and 300 and printing was repeated with a screen producing a 146 µm thick layer. The lowest degree of polymerization binder was problematic because of the formation of massive air bubbles during printing. Samples were evaluated by linear burning rate (Test flames – 50W horizontal flame test method, ČSN EN 60695-11-10) and oxygen index (Determination of burning behavior by oxygen index, EN ISO 4589-2)

The best performance was recorded for the 146 µm thick layer. The mixed fire retardant based on Cloisite-Na+ bentonite and mica protected most of the archival boxes during a medium-scale fire test. Its effect probably consists mainly in the formation of a barrier [5] for the evaporation of flammable volatile compounds to a vapor phase and limiting the access of oxygen to a condensed phase.

7. Conclusion

The above overview of printed elements and layers shows the wide applicability of material printing techniques in research and applications.

Acknowledgement

Authors thank to Technological Agency of Czech Republic for support by projects TA03010548, FW03010006, TH03030197, TN02000051 and Ministry of Industry and Trade for support by project OP PIK–Aplikace CZ.01.1.02/0.0/0.0/20 _321/0024435.

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Biochar-based screen-printed electrochemical sensors: sustainable tools for advanced analytical applications

Švorc Ľ. [1], Sarakhman O. [1], Hatala M. [2], Gemeiner P. [2]

[1] Institute of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia
[2] Department of Graphic Arts Technology and Applied Photochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia
lubomir.svorc@stuba.sk

Abstract. *The increasing focus on sustainability has sparked significant interest in repurposing waste materials as cost-effective, renewable and abundant sources of energy and raw materials. Transforming waste materials presents a promising strategy for renewable energy production, the development of advanced materials and fostering environmental sustainability. Among these materials, biochar–a carbon-rich solid product derived through the pyrolysis of biomass under oxygen-limited conditions–has gained attention as a versatile and sustainable material with diverse applications [1]. This study investigates the potential of biochar as a foundation for the next generation of high-performance printed electrochemical devices. Key factors influencing biochar properties, including biomass type, pyrolysis conditions (temperature, duration, and heating rate) and activation treatments, were systematically analyzed. The integration of biochar into fully screen-printed electrochemical sensors was demonstrated, with a focus on morphological, spectral and electrochemical characterization [2]. Additionally, the performance of these printed sensors in detecting "phenol-like" analytes for pharmaceutical quality control was evaluated, with particular attention to critical analytical features such as sensitivity, linear concentration range, detection limits and method validation. The findings of this study contribute to the advancement of printed electrochemical sensor design, shedding light on current trends, challenges and opportunities for real-world applications.*

Keywords: *biomass, biochar, electrochemical sensor, screen-printing*

Acknowledgement

The authors thank the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences (VEGA No. 1/0036/24 and VEGA No. 2/0136/24), the Slovak Research and Development Agency under the Contract No. SK-PL-23-0013 and APVV-23-0066 and Call for doctoral students and young researchers of Slovak University of Technology in Bratislava to start a research career (Grant 23-04-01-B).

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Tlačené hybridné solárne články pre interiérové aplikácie

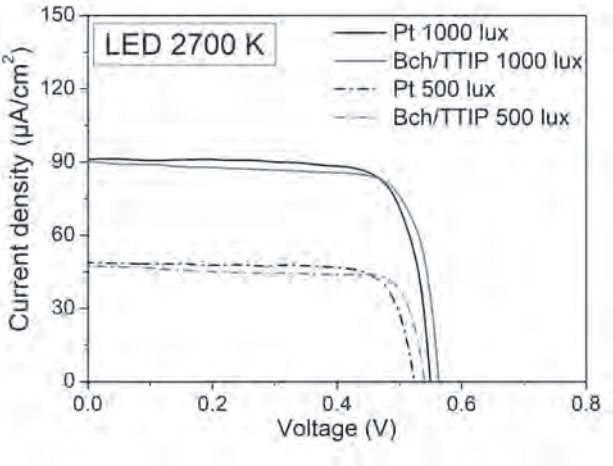
Pavol Gemeiner, Tatiana Buchlová, Michal Hatala, Milan Mikula

Oddelenie polygrafie a aplikovanej fotochémie, Fakulta chemickej a potravinárskej technológie STU v Bratislave, Radlinského 9, 812 37 Bratislava
pavol.gemeiner@stuba.sk

Hybridné solárne články patria do tretej generácie fotovoltiky. Oproti konvenčným kremíkovým solárnym článkom (prvá generácia fotovoltiky) majú výhody ako napr. možnosť prípravy lacnejšími aditívnymi technológiami, použitie dostupnejších materiálov, príprava na flexibilných substrátoch, nízka hmotnosť, priehľadnosť elektród, variabilita dizajnu a vysoká účinnosť pri interiérovom osvetlení. Do tejto generácie patria aj farbivom senzibilizované solárne články (z angl. Dye-sensitized Solar Cell–DSSC). Štandardná štruktúra DSSC pozostáva z troch kľúčových komponentov: fotoanódy zloženej z mezoporéznej vrstvy TiO_2 senzibilizovanej organo-kovovým ruténiovým farbivom, kvapalného elektrolytu a Pt protielektródy. Vysoká cena Pt (~ 40 % nákladov na výrobu DSSC [1]) je jedným z dôvodov, prečo sa výskum zameriava na alternatívne materiály ako napr. vodivé polyméry, rôzne alotropy uhlíka, zmesi kovov a pod. [2]. Navyše, merania DSSC s alternatívnymi CE vykazujú vyššie účinnosti ako pri použití štandardnej Pt.

Jedným z týchto alternatívnych materiálov pri príprave CE je biochar–uhlikatý materiál pripravený pyrolýzou biomasy rastlinného alebo živočíšneho pôvodu. Vlastnosti biocharu ako jeho vysoká porozita, elektrická vodivosť, veľký špecifický povrch, prítomnosť rôznych funkčných skupín a rôznych atómov kovov sú kľúčovými faktormi pre jeho výskum ako CE v DSSC [3].

V našej práci sme študovali sieťotlačené kompozitné CE zložené z biocharu a tetraisopropoxidu titaničitého (TTIP). Biocharové častice boli pripravené pyrolýzou kukuričnej siláže a drevnej štiepky. TTIP bol použitý za účelom náhrady štandardného polymérneho spojiva–etylcelulózy, využívanej pri príprave sieťotlačových disperzií. Pri meraní fotovoltických parametrov pri interiérovom LED osvetlení (500 a 1000 lux) dosiahli DSSC s biocharovými/TTIP protielektródami porovnateľné účinnosti ako pri meraní DSSC so štandardnými Pt CE (Obr. 1). Výsledky tejto práce ukazujú na potenciál biocharu ako lacnej a ekologickej alternatívy k štandardným Pt CE [4].



Obr. 1 Porovnanie voltampérových charakteristík farbivom senzibilizovaných článkov s Pt CE a tlačenou Biochar/TTIP CE. Merania pri interiérovom osvetlení LED 2700 K s intenzitou 500 lux a 1000 lux. Hodnoty PCE predstavujú konverznú účinnosť solárneho článku.

Kľúčové slová: *hybridné solárne články, tlačené elektródy, biochar, obnoviteľné zdroje energie, sieťotlač*

Poďakovanie

Za podporu nášho výskumu ďakujeme *Agentúre na podporu vývkumu a vývoja* (projekt APVV-23-0066) a *Vedeckej grantovej agentúre MŠVVaM SR* (projekt VEGA 2/0136/24).

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Printed Photoelectrochemical Cells For Sensing, Remediation And Energy Harvesting

Petr Dzik, Radim Bartoš, Michal Veselý

Brno University of Technology, Faculty of Chemistry, Purkynova 118, 612 00 Brno, Czech Republic, dzik@fch.vut.cz

Abstract: *Photoelectrochemical cells consisting of a planar nanoparticular titania coated photoanode and an integrated digitated cathode were made by materials printing. TCO coated glass and PET were used for substrates, nanocrystalline titania dispersion bonded by a novel organosilica binder was used for the fabrication of the planar photoanode and silver or carbon inks for the fabrication of the cathode. Due to the digitated shaping of the cathode, photoelectrochemical response was not suffering from iR drop down to low electrolyte ionic strengths. The printed cells can be used in electroassisted photocatalytic oxidative treatment of wastewater as well as for small-scale sensing applications. With particular combination of cathode/anode material, the cell is capable to work as solar cell and energy harvesting becomes possible.*

Keywords: *Electroassisted photocatalysis, titania, titanium dioxide, materials printing*

1. Introduction

A photoelectrochemical cell is a device in which at least one working electrode is made of a semiconductor supported on an electrically conductive substrate. The photocatalytic activity of any immobilized semiconductor photocatalyst can be boosted by the application of external electrical bias. The strategy is based on enhancing the electron–hole separation and consequently increasing the quantum yield of the redox reactions taking place at the electrodes by the application of electrical bias, which is possible when the photocatalyst is deposited on an electrically conducting substrate. In the case of an n-type semiconductor, the working electrode acts as a photoanode to which a positive bias is applied. It consists of an electrical conductor covered by a semiconducting metal oxide (e.g. titanium dioxide). The counter electrode material is not critical as long as sufficient electrical conductivity and corrosion resistance is provided.

The photocurrent generated in an irradiated cell depends on many factors, including but not limited to electrolyte composition, irradiance, material of the electrodes, physical construction of the cell etc. Depending on the design, the cell can be used for a number of important applications, such as sensing, remediation and energy harvesting.

Materials printing is a promising microfabrication method well applicable for the production of planar layered devices, including photoelectrochemical cells. The

technique is based on sequential laying of patterned functional layers by means of modified conventional printing techniques. While generally all traditional printing techniques can be adopted for printing functional layers and patterns, inkjet printing occupies quite a prominent position. Despite its quite narrow viscosity and particle size limits, it seems to be the most suitable technique for lab scale prototype development as no hardware printing form is necessary, i.e., patterns designed on a printer driving computer can be printed directly without the need for physical printing form manufacturing. Moreover, up-scaling is very smooth and easy, because industrial inkjet printers with several meters working width are readily available, so transfer from prototype level to a small series level is reduced to switching to a bigger printer.

In this contribution, we describe the adoption of the principle of planar electrochemical cells to the versatile method of materials printing allowing for rapid processing and essentially unlimited upscaling. We report about our approach and experience with printing the key materials (insulating, semiconducting and conducting). Three application possibilies, i.e. sensing, remediation and energy harvesting, will be covered in detail, together with the physical, electrochemical and photocatalytic properties of the described cell types.

2. Printable Materials With Electronic Functionality

Recently, major developments in the technology of electronic component fabrication have taken place. The dominant position of subtractive fabrication processes based on sequential etching through temporary resists masks has been challenged by a new additive approach. The so called materials printing techniques [1] seem to be a promising microfabrication method well applicable for the production of planar structures with a low level of integration. The technique is based on sequential laying of patterned functional layers by means of modified conventional printing techniques. Strictly speaking, material printing has been around for several decades, but limited to screen printing [2-4] which has been widely applied in the electronic industry. During the past decade, the concept of materials printing has been significantly broadened and the portfolio of applicable techniques has included off-set, gravure, flexo, and inkjet printing.

- Electrical conductors: Transparent conductive oxides (TCOs) represent a highly attractive support material for the fabrication of titania photoanodes, as the photocatalyst layer can be irradiated through the substrate rather than from the electrolyte side which adds some interesting possibilities for reactor design [5].
- n-type semiconductors: The most straightforward fabrication route for metal oxide coated photoanodes is anodic oxidation [6] which is capable of providing oxide coating with various topology [7] and doping options [8]. Oxide coated photoanodes can also be deposited by methods which are more suited for upscaling, amongst them sol-gel based ones [9] and spray pyrolysis [10]. Materials printing is a novel approach to the task of functional material patterning and has already convincingly demonstrated its benefits[11].
- Electrical Insulators: A wide range of conventional printable materials can be

employed for the fabrication insulating layers, e.g. UV-curable inks. However, in order to get improved and reliable performance, more sophisticated materials need to be introduced. For example, barium titanate is a popular insulator with high dielectric constant, ensuring sufficient insulating capacity even wit thin layers originating from inkjet printing.

3. Photoelectrocatalytic Cell Design

The photocatalytic activity of any immobilized semiconductor photocatalyst can be boosted by the application of external electrical bias.[12] The strategy is based on enhancing the electron–hole separation and consequently increasing the quantum yield of the pollutant degradation by the application of electrical bias, which is possible when the photocatalyst is deposited on an electrically conducting substrate[13-15].

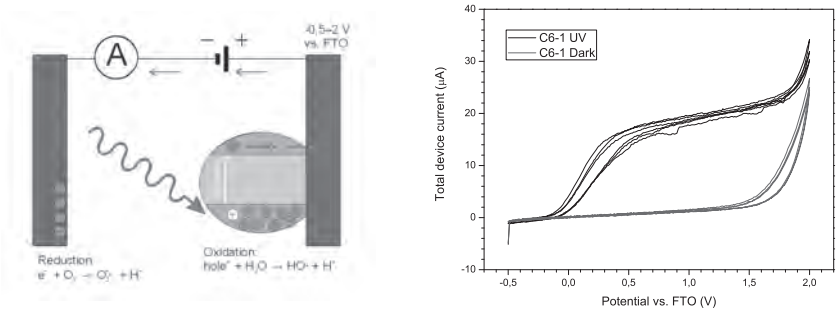

Fig. 1: A scheme of electroassisted photocatalytic process showing the photoexcited electron path (left) and typical polarization curves for titania photoanode (right)

The enhancement of photocatalytic activity of an immobilized semiconductor photocatalyst by the application of external electrical bias has been convincingly demonstrated [12]. However, when using electrolytes of low conductivity, iR drop is one of the factors limiting high current throughput at moderate bias. Supporting electrolyte may be added to increase the electrical conductivity in traditional electrochemical cells, but if the treatment of inevitably low ionic strength media (drinking water) is envisaged, other means for minimizing the iR drop must be secured.

The iR drop may be reduced by the use of a parallel plate reactor with two opposite electrodes and a small space between them where the electrolyte is passed through [16]. However, this configuration is prone to the pressure build-up in a module consisting of many such cells. This drawback can be avoided by placing both electrodes onto a single substrate and shaping them into a close mutual proximity with a very long boundary, i.e. creating interdigitated electrodes (IDE). The working electrode consists of an electrical conductor covered by semiconductor like titanium dioxide. The counter electrode material is not critical as long as sufficient electrical conductiv-

ity and corrosion resistance is provided and interdigital geometry is respected. Such a design ensures two key functions: (1) it suppresses the main obstacle to efficient use of absorbed photons, i.e. the recombination of photogenerated charge carriers, by applying external electrical bias to the semiconducting photocatalyst and (2) it avoids the reduction of the generated photocurrent due to iR drop, even in electrolytes of low ionic strength. These features qualify the device as an interesting candidate for photoelectrocatalytic purification of drinking water. Decomposition of model pollutants has been observed on centimeter-scale prototype devices fabricated by conventional lithographic techniques using optical copying through contact masks for resist patterning [17]. Although the lithographic approach allows for very fine patterns to be fabricated, it is totally unsuitable for the fabrication of large foot-print cell modules.

While utilizing an interdigitated cell design in our recent work [18] with photoelectrochemical cells, a remarkable drawback became evident: a significant fraction of the cell area is occupied by the inter-finger gaps and counter electrodes. A counter-electrode is unavoidable and gaps between the electrodes can be minimized, but still some fraction of the cell can be considered a "dead area" not taking active part in the desired redox processes. Therefore, a new cell design has been introduced where nanoparticulate titania is printed onto an unpatterned layer of TCO, which is almost entirely covered with the exception of a small patch allowing the connection of the positive bias terminal. A digitated insulator layer is printed onto the titania photoanode and the cathode is printed on top of the insulator. In this way we eliminated the gaps of the original interdigitated design and also significantly simplified the fabrication sequence, since no FTO patterning is necessary any more. The cell design is depicted in Figure 2.

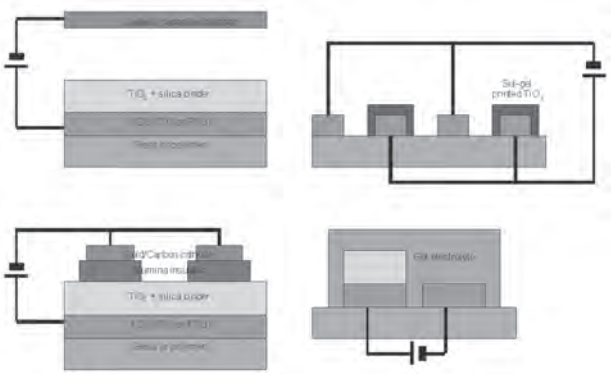

Fig. 2: Various cell designs: a conventional one with physically separated photoanode and cathode (top left), a planar interdigitated one (top right), a planar one with vertically separated cathode (bottom left) and a simplified UV-sensing one with a gel electrolyte layer (bottom right).

4. Investigation of Cell Properties

Photoelectrochemical characterization was performed by linear sweep voltammetry at room temperature using a two terminal setup. Apart from the measurement of the complete all-printed cells themselves, the electrochemical properties of various model cells consisting of separate 1 cm2 titania photoanodes and cathodes made of various materials were investigated in order to elucidate the influence of the material and/or the printing and processing variables. The studied cell was fitted into a custom build quartz cuvette filled with 0.1 M perchloric acid and placed onto an optical bench equipped with a fluorescent UV-A lamp emitting a broad peak centered at 365 (Sylvania Lynx-L, 11 W). A magnetic stirrer was placed beneath the cuvette and a magnetic flea inside the cuvette provided efficient electrolyte mixing. The lamp emission was monitored by a Gigahertz Optic X97 Irradiance Meter with a UV-3701 probe and the irradiance was set to 2 mW/cm2 by adjusting the lamp-to-cuvette distance. Measurements of generated photocurrents were performed with an electrometer build on the basis of the National Instruments Labview platform supplying linear voltage gradients.

5. Application Examples

The following redox processes take place at an illuminated n-semiconductor/electrolyte interface when conduction band electrons are channeled to a counter electrode due to applied reverse bias:

$$h_{vb}^{+} + H_2O \rightarrow HO\bullet + H^{+} \quad (1)$$

$$h_{vb}^{+} + OH^{-} \rightarrow HO\bullet \quad (2)$$

where h_{vb}^{+} is a valence band hole.

In the absence of an oxidisable solute, R, over a number of steps, water is oxidised to oxygen–in summary:

$$h_{vb}^{+} + 1/2\ H_2O \rightarrow H^{+} + ¼\ O_2 \quad (3)$$

If an oxidisable solute, R, is present in the electrolyte, the following reactions also occur:

$$h_{vb}^{+} + R \rightarrow R^{+} \quad (4)$$

$$HO\bullet + R \rightarrow R_{ox} \quad (5)$$

The total current is then composed of two sources: the oxidisable solute oxidation rate and the water oxidation rate [5], where the former increases with its concentration, c_{ox}. The Faradaic efficiency, f, reflecting the competition between reactions 3, 4 and 5 is a convenient measure for the description of the net efficiency of the initial oxidation step and is suitable for comparison of results obtained under various conditions:

$$f = V(dc_{ox}/dt)\ \ F / i_{photo}, \quad (6)$$

where V is the total volume of the batch reactor and F is Faraday's constant.

The oxidized species, R^+ or R_{ox}, undergo further electron transfer reactions and all intermediates may eventually be fully mineralized through a series of oxidative cleavage reactions into water and carbon dioxide.

To illustrate these processes, an example of photodegradation of a solution of terephthalic acid under UVA irradiation and assisted by electrical bias of 1 V, using the interdigitated 1000-1000-1000-1000 micron device with 200 nm thick TiO_2 fingers is shown at Figure 3. During this experiment the photogenerated holes act as strong oxidizing species presumably producing OH· radicals[19]. Although the exact mechanism is still being debated[20], the net oxidative effect is evident and can be easily monitored by various probes yielding fluorescent oxidized products[21-23]. During the course of the experiment, the fluorescence due to an intermediary product (OH-substituted, HTPA) increased and would eventually decrease down to zero as the fluorescent intermediate is further oxidised. The fluorescence at 425 nm plotted as a function of time reflects the initial reaction rate. While the blank checks show essentially no reaction, we can observe a doubling of the reaction rate (with respect to the unbiased case) when an external bias of 1 V was applied. From the initial slopes of the traces, the production rates, v, can be calculated taking into account the total volume of the solution. These production rates, considering Farday's law of electrolysis, are related to the electrical charge passed (photocurrent, i_{photo}). The Faradaic efficiency, f, of the process is calculated using $f = vF / i_{photo}$. The value of 0.009 obtained for the experiment shown is satisfactory given the fact that a very low concentration of electroactive species (1.10^{-5} M) was used. Polychromatic light centered at 365 nm was used for this experiment. The IPCE (incident photon-to-current efficiency) was 0.13 at 365 nm for 200 nm thick electrodes. Values of f were found close to values obtained for the degradation of phthalic acid in a parallel plate reactor [5]. While the datasets of the irradiated samples were measured continuously in 10 s intervals, the dark ones needed to be measured discontinuously only a few times during the reaction duration because a single radiation source was used for both catalyst activation and fluorescent probe excitation.

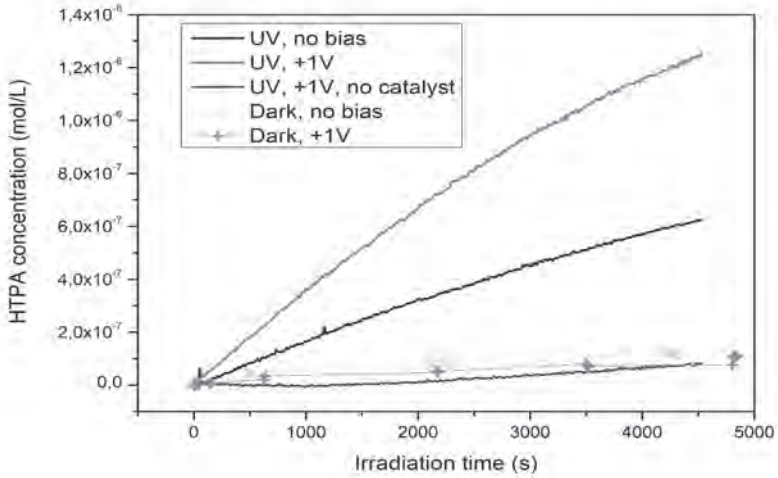

Fig. 3: Concentration profiles of HTPA at various experimental conditions.

Further electrochemical investigation was focused on the study on the influence of the cathode material. The voltammetric curves presented in 4 are the result of combined working and counter electrode response. As the working electrode (titanium dioxide) was identical in all devices, the resulting voltammograms reflect directly the behaviour of the counter electrodes, i.e. their ability to afford reductions at a low overvoltage, thereby shifting the onset of the photocurrent below the cell potential of 0 V. Two possibilities of reduction reactions are offered in the supporting electrolyte used: reduction of dissolved oxygen or reduction of water. Without analysing gaseous products, water reduction cannot be ruled out, but is unlikely given the known electrochemical response of the materials. On the other hand, considering oxygen reduction, carbon has been used successively in fuel cells for this reaction[24]. In fact, using carbon as cathode, the photocurrent delivered at 0 V is around 80% of the maximum (plateau) photocurrent. That means that cells equipped with a carbon counter electrode can be operated under short circuit without much loss and avoiding an external electrical circuit providing bias. If used for scaled-up implementations of the present device, this would reduce cost and complexity of electrochemical reactors immensely. However, this advantageous behaviour is observed only when the surface area of the cathode is large enough to generate currents of similar magnitude as the photocurrents produced at the anode.

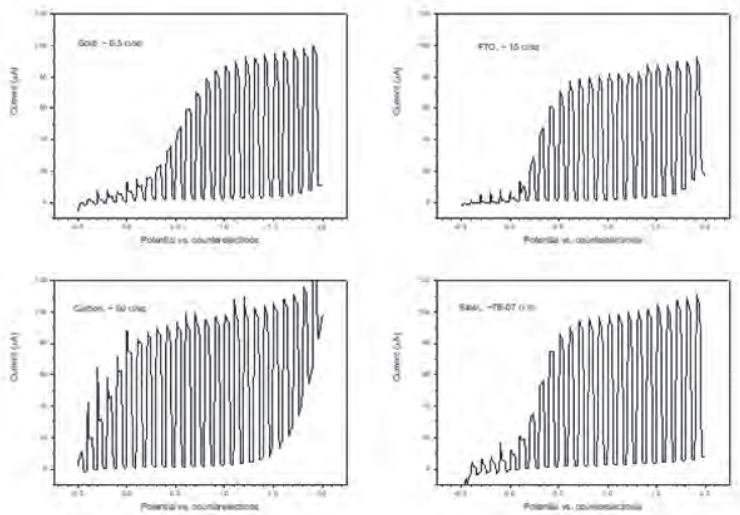

Fig. 4: Chopped linear-sweep voltammetric curves for cells consisting of titania photoanodes (1 layer, thermally sintered on FTO, 1 cm^2) and cathodes of approximately the same surface area facing each other at a distance of 15 mm. Cathodes were made of various materials (see graph legends) and cells were immersed into 0.1 M perchloric acid and irradiated by a broad-band UV-A fluorescent lamp set to 2 mW/cm^2.

A further application niche of the discussed photoelectrochemical cells stems from the obvious and natural fact that the magnitude of the generated photocurrent is proportional to the incident photon flux. This enables the cell to work as a UV sensor, the electrical current of which is proportional to the incident UV irradiance. Such dependence is illustrated in Figure 5. While this behaviour is rather unwelcome during ordinary photoelectrochemical experiments and calls for permanent checking of the lamp condition by the means of a reliable radiometer in order to make experimental results repeatable, it becomes an advantage when UV intensity measurement is the goal.

However, for sensing purposes the cell design needs to be modified: The electrode system can be simplified to a large extend: essentially two planar electrodes would be sufficient, but the liquid electrolyte needs to be replaced with a gel electrolyte. Both these tasks are at present being investigated in our lab and first promising results have been obtained as illustrated at Figure 6.

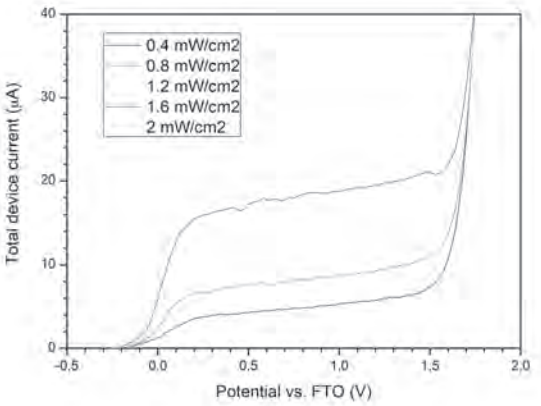

Fig. 5: Linear sweep voltammetry polarization curves for cells consisting of titania photoanodes (1 layer, thermally sintered on FTO, 1 cm2) and FTO cathodes in 0.1 M perchloric acid using a broad-band UV-A fluorescent lamp set to variable irradiance values.

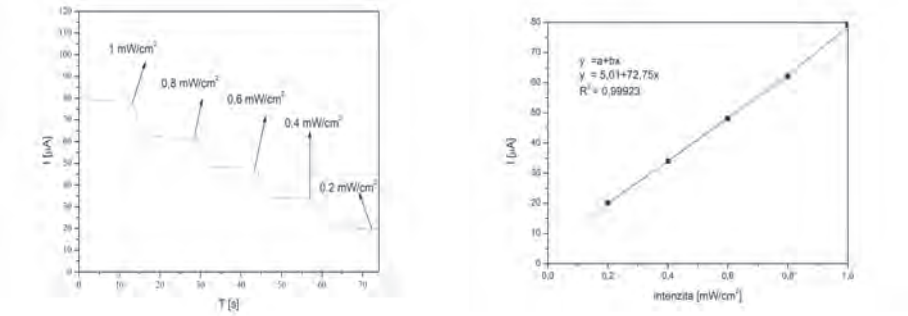

Fig. 6: Figure 6: Chronoamperometric record (left) and resulting calibration curve (right) for an optimized UV-sensing cell with a gel electrolyte using a broad-band UV-A fluorescent lamp set to variable irradiance values.

6. Conclusion

The disclosed overview briefly summarizes our know-how on printed titania photoanodes and their utilization for electrophotochemical cells which can be optimized for various application niches. In any case, materials printing was successfully employed for the deposition of all the functional and auxiliary layers. Inkjet printing proved to be an elegant method for sol delivery to the substrate. It provides a complete control over the deposition process parameters together with an excellent efficiency of precursor use.

Comparative photocatalytic and electrophotocatalytic experiments with terephtalic acid as model contaminant compound proved the beneficial role of external electrical bias in suppressing photogenerated electron-hole recombination in the semiconducting photocatalyst. In this way, more efficient charge separation in the electric field of the IDE device has been demonstrated by the acceleration of terephtalic acid oxidation, which was conveniently monitored by the fluorescent signal of its dominant oxidation product, hydroxyterephtalic acid.

The choice of gold as a counter electrode material is beneficial to the rate of oxygen reduction in air saturated working electrolytes. As a consequence, especially at low external bias or in the absence of external bias, if the electrodes are short circuited, the larger current output of the device is directly leading to increased rates of photoelectrocatalytic reactions. That means that cells equipped with a gold counter electrode can be operated under short circuit without much loss and avoiding an external electrical circuit providing bias.

Simplified planar design of such cells covered with a semi-dry layer of gel electrolyte represent an interesting approach to the manufacture of all-printed low-cost UV sensor.

Acknowledgement

Authors thank to Technological Agency of Czech Republic for support by projects TA03010548, FW03010006, TH03030197.

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Printed Textile Electrodes for ECG Recording

Michal Hatala, Lukáš Vályi, Barbora Dikošová, Pavol Gemeiner

Department of Graphic Arts Technology and Applied Photochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, michal.hatala@stuba.sk

The research on smart textiles explores their applications in various fields, including medicine, military and energy storage. These advanced technology have the potential to revolutionize industries by integrating electronic functionalities into fabrics, enhancing both usability and convenience. This study focuses on smart textiles equipped with electrodes for bioelectrical signal measurement. With medical advancements, acquiring high-quality data is crucial for disease treatment and prevention. However, conventional devices are often non-portable or uncomfortable, limiting data collection in real-life conditions. Smart textiles offer a solution by providing continuous, comfortable, and discreet monitoring without disrupting daily activities.

This work investigates the preparation of dispersions containing a conductive mixture of graphite and carbon black. These dispersions were analyzed in terms of printing and rheological properties, with a focus on sheet resistance, print resolution, and elasticity of the screen-printed layers. Both direct and transfer screen printing methods were used on two types of textiles, ensuring a comprehensive evaluation of printing quality and electrical performance.

Additionally, a prototype dry contact electrode was developed for electrocardiogram (ECG) recording. The study aimed to create functional printed layers applicable in smart textiles. Two prepared dispersions type were formulated – one based on plastisol (PVC based) and another based on silicone. Formulations were modified to optimize adhesion, conductivity, and mechanical properties, making them suitable for practical applications in wearable health-monitoring systems.

Rheological measurements confirmed pseudoplastic behavior in all samples, with increasing viscosity as carbon content increased. Some samples exhibited weak viscosity recovery, leading to layer spreading and edge deformation, which could affect the precision of printed patterns. Oscillatory measurements indicated no linear viscoelastic region, suggesting structural breakdown from the begining of the mechanical stress. These findings highlight the importance of optimizing the dispersion formulation to maintain printing consistency and electrical performance.

Printing results showed that mesh count 32 provided better prints than mesh count 54, which had incomplete ink transfer and inconsistent layer thickness. Sheet resistance decreased with higher carbon content until printing inconsistencies appeared, which impacted the overall conductivity and uniformity of the layers. Transfer-printed silicone dispersions had higher sheet resistance than direct-printed ones, likely due to differences in layer thickness and adhesion. Additionally,

silicone-based layers on non-elastic textiles exhibited higher resistance than those on elastic textiles. Plastisol-based samples showed lower sheet resistance than silicone-based ones, with the lowest recorded value at Rs = 26.1 ± 2.2 Ω/sq, demonstrating the superior conductivity of plastisol formulations.

Elasticity tests indicated that silicone layers printed via transfer printing were more stretch-resistant than those printed directly, suggesting that the transfer method enhanced mechanical durability. Microscopic analysis revealed structural differences, with transfer-printed layers appearing more homogeneous but showing textile structure imprints. This structural distinction may influence the flexibility and long-term stability of the printed layers, particularly in applications requiring repeated movement and bending.

The narrowest printed line was 300 μm for plastisol dispersions and 200 μm for silicone dispersions, highlighting the resolution limits of each formulation. ECG electrodes developed from selected dispersions and commercial carbon paste successfully recorded P waves, T waves, and QRS complexes, validating their functionality in biometric monitoring. However, silicone-based dispersions produced less stable ECG signals compared to plastisol-based dispersions, which yielded more consistent and reliable recordings. This suggests that the choice of dispersion formulation plays a crucial role in optimizing signal clarity and sensor performance.

Future research could explore the impact of fiber orientation on conductivity, alternative solvents, and detailed elasticity analysis, including repeated stretching, bending, and abrasion effects on electrical resistance. Further improvements in formulation design and printing settings could enhance the integration of smart textiles into everyday applications, particularly in healthcare, sports monitoring, and military wearables. Expanding the range of conductive materials and optimizing the interaction between printed layers and textile substrates will be key to advancing the development of high-performance smart textile solutions.

Acknowledgements

The authors would like to thank the grant agencies VEGA and APVV for financial support of the research through projects VEGA 2/0136/24, VEGA 1/0036/24 and APVV-23-0066.

Biochar–príprava, vlastnosti a využitie v tlačenej elektronike

[1]Miroslav Kováč, [1]Michal Hatala, [2]Lenka Lorencová, [3]Alena Šišková-Opálková, [3]Martin Nosko, [4]Ľubomír Švorc, [1]Pavol Gemeiner

[1]Oddelenie polygrafie a aplikovanej fotochémie, Fakulta chemickej a potravinárskej technológie, Slovenská Technická Univerzita v Bratislave, Radlinského 9, 812 37 Bratislava, miroslav.kovac@stuba.sk

[2]Chemický ústav, Slovenská Akadémia Vied, Dúbravská cesta 5807/9, 845 38 Bratislava, chemlelo@savba.sk

[3]Ústav materiálov a mechaniky strojov, Slovenská Akadémia Vied, Dúbravská cesta 9/6319, 845 13 Bratislava, alena.opalkova-siskova@savba.sk

[4]Ústav analytickej chémie, Fakulta chemickej a potravinárskej technológie, Slovenská Technická Univerzita v Bratislave, Radlinského 9, 812 37 Bratislava, lubomir.svorc@stuba.sk

Abstrakt: *Biomass encompasses organic materials derived from living organisms or their combinations with inorganic substances. This includes plants, animals, animal waste, sludge, and waste wood. Thermochemical processes convert biomass into synthesis gas (syngas), bio-oil, and biochar. Syngas and bio-oil are considered alternatives to fossil fuels. Biochar, a solid material produced during biomass carbonisation, is cost-effective, environmentally friendly, and applicable in soil remediation, waste management, and energy production. It primarily contains carbon (C), along with hydrogen (H), oxygen (O), ash, and trace amounts of nitrogen (N) and sulfur (S). The composition depends on the biomass type and the carbonisation process conditions. Modification techniques enhance the physical, chemical, and electrical properties of biochar, allowing its use for various purposes, including the removal of contaminants from soil and water, elimination of organic pollutants, as a catalyst, in wastewater treatment, composting, energy storage, carbon sequestration, and improving soil quality.*

Kľúčové slová: *Biochar, Carbon materials, Carbonization, Printed electronics*

Biochar je podľa *International Biochar Initiative* definovaný ako „pevný materiál získavaný karbonizáciou biomasy". Fyzikálne vlastnosti biocharu ovplyvňuje povaha biomasy a podmienky karbonizácie, ako sú predúprava, teplota, rýchlosť ohrevu, prietok plynu, tlak a metódy modifikácie. Tieto faktory vedú k abrazívnym procesom, tvorbe trhlín a zmene mikroštruktúry biomasy. Počas karbonizácie dochádza k úbytku hmotnosti a zmršťovaniu biomasy v dôsledku uvoľňovania prchavých látok. [1,2]

Kľúčovú úlohu zohráva distribúcia pórov, ktorá ovplyvňuje povrchovú plochu a adsorpčné vlastnosti. Vyššie teploty zvyšujú početnosť mikropórov a podporujú tvorbu nových pórov. Fyzikálne vlastnosti biocharu závisia aj od chemického zlože-

nia biomasy. Tepelný rozklad organických látok začína nad 120 °C, pričom hemicelulóza, celulóza a lignín sa rozkladajú v rozmedzí 200–500 °C. Miera štrukturálnych zmien závisí od podielu týchto zložiek počas karbonizácie. [3,4]

Karbonizácia spôsobuje chemické zmeny v biomase, čo vedie k tvorbe biocharu s rôznorodými vlastnosťami. S rastúcou teplotou klesá výťažnosť biocharu, zatiaľ čo jeho pH stúpa (o 0,5–1,4 jednotky na 100 °C) v dôsledku rozkladu hydroxylových väzieb. Naopak, katiónová výmenná kapacita klesá kvôli úbytku kyslíkatých funkčných skupín. Biochar má spomedzi tuhých biomateriálov najvyššiu výmennú kapacitu vďaka obsahu minerálov. V procese karbonizácie dochádza k znižovaniu pomerov H/C a O/C, čo naznačuje dehydratáciu a dekarboxyláciu do 500 °C. Nad 600 °C je FTIR na detekciu funkčných skupín neúčinná a preto sa využíva Ramanova spektroskopia, odhaľujúca aromatické štruktúry. Pomer I_D/I_G poukazuje rast veľkých aromatických kruhov pri teplotách nad 750 °C. Obsah prchavých látok klesá lineárne s teplotou, zatiaľ čo podiel popola stúpa v dôsledku reziduálnych anorganických minerálov po rozklade biomasy. [5–7]

Elektrická vodivosť biocharu závisí od vnútorného elektrického odporu častíc a elektrického odporu medzi nimi (kontaktný elektrický odpor). Oba faktory sú závislé od teploty [8]. Zníženie vnútorného odporu súvisí so zlepšením usporiadania uhlíkovej štruktúry a lepšou perkoláciou medzi usporiadanými uhlíkovými fázami pri vyšších teplotách. Biochar vyrobený pri 900 °C vykazuje široký rozsah vodivosti od 1,9 x 10^{-5} S/cm do 63 S/cm. Okrem už spomenutých faktorov (teplota, typ biomasy, podmienky predúpravy...) vplývajú na vodivosť aj obsah kovov, kyslíka, plocha povrchu, hustota, obsah uhlíka a veľkosť grafitových kryštalitov. Pochopenie týchto mechanizmov je kľúčové pre optimalizáciu biocharu ako elektricky vodivého materiálu. [9,10]

Nemodifikovaný biochar vykazuje nedostatočné štruktúrálne vlastnosti, s minimálnou plochou povrchu a pórovitosťou. Surový biochar má nedostatočné chemické povrchové vlastnosti, nízku zásaditosť a obmedzený počet funkčných skupín. [11] Úpravy a modifikácie biocharu sa zvyčajne delia na fyzikálne, chemické, impregnácie minerálnymi adsorbentmi a magnetické modifikácie [12]. Tieto techniky môžu zvýšiť plochu povrchu biocharu, zmeniť alebo zosilniť jeho povrchovú reaktivitu, zlepšiť adsorbčné vlastnosti a pridať nové funkčné skupiny na povrchu.

Jednou z oblastí aplikácie biocharu je príprava elektrochemických senzorov, využívaných na environmentálne, potravinové a klinické analýzy. [13] Biocharom modifikované elektrochemické senzory sú využívané vo voltamperometrických meraniach stanovovania anorganických iónov a organických látok. Oliveira et al. použili biochar ako modifikátor elektródy pri detekcií Cu^{2+} iónov vo funkčných nápojoch. [14] Okrem toho sa biochar ukázal ako ideálny materiál pre elektrochemické biosenzory. Ateş et al. syntetizovali Fe_3O_4-biochar nanokompozity na detekciu H_2O_2, pričom senzory vykazovali vynikajúcu selektivitu a citlivosť [15]. Kalinke et al. vyvinuli nenzymatický elektrochemický biosenzor na detekciu glukózy v ľudskom slinách a krvnej plazme, ktorý vykazoval vysokú opakovateľnosť. [16]

Výskum tiež ukazuje využitie biocharu na detekciu interleukínu-6 (IL-6) v sére a krvnom vzorke, pričom senzory vykazovali výbornú analytickú výkonnosť. [17]

Skupina Compagnone vytvorila vodnú fázu exfoliovaných biocharových nanovlákien, ktoré použili na modifikáciu obrazových elektrod a vytvorenie vodivého filmu. [18]

Poďakovanie

Autori by touto cestou radi poďakovali grantovým agentúram VEGA a APVV za finančnú podporu výskumu prostredníctvom projektov VEGA 2/0136/24, VEGA 1/0036/24 a APVV-23-0066.

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Lepidlá pre obalový priemysel–súčasnosť a nové trendy

Karol Vaško

EUKALIN je nemecká spoločnosť špecializujúca sa na vývoj a výrobu vysoko kvalitných priemyselných lepidiel. Jej história siaha do roku 1904 a aktuálne sa venujeme hlavne priemyselným lepidlám pre obalový priemysel, špeciálne pre papierové a kartónové obaly. Podiel lepidla v týchto obaloch sa pohybuje medzi 1–5 %, ale bez týchto lepidiel by výroba a použite papierových obalov nebolo možné. Pri výrobe sa používa niekoľko druhov lepidiel:

Tavné lepidlá EVA/PO/SIS
Disperzné lepidlá PVAC/VAE/Akyláty
Škrobové lepidlá
Kazeínové lepidlá
Glejové lepidlá

V blízkej budúcnosti očakávame významné zmeny pri výrobe a dizajne papierových obalov vzhľadom na nariadenie PPWR (Packaging and Packaging Waste Regulation). Ide o nariadenie EÚ, ktoré sa zameriava na predchádzanie vzniku odpadu z obalov, zlepšenie recyklácie a znižovanie environmentálnych vplyvov obalových materiálov. Tento regulačný rámec sa snaží sprísniť požiadavky na výrobcov a distribútorov obalov a ich zodpovednosť za obaly, ktoré uvádzajú na trh, s cieľom minimalizovať ich negatívny dopad na životné prostredie.
Hlavné ciele PPWR sú:

- **Znížiť množstvo odpadu z obalov**: Cieľom je, aby obaly, ktoré sa uvádzajú na trh, mali minimalizovaný vplyv na životné prostredie, a to prostredníctvom lepšej návrhovej praxe, ktorá zahŕňa obaly, ktoré sa dajú ľahšie recyklovať alebo opätovne použiť.
- **Zlepšiť recyklovateľnosť obalov**: PPWR kladie dôraz na používanie materiálov, ktoré sú lepšie recyklovateľné a zabraňuje používaniu materiálov, ktoré sú ťažko spracovateľné v recyklačných procesoch.
- **Rozšírená zodpovednosť výrobcov (EPR)**: Tento koncept znamená, že výrobcovia obalov budú musieť zabezpečiť, aby obaly, ktoré uvádzajú na trh, boli správne spracované po ich použití. To zahŕňa recykláciu alebo iné formy zhodnocovania odpadu.
- **Podpora obehového hospodárstva**: Zameriava sa na prechod od lineárneho modelu (kde sa výrobky vyrábajú, používajú a vyhadzujú) k obehovému hospodárstvu, kde sú materiály recyklované a opakovane použité.

PPWR by mal pomôcť dosiahnuť ambiciózne ciele EÚ v oblasti udržateľnosti a znižovania odpadu, najmä v súvislosti s obalovými materiálmi, ktoré sú jedným z hlavných prispievateľov k environmentálnemu znečisteniu.

Všetky obaly uvedené na trh sa teda budú musieť recyklovať. Preto sa do pozor-

nosti dostávajú všetky zložky obalu, ako je samotný papier, rôzne funkčné vrsty, tlačové farby a v neposlednom rade aj lepidlá. Z tohto dôvodu sa v rôznych štúdiách zisťovali vplyvy lepidiel používaných pri výrobe obalov na ich recyklovateľnosť. Pri tavných lepidlách je dôležité, aby boli triediteľné a mohli by takto byť z obalu odstránené. Na posúdenie boli vypracované kritéria, tzv. EPRC Scorecard, kde je odstrániteľnosť tavného lepidlo posudzovaná podľa fyzikálnych hodnôt, ako je bod mäknutia, hrúbka nanesenej vrstvy a jej rozmery. Disperzné lepidlá nepredstavujú pri recyklovateľnosti žiaden problém a všetky obaly z domácnosti sú plne recyklovateľné. Naopak, problémom sú PSA lepidlá na akrylátovej báze, ktoré sa nedajú plne odstrániť a v procese recyklácie z nich zostávajú trvalo lepivé častice. Ako technické riešenie je možné použiť vodeodolné filmy s vysokou kohéziou.

Obalový priemysel sa snažívyužívať lepidlá na prírodnej báze. Živice zo stromov sa úspešne pridávajú do tavných lepidiel, kde sa aktuálne dosahuje podiel prírodnej zložky okolo 50 %, aktuálne vývoj smeruje k podielu až 70 %. Už dlhé roky sa v Európe používa prírodný kaučuk na tzv. Coldseal, alebo lak zvarovaný za studena. Vzhľadom na EU-Normu 2023/1115 (EU Deforestation Regulation) sa dá do budúcnosti očakávať postupné zhoršovanie dostupnosti prírodného kaučuku a tým pádom nárasty cien. Rôzne firmy takisto experimentujú s možnosťami syntézy Vyinylacetát-Etylén kopolymérov z prírodných zdrojov (potrebné na výrobu disperzných lepidiel). Príkladom môže byť využitie bioetanolu z Brazílie, alebo zvyškových produktov z drevárskeho priemyslu (kyselina octová). Často sa ale naráža na problémy ako je obmedzená dostupnosť týchto zdrojov.

Priemyselným štandardom je už dlhé roky využite škrobových a dextrínových lepidiel. Často je ale potrebné tieto lepidlá upravovať prídavkom syntetických produktov na zlepšenie ich spracovateľnosti na moderných strojoch.

Firma EUKALIN, ale iné firmy na trhu na aktuálne snažia upraviť škrobové lepidlá tak, aby boli plne použiteľné pre moderné stroje pri výrobe kartonáže a krabičiek, a to tak pre tryskové ako aj pre kolečkové nanášanie. Aktuálne sa darí dostať na 90 %-ný obsah biogénnych látok.

Takisto sa často stretávame s glejovými lepidlami, napríklad by výrobe poťahovanej kartonáže. Tento čisto prírodý produkt ale sprevádza niekoľko problémov, ako je zápach počas spracovania alebo plná závislosť od Číny. Čoraz častejšie sú preto nové stroje na výrobu poťahovanej kartonáže vybavené zariadeniami na aplikáciu disperzných alebo tavných lepidiel.

Ďalším z lepidiel z prírodných zdrojov sú kazeínové lepidlá, používané napríklad na mokré etiketovanie fliaš. V tomto prípadne sa často stretávame s kolísavou kvalitou ako aj zhoršenou dostupnosťou a nárastom cien. Preto je tu tiež trend prechodu na disperzné lepidlá, hlavne pri nových vysokovýkonných etiketovacích zariadeniach.

Záverom sa dá skonštatovať, že budúcnosť lepidiel pre obalový priemysel je hlavne vo zvyšovaní obsahu biogénnych látok v tavných a disperzných lepidlách na čo najvyššiu úroveň pri zachovaní ich vhodnosti na použitie na moderných vysokovýkonných lepiacich zariadeniach.

Preliminary study on the impact of digitalization methods on assessing skin tone color reproduction accuracy in inkjet printing using area-based open-source image analysis tool

Sandra Dedijer, Ivana Jurič, Miljana Prica, Magdolna Pál,
Nemanja Kašiković, Živko Pavlović, Saša Petrović

University of Novi Sad, Faculty of Technical Sciences, Graphic Engineering and Design,
Trg Dositeja Obradovića 6, Novi Sad, Serbia,
dedijer@uns.ac.rs

Abstract: *Accurate color monitoring is of utmost importance in the graphic industry, where maintaining high-quality color reproduction is essential. This need becomes particularly critical in the reproduction of skin tones, a topic of significant research interest due to its impact on the perception of human images. Studies have demonstrated that standard observers can discern subtle variations in skin color, including minor shifts in chroma and hue toward reddish tones compared to actual skin shades. Traditional methods for objective color reproduction analysis typically rely on standard colorimetric measurement techniques and devices, which are commercially available but often expensive and cumbersome. There is growing interest in leveraging affordable, user-friendly software solutions in combination with low-cost imaging technologies to make objective colorimetric analysis more accessible. This study investigates the potential of employing the area-based open-source image analysis tool Trigit alongside two distinct digitalization methods, scanning and digitalization using a camera, to evaluate skin tone color reproduction accuracy. Skin tone samples were inkjet-printed, digitalized using the proposed methods, and analyzed to extract colorimetric coordinates. These results were compared to direct spectrophotometric measurements of the printed samples. By calculating and comparing color differences, the performance of the digitalization methods was evaluated.*

Keywords: skin tone reproduction, digitalization method, image analysis tools, inkjet printing.

1. Introduction

A pivotal role in human visual cognition plays color perception, particularly in the perception of skin tones. Research has consistently demonstrated that the way facial skin color is perceived differs fundamentally from the perception of other colors. Individuals with normal trichromatic vision exhibit an extraordinary ability to detect subtle variations in human skin tones with high precision. Furthermore,

skin color perception serves as a crucial determinant of perceived attractiveness and is closely associated with judgments about an individual's health based on facial appearance [1]. Skin color is categorized as a memory color, playing a fundamental role in how individuals are perceived in images. With the proliferation of mobile devices, including smartphones and tablets, alongside the increasing popularity of image capture and sharing applications, user preferences have shifted beyond traditional color accuracy toward preferred color reproduction [2]. Consequently, achieving visually appealing and natural-looking skin tones remains a key aspect of color reproduction. Since individuals often rely on memory-based color perception to evaluate the fidelity of reproduced colors, it is essential to understand both the preferred reproduction range of skin tones and the methodologies employed for color measurement to optimize preference-based reproduction [3]. Fields such as photography, printing, medicine, lighting, retail, and cosmetics all rely on precise skin tone reproduction to ensure consistency, diagnostic accuracy and product compatibility [4]. From a quantification standpoint, objective color measurement necessitates empirical modeling within a defined color space, where the CIE Lab* color space and associated color difference equations being the most widely adopted [5].

There has been growing interest in the quantitative assessment of color using images captured with cost-effective commercial imaging technologies, including smartphones, scanners and digital cameras, for scientific applications. The continuous advancement of affordable imaging systems has facilitated objective colorimetric analysis during image acquisition. This study investigates the feasibility of utilizing Trigit, an open-source, area-based image analysis tool, for evaluating the accuracy of skin tone reproduction in images digitized via a scanner and a mobile phone camera. Specifically, selected skin tones were printed using an inkjet printing system, digitized and analyzed to extract colorimetric coordinates using the proposed tool. Color measurements were conducted directly on the printed samples using a spectrophotometer. By computing color differences, the effectiveness of the employed digitalization methods was systematically assessed.

2. Methods and materials

For the objectives of this research, a custom-designed test chart consisting of twenty skin tone patches from Adobe's standard skin color palette was developed (Figure 1). The finalized PDF file was prepared for printing while adhering to the color specifications embedded within the Coated Fogra 39 profile. The printing process was executed using two distinct, fully calibrated inkjet printing systems: a solvent-based SOLJET Pro 3 Print and Cut XC-540 and a UV-based UV Print and Cut LEC-540. Each printer operated at two predefined output resolutions 360×720 dpi and 720×1440 dpi representing the lower and upper resolution thresholds, respectively. To ensure uniformity, all additional printing parameters remained constant across both devices, including the application of a dither algorithm for rasterization, the employment of the nearest-neighbor method for interpolation and the

activation of bi-directional printing for the print head's movement. As a printing substrate, a commercially available Display PP paper was utilized.

Fig. 1: Test chart

L*a*b* values of the printed samples were measured using a Techkon SpectroDens spectrophotometer, with a measurement geometry of 0/45, an illuminant D50, and a 2° standard observer setting. Each color patch underwent six individual measurements, with the mean values subsequently used for data analysis. The digitization of printed samples was performed via two methodologies: scanning and photographic capture. For the scanning process, a CANON CanoScan 5600F scanner was employed at its native resolution of 1200 dpi, with all automatic image enhancement features disabled to prevent data alteration. The photographic method, on the other hand, utilized a mobile phone camera, given its widespread accessibility as a standard digital imaging device. Specifically, the primary camera (24 mm, f/1.78, ISO 80, 0 eV) of an iPhone 14 Pro Max was used. The printed samples were positioned inside a color viewing cabinet (Agile Radiat CVC5-2E – 5) at a 45° angle under standardized D50 illumination. The camera was positioned within the cabinet at a perpendicular angle (0°) and maintained a fixed distance of 260 mm from the samples, simulating real-world conditions for routine color evaluation. Following digitization, L*a*b* values were extracted from the scanned and photographed images using Trigit, an open-source, area-based image analysis tool [6]. The square selection tool was employed to delineate the region of interest corresponding to each color patch. The computed color differences, ΔE00 [7], were derived by comparing the L*a*b* values obtained via spectrophotometric measurements with those extracted using image analysis. These calculations facilitated the characterization of the proposed color measurement methodology, assessing its feasibility and accuracy.

3. Results and discussion

Figure 2 illustrates the computed differences in color (ΔE00), lightness (ΔL), hue (ΔH) and chroma (ΔC) between the L*a*b* values of each color patch, as measured by a spectrophotometer, and those extracted from scanned and photographed images using the open-source image analysis software. The figure presents these differences for samples printed using both a solvent-based inkjet digital printing machine and a UV digital printing machine at low and high printing resolutions.

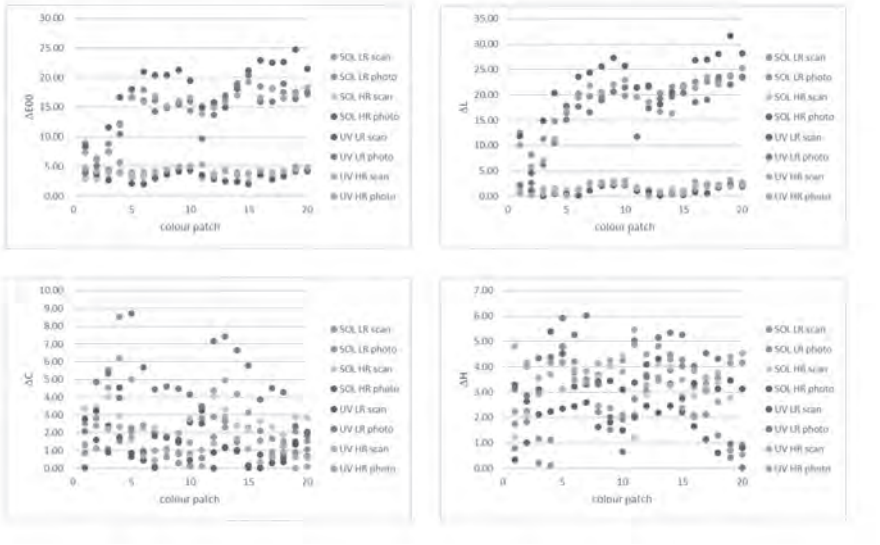

Fig. 2: Upper left: color difference values (ΔE00), upper right: lightness difference values (ΔL), lower left: chroma difference values (ΔC), lower right: hue difference values (ΔH)

The analysis of the graphs reveals that the calculated color differences range from a minimum of 2.03 ΔE00 for scanned samples to a maximum of 24.77 ΔE00 for photographed samples. Notably, higher color difference values were observed for lighter color patches compared to darker ones. The results clearly indicate that the color discrepancies between the measured L*a*b* values and those extracted using Trigit software are lower for scanned images than for photographed ones. This significant deviation in the photographed samples may be attributed to the lighting conditions during the photographic process and the physical distance between the sample and the camera. Furthermore, the impact of the digital printing method and output resolution was found to be more pronounced in the case of photographed samples compared to scanned ones, with lower color difference values observed for UV-printed samples. The analysis of differences in lightness, hue, and chroma demonstrated that the digitalization process predominantly affects the lightness component, with the highest numerical discrepancies observed in the L coordinate, followed by hue and chroma. Interestingly, the digitalization process using a camera appears to exert a lesser influence on the distortion of chromatic values (average ΔC photo/scan 2.29/1.98, average ΔH photo/scan 2.90/3.31) compared to lightness values, whereas scanning is potentially more influential on chromatic coordinates than on lightness (average ΔC photo/scan, average ΔH photo/scan 19.00/1.51).

4. Conclusions

This study presents a preliminary investigation into the feasibility of employing two digitalization methods for subsequent color coordinate extraction via the area-based, open-source image analysis software Trigit in the context of skin tone color reproduction. The findings highlight the impact of the chosen digitalization method on the final results. The computed color differences between instrumentally measured L*a*b* values and those extracted from scanned and photographed images of selected skin color patches ranged from 2.03 ΔE00 to a maximum of 24.77 ΔE00, indicating variations from minimal to highly perceptible differences. It was observed that color discrepancies were more pronounced in lighter color patches compared to darker ones. Moreover, lower color differences between measured and extracted L*a*b* values were obtained from scanned images as opposed to photographed ones. The analysis of differences in lightness, hue and chroma revealed that the digitalization process had the most significant effect on the lightness component, with the highest discrepancies recorded for the L coordinate, followed by hue and chroma. Notably, digitalization using a camera appeared to exert less influence on chromatic value distortion compared to its effect on lightness, whereas the scanning process was potentially more impactful on chromatic coordinates than on lightness values. The potential application of open-source image analysis tools in evaluating color reproduction accuracy is considerable; however, further research is required to assess the influence of different digitalization setups and to determine their reliability as an alternative to device-based color measurements. This is particularly crucial in the domain of skin color reproduction accuracy, as even minor deviations can be perceptible to the human eye.

Acknowledgement

This research has been supported by the Ministry of Science, Technological Development and Innovation (Contract No. 451-03-137/2025-03/200156) and the Faculty of Technical Sciences, University of Novi Sad through project "Scientific and Artistic Research Work of Researchers in Teaching and Associate Positions at the Faculty of Technical Sciences, University of Novi Sad 2025" (No. 01-50/295).

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New ecological materials for FDM 3D printing

Michal Ďurfina, Roderik Plavec, Vojtech Horváth, Pavel Alexy

Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology
Radlinského 9, 812 37, Bratislava, Slovakia,
e-mail: michal.durfina@stuba.sk

Abstract: *In the pursuit of sustainable manufacturing practices, the development of biodegradable materials has gained significant attention. Following study investigates the potential of creating a flexible, fully biodegradable polymer blend tailored for Fused Deposition Modeling (FDM) 3D printing technology. By leveraging the unique properties of PHAs and optimizing their composition, researchers have developed materials that combine flexibility, toughness, and eco-friendliness. The reduced glass transition temperature further enhances their versatility, ensuring performance across a wide range of temperatures.*

Keywords: *3D printing, polymers, renewable, biodegradable*

1. Introduction

3D printing has gained significant attention in recent years, becoming popular among professionals and the public. As part of additive manufacturing, it enables rapid prototyping and production of complex parts, saving time and costs. A key advantage is its ability to create intricate geometric shapes, benefiting industries like medicine (personalized implants, prosthetics), robotics, aerospace, and automotive manufacturing. However, additive manufacturing has a limited material selection compared to traditional methods. Research is expanding material options, particularly biodegradable polymers, to improve mechanical durability and sustainability. [1, 2] Since prototyping generates waste, biodegradable materials could help reduce its environmental impact.

2. FDM 3D Printing

Fused Deposition Modeling (FDM), or Fused Filament Fabrication (FFF), is a widely used additive manufacturing method. It involves depositing molten thermoplastic filament (1,75 or 2,85 mm) layer by layer via a heated nozzle. FDM is cost-effective, user-friendly, and supports various materials, making it ideal for prototyping and hobby applications. Its advantages include affordability, multi-material compatibility, and broad industry applications. However, it offers lower precision and surface quality than other additive techniques. [3] Despite these drawbacks, FDM remains one of the most widely used and evolving 3D printing technologies.

3. Bioplastics

Biopolymers originate from fossil or renewable sources. Synthetic biodegradable plastics include polyvinyl alcohol (PVOH), polycaprolactone (PCL), and polybutylene adipate terephthalate (PBAT). PVOH dissolves in water but degrades slowly. PCL, used in medicine, breaks down gradually in the body. PBAT, commonly used in packaging, degrades faster.

Renewable-source polymers like polylactic acid (PLA), polyhydroxyalkanoates (PHA), and thermoplastic starch (TPS) are more sustainable. PLA, derived from plants, is compostable and used in packaging, 3D printing, and medicine. PHA, produced by microorganisms, degrades naturally and is used in medicine, packaging, and agriculture as an eco-friendly alternative to conventional plastics. [4]

4. Materials and testing

Two different types of PHAs (polyhydroxybutyrate copolyesters), differentiating in crystallinity (PHA1 = 52 %, PHA2 = 36,2 %), and a toughness modifier (which was in solid form and chemically is a polymer as well) were used. As a reference material, generic PLA filament (Turtle s.r.o, Slovakia) was used.

Composition of polymer blends was calculated with regard to two factors, X1 which represents ratio between modifier and matrix and X2 which represents ratio between PHA1 and PHA2 in matrix.

Polymer blends were prepared by blending in a co-rotating twin screw extruder (LabTech, Thailand). The melt was cooled in a water bath, pelletized and dried at 50°C for 24 hours.

Filaments suitable for FDM 3D printing was prepared from dry pellets in a single screw extruder (Plasticorder Brabender, Germany). The melts were cooled in a water bath at 45 °C and the diameter was controlled via variable pulling speed. We were able to produce filaments with diameter of 1,75 mm (standard) ± 0,15 mm.

Test samples were produced on a FDM 3D printer Ender 3 (Creality, China), modified to be able to print flexible filaments. All samples were printed with standard 0,4 mm nozzle on a textured PEI print plate (not heated during printing). Print parameters were as follows: cooling fan speed 100%, print speed 10 mm/s, (0,7 – 0,5 mm^3/s), layer height 0,2 mm.

4.1 Thermal properties

The thermal properties of the studied blend were determined using a differential scanning calorimetry DSC 1 (Mettler-Toledo Inc., USA). The basic thermal characteristics such as the glass transition temperature, the crystallization temperature, and the melting point of the crystallites were evaluated from the measurements.

The glass transition temperature (Tg) of these blends is critical, as lower Tg values signify greater elasticity and toughness at lower temperatures. Additionally, polymers with lower Tg may exhibit improved biodegradability. All studied blends

exhibited Tg values significantly below the reference material, polylactic acid (PLA, Tg = 61 °C), allowing for toughness across broader temperature ranges, including sub-zero conditions.

The melting temperatures of crystalline structures indicate that blends containing more PHA1 show higher melting temperatures and enthalpies, denoting increased crystallinity (figure 1).

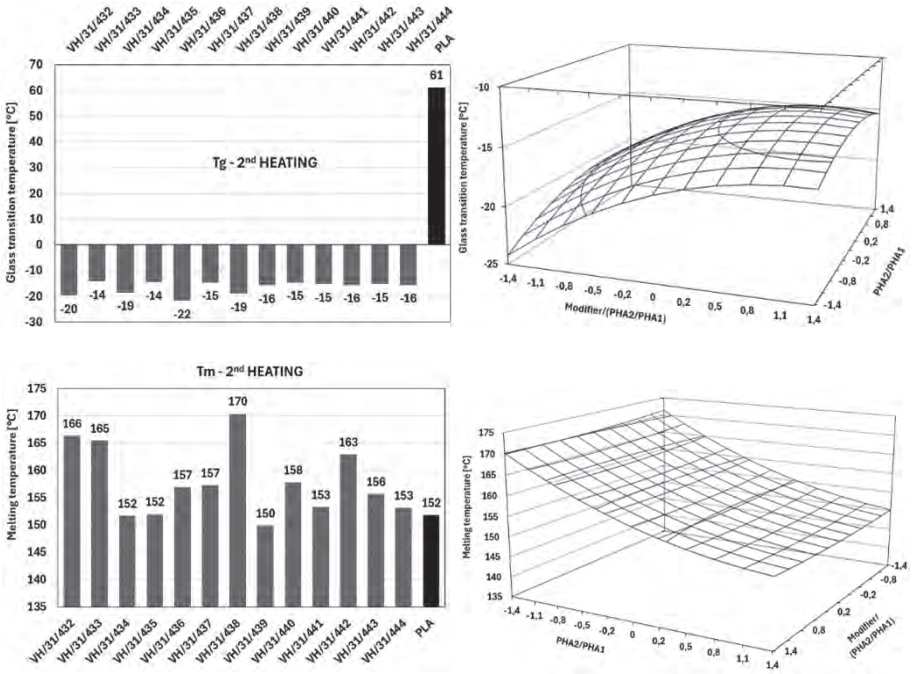

Fig. 1: Results from thermal analysis

4.2 Impact toughness

For the measurements of impact strength, 80x10x4mm specimens (STN ISO 179 (64 0612)) were printed using FDM 3D printer. Each sample was examined using an impact pendulum (Instron, USA) according to STN ISO 179 (64 0612). The specimens were unnotched and prior to testing, all specimens were cooled to – 30 °C for 30 minutes.

The study revealed a significant influence of content of toughness modifier (X1) on impact strength, although the significance is not linear (figure 2). This suggests a complex interplay between the composition of the polymer matrix and the

toughness modifier. Factor X2 (the ratio of PHAs in the polymer matrix) demonstrated a significant effect on impact toughness across the entire concentration range of the toughness modifier. Interestingly, the influence of factor X2 reverses as factor X1 transitions into positive values, suggesting a nonlinear and interdependent relationship between these variables. By optimizing the composition of the biodegradable polymer blend based on matrix composition and incorporating an appropriate amount of the toughness modifier, we successfully produced a material with enhanced toughness properties. Specifically, the resulting material exhibited an impact toughness several times greater than that of the reference material, polylactic acid (PLA). This finding highlights the potential of PHA-based blends as superior alternatives to traditional polymers for applications requiring enhanced impact resistance.

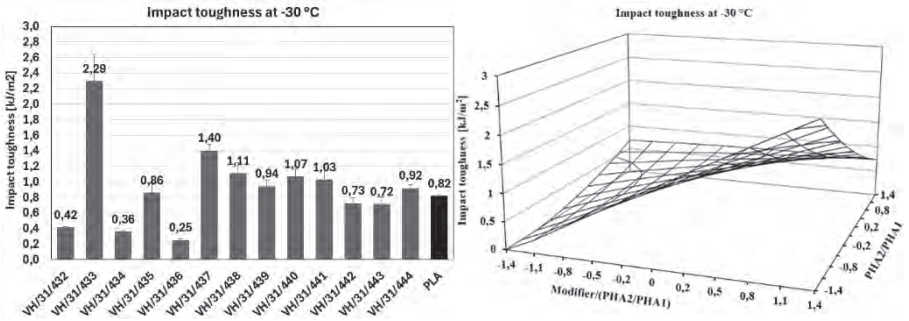

Fig. 2: Impact toughness of tested polymer blends

4.3 Flexural properties

For the measurements of flexural properties, 80x10x4mm specimens (STN ISO 179 (64 0612)) were printed using FDM 3D printer. The three-point bending test was performed on a universal testing machine (Zwick Roell, Germany) according to STN ISO 178 (64 0607). The distance of the support points was set to 64 mm (L =16.h) and the load was applied using a load pin in the middle of the span length with a cross-head speed of 5 mm/min. During the test, the stress-strain dependency of the test specimen was recorded. Flexural strength was evaluated by STN 64 0607 standard.

The flexural modulus represents the material's resistance to deformation under bending stress, with higher modulus values requiring greater stress to induce deformation. As expected, increasing the concentration of the toughness modifier reduced the flexural modulus values. Comparisons of polymer blends containing identical toughness modifier concentrations revealed that increasing the proportion of PHA2 in the matrix further decreased the modulus values (e.g., VH/31/433

vs. VH/31/435; VH/31/432 vs. VH/31/434; VH/31/438 vs. VH/31/439). The results (figure 3) indicate that increasing the toughness modifier concentration enhances flexibility of the studied polymer materials. However, this improvement comes at the cost of reduced resistance to shape changes under bending stress, which is logical and strongly dependent on the final material use case.

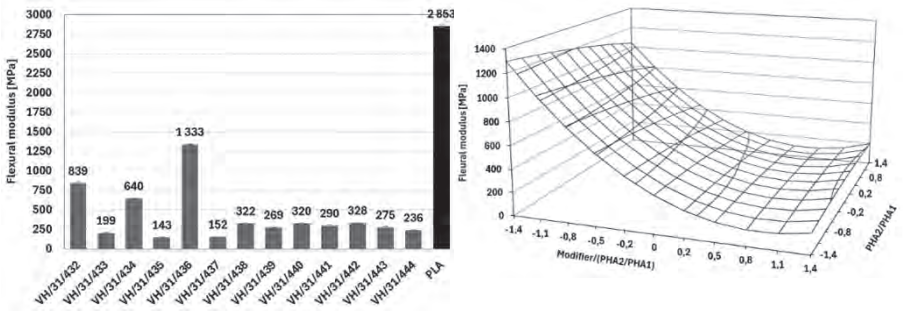

Fig. 3: Flexural modulus of tested polymer blends

4.4 Hardness

Hardness of each material was determined from the same specimens as for flexural properties and impact toughness, using manual Shore D durometer. Hardness values were determined after 15 seconds according to ISO 868.

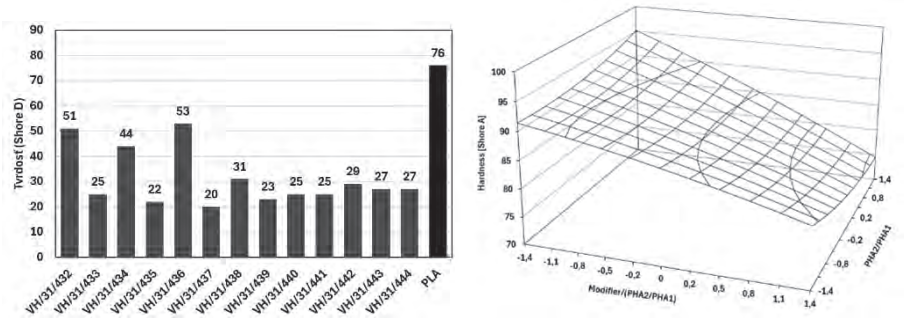

Fig. 4: Shore D hardness of tested polymer blends

According to the Shore D scale, the final hardness of studied polymer blends varied from 20 to 53 Shore D, which is significantly lower compared to reference (PLA), which exhibited value of 76 Shore D. As expected, we can see that by adding

more toughness modifier to the blend, the hardness value decreases. The results (figure 4) suggest that factor 1 (toughness modifier content) has a pronounced impact on material hardness, while factor 2 (matrix composition) has a not significant effect.

5. Conclusion

The investigated polymer blends demonstrated good suitability for FDM 3D printing, offering processing parameters comparable to PLA, with added benefits, such as flexibility, low hardness and good impact strength, that make them stand out as unique materials for additive manufacturing. Key advantages of these materials include a low glass transition temperature which is necessary foundation for flexibility across a wide temperature range (even in freezing conditions), enhanced biodegradability, and mechanical properties such as low hardness, flexibility and toughness. Importantly, these blends are derived from bio-based, renewable sources, making them a sustainable and environmentally friendly alternative for 3D printing. The ability to tailor mechanical and thermal properties through composition adjustments offers unprecedented versatility, enabling these materials to meet the specific requirements of various applications. These attributes make the investigated polymer blends a one-of-a-kind solution for FDM 3D printing, combining functionality, sustainability, and adaptability in ways that conventional materials cannot.

6. References

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Drupa 2024

Vladimír Dvonka

Fakulta chemickej a potravinárskej technológie STU v Bratislave,
Oddelenie polygrafie a aplikovanej fotochémie ÚPSP
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Drupa–najväčšia výstava polygrafických technológií a materiálov vo svete.

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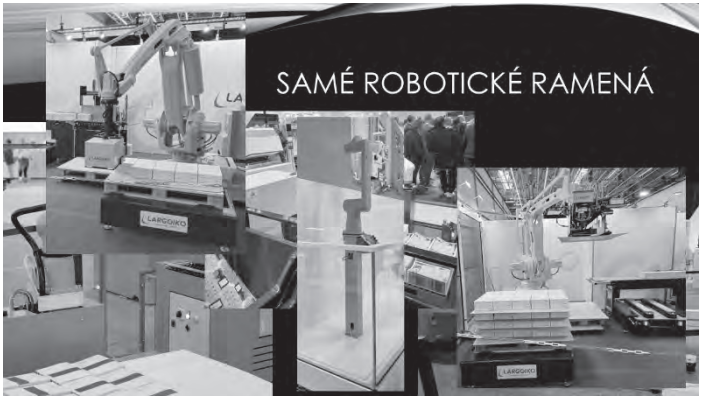

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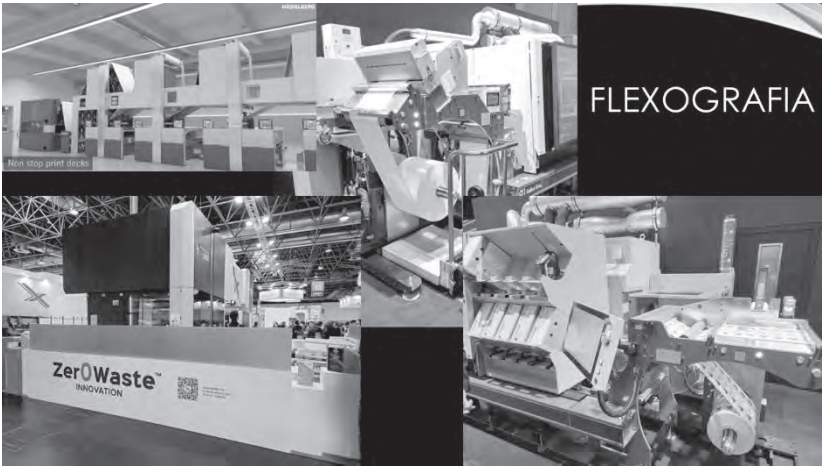

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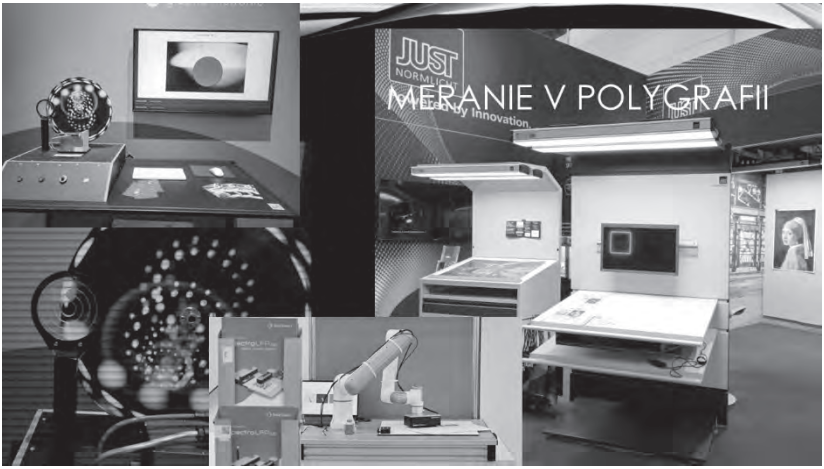

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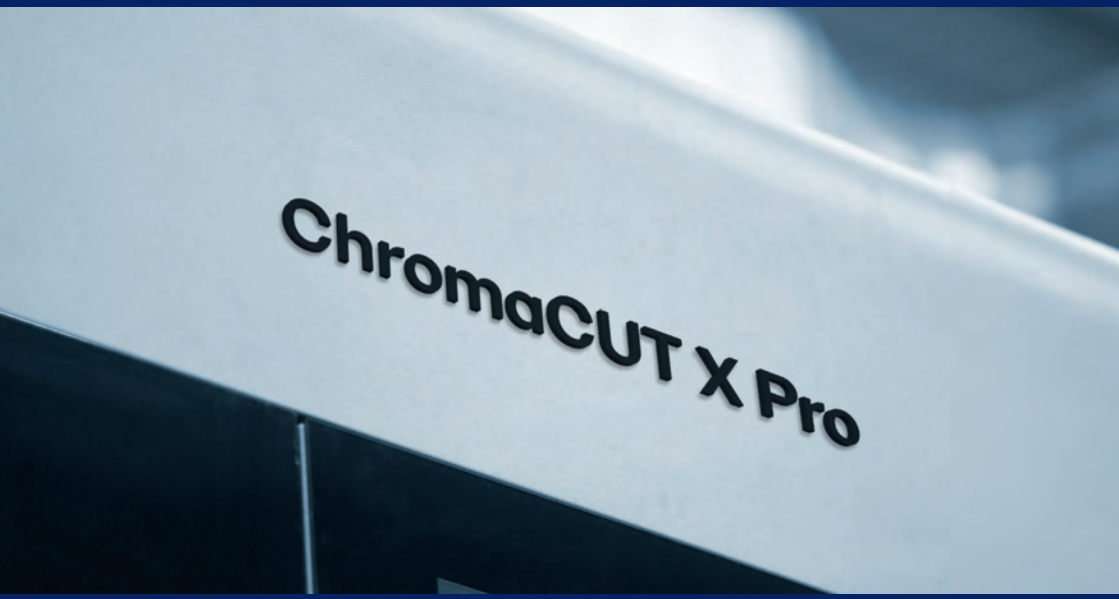

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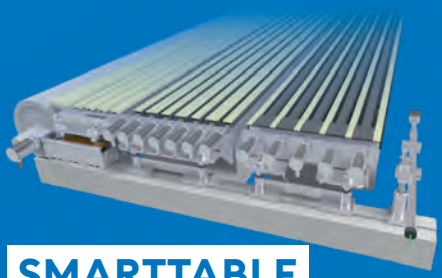

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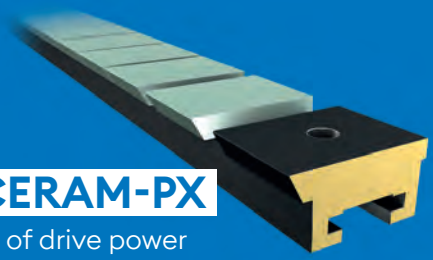

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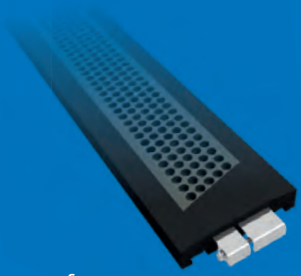

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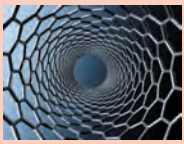
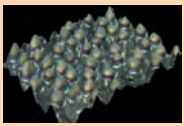
Výskum a výroba tlačenej elektroniky a solárnych článkov



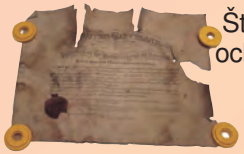
Tlačená elektronika: solárne články perovskitové a DSSC; RFID, OLED, batérie, pamäte, reproduktory. 3D materiálová tlač, testovanie materiálov a úprava povrchov plazmou. Spolupracujeme s Ústavom polymérov SAV, s Fakultou chemickou VUT v Brne a s Univerzitou Pardubice FCHT.

Forenzná analýza dokumentov



Kriminalisticko-expertízne analýzy, metódy analýzy dokumentov a potencionálnych falzifikátov. Ochranné prvky dokumentov – hologramy, laserové rytie, fluorescencia, termochrómne a infračervené farby… Spolupracujeme s Kriminalistickým a expertíznym ústavom Policajného zboru.

Moderné technológie ochrany kultúrneho dedičstva



Štúdium OMOD sa zameriava na kultúrne a historické dedičstvo a jeho ochranu, chémiu, materiály, techniku a technológie ochrany v galériách, knižniciach, archívoch a múzeách. Spolupracujeme so Slovenskou národnou galériou, SNM a Slovenským národným archívom.

Prepress, Press a Postpress

Digitálne spracovanie textu a obrazu, tlač klasickými a digitálnymi technikami, kontrola kvality tlače spektrofotometrom, fluorescencia, dokončovacie spracovanie tlačových médií a potlačených obalov. Spolupracujeme s polygrafickými podnikmi na riešení zaujímavých problémov z praxe.

Cestovanie – Ceepus, Erazmus

Náš európsky vedecký a študijný program Ceepus je určený pre študentov a učiteľov na univerzitách s rôznym zameraním.

Ing. Vladimír Dvonka, PhD., vladimir.dvonka@stuba.sk
Fakulta chemickej a potravinárskej technológie STU
Ústav prírodných a syntetických polymérov
Oddelenie polygrafie a aplikovanej fotochémie, opaf.sk
Radlinského 9, 812 37 Bratislava 1, Tel.: 02/59 32 52 21, 24

WPP PA

Wood, Pulp and Paper 2025

Špeciálne papiere na báze nanocelulózy a nanofibrilovanej celulózy s multifunkčnými vlastnosťami

Štefan Boháček, Stankovská Monika, Pažitný Andrej, Ihnát Vladimír

Výskumný ústav papiera a celulózy, a.s. Bratislava

Abstrakt: *Špeciálne filtračné papiere, ktoré boli vyvinuté pre zariadenie na deaktiváciu vzdušných patogénov prenášaných kvapôčkovým spôsobom obsahujú špeciálnu vrstvu nanofibrilovanej celulózy a nanocelulózy, obsahujúcu antiseptické kovové ióny a pomocné látky (adjuvancie) v zadržanej zvyškovej vode, v ktorých sa spájajú deaktivačné a dezinfekčné účinky niektorých kovových iónov a UV-C žiarenia v špeciálnom rozsahu vlnových dĺžok elektromagnetického žiarenia, pri ktorom sa nevytvára ozón. Mikrokvapôčky sa zachytávajú pri filtrácii kontaminovaného vzduchu na povrchovo upravenom filtračnom papieri. Vzduch je nasávaný otvorom nanofiltračného zariadenia umiestneným v spodnej časti a prechádza do stredu filtračnej vložky, kde je umiestnený žiarič UV-C žiarenia. Následne prechádza cez filtračný papier obsahujúci soli antiseptických kovov od stredu žiariča smerom von cez filtračný papier hermeticky vložený do filtračnej vložky. Filtračná prepážka je harmonikovo poskladaná tak, aby bol jeho povrch maximálne a celý ožiarený UV-C žiarením. Do zachytených kontaminovaných mikrokvapôčok difundujú antiseptické ióny, ktoré spolu s pôsobením UV-C žiarenia deaktivujú vírusy a dezinfikujú baktérie. Pôsobením UV-C žiarenia a prúdenia vzduchu s relatívne nízkou vlhkosťou, kvapôčky postupne vysychajú a deaktivované vírusy a dezinfikované baktérie sú odnášané vzduchom. Mikróby sú na povrchu pokryté pomocnými látkami (adjuvanciami). Vďaka tomu sa deaktivované vírusy a dezinfikované baktérie ľahšie dostávajú do imunitného systému ľudského teľa, kde sa pomocné látky rozpustia, odhalia spike proteíny ako aj celý bielkovinový obal deaktivovaného vírusu alebo dezinfikovanej baktérie–neschopnej replikácie. Imunitný systém sa naučí bojovať proti takto odhaleným cudzorodým látkam a po vniknutí aktívneho vírusu, prípadne živej baktérie už organizmus bude mať zvýšenú imunitu proti aktuálnej mutácii vírusu, či baktérie. Zariadenia takto prispejú ku zvýšeniu celkovej imunity populácie.*

Kľúčové slová: *nanocelulóza, katióny, UV-C žiarenie, filtrácia, deaktivácia, vírus*

Úvod

Boj proti pandémii ostatných rokov, zapríčinených vzduchom kvapôčkovým spôsobom prenášanými a neustále sa mutujúcimi enterovírusmi môže byť účinný vtedy, ak sa imunitný systém populácie vystaví deaktivovaným vírusom s aktuálnou mutáciou ich RNA (DNA v prípade DNA vírusov). Ako sa ukazuje na príkladoch ostatných rokov navrhované riešenie je účinné pre všetky infekčné choroby pre-

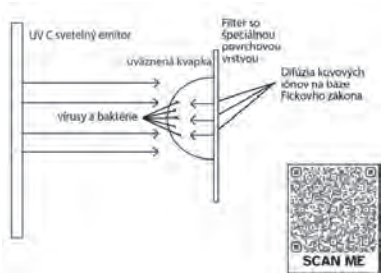
nášané týmto spôsobom. Jedná sa o boj proti chrípke, covidu, angíne, vírusovému zápalu pľúc, tuberkulóze, nádche a podobným vzduchom prenášaným chorobám spôsobujúcich epidémie až pandémie.

Prístroj na deaktiváciu vzduchom prenášaných patogénov a na zvýšenie imunity populácie

Špeciálne filtračné papiere, ktoré boli vyvinuté pre zariadenie na deaktiváciu vzdušných patogénov prenášaných kvapôčkovým spôsobom obsahujú špeciálnu vrstvu nanofibrilovanej celulózy[4] a nanocelulózy[3], obsahujúcu antiseptické kovové ióny a pomocné látky (adjuvancie). Samotné patentované zariadenie[2] Výskumného ústavu papiera a celulózy je zariadenie slúžiace na filtráciu vzduchu, v ktorom sa spájajú deaktivačné a dezinfekčné účinky niektorých kovových iónov a UV-C žiarenia v špeciálnom rozsahu vlnových dĺžok elektromagnetického žiarenia. Úprava filtračného papiera zanáškou optimálnej zmesi nanofibrilovanej celulózy a nanocelulózy je za účelom optimalizácie pórovitosti filtračnej prepážky s ambíciou zachytiť kontaminované mikrokvapôčky na povrchu – prípadne hlbšie v materiáli filtračnej prepážky pri filtrácii kontaminovaného vzduchu.

Princípy fungovania

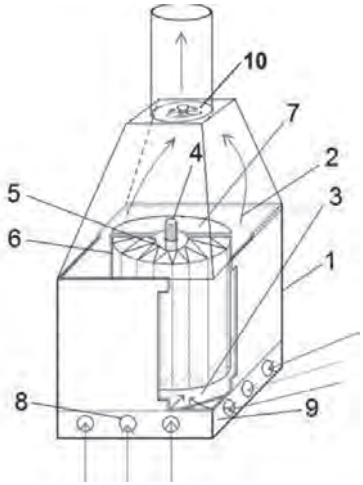
Zariadenie na deaktiváciu vzdušných patogénov prenášaných v kvapôčkovej forme, zachytených na filtračnom papieri so špeciálnou vrstvou nanofibrilovanej celulózy a nanocelulózy, obsahujúcou antiseptické kovové ióny a pomocné látky (adjuvancie) v zadržanej zvyškovej vode, v ktorých sa spájajú deaktivačné a dezinfekčné účinky kovových iónov a žiarenia v špeciálnom UV-C rozsahu elektromagnetickej vlnovej dĺžky



Obr. 1: Princíp fungovania deaktivácie vírusov

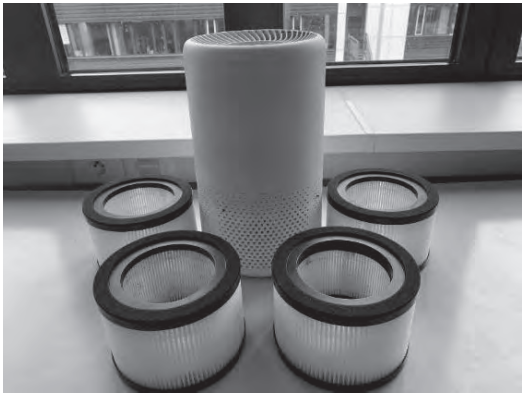
Vzduch je nasávaný otvorom nanofiltračného zariadenia umiestneným v spodnej časti a prechádza do stredu filtračnej vložky, kde germicídny žiarič vyžaruje žiarenie v takom rozsahu elektromagnetických vlnových dĺžok UV-C, pri ktorých nevzniká ozón. Kontaminovaný vzduch následne prechádza cez filtračný papier

obsahujúci soli antiseptických kovov, od stredu žiariča smerom von cez filtračný papier[7] hermeticky uzatvorene vložený do filtračnej vložky. Filtračná prepážka je harmonikovito poskladaná tak, aby bol jeho povrch maximálne a celý ožiarený UV-C žiarením. Do zachytených kontaminovaných mikrokvapôčok difundujú antiseptické ióny[5], ktoré spolu s pôsobením UV-C žiarenia deaktivujú vírusy a dezinfikujú baktérie. V prípade zachytenia mikrokvapôčky hlbšie vo filtračnom materiáli[10], prípadne na mieste kde akákoľvek iná prekážka (ako napríklad ďalšia kvapôčka) tieni na nami sledovanú infikovanú kvapôčku a UV-C žiarenie nemôže tieto mikróby zasiahnuť a vírusy deaktivovať, nastupuje proces deaktivácie iónmi kovov, difundujúcich do vnútra takejto kvapôčky. Pôsobením UV-C žiarenia a prúdenia vzduchu s relatívne nízkou vlhkosťou, kvapôčky postupne vysychajú a deaktivované vírusy prípadne dezinfikované baktérie sú odnášané vzduchom. Mikróby sú na povrchu pokryté pomocnými látkami (adjuvanciami). Vďaka tomu sa deaktivované vírusy a dezinfikované baktérie ľahšie dostávajú do imunitného systému ľudského teľa, kde sa pomocné látky rozpustia, odhalia spike proteíny, ako aj celý bielkovinový obal deaktivovaného vírusu alebo dezinfikovanej baktérie–neschopnej replikácie. Imunitný systém sa naučí bojovať proti takto odhaleným cudzorodým mikróbom. Neskôr po infekcii aktívnym vírusom, prípadne živou baktériou, organizmus už bude mať zvýšenú imunitu proti aktuálnej mutácii vírusu, či baktérie. Opísané zariadenia takto prispejú ku zvýšeniu celkovej imunity populácie.



1. Nanofiltračné zariadenie cylindrického alebo hranolového tvaru na deaktiváciu vzduchom prenášaných patogénov cez filter obsahujúci organické a anorganické aditíva vo zvyškovej vode na celulózovom nosiči
2. Perforovaná základňa
3. Vnútorný priestor
4. V strede obsahuje pozdĺžne umiestnený germicídny žiarič vo forme cylindra alebo U-rúrky
5. Pórovité steny filtračného papiera poskladané do harmonikovitého tvaru
6. Filtračná kazeta
7. Nepriepustná bariéra
8. Vstupné otvory pre vzduch
9. Prívod infikovaného vzduchu s kvapôčkami
10. Ventilátor[9]

Obr. 2: Prístroj na deaktiváciu vzduchom prenášaných patogénov a na zvýšenie imunity populácie



Obr. 3: Realizácia funkčného modelu prístroja na deaktiváciu vzduchom prenášaných patogénov v praxi s náhradnými účinnými filtrami

Na ochranu a presadzovanie práv duševného vlastníctva – bol uplatnený medzinárodný patent PCT (Patent Cooperation Treaty) – patentová prihláška bola zverejnená na WIPO (World Intellectual Property Organisation) WO/2023/128878[1,2] autorov: Bohacek, S.,, Soos, L., Toth, M., Stankovska, M., Pazitny, A., Ihnat, V., Kuna, V., Balbercak, J.,Schwartz, J. „Nanofiltration device for deactivation of air-filtered pathogens on surface-treated filter material", Výskumný ústav papiera a celulózy, a.s. Bratislava – patentové konanie prebieha – podania sa uskutočnili v rámci platných lehôt – v Európe (Európska patentová prihláška č.21970127.3 na spoločný európsky patent), v USA (US patentová prihláška č. 18/725,673), v Kanade (číslo patentovej prihlášky ešte neoznámili), v Ruskej federácii (patentová prihláška č. 2024121382), v Japonsku (patentová prihláška č. 2024-539957), v Juhokórejskej republike (patentová prihláška č. 10-2024-7022275), v Číne (patentová prihláška č. 202180105329.2), v Indii (patentová prihláška č. 202417052673) a v Austrálii (patentová prihláška č. 2021481015).

Účasť na výstave COFO27

Vynález bol vybraný na výstavu COFO27 spojenú s 27. zasadnutím Výboru pre lesné hospodárstvo (COFO) Záujem o zariadenie prejavili firmy z celého sveta, takisto záujem o zastupovanie Výskumného ústavu papiera a celulózy na Úradoch na ochranu priemyselného vlastníctva vyjadrili desiatky kancelárií z celého sveta.

Účasť na výstave CEPI Bioeconomy Lab

Vynález bol vybraný Konfederáciou európskeho papierenského priemyslu CEPI (Confederation of European Paper Industries) na Výstavu CEPI Bioeconomy Lab, kde sa vystavovali vybrané vynálezy, technické riešenia a inovatívne produkty v Bruseli na Radnici pre novozvolených členov Európskeho parlamentu.

Obr. 4: Fotografie z Výstavy COFO 27, 22.–26. júla 2024 v sídle FAO (OSN) v Ríme v Taliansku.

Obr. 5: Výstava CEPI Bioeconomy Lab for MEP, Brussels Town Hall, 23.-24.9.2024

Záver

Výskumné aktivity nášho tímu sa v súčasnosti orientujú hlavne na výskum a na testovanie efektívnosti a účinnosti deaktivácie vírusov a dezinfekcie baktérií pri rôznych prietokoch vzduchu a tiež na sledovanie efektívnosti filtrov a jej poklesu v závislosti od dĺžky používania. Zhromažďujeme dáta potrebné na určenie optimálneho časového intervalu na výmenu filtra za nový, teda aktívny. Všetky tieto informácie budú potrebné na dimenzovanie zariadení na veľkosti priestorov, v ktorých budú nasadené a na optimalizáciu režimu ich aplikácie.

Acknowledgement

The project leading to this application has received funding from the European Union's HORIZON EUROPE research and innovation programme under grant agreement No 101059552, Project name: Upgrade of the Centre of Excellence LignoSilva (Call: HORIZON-WIDERA-2022-ACCESS-01-two-stage).

Co-funded by
the European Union

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Hardwood kraft pulp bleaching costs reduction at Mondi SCP, Ružomberok

Michal Kebísek

Mondi SCP a.s., Tatranská cesta 3 Ružomberok, michal.kebisek@mondigroup.com

Abstract: *Recent years have presented pulp and paper inustry with many challenges. Among these the dramatic increase of energy and chemicals prices has been one of foremost concerns. This material presents a case study of a systematic approach to reduce heat, electricity and chemicals costs in an integrated BHK pulp mill located in the Central Europe environment. Various examples of applied projects and initiatives are presented along with their impact to production costs and environmental footprint of bleached hardwood kraft pulp production.*

New paper machine PM19

Jaroslav Majer, Kristína Ševčíková

Mondi SCP, a.s., Tatranská cesta 3, 034 17 Ružomberok, Jaroslav.Majer@mondigroup.com, Kristina.Sevcikova@mondigroup.com

Abstract: *The new paper machine PM19 has been one of five machines at Mondi SCP for four years. It is the most modern paper machine and uses new technologies from Valmet. The paper produced is a combination of virgin and recycled fiber. It was built with the aim of saving the environment and waste materials. The most modern technologies contribute to the intelligent and optimal management of the use of all input materials, as well as emerging by-products. One of these tools is the APC /Advanced Process Controls/, tool for online strenght properties and visual appearance information and control; optimization inputs like raw materials, chemical consumptions or energy. Quality models and predictions are fully implemented through continuous learning by each laboratory results.*

Less effort, more impact: Reduction of driving power by using a unique ceramic material

Markus Magauer

Röchling Industrial Oepping GmbH & Co. KG Röchlingstraße 1 | 4151 Oepping | Austria

Abstract: *ROBACERAM PX is a unique premium ceramic material for dewatering elements from Röchling Industrial Oepping for machines with the highest demand in regards to friction and the highest machine speeds. Thanks to its unique material composition and the special production process, this material grade brings numerous benefits to achieve an efficient paper production process.*

Renovácie ložísk ako cesta k cirkulárnej ekonomike

Marek Vrábel

SKF Slovensko spol. s r. o., Plynárenská 7B, 821 09 Bratislava

Abstrakt: *Cieľom prednášky SKF je priblížiť účastníkom konferencie ako dokážeme našim zákazníkom a partnerom pomocou služby Renovácie ložísk dosahovať a napĺňať KPI a normy zelenej a cirkulárnej ekonomiky. Predstavíme výhody Renovácii ložísk (redukcia CO2 emisii až o 90 % vrátane certifikácie o úsporách energii a materiálov, efektívne prevádzkovanie ložísk a dosahovanie maximálnej životnosti náhradných dielov, zníženie dodacích termínov a nákladov na prevádzku, a pod.). Vysvetlíme princípy a procesy samotnej renovácie, benefity technického reportu z analýzy ložísk a zdieľanie cenného know-how s našimi zákazníkmi a samozrejme aj konkrétne príklady z praxe.*

Evaluation of Black Liquor Physical Properties Before and After Spruce Chips Impregnation

Michaela Peciarová, Peter Peciar, Martin Juriga, Roman Fekete

Slovak University of Technology in Bratislava, Faculty of Mechanical Engineering, Institute of Process Engineering, Námestie Slobody 17, 812 31 Bratislava, Slovakia
michaela.peciarova@stuba.sk, peter.peciar@stuba.sk, martin.juriga@stuba.sk, roman.fekete@stuba.sk

Abstrakt: *This study investigated the impact of a batch impregnation process on black liquor properties, specifically focusing on effective alkali (EA) concentration and viscosity. Black liquor, a complex aqueous solution comprising organic and inorganic fractions, was used to impregnate softwood chips. The EA concentration of black liquor exhibited a time-dependent decrease during the impregnation cycle, with the most significant drop observed within the first 10 minutes. This decline is attributed to various process parameters, including pressure and temperature. Viscosity, a crucial factor influencing liquid flow through the wood structure, was also monitored. While the initial viscosity is influenced by factors like temperature and dry solids content, the study observed that post-impregnation black liquor samples exhibited viscosities comparable to the original solution. These findings provide valuable insights into the dynamic behavior of black liquor during the impregnation process, highlighting the interplay between EA concentration, viscosity, and process parameters.*

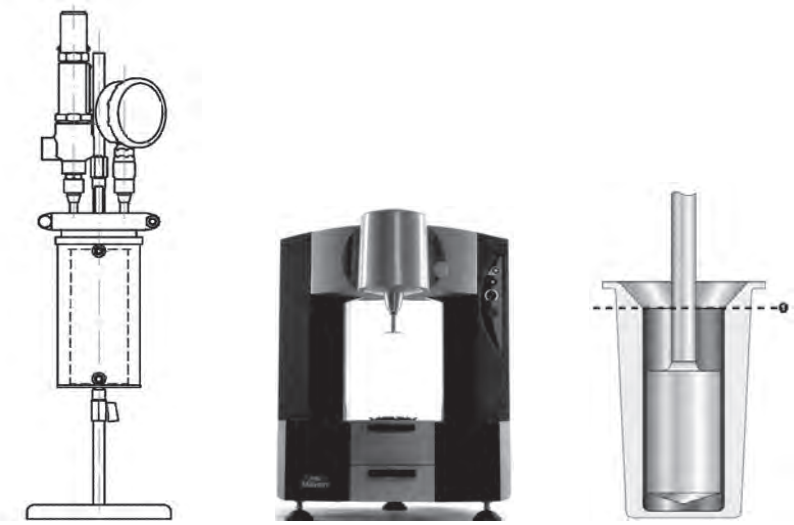
Kľúčové slová: *Impregnation, Spruce Chips, Black Liquor, Physical Properties*

1. Úvod

V súčasnosti, keď sa pozornosť upriamuje na znižovanie spotreby energie a surovín, je dôležité venovať pozornosť často opomínanému kroku kraftových várok, a to procesu impregnácie. Počas impregnácie sú štiepky penetrované čiernym lúhom (zmesou vysoko alkalického bieleho lúhu a slabého pracieho filtrátu) s následnou difúziou. Počas prenikania čierneho lúhu do štruktúry drevných štiepok sa jeho počiatočná koncentrácia znižuje. Toto zníženie je ovplyvnené viacerými faktormi, medzi ktoré patria: rozmery štiepok (najmä ich hrúbka), obsah vlhkosti, množstvo zachyteného vzduchu v štruktúre dreva a tiež procesné parametre, ako sú teplota, tlak a dĺžka trvania samotnej impregnácie. Viskozita impregnačnej kvapaliny, ktorá indikuje ľahkosť prenikania lúhu do štruktúry dreva, je nepochybne silne závislá od teploty impregnácie. Hodnota dynamickej viskozity čierneho lúhu v prvom rade závisí aj od množstva tuhých častíc rozpustených v ňom [1-8].

2. Experimentálna stanica

Reaktor (obr. 1a) s objemom približne 1,6 litra je vyhrievaný pomocou duplikátora. Je vybavený snímačom tlaku a teploty, ktorý je pripojený k modulárnemu systému ALMEMO 5690-1M09. Tento systém zabezpečuje zber a zobrazenie údajov v reálnom čase. V spodnej časti reaktora sa nachádza vzorkovací ventil, cez ktorý sa odoberali vzorky impregnačného média počas impregnácie. Na tlakovanie reaktora bol použitý inertný plyn – dusík. Vo vnútri reaktora je umiestnený vyberateľný košík, do ktorého sa vkladá experimentálny materiál–štiepky [9-11].



a) b) c)

Obr. 1: Experimentálna stanica [9-11]: a) patentovaný laboratórny reaktor; b) rotačný reometer Malvern Kinexus; c) meracia komora rotačného reometra

3. Experimentálne merania

Pre získanie časového priebehu znižovania koncentrácie čierneho lúhu boli vykonané experimenty s ihličnatým drevom, ktoré bolo po dobu 30 minút impregnované roztokom s počiatočnou koncentráciou 5 g/l NaOH. Experimenty prebiehali pri tlaku 5 bar a teplotách 70, 80 a 90 °C. Vzorkovanie bolo nastavené na frekvenciu 5 minút. Okrem toho bolo sledované možné zvýšenie/zníženie viskozity čierneho lúhu, ktoré súviselo so stratou obsahu sušiny, ktorá prenikla do dreva spolu s roztokom [13].

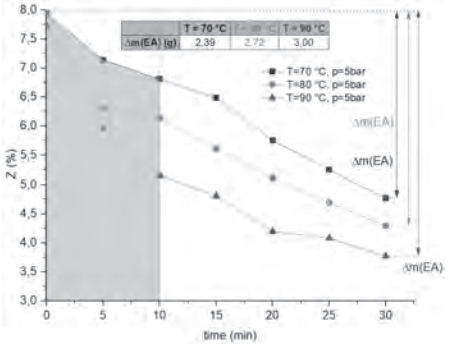
4. Analýza merania

Na získanie údajov o sušine, a teda aj o obsahu vlhkosti skúmaného materiálu, bola použitá metóda podľa SCAN-CM 39:94 [12]. Gravimetrická analýza bola použitá na určenie množstva lúhu impregnovaného do dreva. Pokles koncentrácie impregnačného lúhu v čase bol stanovený titračnou analýzou podľa metódy K. Wilsona [8]. Vzorka bola pipetovaná do kadičky s destilovanou vodou a 20 % roztokom BaCl2 a následne titrovaná 1 molárnym roztokom HCl až do dosiahnutia pH 11. Okrem toho bola skúmaná viskozita lúhu pred a po impregnačných testoch [13].

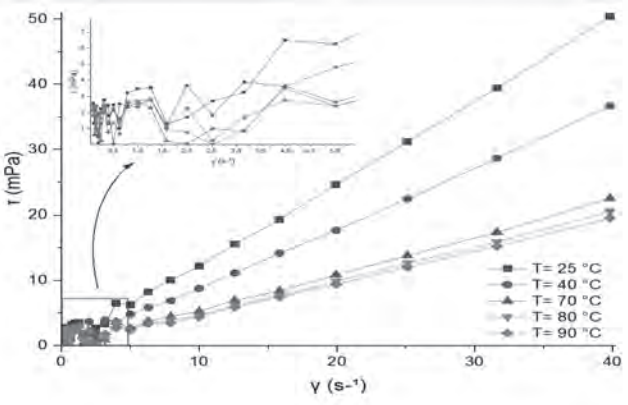
5. Výsledky a diskusia

Titračné experimenty so vzorkami odoberanými počas impregnácie štiepok ihličnatého dreva viedli ku grafickej závislosti klesajúcej zanášky efektívnych alkálií vztiahnutých na hmotnosť absolútne suchého dreva v čase. Táto závislosť jednoznačne ukazuje, že čím vyššia je teplota čierneho lúhu, tým vyššia je spotreba efektívnych alkálií. So zvyšujúcou sa teplotou klesá dynamická viskozita čierneho lúhu. Čím nižšia je hodnota viskozity, tým ľahšie preniká impregnačný roztok do štruktúry dreva.

Zvýšením teploty o 20 °C sme preukázateľne potvrdili možnosť skrátenia doby impregnácie za predpokladu, že požadovaný výstup zanášky efektných alkálií bol približne 4,77 %. Dynamická viskozita čierneho lúhu pred impregnáciou pri 70 °C mala hodnotu 0,55 mPa.s a hodnota sušiny xs = 10,133 %, po impregnácii mala hodnotu 0,56 mPa.s a hodnotu sušiny xs = 10,311 %. Napriek výraznému poklesu koncentrácie efektívnych alkálií v roztoku a po kontakte kvapaliny s poréznymi drevným materiálom v podobe štiepok nebol pozorovaný žiadny významný vplyv na zmenu dynamickej viskozity. Výsledky meraní dynamickej viskozity sú uvedené v tabuľke 1.



Obr. 2: Závislosť zanášky efektívnych alkálií od času impregnácie. Tabuľka v hornej časti obrázku zobrazuje vypočítané hodnoty rozdielu hmotnosti efektívnych alkálií na začiatku a na konci impregnácie [13].



Obr. 3: Reogram čierneho lúhu pred impregnáciou [13].

Tab. 1: Namerané hodnoty viskozity čierneho lúhu pred impregnáciou a vzoriek po impregnácií pri teplotách 70, 80 a 90°C pri vybraných teplotách merania [13].

Meranie pri teplote	25°C	40°C	70°C	80°C	90°C
ČIERNY LÚH	η **(mPA. s)**				
počiatočný pred impregnáciou	**1,25** ±0,023	**0,89** ±0,019	**0,55** ±0,014	**0,49** ±0,015	**0,47** ±0,017
impregnácia pri teplote 70 °C	**1,24** ±0,024	**0,90** ±0,020	**0,56** ±0,018	**0,51** ±0,023	**0,49** ±0,020
impregnácia pri teplote 80 °C	**1,24** ±0,030	**0,89** ±0,031	**0,55** ±0,019	**0,51** ±0,019	**0,48** ±0,017
impregnácia pri teplote 90 °C	**1,26** ±0,028	**0,90** ±0,016	**0,55** ±0,014	**0,50** ±0,013	**0,47** ±0,010

6. Záver

Pokles koncentrácie efektívnych alkálií čierneho lúhu počas impregnácie štiepok ihličnatého dreva je najvýraznejší v prvých okamihoch kontaktu impregnačného média s poréznym materiálom. Impregnácia čiernym lúhom pri 70 °C spôso-

bila zníženie koncentrácie o 35 % z počiatočnej hodnoty. Pri teplote čierneho lúhu 80 °C bol pokles približne 53 % a pri 90 °C pokles z počiatočnej hodnoty efektívnej koncentrácie alkálií dosiahol až 64 %. Koncentrácia čierneho lúhu teda vykazovala klesajúci trend, ktorý sa však výrazne neprejavil na jeho dynamickej viskozite ani na obsahu sušiny v nej.

Poďakovanie

Autori by radi poďakovali Ministerstvu školstva, výskumu, vývoja a mládeže Slovenskej republiky za finančnú podporu výskumu prostredníctvom grantu KEGA 003STU-4/2023.

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Lignin As A Key Player In Sustainable Materials: Isolation, Market Trends, And Industrial Potential

Richard Nadányi[1,2], Aleš Ház[1]

[1]Department of Wood, Pulp and Paper, Institute of Natural and Synthetic Polymers, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia, richard.nadanyi@stuba.sk
[2]Christian Doppler Laboratory for Next-Generation Wood-Based Biocomposite, Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria, richard.nadanyi@tuwien.ac.at

Abstract: Lignin, the second most abundant natural polymer after cellulose, plays a key role in sustainable material applications. Despite being a major byproduct of the pulp and paper industry, lignin remains underutilized, primarily burned for energy. However, advances in lignin isolation and valorization are unlocking its potential in high-value applications. This abstract provides an overview of lignin's potential, focusing on isolation methods, market trends, and industrial applications, based on previous research findings.

Keywords: *Lignin, sustainability, biorefinery, isolation techniques, market trends, industrial applications*

1. Introduction

Lignin is a complex phenolic biopolymer with growing interest for industrial applications due to its structural versatility and chemical properties. It is primarily produced from Kraft and sulfite pulping, where most of it is used for energy generation. However, its potential as a bio-based raw material is gaining attention [1].

2. Lignin Isolation, Market Trends, and Industrial Applications

Lignin isolation significantly impacts its usability. The LignoBoost™ process and other precipitation-based methods improve lignin recovery from black liquor. Techniques like membrane filtration and solvent extraction allow for tailored properties, enhancing application possibilities [2,3].

The lignin market is expanding due to demand for sustainable alternatives to fossil-based chemicals. Commercial products like Kraft lignin and lignosulfonates serve as dispersants and adhesives, while advancements in processing enable higher-value applications in composites, bio-based resins, and carbon fibers [1].

Lignin-based materials offer promising substitutes for petrochemical-derived components in bioplastics, rubber, and specialty chemicals. Studies show im-

proved mechanical properties in polymer matrices, supporting lignin's role as a sustainable alternative. Additionally, its antioxidant and UV-resistant properties enhance coatings and protective formulations [1,2,4].

3. Conclusion

Lignin's potential as a sustainable material is increasingly recognized. Its successful integration into industrial processes relies on optimizing isolation and expanding applications. Pulp mills can capitalize on lignin valorization, contributing to both profitability and the circular bioeconomy [1,4].

Acknowledgements

The Slovak Research and Development Agency is acknowledged for their funding of the projects under the contracts APVV-22-0388, and VEGA 1/0743/24.

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Quo Vadis Papier?

Štefan Šutý

ODCP, ÚPSP, FCHPT STU, Bratislava

Abstrakt: *Paper is a special material, the origin of which historians mention at the beginning of our era, a little more than 2000 years ago in China. This paper was identical in structural form, made of separate plant cells, to the paper produced at the present time. The potential of paper as a very effective carrier of information at the time of its creation was greatly appreciated. This function has dominated so far, despite the fact that various new functionalities of paper have been developed, which have expanded the portfolio of its use and also the variety of paper types. In Europe, paper began to be used more intensively only in the 12th and 13th centuries after its path of spread from China through Arab countries to Spain and gradually to the whole of Europe. The demand for paper increased enormously in the 15th century with the development of the printing press and in the 18th and 19th centuries with the method of producing an endless sheet of paper on the Roberts and Foudrinier paper machine, as well as the raw material transition from rag to wood pulps. In the 20th century, paper became an indispensable material in schools, offices, printers and in everyday communication. At present, the largest paper machine produces about 4.5 tons of paper/day, with a production speed of up to 2000 m/min and a machine width of 11.8 m, and the length of the machine is up to 600 m. The subject of this paprer is to try to answer some questions about the future of paper. For example: Does paper have a perspective in the future? What challenges will paper production face in the future? How will the paper change?*

Kľúčové slová: *budúcnosť papiera, digitalizácia, recyklácia, automatizácia*

1. Úvod

Papier ako technický plošný materiál vytvorený z izolovaných rastlinných buniek, mechanicky opracovaných mletím, samotných alebo s prídavkom pomocných látok zo suspenzie (vodnej) postupným odstraňovaním vody filtráciou, lisovaním a sušením. Pôvodné využitie papiera bolo na zaznamenávanie informácii a kultúrneho dedičstva.

Podľa odhadov bolo do roku 2010 vytlačených približne 129 miliónov kníh, nepočítajúc rukopisy, časopisy a noviny. Každý rok sa vytlačia miliardy strán dokumentov, kníh a novín. Veľké knižnice ako Library of Congress v USA obsahujú približne 170 miliónov položiek, z toho väčšina je na papieri. Celkové množstvo informácií uchovaných na papieri sa odhaduje na petabajty (PB) až exabajty (EB) dát, pričom moderné digitálne úložiská už túto kapacitu výrazne presahujú.

OBR:1. Vývoj produkcie papiera v hárkoch A4/min.

Táto funkcionalita papiera stále dominuje a bolo to evidentné až do roku 2008 kedy produkcia hlavne grafických papierov dominovala a neklesla ani s počiatočným príchodom digitálnych informačných technológii ba naopak vzrastala každoročne. Až s rozvojom rýchlosti počítačov, zvyšovaním kapacít pamäťových úložísk a vývoj digitálnych sietí priniesol dominanciu digitálnych informačných technológii a pokles dopytu po grafických papieroch. Naopak globalizácia, rozvoj trhov a vznik„ e-comerce" enormne zvýšil dopyt po obalových materiáloch hlavne vlnitej lepenke ale aj iných obalových papierov. Dá sa povedať, že obalové papiere dominujú v segmente papierenských technológii. Veľmi stabilná je aj oblasť produkcie hygienických papierov. V roku 2023 sa ako top produkty dostali do popredia recyklovaný fluting, testliner a recyklovaný skladaný kartón–všetky druhy obalov–a tvorili 63 % z 10 najlepších tried. Išlo o významný posun oproti roku 2008, keď bol bežnejší novinový papier a kopírovací papier (1). Tu sa dá predpokladať nárast dopytu v budúcnosti a tým aj produkčných technológii. Tu treba poznamenať, že tieto papiere je možné predávať len do určitej vzdialenosti od produkčných jednotiek. Rozvoj papierenského priemyslu silne závisí od pomeru dopytu a výrobných kapacít v určitom regióne sveta. Perspektíva rozvoja buničiny a papiera závisí od regiónu a výrobného segmentu (2). V Európe a Severnej Amerike je dopyt saturovaný výrobnými kapacitami v posledných desaťročiach výrobné kapacity prevyšujú dopyt. V poslednom období najväčší rozmach papierenských kapacít narástol v Ázii a južnej Amerike. Súvisí to s nízkou spotrebou papiera na obyvateľa.

2. Faktory ovplyvňujúce rozvoj papierenského priemyslu

Dostupnosť surovín pre papierenský priemysel v budúcnosti bude závisieť od viacerých faktorov, ako sú klimatické zmeny, regulácie lesného hospodárstva, technologické inovácie a dopyt po recyklovaných materiáloch (3).

Energetická efektivita papierenského priemyslu sa bude v najbližších desaťročiach zlepšovať vďaka kombinácii inovácií v technológiách, digitalizácie, využívania obnoviteľných zdrojov a prísnejších environmentálnych regulácií. Najväčší potenciál úspor sa očakáva v optimalizácii výrobných procesov, efektívnejšom sušení, automatizácii a využití recyklácie.

Nízky alebo nulový vplyv na znečisťovanie životného prostredia je ambiciózny cieľ a hoci je dosiahnutie nulových emisií v papierenskom priemysle náročné, kombináciou moderných technológií, obnoviteľných zdrojov energie, cirkulárnej ekonomiky a digitalizácie je možné výrazne znížiť ekologický dopad. Kľúčovými faktormi sú uzavreté materiálové a vodné cykly, zelená energia, využitie vedľajších produktov a automatizácia procesov.

Zvyšovanie efektivity práce a znižovanie podielu človeka na výrobe v budúcnosti dosiahneme tak že, papierenský priemysel prejde revolučnou automatizáciou (4), ktorá dramaticky zníži potrebu manuálnej práce a zvýši efektivitu. Výroba sa bude riadiť AI, robotikou, IoT a prediktívnou údržbou, čím sa dosiahne nižšia spotreba energie, menej odpadu a vyššia kvalita produktov (5). Hoci podiel človeka na výrobe sa zníži, dopyt po odborníkoch v oblasti IT, dátovej analýzy a držby robotov sa zvýši.

3. Záver

S papierom ako materiálom možno počítať aj v budúcnosti. Je to unikátny materiál, ktorého funkcionalita a tým aj rozmanitosť výrobkov a ich spracovanie dáva tomuto materiálu veľkú perspektívu v budúcnosti. Papierenský priemysel však bude čeliť veľkým výzvam v oblastiach surovinových zdrojov, energetickej efektivity a diverzity so zameraním na obnoviteľné zdroje energii, stály trend znižovania dopadu na životné prostredie bude pokračovať a zvyšovanie automatizácie a robotizácie procesov výroby a spracovania papierov je nevyhnutný trend pre jeho trvalú konkurencieschopnosť.

Poďakovanie

Táto publikácia vznikla vďaka podpore agentúry APVV a projetu APVV-22-0277 a Vededeckej grantovej agentúre Ministersterstva školstva, vedy, výskumu a športu SR a Slovenskej akadémie vied za podporu projektom VEGA 1/0651/23.

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Ochrana mestskej zelene inovatívnym lignocelulózovým produktom

Daniela Majerčáková, Filip Šubín

Výskumný ústav papiera a celulózy, a. s. Bratislava

Abstract: *The study of the adsorption capacity of compressed cylindrical cellulose fibres in the form of an innovative adsorber, enabling the adsorption of road salts and biological properties, is the subject of the project, which also resulted in this study. The effectiveness of the adsorber depends on its physicochemical properties and its packaging method in desalination foils. The cellulose adsorber should be packed into modified desalination foils to ensure free water flow into the soil and increase the adsorption surface for soluted salt. The aim of the system is to achieve 90 % efficiency in the adsorption of road salt. While all tested samples absorbed salt water, the most effective were those with 87%, a diameter of 19mm, a length of 26mm, and 6.76 % moisture content. Cellulose pellets were more effective in adsorbing salt than willow chips (Salix vinalis)*

Kľúčové slová: *buničina, posypová soľ, lignocelulóza, ochrana stromov*

1. Úvod

Negatívne účinky posypových solí vo vysokej koncentrácii v pôde sa prejavujú narušením osmotickej rovnováhy rastlín, čo sťažuje príjem vody a živín a preto používanie posypových solí môže viesť k vysychaniu rastlín, dokonca aj vtedy, keď je pôda dostatočne vlhká a rovnako tak posypové soli vplývajú na chemické zloženie pôdy. Riešenie ochrany stromov pred účinkami cestnej posypovej soli v kombinácii s riešením nadmerného množstva použitého kartónového odpadu a nevyužiteľnosti krátkych vlákien celulózy, ktoré nemožno ďalej cirkulovať.

Pri recyklácii papiera vznikajú celulózové vlákna, ktoré nie je možné použiť na vytváranie tradičného papiera a z toho dôvodu sa vyhadzujú na skládky alebo pália (Venkatesan et al, 2023). Tieto vlákna by mohli byť využité na vstrebávanie soli používanej na odmrazenie ciest a tým ochraňovať zalesnenie v obývaných oblastiach (Equiza et al, 2017). Prítomnosť NaCl v pôde znižuje schopnosť vody prenikať hlbšie do pôdy, zvyšuje jej zásaditosť (Fay & Shi, 2012). Stres zo slanosti vytvára rušenie prenosu iónov naprieč membránami buniek koreňov, taktiež limituje vstrebávanie vody a nutrientov ako draslík, ktorý je nutný na správne fungovanie rastlinných buniek (Lynch J. Läuchli, 1984). Novou aktívnou metódou na zachytávanie cestnej soli je použitie vŕbových štiepok (Salix viminalis) umiestnených v špecializovaných podnosoch. Tento systém je výnimočný tým, že na rozdiel od tradičných pasívnych bariér aktívne odstraňuje cestnú soľ z prostredia. Vŕbové štiepky odstránili časť soli z roztoku soľanky,

čo umožnilo preniknúť do pôdy iba vode s nízkou slanosťou. Účinnosť zachytávania soli sa v rámci systémov výrazne líšila, v rozmedzí od 31 % do 95 %, v závislosti od konkrétnej použitej konfigurácie (Spisak et al., 2020).

Nová aktívna metóda zachytávania posypovej soli využíva vŕbové triesky (*Salix viminalis*) umiestnené v špecializovaných vaničkách. Na rozdiel od tradičných pasívnych bariér je tento systém jedinečný, pretože aktívne odstraňuje posypovú soľ z prostredia. Vŕbové triesky boli usporiadané v troch rôznych konfiguráciách: mikro-stĺpce, mikro-stĺpce s retenčnými pohármi a monovrstvový stĺpec. Každá konfigurácia účinne eliminovala časť soli zo soľného roztoku, čím umožnila prienik do pôdy len vode s nízkou slanosťou. Účinnosť systému, určená meraním obsahu soli v adsorbéri po zimnej sezóne, zdôrazňuje jeho potenciál ako inovatívneho prístupu k ochrane pobrežnej vegetácie, podzemnej vody a pôdy pred nepriaznivými účinkami rozmrazovacej posypovej soli. (Spisak et al., 2020)

2. Materiál a metódy

Po viacnásobnej recyklácii papiera vznikajú veľmi krátke, takzvané nulové vlákna, ktoré znižujú kvalitu papiera a vytvárajú prašné, potenciálne výbušné prostredie. Tieto vlákna sa hromadia v kale, čo zvyšuje náklady na skládkovanie. Navrhujeme ich využitie po fibrilácii na výrobu peliet pre efektívne zachytávanie soli. Tieto vlákna sú pre adsorpciu solí ideálne, ekonomicky výhodné a riešia problém kalu. Pre lepšiu pevnosť peliet boli primiešané netriedené sekundárne vlákna.

Tab. 1: Špecifikácia frakčného zloženia vlákien celulózového adsorbéra

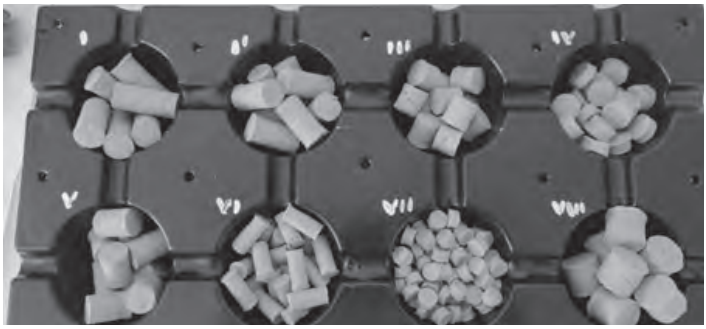
		Vzorka celulózy–nulové vlákna
Sušina		31,651 %
Frakcionácia na Bauer-McNett Classifier	26	19,864 %
	50	28,815 %
	100	14,850 %
	200	2,544 %
	-200	33,927 %

Valcové celulózové adsorbéry rôznych parametrov (rozsah výšky v rozmedzí od 0,5 cm do 8 cm s priemerom 0,5 cm až 5 cm) boli vytvarované manuálne pomocou laboratórneho zariadenia našej výroby (Obr. 1). Spôsob výroby–lisovanie krátkovláknitej celulózovej vlákniny pri rôznych tlakových silách v rozsahu od 0,1 do 12,0 MPa. Celulózové adsorbéry boli vyrobené z krátkovláknitej buničiny.

Odsoľovacia fólia (Obr. 1) s výškou 4 cm, vyrobená z HDPE s hrúbkou 2 mm. Fólia má dvanásť retenčných nádob v tvare pologúľ, zospodu vystužených priehlbinami v tvare torusu. Retenčné nádoby sú prepojené otvorenými žľabmi, určenými na odvádzanie prebytočnej málo slanej vody

Metodika stanovenia koncentrácie NaCl adsorbéra

Adsorpčná kapacita bola hodnotená s použitím 20 % roztoku soli pri teplote 20 °C a okolitej vlhkosti 40 %. Testy sa uskutočnili na odsoľovacej fólii obsahujúcej 12 retenčných komôr, každá s objemom 125 cm3. V každej komore boli umiestnené rôzne typy adsorbérov a každý z nich bol naraz nasýtený 100 ml 20 % roztoku NaCl. Potom sa adsorbéry nechali vysušiť pri teplote 20 °C. V experimente merania špecifickej adsorpcie bol z každej komory vybraný a označený práve jeden absorbér, ktorý bol odvážený pred zaplavením slanou vodou a po impregnácií a odparení. Týmto spôsobom je možné určiť množstvo adsorpcie NaCl z roztoku jediným adsorbérom.



Obr. 1: Vybrané typy adsorbéra umiestneného v záchytných nádobách s kapacitou 125cm^3

Koeficient povrchového odparovania (ESC)

Koeficient povrchového odparovania je funkciou dvoch premenných: priemeru (D) a výšky (H). Priemer jadier je striktne určený obrábacím strojom použitým na tvarovanie, avšak dĺžka adsorbérov sa dá ľahko upraviť počas výrobného procesu zmenou množstva použitého materiálu alebo stupňa kompresie. Preto bola optimalizácia koeficientu odparovacej plochy vykonaná za predpokladu, že priemer adsorbérov sa bude považovať za parameter funkcie, zatiaľ čo dĺžka sa bude považovať za nezávislú premennú. Vzorec pre koeficient v prípade valca je:

$$ESC=P/O=2\ (D+2h)/Dh\ [cm]\text{^}(-1) \quad (1)$$

kde P je plocha a O je objem.

3. Výsledky a diskusia

Najvyššia hodnota ESC (6,19) bola dosiahnutá s najmenším priemerom (1,20 cm) a najmenšou výškou (0,73 cm), čo naznačuje, že menšie adsorbéry prispievajú k lepšiemu výkonu odparovania a taktiež mali aj najvyššiu absorpčnú účinnosť pre jeden absorbér (74 %), ale adsorpcia NaCl priamo nekorelovala iba s ESC. Najvyššia

absorpčná účinnosť (91 %) bola dosiahnutá s priemerom 1,20 cm a 94 adsorbérmi, čo naznačuje, že väčší počet adsorbérov môže výrazne zlepšiť absorpčnú kapacitu NaCl. Za zmienku tiež stojí, že najslabším adsorbérom s účinnosťou 43 % bola drevná štiepka Salix viminalis.

4. Záver

Na každom z 12 adsorbérov sa vyskytujú rôzne vzory a veľkosti kryštálov soli, čo naznačuje, že kryštalizácia prebiehala odlišne v závislosti od vlastností povrchu adsorbéra. Z pozorovanie môžeme vyhodnotiť, že najviac soli mimo absorbéra bolo zanechané vŕbovými trieskami, ktoré mali taktiež najnižšiu absorbciu soli. Pri bližšom pozorovaní boli viditeľné soľné nánosy na povrchu a malé ložiská soli v mikropóroch absorbéru.

Aby sa potvrdilo, že látkou vstrebanou adsorbentmi na báze celulózy bol chlorid sodný (NaCl), uskutočnilo sa skenovanie elektrónovým mikroskopom (SEM) v spojení s energeticky disperznou röntgenovou spektroskopiou (EDS). Okrem zobrazovania SEM sa na zachytenie povrchových obrazov pri rôznych zväčšeniach použila optická mikroskopia, ktorá odhalila distribúciu NaCl na povrchoch adsorbéra. EDS analýza poskytla podrobné elementárne údaje potvrdzujúce prítomnosť sodíka (Na) a chlóru (Cl) ako charakteristických zložiek NaCl nie len na povrchu, ale tiež sa detegoval vo vnútornej štruktúre.

Použitie adsorbérov na báze celulózy ponúka dvojitý environmentálny prínos tým, že rieši dva významné problémy súčasne. Poskytuje efektívne riešenie na riadenie akumulácie celulózového odpadu a pomáha zmierniť salinizáciu pôdy spôsobenú kontamináciou cestnou soľou, najmä chloridom sodným (NaCl).

Poďakovanie

Táto práca bola podporená projektom „Inovatívny celulózový adsorbér na zvýšenie ochrany stromov pred účinkami cestných solí“ (INNOCEL) v rámci výzvy EUREKA Danube Call 2022 pod číslom 2022-17613/NP/DANUBE 2022 Call.

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Sustainable Utilization of Sawmill Byproducts for High-Performance Biocomposites

Luis Zelaya-Lainez[1], Gabriel Unsinn[1], Markus Lukacevic[1], Nauman Wahab[1], Cornelia Hofbauer[1], Luisa Scolari[1], Florian Zikeli[2], Thomas Harter[1], Richard Nadányi[1], Hinrich Grothe[1], Anton Friedl[1], Michael Harasek[1], Josef Füssl[1]

[1] Christian Doppler Laboratory for Next-Generation Wood-Based Biocomposite, TU WIEN, Austria
[2] University of Tuscia, Italy

Email: luis.zelaya@tuwien.ac.at, Gabriel.unsinn@tuwien.ac.at, markus.lukacevic@tuwien.ac.at, nauman.wahab@tuwien.ac.at, cornelia.hofbauer@tuwien.ac.at, luisa.scolari@tuwien.ac.at, florian.zikeli@tuwien.ac.at, thomas.harter@tugraz.at, richard.nadanyi@tuwien.ac.at, hinrich.grothe@tuwien.ac.at, anton.friedl@tuwien.ac.at, Michael.harasek@tuwien.ac.at, josef.fuessl@tuwien.ac.at

Abstract: *This study presents a sustainable approach to transforming sawmill byproducts into high-performance biocomposites. By optimizing mechanical properties across different scales, we aim to enhance material efficiency while gaining a fundamental understanding of binding mechanisms through chemistry, advanced analytics, and multi-scale simulations. Additionally, we investigate the impact of less resource-intensive production parameters on mechanical performance to develop more efficient and sustainable processing methods. Conducted within the Christian Doppler Laboratory for Next-Generation Wood-Based Biocomposites, our research contributes to the advancement of durable, eco-friendly biocomposites with reduced environmental impact.*

Acknowledgement

The financial support by the Austrian Federal Ministry of Labour and Economy, the National Foundation for Research, Technology and Development and the Christian Doppler Research Association is gratefully acknowledged. Furthermore, the authors would also like to express their gratitude to the CD laboratory company partner HS Timber for their financial support. The first author would also like to thank the support from the Austrian Science Fund (FWF) through the Y1093 START-project.

Selected mechanical properties of hornbeam from coppice stands for structural applications

Přemysl Šedivka

Czech University of Life Sciences Prague, Faculty of Forestry and Wood Sciences, Kamýcká 129, 165 00 Prague – Suchdol, Czech Republic, sedivka@fld.czu.cz

Abstract: *As a result of climate change, the availability of soft wood and the potential for the more climate-resistant hornbeam wood (Carpinus betulus) to be used for structural applications are decreasing. However, due to cultivation measures, lower yield and lower quality parameters of the produced structural lumber, the price level of hornbeam wood on the market is higher than that of spruce wood, and it is also variable. Therefore, a possible solution is to change the system of growing wood, namely by switching from traditional first-generation growing systems to second-generation, or sapling, systems. To verify the parameters of hornbeam wood from coppice stands for potential structural applications, selected mechanical parameters were investigated. Analyzes of the mechanical behavior of sawn timber from hornbeam saplings show comparable results compared to wood from first-generation stands from low to medium forests.*

Keywords: *Hornbeam; structural wood; mechanical properties*

1. Introduction

As a result of climate change and an increase in average temperatures and uneven distribution of annual precipitation averages, spruce forest stands are dying in Central Europe due to bark beetle infestation (Nardi *et* al. 2022; Yadav and Kumar 2021). The absence of spruce wood on the market for processing into final products due to the bark beetle calamity and the gradual change in the species structure of forest stands more resistant to climate change in the future. It can potentially be replaced by selected broadleaf species. Hardwood is already commonly used in a number of end products (Krackler *et* al. 2011). Hornbeam wood is a potentially interesting alternative to spruce wood for interior and exterior structural applications due to the advantageous ratio of structural wood's mechanical properties. Due to its higher density and cellular structure, it has favorable strength properties. However, the disadvantage is the high hardness of hornbeam wood, which is problematic during mechanical processing of the surface. There are many types of surface treatments for wood before gluing. The influence of the mechanical structure of the surface of plywood panels before gluing on the strength of the glued joint was dealt with by Aydin (2004) and the study shows that the smaller the surface roughness after the grinding process before gluing, the higher the strength

of the glued joint. Bongers *et* al. (2016) focused in his study on the bonding of wood for non-structural applications with a chemically treated wood surface by acetylation. During delamination tests, the increased strength of the glued joint was demonstrated for acetylated wood. A study by Klébert *et* al. (2022) mentions the possibility of increasing the adhesion of the wood surface by plasma modification, while the effectiveness of this type of surface treatment depends on the type of gas used, and the plasma system during plasma treatment of the surface can increase its adhesion. Nevertheless, compared to chemical treatment, this procedure is technologically and financially demanding. In a study by Tymyk *et* al. (2013) the positive effect of the chemical modification of the surface of the veneers with the chemical modifier hydrogen peroxide on the increase of surface adhesion was demonstrated.

The study focuses on the difference in the mechanical properties of hornbeam wood from non-clearing and clear-cutting stands from low to medium forest, for the potential of its use for non-structural and structural applications in the interior and exterior.

2. Material and Methods

2.1 Wood samples

The test bodies for conducting the experiments were made of hornbeam wood (*Carpinus betulus*) (Tab. 01), designed according to the procedure defined in ČSN 49 0115 and ČSN 49 116. As input material, wood from normal (Hornbeam N) and cuttings (Hornbeam C) stands from hornbeam forest of medium height (Fig. 01) were used. Cut-outs of logs for the production of test specimens were taken from the hornbeam growth of a medium-sized forest near the village of Neveklov, Czech Republic. From the cutouts of the logs, prismatic lumber was produced, qualitatively and strength-graded to class D32 according to EN 338. Prisms with a thickness of 50 mm were formatted into lamella blanks cut in the radial direction with a thickness of 20 mm with an allowance for thickness milling, while mechanical defects such as suk cracks were cut out (Fig. 01). The slats were technologically conditioned for seven days in an air-conditioning chamber (Weisstechnik, Germany), i.e. in our case at a temperature of 20 ± 2 °C and a relative air humidity of 65 ± 5 % so that the moisture content of the wood was stabilized and maintained at 12 ± 1 %. Individual moisture and density were determined after conditioning according to ISO 13061-1 and ISO 13061-2. Test bodies with a size of 20 × 20 × 300 mm (width × height × length) were cut from the blanks (Fig. 01). Based on the type of surface treatment, two groups of slats of the respective wood species were created. The lamellae were processed by grinding on a wide belt sander with a P60 grit belt with an accuracy of 0.01 mm. Milling was performed on a reference milling machine with a head equipped with four knives with an accuracy of 0.01 mm (feed speed 4 m/min).

Tab. 01 Density of tested normal and coppice hornbeam wood

Sign.	A type of hornbeam wood (*Carpinus betulus*)	Designation	Average density (kg/m^3)
1.	Normal forest growth of medium height	Habr N Hornbeam N	828.80
2.	Coppice medium-sized forest	Habr V Hornbeam C	806.86

2.2 Testing Methods

The basic mechanical properties of the wood were determined by testing the strength limit in static three-point bending according to the procedure ČSN 49 0115. Wood from normal saplings from a medium-sized hornbeam forest was used as input material. For each measured group, 76 test specimens were produced so that a minimum of 70 valid measurements were always achieved. So a total of 152 test specimens were achieved to achieve 140 valid measurements. For the test of static three-point bending, the test device of the universal test tearing machine type TIRA test 2850 (manufacturer TIRA GmbH, Germany) with feed was used (Fig. 01). The test bodies were placed on the fixtures of the test universal tearing machine according to the diagram in Fig. 01. Finally, the test specimens were loaded with compressive force until the test specimen failed. The highest developed force F_{max} in Newtons (N) was recorded. The feed speed of the tensile testing machine was quoted at 5 mm/min. The results of the specified strength are shown in Fig. 02.

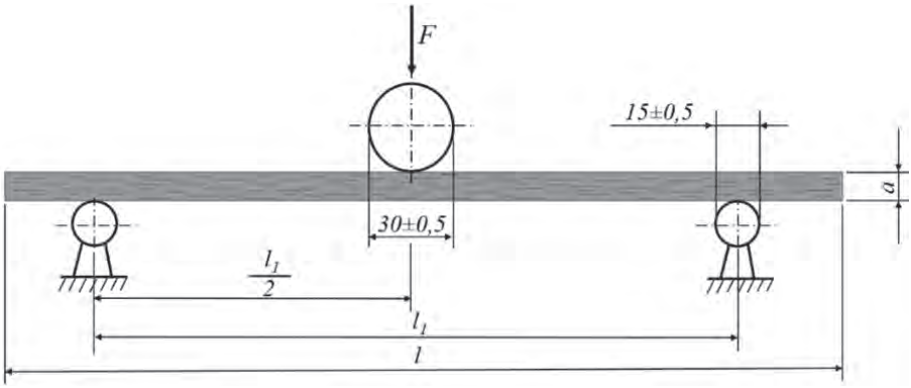

Fig. 01: Scheme of loading test specimens of hornbeam wood.

3. Results

3.1 Expression of results according to ČSN 49 0115

Bending strength perpendicular to the fibers in the radial or tangential direction σ_w is expressed in MPa and calculated according to Eq. [1] (ČSN 49 0115),

$$\sigma_w = \frac{3.F_{max} \cdot l_0}{a \cdot h^2} \quad (1)$$

where F_{max} is the ultimate force (N), l_0 is the distance between the centers of the supports (mm), b is the width and h is the height of the test specimen (mm).

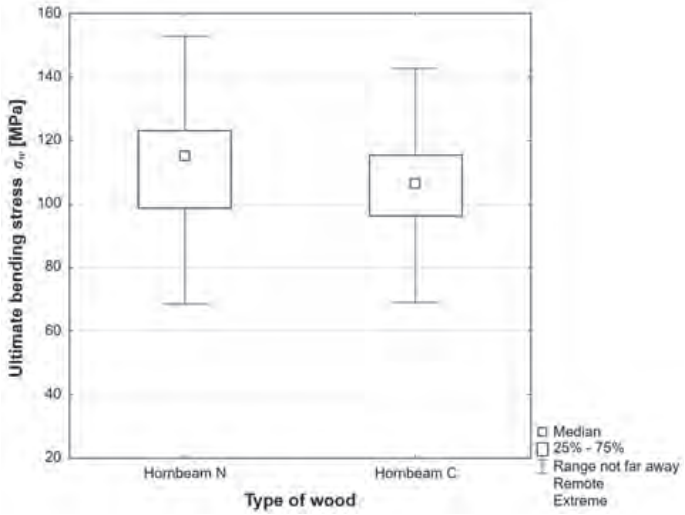

Fig. 02 Bending strength limit perpendicular to the fibers of hornbeam wood of normal and coppice stands

The resulting values of the bending strength perpendicular to the fibers in the radial and/or tangential direction are presented in a box graph (Fig. 02). The results show a difference in the strength limit between hornbeam wood from normal and coppice stands, where hornbeam wood from normal stands has a higher strength limit. However, this difference is not statistically insignificant, only within the margin of statistical error. This hypothesis is also confirmed by the difference in density values (Tab. 01), where hornbeam wood from normal stands has a demonstrably higher density than wood from coppice stands. Research has shown that there is no

statistically significant difference in the mechanical properties of hornbeam wood from normal and sapling stands of low to medium forest. Based on the results of the research, it is possible to support the hypothesis that hornbeam sapwood can be used, as well as wood from normal low to medium forest stands, for structural applications such as the glulam program.

4. Conclusion

The aim of the presented study was to compare selected mechanical properties of hornbeam wood from normal and cutting stands of low to medium forest to determine the potential of its use for non-structural and structural applications. The characteristics of the bending strength perpendicular to the fibers in the radial or tangential direction were compared, where a difference was demonstrated. However, this difference was only within statistical error. When comparing the density characteristics, a statistical difference was demonstrated and the results correspond to the bending strength limit perpendicular to the fibers. The study showed that, according to the selected monitored characteristics, hornbeam wood from the cuttings of low to medium forest has similar properties as from normal stands. The study shows the possibilities of using hornbeam wood from low to medium forest cuttings for interior and exterior structural applications, just as it is the case with hornbeam wood from normal stands.

Acknowledgements

The research was carried out as part of the project entitled "Optimization of core wood surface adhesion to increase the strength of the glued joint", no. A_04_22 of the program of the Internal Grant Agency of the Faculty of Forestry and Wood Sciences, Czech University of Life Sciences Prague.

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The wet spinning process based on cellulose

Mária Petková, Anna Ujhelyiová

Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology,
Institute of Natural and Synthetic Polymers, Department of Plastics, Rubber, and Fibers

Abstract: *Wet spinning is a key technology in the textile and material industry, with modern trends focusing on greener solvents and process optimization. The wet spinning of cellulose remains a classic cellulose fiber production process that also continues to evolve, aiming for greater efficiency, environmental sustainability, and enhanced fiber quality. New trends in cellulose dissolution include Deep eutectic solvents (DES) and ionic liquids, offering more sustainable alternatives to traditional chemicals. Another approach deals with methods of cellulose modification for better dissolution. Solutions with dissolved cellulose are also used in electrospinning processes. Innovative nanotechnologies enable its wider use in various industries. Historically, Slovakia was among the global leaders in cellulose fiber production. Although the fiber industry has been pushed into the background in recent years, the groups of scientists continue to bring a new dimension (innovations) to the field of cellulosic fibers.*

Keywords: *Cellulose, spinning, regeneration, solution*

1. Introduction

Cellulose is a highly molecular substance, a polysaccharide composed of glucose units connected by β-1,4-glycosidic bonds. Cellulose forms the basic structure of higher plants, where it is the building block of plant primary cell walls and, together with lignin, participates in the construction of secondary cell walls. It gives plant cell walls strong structural support and strength. Due to its long chain length and high crystallinity, cellulose has high stability and is insoluble. The chains form a rigid lattice structure through hydrogen bonds and Van der Waals forces. [1,2]

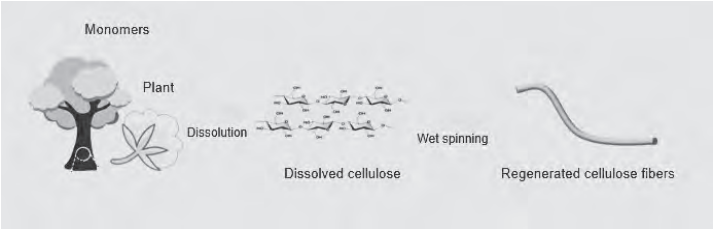

Fig. 1: The parts of preparing cellulose fibers by wet spinning. [3]

The sources of cellulose for distinct processing methods are plants with different cellulose content. Cellulose fibers can be obtained directly from cotton or hemp. Cotton fibers can contain up to 99% cellulose. However, cellulose is also obtained by chemical dissolution when we need to separate the cellulose from other components that make up the plant. Examples of such plants are bamboo and various trees, with around 32-56% cellulose content. The obtained cellulose always has different properties of the obtained polymer fibers and therefore its use is different for various applications. [4,5]

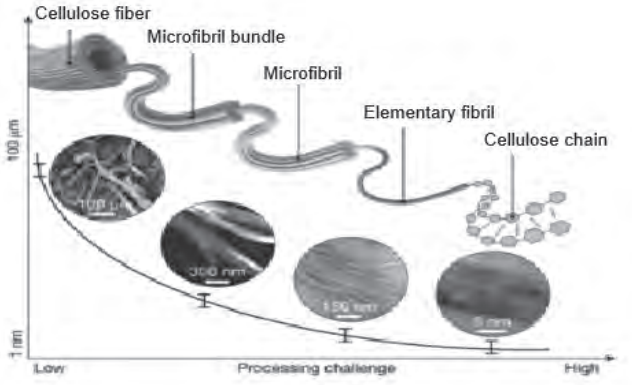

Fig. 2: Cellulose – from plants to polymer chains. [6]

Cellulose was the first natural polymer used to produce textile fibers chemically. Cellulose fibers are prepared either from regenerated cellulose or from cellulose derivatives.

The history of cellulose fibers dates back to 1884 when a successful attempt was to produce fibers from natural polymer based on nitrocellulose. It was invented by Frenchman Hilaire de Chardonnet and is known as Chardonnet's silk. However, this material was highly flammable, which limited its use.

The year 1892 is associated with the development of viscose silk – Rayon. Charles Frederick Cross, Edward Bevan, and Clayton Beadle in England developed a safer method of dissolving cellulose using sodium hydroxide and carbon disulfide (CS_2) to form a viscous solution. This process was industrialized in 1905. The fibers produced in this way are known as viscose fibers or artificial silk. [7]

In the city of Senica in Slovakia, the textile industry has a long history thanks to an important textile company in this region called Slovenský hodváb (Slovak silk), which produced viscose fibers from the 1920s to the 1980s. It played an important role in the Slovak textile industry as a raw material base for chemical fibers from natural polymers. The viscose fiber preparation process has undergone several changes during its almost seventy-year history, but they could not prevent its

termination. Currently, however, production of viscose fibers is no longer carried out in Senica. Changes in the global market, economic factors, and environmental requirements led to the termination of these activities in this region.

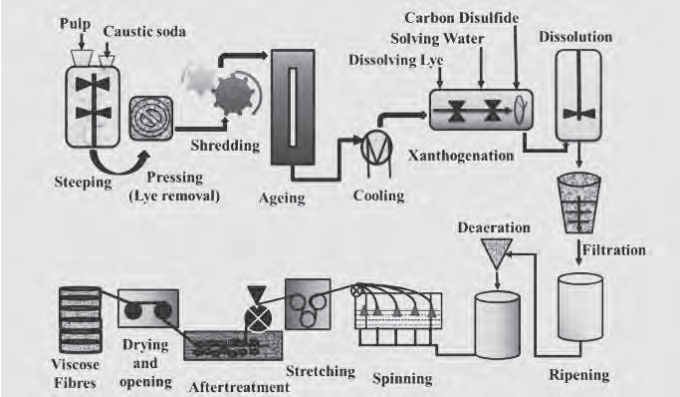

Fig. 3: Preparation of cellulose fibers by the viscose method. [6]

The year 1930 brought a new way of producing fibers from cellulose, namely the production of acetate silk. The steps that preceded the dissolution of cellulose were the acetylation of cellulose with acetic acid and acetic anhydride, where a catalyst was also added. The cellulose diacetate thus prepared was solvable in organic solvents (e.g. acetone). This process allowed the production of other types of cellulose fibers, in a less toxic way than the viscose process. [8]

Research is currently focused on ionic liquids and deep eutectic solvents (DES), which are less toxic and enable more efficient dissolution of cellulose. So it is not a change in the principle of the production process, it is rather a change in the dissolution and preparation of the solution from which cellulose-based fibers are subsequently prepared. The Austrian company Lenzing AG began developing a lyocell process in which cellulose is dissolved in N-methylmorpholine-N-oxide (NMMO). This process was commercialized in the 1990s and is considered environmentally acceptable. Production is still working today. It primarily uses a viscose process to produce its fibers, focusing on sustainability and eco-friendly practices. In addition to viscose, the company has also developed innovative cellulose fibers that are produced using environmentally friendly technologies, thanks to the fact that the solvent is almost completely recyclable, the process produces fewer emissions, and water consumption in the production process is lower. [10]

Deep Eutectic Solvents (DES) are innovative and ecological solvents that find application in various industries. However, their commercial use is still in the initial stages of development and subsequent implementation. [10]

New technologies for the preparation of cellulose-based nanofibers are also being developed, such as the electrostatic spinning of cellulose, the production of

nanocellulose fibers, and hybrid materials. In this case, cellulose solutions prepared using classic solvents or DES-based solvents are used, so it is not a change in cellulose dissolution, but a change in the principle of the fiber production process. The spinning process takes place in a bath with a metal nozzle connected to high voltage (10-50 kV). Electrostatic forces draw the solution into the nozzles, creating extremely thin filaments. After evaporation of the solvent, a solid nanofiber is formed. The fibers are deposited on a metal collector (fixed plate or rotating drum). The resulting cellulose nanofibers can form randomly arranged structures – nonwoven fabrics or infinite fibers wound on a spool. [11]

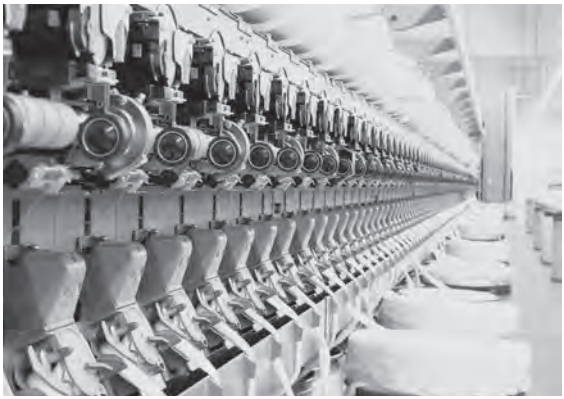

Fig. 4: Textil yarns prepared for textile processing – a portfolio of Lenzing AG. [9]

Cellulose spinning is a process in which cellulose is converted into fibers using chemical and physical processes. This process is important for the production of textile materials, paper, filter membranes, and biomedical products. Cellulose fibers remain an important part of the industry with a growing emphasis on green solutions and innovation.

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Use of waste biomass for paper production

Kateřina Hájková & Josef Bárta

Czech University of Life Sciences Prague, Faculty of Forestry and Wood Sciences, Kamýcká 129, 165 00 Prague – Suchdol, Czech Republic, hajkovakaterina@fld.czu.cz

Abstrakt: *Due to the scarcity of wood in some countries, it is necessary to replace it with other raw materials and, at the same time, use the waste material. This research aims to use waste biomass to convert potential lignocellulosic materials efficiently. Their suitability for the production of composites is assessed based on selected mechanical properties. Tensile and burst indexes have been identified as critical properties of pulp from waste biomass. Better mechanical properties, i.e., tensile strength index, were achieved for poppy straw at 52.7 N·m·g^{-1} for sodium pulp, but the nitrate-alkali method also showed corresponding values of 45.9 N·m·g^{-1}. The results of this research are used to evaluate the waste biomass as an alternative feedstock for the production of biocomposites.*

Kľúčové slová: *Straw; nitrate-alkaline pulp; soda pulp; mechanical properties.*

1. Introduction

Waste management and renewable energy have become key strategies for mitigating environmental damage and optimizing resource use [1;2]. Using lignocellulosic waste to produce valuable products implies a sustainable and environmentally friendly resource potential [3]. The global annual production of lignocellulosic biomass is estimated to be approximately 181.5 billion tonnes [4]. The use of agricultural residues containing lignocellulosic materials as biomass offers advantages. These advantages include abundant availability, renewable resources, and cost-effective production [5]. Due to concerns about deforestation, extensive studies have been conducted investigating alternative non-timber sources for the forest products industry, particularly for producing biocomposites and paper [6]. As a result, many agricultural wastes/wastes and naturally growing annual plants worldwide exhibit chemical and physical properties similar to wood [6]. These include materials such as poppy stalks [7], cotton stalks [8], rice straw [9], sunflower stalks [10], sugarcane waste [9].

Using biomass in paper production makes an important contribution to the conservation of natural resources. There is a growing interest in using alternative raw materials to reduce the ecological footprint and conserve natural resources. The raw materials used in paper production must contain a high cellulose content, a criterion met by lignocellulosic biomass composed of cellulose, hemicellulose, and lignin [11]. Higher cellulose content and lower lignin content in biomass are associated with increased durability of paper [12].

This study investigates the possibility of using waste biomass for papermaking using delignification processes (nitrate-alkali and sodium) with an evaluation of their properties and environmental and economic impacts.

2. Materials and methods

2.1. Materials

The waste biomass (corn, flax, hemp, poppy, and sisal) was grown and harvested in fields in the Czech Republic. The waste material had to disintegrate to a chip length of 1–2 cm to be used for further processing.

2.2. Chemical analysis

Waste material was grounded using an MF 10 BASIC knife mill from IKA (Germany). For chemical analysis, the following methods were performed using Tappi methods: extraction, ash, cellulose, and lignin analysis.

The representation of ash as an inorganic fraction in straw was determined by exposure to 525°C according to the Tappi T211 om-02. Before further chemical analyses, unwanted extractives were removed. Namely, the sample was extracted in a binary mixture of ethanol-toluene for six hours in Soxhlet apparatus according to the Tappi T280 wd-06. Macromolecular substances were determined as cellulose, and lignin. The analysis of cellulose was carried out using the Seifert method. Lignin was determined in the sulphuric acid Klason method according to Tappi T13 wd-74.

2.3. Nitrate-alkaline pulp

In the case of the nitrate-alkaline method, 6 % nitric acid was used as the cooking chemical, which nitrated the lignin in our pulp and partially oxidized it to nitro-lignin, which was removed in the second stage of extraction using 5% sodium hydroxide. These two stages took only 45 minutes, then neutralization with 1% acetic acid and a thorough washing.

2.3. Soda pulp

The chips were placed in a laboratory cooker where the soda cook was run. The cooking chemical used was 19 % sodium hydroxide with a hydromodul of 5:1. The process of soda cooking consisted of four phases. In the first phase, the raw material was cooked to 105°C then impregnated at this temperature for 30 minutes in the second phase. In the third phase, cooking to 160°C followed, and at this temperature, the raw material was cooked to an H-factor of 1250 h. The cooking time was 4 hours. Subsequently, the pulp was stripped of the black liquor by a four-stage

washing process, pulped, separated from rejects, and prepared to produce laboratory handsheets.

2.4. Mechanical properties

The laboratory sheets were produced on a RAPID-KÖTHEN RK-2A laboratory sheeting machine (Germany) with a weight of 80 g·m^{-2} and subsequently conditioned according to standard conditions for testing according to ISO 5269-2.

For both soda and nitrate-alkaline pulp made from waste, laboratory hand sheets were analysed, specifically for tensile properties ISO 1924-2, burst strength according to ISO 2758:2014.

3. Results and discussion

3.1. Chemical analysis

The chemical composition of the plant has a significant effect on fibre properties and pulp yield. Table 1 shows the chemical composition of waste biomass. The chemical composition of each component may vary according to climate, cultivation, plant part, and other aspects, so these values may differ from other publications on waste processing.

Tab. 1: Chemical composition (in mass % of oven dried samples).

Raw	Ash	Extractives	Cellulose	Lignin
Corn	8.4	9.9	47.6	20.1
Flax	2.9	1.5	39.2	25.1
Hemp	3.6	1.3	37.7	24.8
Poppy	1.7	7.5	35.2	22.7
Sisal	1.4	0.2	43.2	19.7

For raw materials, the highest ash content was found for corn, 8.4%, which may be due to the high silicate content of the flesh. Similar values were obtained for sunflowers at 8.2% [10]. The other crops are more straw-like, hence their lower ash content. As regards the amount of cellulose, all crops contain sufficient quantities suitable for paper production.

3.2. Characteristics of pulp

Table 2 shows the pulp characterization variables, Kappa number indicates the amount of pulp cooked, other parameters are the total production yield and the amount of rejects.

Tab. 2: Characteristics of pulp.

Pulp	Nitrate-alkaline pulp			Soda pulp		
	Kappa number	Total yield, %	Amount of rejects, %	Kappa number	Total yield, %	Amount of rejects, %
Corn	22.2	14.1	22.2	45.8	16.9	1.44
Flax	26.6	37.0	26.6	36.8	33.8	1.04
Hemp	27.8	38.8	27.8	33.0	40.2	0.60
Poppy	34.2	37.8	34.2	27.1	40.3	1.03
Sisal	29.8	47.5	29.8	24.7	48.8	0.71

In terms of total yield, corn pulp was the worst. From the Kappa numbers above, although the nitrate-alkaline cook is significantly shorter, it achieves a high degree of delignification and has almost similar results to the industrially used soda cook.

3.3. Mechanical properties

The mechanical properties of the 80 g·m^{-2} paper made from these raw materials are shown in the graphs in Figures 1 and 2.

Figures 1 and 2 show that the pulp made by the soda method from corn is the best behaved, but with this pulp, again, only a minimal yield was achieved. Therefore, poppy stalks are the most suitable raw materials. Although the soda cook achieved better yields for poppy straw, the nitrate-alkaline method did not achieve low values either. Other crops such as hemp, flax, and sisal have very low values for the industrial use of these raw materials for soda pulp production.

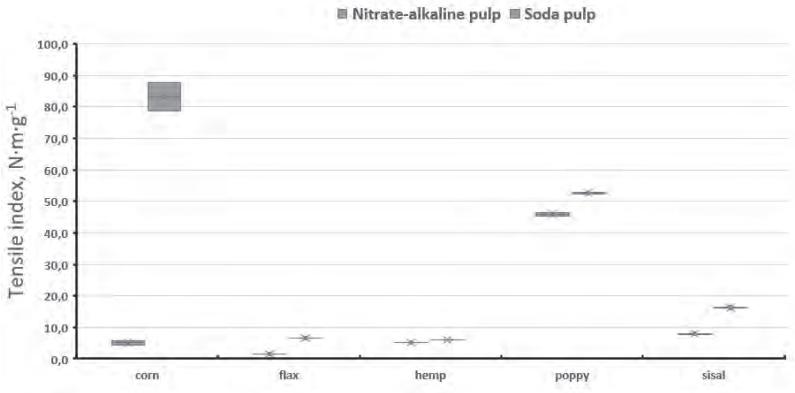

Fig. 1: Tensile index.

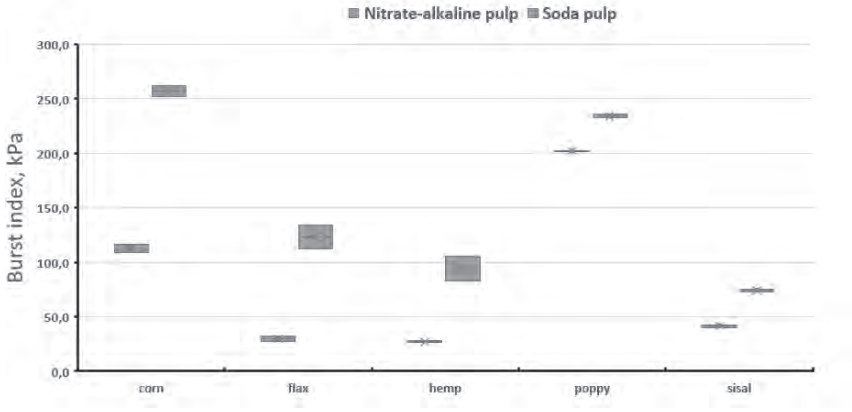

Fig. 2: Burst index.

4. Conclusion

Compared with other raw materials, waste poppy is an alternative for pulp production, mainly because of its mechanical properties. Because poppy pulp outperforms many agrarian residues in tensile strength and burst index. Using poppy straw has environmental benefits such as reducing deforestation and the carbon footprint, which should position poppy straw as a sustainable alternative as demand for renewable materials increases.

Acknowledgement

Thanks to the support of the Department of Wood Processing and Biomaterials at the Faculty of Forestry and Wood Technology.

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Effect of the FeTNa solvent on agricultural residues of wheat, rapeseed, flax and hemp

Josef Bárta, Kateřina Hájková and Adam Sikora

Česká zemědělská univerzita v Praze, Kamýcká 129, 165 00 Praha-Suchdol, bartajosef@fld.czu.cz

Abstrakt: *Effect of FeTNa solvent on agricultural residues of flax, hemp, rapeseed and wheat without chemical separation of the material and its impact on the degree of polymerization. Determination of the chemical composition of the material from agricultural residues. Assessment of liquid properties such as density, surface tension and viscosity and their effect on the possible coating of the resulting pulp particles on paper products. Density, surface tension and viscosity of the solvent increase due to dissolution. By appropriate cleaning and dilution treatments of the solution, adequate properties can be achieved for the application of the material to paper products.*

Keywords: *Cellulose solvent, agricultural residues, liquid properties, degree of polymerization*

1. Introduction

Agricultural residues of flax (*Linum usitatissimum*), hemp (*Cannabis sativa*), oilseed rape (*Brassica napus*) and wheat (*Triticum aestivum*) were used for this research. The utilization of agricultural residues for pulp production has been investigated in a number of studies. The use of wheat, barley and triticale can replace conventional wood pulp in recycled paper up to 30 % of the pulp content [1]. Another study describes the production of bleached pulp from wheat for commercial papermaking with a production rate of 150 t/day [2]. Most research describes the use of agricultural residues for pulp production, as a substitute for conventional wood pulp, or for the production of special paper products with specific properties. The use of these post-harvest residues for the production of nanoparticles has been addressed by a number of studies up to now, as an adequate production method has not yet been found from an ecological and economic point of view. One study produced pulp by cooking with isobutanol and peracetic acid from wheat, flax straw and kenaf. Subsequent acid hydrolysis using 43 % sulfuric acid and a temperature of 60 °C produced nanocellulose particles, which they applied in the pulp and on the surface of the paper and paperboard product to improve physical and mechanical properties [3]. Another study fabricated CNFs (cellulose nanofibrils) from wheat straw using steam explosion, acid and mechanical treatments to produce nanocomposite materials with thermoplastic starch [4]. Another study fabricated CNFs from wheat straw and soybean hulls using alkaline pretreatment, acid hy-

drolysis with hydrogen chloride, and mechanical treatment by crushing after freezing in liquid nitrogen [5]. Another approach by was used chemical pretreatment to remove wax, delignification in acidified sodium chlorite, removal of hemicelluloses by potassium hydroxide in a repetitive process to produce relatively pure cellulose. The cellulose was then hydrolyzed with sulfuric acid and CNC (cellulose nanocrystals) were produced from wood, bamboo and wheat straw using ultrasonication [6]. FeTNa is a complex compound of iron, tartaric acid and sodium in a 1:3:6 molar ratio for a stable mixture. So far, FeTNa solvent has only been used to assess the degree of polymerization of lignocellulosic materials. The dissolution mechanism of cellulose in the FeTNa complex is attributed to the strong interaction of the FeTNa complex with cellulose due to some formation of new bonds between the central iron atom and the free hydroxyl groups at the C2 and C3 positions in the cellulose structure. It is further suggested that these hydroxyl groups replace the tartrate branch molecules at the central iron position of the complex in the FeTNa complex [7].

2. Materials and methodology

2.1. Materials

Agricultural residues of flax, hemp, rapeseed and wheat were used to dissolve the material. These materials were first pre-dried at 60 °C for 12 hours in a MEMMERT dryer (Swabach, Germany).

Then the agricultural residue sample was crushed in a knife mill MF 10 BASIC from IKY (Staufen, Germany) with a 3.0 mesh size screen. The material thus crushed was then sieved into individual fractions, where the fraction 1.50 mm to 3.15 mm was used for chemical analysis. The same size fraction was also used for dissolution in FeTNa solvent.

2.2. Chemical analysis

Prior to chemical analysis, the extractives were removed using a binary mixture of ethanol toluene 7:3 according to Tappi T5 wd-73 standard [8]. The Seifert method was used for the determination of cellulose [9]. Holocellulose was determined according to Wise [10]. Lignin was determined according to Tappi T222 om-11 and inorganic content in ash was determined according to Tappi T211 om-02 [8].

2.3. FeTNa manufacture

The cellulose solvent FeTNa was made from solutions of sodium tartrate, ferric nonhydrate and sodium hydroxide. The produced solution was filtered using S2 frit before use [10].

2.4. Production of nanocellulose solution

The lignocellulosic material deprived of extractives was loaded at 0.01, 0.02, 0.025, 0.04, 0.05 g/L. The weighed material was placed in 30 ml of FeTNa solution in PE containers. Then, a number of glass beads were added such that the degree of space filling was 26 %.

2.5. Determination of the properties of the nanocellulose solution

For the resulting solution, liquid parameters such as dynamic viscosity with Ubbelohde viscometer, density pycnometrically and surface tension stalagnometrically were measured.

The degree of polymerization of nanocellulose was determined according to SCAN 266 CM 15:88 [11] and ISO 5351:2004 [12] standards. The viscosity ratio according to equation (1), from it the specific viscosity (2), reduced viscosity (3) and limiting viscosity number (4) were calculated based on the sample discharge time and the solvent discharge time alone. The average degree of polymerization was calculated according to equation (5) [13].

$$\eta_{rel}=\tau_1/\tau_0, \quad (1)$$

$$\eta_{sp}=n_{rel}-1, \quad (2)$$

$$\eta_{red}=\eta_{sp}/\rho, \quad (3)$$

$$LVN=\lim_{\rho\to 0}\eta_{sp}/\rho, \quad (4)$$

$$DP=193.5\cdot LVN^{1.064}. \quad (5)$$

3. Results and discussion

Tab. 1: Chemical composition of materials.

Material	Ash	Extractives	Cellulose	Lignin	Holocellulose
Wheat	4.33 (0.12)	3.54 (0.01)	42.64 (0.06)	28.49 (0.04)	75.55 (0.10)
Rapeseed	8.70 (0.13)	6.83 (0.00)	39.09 (0.01)	27.72 (0.03)	74.66 (0.10)

The individual tables show the properties of wheat, rapeseed, flax and hemp solutions with different concentrations. In general, for all solutions, the average density and dynamic viscosity of the solution increase with increasing concentration. The increase of dynamic viscosity is due to a production of more particles with lower degree of polymerization that react with each other and increase in these

way dynamic viscotiy. In particular higher dynamic viscosity makes solution harder to apply for surface treatment. On the other hand, lower interfacial tension with higher concentration makes solution easier to absorb when it is applied on the surface of samples.

Tab. 2: Solution properties of wheat.

Material solution	Concentration g/l	Density kg/m^3	Dynamic viscosity Pa*s	Interfacial tension mN/m	Degree of polymerization
Wheat	0.01	1237.84	3.37	72.39	355
	0.02	1233.70	3.53	71.57	290
	0.025	1238.82	4.70	64.80	327
	0.04	1235.30	5.54	52.41	266
	0.05	1239.07	6.37	56.37	252

With this method of nanocellulose production, we suggest either higher concentration of material dissolving above 2 % of material concentration in solution, gels form should be created. These gels could be cleaned in distilled water several times and used for the application of nanocellulose in the pulp directly. With lower concentrations, nanocellulose solution for surface treatment is produced, but so far without cleaning it changes colour of the final product, but increase mechanical and physical properties The surface tension decreases with increasing concentration. The degree of polymerisation decreases with increasing concentration.

Tab. 3: Solution properties of rapeseed.

Material solution	Concentration g/l	Density kg/m^3	Dynamic viscosity Pa*s	Interfacial tension mN/m	Degree of polymerization
Rapeseed	0.01	1235.88	3.17	66.06	263
	0.02	1233.20	3.30	63.88	165
	0.025	1237.18	3.52	58.98	165
	0.04	1234.61	4.10	61.63	156
	0.05	1238.02	4.59	-	153

Tab. 4: Solution properties of flax.

Material solution	Concentration g/l	Density kg/m^3	Dynamic viscosity Pa*s	Interfacial tension mN/m	Degree of polymerization
Flax	0.01	1238.40	3.95	76.22	571
	0.02	1236.35	5.67	65.84	546
	0.025	1239.00	7.12	62.09	569
	0.04	1236.25	10.33	-	487
	0.05	1233.20	11.96	-	432

Tab. 5: Solution properties of hemp.

Material solution	Concentration g/l	Density kg/m^3	Dynamic viscosity Pa*s	Interfacial tension mN/m	Degree of polymerization
Hemp	0.01	1233.70	4.80	79.83	853
	0.02	1239.34	6.79	78.70	675
	0.025	1235.04	10.04	74.71	764
	0.04	1238.79	10.50	68.93	491
	0.05	1236.31	11.25	71.11	412

Acknowledgement

We are grateful to the Faculty of Forestry and Wood Technology, Czech University of Life Sciences in Prague and the Internal Grant Agency for financial support for the research (A_03_24).

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Interakcia celulózy a dreva vo forme štiepok s vodou

Hrčka Richard[1]–Kučerová Viera[2]

[1]Technická univerzita vo Zvolene, Drevárska fakulta, Katedra náuky o dreve, T.G. Masaryka 24, 96001 Zvolen, Slovensko, hrcka@tuzvo.sk
[2]Technická univerzita vo Zvolene, Drevárska fakulta, Katedra chémie a chemických technológií, T.G. Masaryka 24, 96001 Zvolen, Slovensko, viera.kucerova@tuzvo.sk

Abstract: *Water remains in wood even after its processing into chips. The initial moisture content of wood is not the same in all chips, which causes problems in their subsequent processing. The aim of the paper is to point out the assumptions for homogenizing the moisture content of the chips according to the interactions of cellulose and wood in the form of chips with water. The initial moisture content of spruce chips placed in a pile reached values ranging from units to tens of percent. Moisture adjustment is possible up to maximum saturation. Saturation was influenced by wood species and the maximum amount of bound water determined by a value of up to 35 %. Cellulose reached a significantly higher moisture content of 38.9 % in a liquid water environment. The TCI and LOI of cellulose were determined by the FTIR method. For spruce wood, the TCI and LOI parameters reached values of 0.625 and 1.000.*

1. Úvod

Delignifikácia štiepok pri výrobe celulózy je zintenzívnená oproti podobnému procesu, ktorý by sa vyskytoval len vo výrezoch. Intenzifikácia spočíva vo zväčšení povrchu, a teda plochy kontaktu dreva vo forme štiepky a delignifikačného roztoku. Výrez spracovávaný na buničinu sa preto štiepkuje. Štiepka si zachováva intenzívne vlastnosti výrezu po štiepkovaní. Zvýšenú pozornosť si vyžaduje vlhkosť ako miera množstva vody v dreve výrezu a štiepky. Voda je prirodzenou súčasťou dreva. Zvýšený záujem má dve príčiny: 1. Koľko vody je vnášané do reaktora? 2. Ako veľmi je priepustné drevo štiepky pre tekutiny?

Cieľom príspevku je určenie vlhkosti a jej variability v rámci výberového súboru štiepok zo smrekového výrezu, homogenizácia vlhkosti v rámci výberového súboru a určenie maximálneho množstva voľnej a viazanej vody dreva rôznych druhov drevín.

2. Materiál a metodika

Smrekové drevo (*Picea abies,* L.) vo forme výrezov bolo rozštiepkované. Štiepky s takýmto pôvodom sú vlastné a celý proces ich zhotovenia kopíruje podmienky z výroby a praxe. Štiepky získané rozštiepkovaním piliarskeho odpadu z okrajových častí spracovávanej smrekovej guľatiny na prizmy sú piliarske. Rozmery vlastných,

ako aj piliarskych štiepok boli 25 – 30mm × 20 – 25mm × 5mm v smeroch L × R × T. Počet skúmaných štiepok bol 2 × 30.

Telesá pre určenie maximálnych vlhkostí pripadajúcich na vodu voľnú aj viazanú mali tvar kocky o hrane 1 cm v počte 30 kusov pre jednotlivé dreviny: buk (Fagus), smrek (Picea), dub (Quercus), borovica (Pinus), hrab (Carpinus), jedľa (Abies), topoľ (Populus).

Vlhkosť štiepok bola zisťovaná gravimetrickou metódou podľa STN 49 0103. Hmotnosť mokrého dreva m bola vážená v odvažovačke analytickými váhami s presnosťou 1.10^{-3} g. Po vysušení v prostredí sušiarne so suchým vzduchom pri teplote 105 °C bola určená hmotnosť štiepok v absolútne suchom stave m_0. Potom vlhkosť bola vypočítaná podľa vzorca:

$$w = \frac{m - m_0}{m_0} \times 100\,\%$$

Relatívna vlhkosť bola spočítaná z vlhkosti:

$$w_r = \frac{w}{100 + w} \times 100\,\%$$

Sušina je kladný rozdiel 100 % hodnoty a relatívnej vlhkosti.

Vlhkosť získaná drevom po dlhodobom máčaní vo vode, a ktorá pripadá na vodu viazanú w_{Bmax} sa nazýva medza nasýtenia bunkových stien (Babiak & Kúdela 1995). Spolu s vlhkosťou reprezentujúcou vodu voľnú w_{Fmax}, ktorá bola získaná drevom po dlhodobom máčaní vo vode, tvoria maximálnu vlhkosť dreva w_{max}.

Vlhkosť w_{Bmax} je možné určiť meraním hmotnosti dreva váženého v prostredí vody a určení tzv. zdanlivej hmotnosti m_z. Vlhkosť w_{Fmax} je možné určiť meraním hmotnosti m_{vv} telesom vytlačenej vo vode. Potom celková hmotnosť vody v dreve je súčtom hmotností voľnej a viazanej vody. Napokon maximálna vlhkosť je určená súčtom maximálnej vlhkosti pripadajúcej na vodu voľnú a maximálnej vlhkosti pripadajúcej na vodu viazanú (Hrčka a kol. 2020).

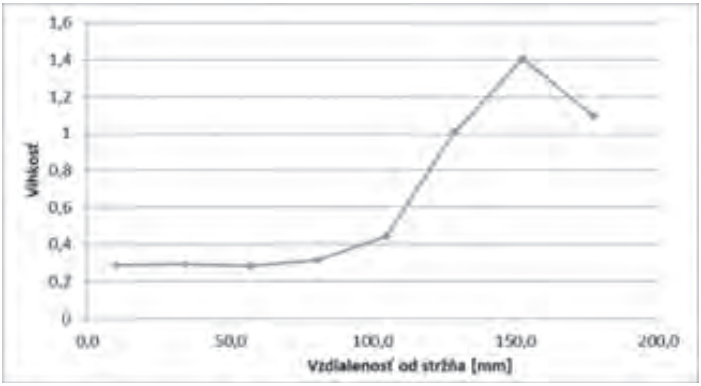
$$w_{max} = \left(\frac{m_w - m_0}{m_0} \right) + \frac{m_z}{m_0} = (w_{F\,max}) + w_{B\,max}$$

Celulóza bola izolovaná zo smrekového dreva podľa Seiferta (1956). Metóda FTIR bola použitá na zistenie celkového indexu kryštalinity (TCI) a indexu laterálneho usporiadania (LOI) celulózy. TCI a LOI bol vypočítaný ako pomer medzi intenzitami pásov, v tomto poradí: 1370/2900 cm^{-1}, 1424/898 cm^{-1} (Poletto a kol. 2014).

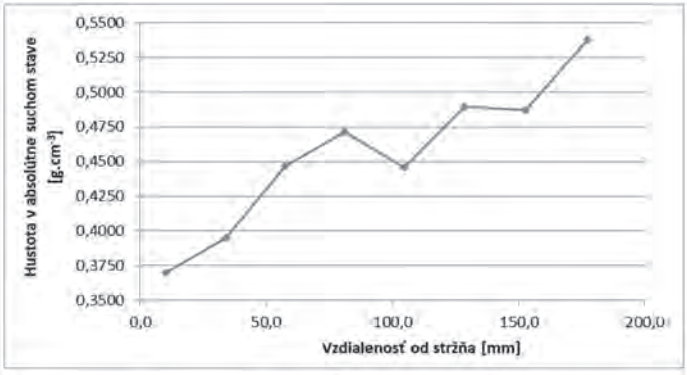
3. Výsledky a diskusia

Vonkajšia beľová časť smrekového výrezu je podstatne vlhkejšia než oblasť zrelého dreva, obr. 1.

Uvedené je spôsobené zväčšeným množstvom vody v oblasti beli a nie zvýšenou hustotou v suchom stave, ktorá je nepriamo úmerná maximálnej hodnote vlhkosti pripadajúcej na vodu voľnú, obr. 2:



Obr. 1: Vlhkosť smrekového výrezu v závislosti od vzdialenosti od stržňa.



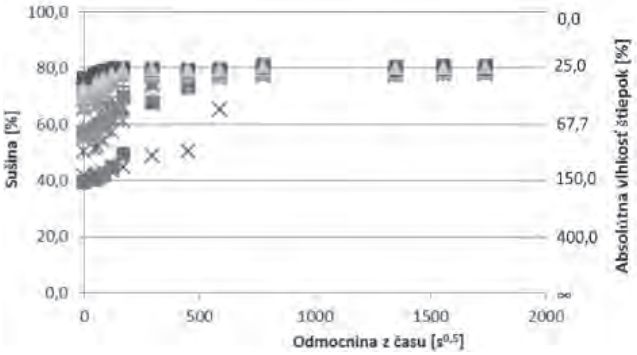
Obr. 2: Hustota v suchom stave smrekového výrezu v závislosti od vzdialenosti od stržňa.

Zvýšená vlhkosť v oblasti beli spôsobuje aj zväčšenú vlhkosť štiepky z tejto časti priečneho rezu kmeňa. Teda piliarska štiepka dosahovala v priemere vyššiu vlhkosť než štiepka vlastná, ktorá bola vymanipulovaná aj z oblasti zrelého dreva.

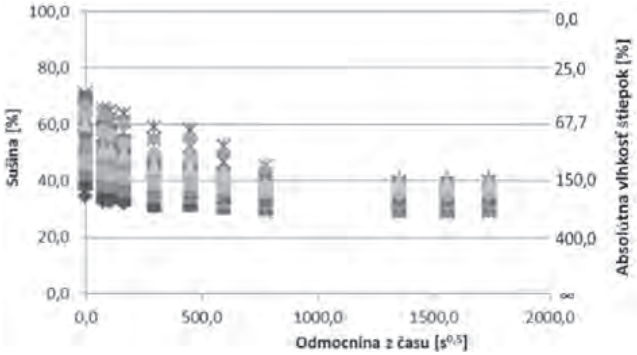
Zníženie rozptylu vlhkosti štiepok si vyžaduje buď:

– sušenie príliš vlhkých štiepok alebo
– vlhčenie suchých štiepok na dohodnutú rovnovážnu vlhkosť.

Sušenie a vlhčenie štiepok znázorňujú obr. 3, 4:



Obr. 3: Zmena sušiny a absolútnej vlhkosti smrekových štiepok pri dosahovaní rovnovážnej vlhkosti sušením od odmocniny času



Obr. 4: Zmena sušiny a absolútnej vlhkosti smrekových štiepok pri dosahovaní rovnovážnej vlhkosti máčaním od odmocniny času

Tab. 1: Maximálne vlhkosti vody viazanej a voľnej pre naše najzastúpenejšie dreviny

	w_{Bmax} [%]	w_{max} [%]	Variačný koeficient w_{max} [%]
smrek	32,7	182	11
jedľa	34,3	221	9,8
borovica	31,5	154	23
buk	34,9	120	7,3
dub	33,5	112	32
topoľ	34,6	238	4,5
hrab	29,2	94,8	7,8

Vlhčenie je možné uskutočniť do maximálnej vlhkosti, ktorá je závislá od spracovávanej dreviny. Tab. 1 obsahuje maximálne vlhkosti pripadajúce na vodu voľnú aj viazanú pre naše najzastúpenejšie dreviny.

Zatiaľ, čo maximálna vlhkosť viazanej vody je pre rôzne dreviny takmer konštantná, maximálne množstvo voľnej vody výrazne závisí od dreviny.

Kryštalinitu celulózy izolovanej zo smrekových štiepok sme zistili metódou FTIR. Na určenie pomerného zastúpenia kryštalických a amorfných oblastí celulózy a jej usporiadania sa používajú indexy kryštalinity. Celkový index kryštalinity (TCI) a index laterálneho usporiadania (LOI) celulózy bol 0,63 a 1,00.

Počet molekúl vody na jednotku glukopyranózy bol 3,5. Celulóza dosahovala hodnotu maximálnej vlhkosti viazanej vody 38,9 % v prostredí kvapalnej vody.

4. Záver

Podstatne väčšiu vlhkosť dosahovala piliarska štiepka vymanipulovaná z obvodu oproti vlastnej štiepky vyrobenej z celého prierezu smrekového výrezu. Homogenizáciu vlhkosti v štiepke je možné dosiahnuť sušením. Potom je potrebné počítať s výslednou rovnovážnou hodnotou pod 35 %. Pri zvlhčovaní štiepok je možné dosiahnuť hodnotu vlhkosti aj nad 35 % až po maximálnu vlhkosť, ktorá je daná vlastnosťami použitej dreviny. Celkový index kryštalinity (TCI) a index laterálneho usporiadania (LOI) celulózy zo smrekovej štiepky bol 0,63 a 1,00.

Poďakovanie

Táto práca vznikla v rámci projektov a finančnej podpory Agentúry na výskum a vývoj na základe zmluvy č. APVV-22-0034 a vedeckej grantovej agentúry Ministerstva školstva, výskumu, vývoja a mládeže SR VEGA 1/0027/24.

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Utilization of Waste Liquors from the Paper Industry for Wood Modification in Engineered Wood Products

Tomáš Holeček

Czech University of Life Sciences Prague, Faculty of Forestry and Wood Sciences,
Kamýcká 129, 165 00 Prague – Suchdol, Czech Republic,
holecekt@fld.czu.cz

Abstract: *Current technological advancements and growing environmental awareness are increasing pressure for recycling and efficient use of industrial waste. Black liquor, a byproduct of pulp production, is a significant example. Many studies focus on its processing, primarily on lignin extraction (which constitutes approximately 30% of the raw material). However, this processing is energy-intensive and chemically demanding, increasing the cost of the final product. Our research focuses on the direct utilization of untreated black liquor to enhance the fire resistance of wood-based building materials.*

Keywords: *Fire resistance, composite material, calorimeter, smoke optical density.*

1.Introduction

Lignin, an abundant biopolymeric waste product from pulp production, represents an attractive and sustainable alternative to fossil fuels. Its versatility allows for a wide range of applications, from antioxidants and surfactants to components of biopolymers and other chemicals (1). However, traditional methods of lignin extraction are energy-intensive and economically unfavorable, hindering its wider use. Therefore, current research focuses on the direct utilization of raw lignin, minimizing demanding processing and reducing the carbon footprint. Examples include fire-retardant coatings and polyurethane-based coatings (2, 3, 5, 6, 7), where lignin replaces conventional fossil-fuel-based materials. This approach further supports the principles of circular economy through the efficient use of industrial waste products. The use of waste streams, such as kraft and sulfite black liquor, for wood impregnation and improvement of its fire resistance represents a step towards a more sustainable and environmentally friendly future in construction.

2. Material and Methods

2.1 Material

This research investigates the utilization of kraft black liquor, a waste byproduct from pulp production, as a natural fire retardant in wood composites. Kraft black liquor, a solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), is effec-

tive in lignin degradation and cellulose fiber separation during pulp production. Its properties, such as high alkaline lignin concentration (29.6 g/L) and specific heat capacity (12.74 MJ/kg dry matter), indicate its potential for modifying the properties of wood materials. The black liquor was supplied by Mondi Štětí, a.s. (Štětí, Czech Republic).

For impregnation, peeled veneers of Scots pine from industrial plywood production were used. The veneers were cut oversized to the required format and layered so that the individual layers were mutually perpendicular. Selected layers were then pressure-impregnated in a pressure chamber under a vacuum of 0.8 bar followed by a pressure of 6 bar, using air as a pressurizing medium above the free surface of the impregnation liquid. After impregnation, the veneers were dried and conditioned to a standard moisture content of 12 %. After conditioning, the veneers were bonded with phenol-formaldehyde adhesive in a heated press at a curing temperature of 130 °C. After curing, the boards were cooled to a laboratory temperature of 20 °C. Test specimens for cone calorimeter measurements (dimensions 100 x 100 x 20 mm) and for smoke optical density measurements (dimensions 75 x 75 x 20 mm) were then prepared from these boards. All samples were placed in a conditioning chamber before testing to stabilize the moisture content at approximately 12 % (Tab. 1).

2.2. Methods

Measurements were performed using a cone calorimeter (CLASIC spol. s.r.o.) according to ISO 5660. The procedure involved placing a precisely defined sample in a chamber where it was exposed to controlled radiation with a known heat flux. The instrument continuously recorded the heat release rate (HRR), total heat released (THR), and mass loss of the sample during combustion. Relevant flammability parameters were calculated from this data, including peak heat release rate, time to peak heat release rate, and the mass average of the heat release rate (MARHE). The results provide a comprehensive characterization of the material's behavior in a fire.

Smoke optical density was determined according to ISO 5660-2. A sample with precisely defined dimensions was placed in a chamber and subjected to controlled combustion. During combustion, the light transmission through the produced smoke was continuously measured, from which the time course of the smoke optical density was calculated. The obtained data provide information on the amount and density of smoke produced during combustion, a key parameter for assessing its fire hazard. Results are typically presented as the dependence of optical density on time and allow quantification of the amount of smoke produced.

Plywoods were manufactured from nine veneer layers with a total thickness of 20 mm. Variants A and B contained impregnated veneers: five layers in variant A and seven layers in variant B, while the outer layers remained unimpregmated. A control sample (Ref) was manufactured from unimpregmated veneers.

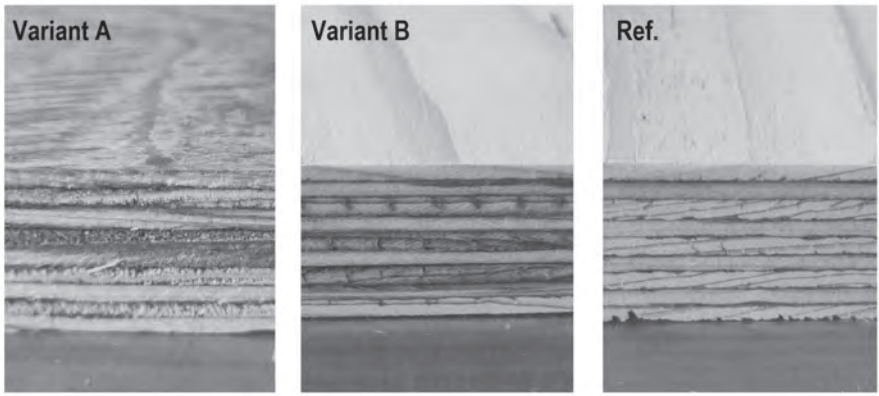

Fig. 1 Modified plywood variants

3. Results

Tab. 1 shows the cone calorimeter test results. The average density of the plywood samples shows only a slight difference, likely due to variations in veneer density. The MARHE (Maximum Average Rate of Heat Emission) parameter, representing the maximum amount of heat released in a given time interval, shows a 10.4 % decrease in variant B compared to the reference sample. Similarly, the total heat released is also lower in variant B, by 13.6%. Other parameters in Tab. 1 provide supplementary information on the material's behavior during the test.

Tab. 1: Cone calorimeter parameters of the composite materials

parameters	variant A	variant B	Ref.
Density in [kg/m^3]	540,3	592,2	629,2
mARHE [kW/m^2]	112,4	103,9	116,0
Calorific value [MJ/kg]	17,1	14,6	16,9
Start of permanent flame [s]	88	80	78
Weight at ignition in [g]	110,4	105,1	103,4
Weight loss rate [g/m^2*s]	4,9	5,2	4,9

Smoke optical density (OD), a key parameter for fire safety, was measured to assess the obscuration of the space during a fire. The rate of obscuration critically affects the speed and success of evacuation. Variant A exhibited the lowest cumu-

lative smoke optical density, which increased over time. As shown in Fig. 2, this variant remained below a value of 100 throughout the test, representing slightly reduced visibility and orientation in the space, thus increasing safety in the event of a fire. In contrast, variant B and the reference sample showed almost identical smoke optical densities. This suggests that for the overall fire development and smoke production, the modification and properties of the top layer of the plywood are most significant.

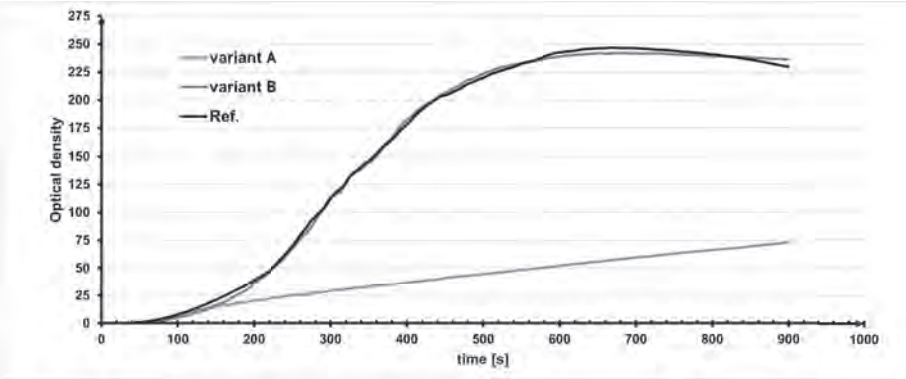

Fig. 2 Time-dependent development of smoke optical density

Figure 3 presents the derivative of smoke optical density (dOD/dt), representing the rate of smoke production as a function of time and providing a more detailed insight into the behavior of the materials when exposed to radiant heat of 20 kW/m^2. Analysis of this derivative reveals differences in the behavior of the individual plywood variants. Variants B and the reference sample show no statistically significant differences in the rate of smoke production, which is due to the identical unimpregmated top layer. After the rupture of the first bonded layer, the rate of smoke production changes temporarily; however, after overcoming this more thermally resistant layer, it increases again until an insulating layer of charred material is formed, which limits further degradation. This phenomenon manifests as a typical acceleration and subsequent deceleration of smoke production. In contrast, variant A, with its impregnated top layer, exhibits a much more homogeneous structure and a smoother smoke production profile without a significant decrease in rate between the wood layer and the adhesive. This indicates a very similar response of both materials to radiant heat. From this perspective, variant A appears to be a much more homogeneous structure.

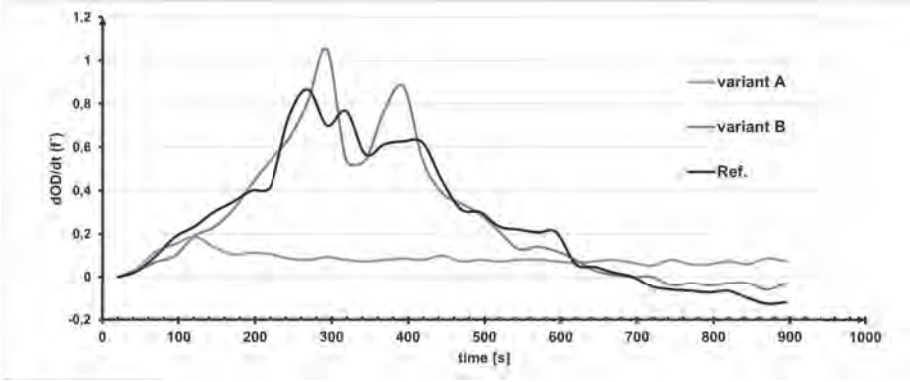

Fig. 3: Rate of smoke optical density development over time

4. Discussion

The cone calorimeter and smoke optical density results demonstrate that kraft black liquor impregnation significantly impacts the fire performance of the resulting plywood. Variant A, with its impregnated top layer, exhibited substantially lower heat release rate (MARHE), total heat released, and smoke optical density compared to both variant B and the reference sample. Variant B, with only internal layers impregnated, showed virtually no difference from the reference sample. This clearly highlights the crucial role of top-layer impregnation in overall fire resistance. Analysis of the smoke optical density derivative (dOD/dt) reveals that variant A displays a more homogeneous response to radiant heat, with no significant changes in smoke production rate between wood layers and adhesive. In contrast, variant B and the reference sample show characteristic changes in rate after the first bonded layer is breached. These differences underscore the importance of top-layer impregnation in reducing smoke production and improving overall fire performance. Further research could focus on optimizing the impregnation process, testing various black liquor concentrations and wood species. Furthermore, spread of flame tests and an assessment of long-term impregnation stability would be beneficial.

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Deep eutectic solvents and their future in the pulp and paper industry

Veronika Majová, Klára Janigová, Ida Skotnicová, Štefan Šutý

Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Department of Wood, Pulp and Paper, Radlinského 9, 812 37 Bratislava, veronika.majova@stuba.sk

Currently, significant attention is being directed toward the development of new eco-friendly solvents in line with the principles of green chemistry. At the beginning of the 21st century, several new types of green solvents were introduced, including deep eutectic solvents (DESs) [1]. These solvents have broad applications in biomass processing and fractionation. DESs are obtained by mixing two or more compounds in a specific molar ratio, where at least one component acts as a hydrogen bond donor (HBD) and another as a hydrogen bond acceptor (HBA). Molecular association occurs through hydrogen bonds and van der Waals forces, resulting in a mixture with a melting point significantly lower than that of its individual components [2]. Research has shown that selected DESs are effective in dissolving primarily lignin and hemicelluloses from lignocellulosic raw materials [3-4].

DESs have great potential for use in the pulp and paper industry as well as in recycling. The application of these solvents to wood chips or annual plants in the pulping or delignification process reduces the energy required for pulp production. From an environmental perspective, DESs are considered eco-friendly solvents due to their biodegradability, recyclability, and reusability.

Most commonly used DESs have a pH below 7 [5]. In recent years, studies have reported the use of alkaline DESs in biomass fractionation. In the study by Lim et al. [6], an alkaline DES based on potassium carbonate and glycerol in a 1:7 molar ratio was used for the pulping process of rice straw. Chemical composition analysis and FTIR analysis confirmed that this alkaline solvent was capable of partially removing hemicelluloses and lignin from the lignocellulosic matrix. Another study [7] utilized two alkaline DESs for lignin extraction from Populus deltoides samples. Specifically, the solvents consisted of a mixture of choline chloride and urea in a 1:2 molar ratio and choline chloride with imidazole in a 3:7 ratio. The reaction was carried out at elevated temperatures (115 and 150 °C) for 15 hours. Both solvents resulted in lignin dissolution and depolymerization.

Oxygen delignification is an essential technology in the production of bleached pulps. It enables the additional removal of 40–50 % of lignin, with the goal of reducing the consumption of chemicals in subsequent bleaching stages. This process leads to partial degradation of the cellulose chain, with a delignification time of 1.5 to 2 hours. Therefore, the aim is to introduce new eco-friendly methods, such as green solvents in combination with oxygen. It is expected that the synergistic effect of solvents and oxygen will enhance lignin removal from pulp/fibers. The

application of this post-delignification stage should increase delignification efficiency by more than 50% while preventing cellulose chain degradation.

Acknowledgement

This work was supported by the call for doctoral students and young researchers of Slovak University of Technology in Bratislava to start a research career (Grant 23-04-04-B). This work was supported by the Slovak Research and Development Agency under the contracts Nos. APVV-22-0277, APVV-22-0388, and VEGA Grant 1/0651/23.

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By-products from the wood-processing industry as a source of added-value compounds

Martin Štosel [a], Aleš Ház [a], Mária Stašová [a], Tetiana Krokhmalna [a]

[a] Slovak University of Technology, Institute of Natural and Synthetic Polymers, Department of Wood, Pulp, and Paper, Rdlinskeho 9, Bratislava, Slovakia, martin.stosel@stuba.sk

The wood processing industry is a major producer of by-products generated during the processing of lignocellulosic biomass [1]. One of the primary by-products of this industry is tree bark, which accounts for approximately 5–25 % of the total weight of trees. During wood processing, the bark is commonly incinerated for energy production [2].

However, several studies have demonstrated that tree bark contains significant amounts of secondary metabolites, including phenolic compounds. These substances play a protective role in plants against fungal, viral, and bacterial infections, as well as protection against UV radiation. The bioactive properties of phenolic compounds have been successfully utilized in human medicine due to their antibacterial, antiviral, and antifungal effects, as well as their demonstrated neuroprotective, anticancer, and cardioprotective activities. Therefore, tree bark remains a subject of scientific interest [3].

The primary objective of this study is to explore alternative extraction techniques that align with the principles of green chemistry and to optimize these methods to maximize both total extraction yield and the recovery of target compounds, such as catechin, quercetin, taxifolin, and resveratrol. For selective extractions, deep eutectic solvents (DES) based on choline chloride and carbohydrates were employed in moral ratios of 1:1 (1,5), 1:3, 1:5. A two-factor, five-level experimental design was applied to bark samples of silver fir (Abies alba) and European beech (Fagus sylvatica). The extraction parameters of our design of experiment (DoE) were extraction time (60–180 minutes) and temperature (30–100 °C). The results of these experiments will be statistically evaluated to determine the optimal extraction conditions for the studied bark samples.

Kľúčové slová: *Extraction, DES, bark, wood-processing industry, by-products, phenolic compounds*

Acknowledgments

This publication was supported by the Slovak Research and Development Agency under contract No. APVV-22-0388 and VEGA 1/0743/24. Furthermore, this publication was supported by the project Extraction of natural substances with added value from different types of biomasses (Grant STU Bratislava for young researchers).

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Changes in paper properties and structure due to aging

Soňa Malečková[a*], Eva Guzikiewiczová[a], Katarína Vizárová[a], Milan Králik[b], František Kačík[c]

a Slovak University of Technology, Faculty of Chemical and Food Technology, Institute of Natural and Synthetic Polymers, Department of Wood, Pulp and Paper, Radlinského 9, Bratislava SK-812 37, Slovakia;
b: Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Institute of Organic Chemistry, Catalysis and Petrochemistry, Department of Organic Technology, Catalysis and Petroleum Chemistry, Radlinského 9, Bratislava SK-812 37, Slovakia;,
cTechnical University in Zvolen, Faculty of Wood Sciences and Technology, Department of Chemistry and Chemical Technologies, T G. Masaryka 24, Zvolen SK-960 53, Slovakia
sona.maleckova@stuba.sk

A significant part of traditional information carriers (books and archival documents) is precisely on acidic paper, which is more easily degraded [1, 2, 3]. The effort to stabilize it and extend its lifespan is the subject of extensive research [3, 4, 5, 6]. The fundamental prerequisite for the successful extension of acidic paper's lifespan is to understand the changes caused by ageing and to look for more effective methods of protection/deacidification [5, 6, 7, 8].

The aim of the study was to observe the impact of paper structure and its chemical composition due to ageing. Four types of paper were selected: two model acidic papers (with the presence and absence of lignin), a real book (published in 1953), and Whatman paper (pure α-cellulose). The paper samples were subjected to accelerated ageing in a sealed environment at a temperature of (98±2)°C according to the ASTM98-02 standard for 10 days. The following properties were tested: chemical (molecular weight distribution via GPC, surface pH), mechanical (folding endurance, zero-span), and spectral (XRD –crystallinity index of cellulose). Additionally, the relationship of the paper to water was monitored using absorption isotherms and contact angle measurements.

Changes in cellulose structure occur across structural levels. The chemical composition of the fibres changes, affecting the mechanical properties of the paper itself. The paper's relationship to water is very important in paper production, processing of the final product, and long-term preservation–in maintaining its functional properties.

Keywords: *cellulose, structure, aging, alum sizing, water, MWD*

Acknowledgment

This work was supported by the Slovak Research and Development Agency under Contract no. APVV-18-0155 and APVV-22-0277.

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Innovations for Improving the Elastic Properties of Paper: Mechanical and Chemical Modifications

Ida Skotnicová[1], Štefan Šutý[1], Lota Chrvalová[1], Juraj Krišta[2], Kristína Kyseľová[1]

[1]Department of Wood, Pulp and Paper, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia
[2]Pulp and Paper Research Institute, JSC, Dúbravská cesta 14, 84104 Bratislava 4, Slovakia
ida.skotnicova@stuba.sk

Abstract: *The enhancement of the elastic properties of paper is an important area of research, especially given the growing demand for materials that combine flexibility, strength and sustainability. This study presents research on mechanical and chemical modifications to improve elasticity of paper. Mechanical treatments, particularly microcreping, were investigated, showing potential in increasing the paper's elongation capacity without significantly compromising its structural integrity [1, 2, 3, 4]. In addition to mechanical modifications, chemical treatments were also investigated, including the use of a dispersion of Duvilax in combination with the cationic polyelectrolyte Magnafloc, polyvinyl acetate (PVAC) and the cellulose-based additive DuraPulp [1, 2, 4. 5]. These additives were tested at various concentrations, showing improvements in the strength properties of the paper, while their effect on elasticity was observed to vary. Specifically, the addition of DuraPulp and PVAC demonstrated some enhancement in the paper's elongation, although the improvements were less pronounced compared to the mechanical modifications [1, 2, 5]. Furthermore, the study also explores the role of pulp refining, with preliminary results suggesting that higher degrees of refining can lead to increased elongation properties. These partial findings lay the groundwork for future research into the mechanisms influencing paper elasticity [4, 6]. The insights gained will help guide further research to develop more effective methods for improving the elastic properties of paper, expanding its potential for a variety of applications.*

Keywords: *elastic properties; elongation; mechanical modification; chemical additives; modification in papermaking*

Acknowledgement

This work was supported by the Research and Development Agency under contract APVV-22-0277 and project VEGA 1/0651/23.

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WPP PA

Wood, Pulp and Paper Polygrafia Academica 2025

Posterová sekcia/Poster section

Corn kernel fiber–alternative source of fiber added to pulp in production of wrapping paper

Andrej Pažitný[a,*], Juraj Krišta[a], Vladimír Ihnát[b]

aPulp and Paper Research Institute, JSC, Dúbravská cesta 14, 84104 Bratislava 4, Slovak Republic, bSlovak Forest Products Research Institute, Dúbravská cesta 14, 84104 Bratislava 4, Slovak Republic,*pazitny@vupc.sk

Abstract: *Nova-Institute study published with CEPI in 2023 shows an increasing interest in paper and paper products made out of non-wood fiber, sourced from the agricultural and textile sectors. Perspective alternative of wood fiber is corn kernel fiber which is the shell or bran around each corn grain, and it is mainly composed of cellulose. Our analysis confirmed that holocellulose content in corn kernel fiber is about 60 % and this type of waste as a by-product of starch production based on corn has an average dry matter content of 46%. This work deals with the selected type of treatment of corn kernel fiber combined with wood pulp–beating. The mixture of corn threshes based on corn grain and softwood pulp was beaten and the effect of addition of corn kernel fiber from corn threshes to coniferous pulp on WRV (Water Retention Value) and °SR (Schopper-Riegler degree) was investigated. The suitability of corn threshes for papermaking was confirmed and the corn kernel fiber is also potentially suitable for board production.*

Keywords: *Beating, corn kernel fiber, holocellulose, °SR (Schopper-Riegler degree), softwood pulp, WRV (Water Retention Value).*

1. Introduction

Corn bran is a by-product of dry – or wet-milling in corn kernel processing [1]. Corn bran mainly comes from the pericarp, which is another by-product derived from the production of corn starch [2]. Dry-milling process involves milling of clean, tempered grain (moisture content of 200 $g.kg^{-1}$) to separate its components: endosperm, germ and bran [3, 4]. The major products of dry milling are corn grits, meals and flour. Wet-milling of corn kernel involves firstly steeping of grains in water and sulphur dioxide. During this process the moisture content increases to about 450 $g.kg^{-1}$ and grains are softened to facilitate separation of the components: starch, gluten, fiber and germ [4, 5]. Both corn bran and corn fiber are mainly composed of the pericarp, however, corn fiber also contains cell wall material from the endosperm, which is not contained in corn bran [6]. The aim of this work was to determine chemical composition of the corn threshes and corn fiber based on corn bran to compare it with kraft pulp and to determine suitability of obtained materials for production of wrapping paper by WRV monitoring.

2. Materials and methods

Corn threshes and corn fiber were obtained from Tate & Lyle Boleraz, Ltd. (Slovak Republic). Non-bleached coniferous kraft pulp was obtained from Mondi Štetí, JSC (Czech Republic). International standards such as ISO 1762, T 264 cm-07, T 222 om-98, Tappi UM 250, Wise's method and ISO 692 were used. Extractives were determined by the extraction method with dichloromethane according to ISO 624. When determining the Klason lignin content, this content was corrected for the ash content. Lignin soluble in sulfuric acid as well as total lignin was determined. The content of holocellulose–cellulose and hemicelluloses, and cellulose itself was determined. Finally, the ash content was also determined.

The beating of pulp suspensions was performed in laboratory beater Valley holander according to the ISO 5264-1. Samples of pulp were taken at period of 0, 20, 40 and 60 minutes. The Schopper-Riegler (°SR) values of the pulp samples were measured according to the STN ISO 5267-1. The water retention value (WRV) was determined according to the ISO 23714:2007. Five types of pulp suspensions were beaten as follows: corn threshes and coniferous pulp in ratio of 75:25 (M1) and 25:75 (M2), corn fiber and coniferous pulp in ratio of 75:25 (M3) and 25:75 (M4) at dry mass weight of components. The kraft pulp was also beaten without additional pulp based on corn kernel (M5).

3. Results and discussion

Chemical composition of corn fiber, corn threshes and coniferous kraft pulp (Fig. 1) is shown in Tab. 1.

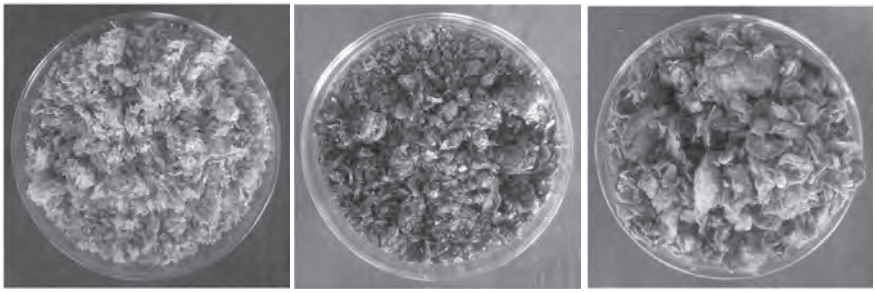

Fig. 1: Corn fiber, corn threshes and coniferous kraft pulp.

Tab. 1: Chemical composition of corn fiber, corn threshes and coniferous kraft pulp.

Component	Proportion of analyzed components (% w/w o.d.)			Method
	Corn Fiber	Corn threshes	Kraft pulp	
Ash	1.67	7.10	0.25	ISO 1762
Extractives	2.91	1.56	2.70	ISO 624
*Klason lignin	6.84	4.00	27.17	Tappi T 222 om-98
Acid soluble lignin (ASL)	8.54	8.80	0.19	Tappi UM 250
Total lignin	15.38	12.80	27.36	-
Holocellulose	60.10	43.10	69.69	Wise
Cellulose	19.90	13.40	41.90	ISO 692

*Klason lignin content was corrected for the ash content.

The holocellulose content in corn fiber (60.10 %) is comparable to that in kraft pulp (69.69 %). In case of corn threshes holocellulose content (43.10 %) is approximately 1.6-times lower than that in kraft pulp. The cellulose proportion in corn fiber (19.90 %) is half that of kraft pulp (41.90 %). The lowest proportion of cellulose is determined in corn threshes (13.40 %). The total lignin in kraft pulp (27.36 %) is approximately half that of corn fiber (15.38 %) and corn threshes (12.80 %). Corn fiber contains ash consisting of inorganic compounds, at a rate almost seven times higher than that of kraft pulp. In case of corn threshes the ash content is about twenty-eight t higher than that in kraft pulp. The extractives content is slightly higher in case of corn fiber (2.91 %) compared to kraft pulp (2.70 %), the lowest content of extractives is in case of corn threshes (1.56 %).

The WRV value was calculated according to formula (1):

$$WRV = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100\ \% \tag{1}$$

where: *WRV*–Water Retention Value [%],
m_{wet}–mass of moist/wet sample of lignocellulosic material [g],
m_{dry}–mass of oven-dried sample of lignocellulosic material [g].

As shown in Tab. 2 the °SR and WRV values rise with increasing beating period. It can be concluded from the results that there is no significant difference in °SR values at time of beating 0 minutes except of M1 beating. It is evident that the initial °SR values for M2 (13 °SR), M4 (11 °SR) and M5 (12 °SR) beatings are more

balanced. The required °SR value ranging from 22 °SR to 38 °SR for terminal beating is achieved in period of 40 minutes. In this checkpoint WRVs for M2 (174.7 %), M3 (171.3 %), M4 (172.3 %) and M5 (171.2 %) are comparable and consistent with our previous findings [7].

Tab. 2: Schopper-Riegler (°SR) and WRV values for pulp types depending on beating period. WRV values are average of 4 measurements.

Sample	Beating period (minutes)	°SR	WRV (%)	Standard deviation of WRV (%)
0/M1	0	21	140.3	1.10
20/M1	20	31	160.6	5.22
40/M1	40	63	168.0	2.31
60/M1	60	77	180.4	1.21
0/M2	0	13	136.0	1.07
20/M2	20	17	157.5	1.65
40/M2	40	23	174.7	1.31
60/M2	60	37	186.1	1.57
0/M3	0	16	151.6	2.12
20/M3	20	23	163.3	1.17
40/M3	40	38	171.3	0.97
60/M3	60	60	178.7	0.29
0/M4	0	11	140.4	0.64
20/M4	20	15	158.8	1.17
40/M4	40	29	172.3	3.48
60/M4	60	39	184.2	5.97
0/M5	0	12	140.6	4.65
20/M5	20	19	160.0	4.18
40/M5	40	22	171.2	0.77
60/M5	60	29	182.7	1.74

As the resulting °SR and WRV values generally suggest, the combination of beaten corn fiber as a by-product of starch and non-bleached coniferous kraft pulp is, from this point of view, suitable for wrapping paper production, as the obtained suspension has similar properties to OCC (Old Corrugated Containers) after pulping into suspension [8]. Obtained lignocellulosic materials converted into suspension are therefore suitable for wrapping paper production and in production of packaging materials. However, studies need to be conducted in the future for the

combination of OCC and corn kernel fiber, the suspension of which will be potentially suitable for production of special wrapping papers based on secondary fiber and waste material.

4. Conclusions

Non-woody material, based on agricultural post-harvest residues, shrubs, or other lignocellulosic materials, is a suitable raw material for the paper industry. Waste from processing of corn grain into starch is also an alternative to wood pulp. Corn fiber and corn threshes are by-products from such processing. The holocellulose content in corn fiber (60.10 %) is comparable to that in kraft pulp (69.69 %). In case of corn threshes holocellulose content (43.10 %) is approximately 1.6-times lower than that in kraft pulp. The total lignin in kraft pulp (27.36 %) is approximately half that of corn fiber (15.38 %) and corn threshes (12.80 %). The impact of beating on suspension of corn fiber and corn threshes combined with kraft pulp was characterized by °SR and WRV values. Both values show rising trend with increasing beating period. With a holocellulose content of about 60 %, corn fiber is a prospective alternative to wood-based pulp and a suitable material for wrapping paper production due its analogical properties with OCC susupension based on determination of °SR and WRV and their comparation with professional literature.

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-23-0651.

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Stabilization of colour layers with verdigris pigment on paper carriers

Dominika Rudinská, Izabela Lukačovič Vajová

Department of Wood, Pulp and Paper, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia
dominika.rudinska@stuba.sk

Abstract: *Verdigris refers to a group of green and blue copper-based pigments that have been widely used throughout various historical periods to adorn and enhance artworks. However, over time, these pigments pose a significant risk to the stability of the paper substrates they are applied to, due to the release of mobile copper ions during the ageing process. These ions can accelerate degradation, threatening both the integrity of the pigment and the paper. Methods of chemical stabilisation offer promising solutions for preserving not only the verdigris pigments themselves but also the underlying paper materials. The model system, which was prepared, was subjected to accelerated ageing and stabilisation processes. Three different stabilizers –1H-benzotriazol, tetrabutylammonium bromide, and calcium phytate – one modifier, sodium hypochlorite, and water which are commonly used in the conservation of verdigris pigment or paper, were tested for their effectiveness in preserving the materials. This research aims to contribute to the understanding of how stabilisers and modifiers influence the paper substrate, providing valuable information for the conservation and long-term preservation of artworks.*

Keywords: *stabilization; verdigris; paper; accelerated ageing*

Acknowledgement

This work was supported by the Research and Development Agency under contract APVV-20-0410, by the project StabPaV: The effect of stabilizers and modifiers on the paper backing in connection with verdigris pigment (Grant STU for young scientist) and by project Identification of materials in cultural heritage collections based on synthetic plastics through their characteristic "fingerprints" (Grant scheme to support excellent teams of young researchers).

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Emission of VOC from wood-rubber particleboards

Tatiana Bubeníková, Iveta Čabalová, Anna Darabošová

Technical University in Zvolen, Faculty of Wood Sciences and Technology, Department of Chemistry and Chemical Technologies, T. G. Masaryka 24, 960 01 Zvolen;
email: bubenikova@tuzvo.sk, cabalova@tuzvo.sk, xdarabosova@is.tuzvo.sk,

Abstract: *Newly prepared composite materials should not endanger the hygiene, health and safety of workers, residents or the environment during their life cycle. For a comprehensive view of the properties of newly prepared single-layer particle boards, VOCs emitted from particle boards (PB) containing waste rubber (GWR) from scrapped cars were therefore analyzed using the HS-GC-MS method. Particle boards (PB) were prepared from spruce wood particles (0.25 mm to 4.0 mm) and granulate (1.0–3.0 mm) from a mixture of waste rubber (carpet, insulators) was used as an additive. The GWR granulate consists of a mixture of processed materials polyester, glass fibers, polyurethane, paper and EPDM (ethylene propylene diene monomer). For the molding of single-layer PB with the addition of GWR, a commercially available UF resin Kronores CB 1100 F was used. 4 tests were performed at different temperatures. In the first test, VOCs emitted from prepared PBs with different GWR contents were analyzed at 30 °C (a temperature that is common in summer and inside buildings). In further tests, at temperatures of 60 °C, 80 °C and 100 °C (temperatures that materials reach e.g. in the summer season or in the initial stages of a fire, when the material is just heating up and thermal degradation begins). For comparison, VOCs emitted from particle boards without the addition of GWR as well as the granulate itself were also analyzed. The analyses of VOC (Volatile Organic Compounds) were performed on an Agilent 7890A GC / 5975C MSD system with an Agilent Headspace Autosampler 7697A. The VOCs were identified by comparing the measured spectra with the NIST20 mass spectra library. At 30 °C and 60 °C, no VOCs were identified that would be released either from the particleboard itself or from PB with different GWR contents. No VOCs were emitted from the GWR granulate itself even at 80 °C, and at 100 °C, only α-pinene was emitted from GWR. Toluene, α-pinene, β-pinene and 3-carene were released from PB without GWR addition at 80 °C. At 100°C, other volatile terpenes and also hexanal were emitted. α-Pinene was dominant, accounting for up to 79 % of VOC emissions from PB. In composite materials with 10 %, 15 % and 20 % GWR content at 80 °C, except for α-pinene, no other volatile organic compounds were identified in the emissions. VOC analysis at 100 °C indicates an 85 % decrease in the total VOC emissions in the sample with 20 % GWR addition. Sorption of the released α-pinene and other VOCs by the GWR granulate is likely to occur.*

Keywords: *VOC, particleboard, spruce wood, recycling, rubber*

Acknowledgments

This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-22-0034 and by the Ministry of Education, Research, Development and Youth of the Slovak Republic under the Contract no. VEGA 1/0027/24.

Wood-rubber/wood-plastic particleboards, evaluation of its mechanical properties

Iveta Čabalová[1], Jozef Krilek[2], Anna Darabošová[1], Tatiana Bubeníková[1], Vladimír Mancel[2]

[1]Technical University in Zvolen, Faculty of Wood Sciences and Technology, Department of Chemistry and Chemical Technologies, T. G. Masaryka 24, 960 01 Zvolen; email: cabalova@tuzvo.sk, xdarabosova@is.tuzvo.sk, bubenikova@tuzvo.sk

[2]Technical University in Zvolen, Faculty of Technology, Department of Environmental and Forestry Machinery, Študentská 26, 960 01 Zvolen, Slovakia; email: krilek@tuzvo.sk, xmancel@is.tuzvo.sk

Abstract: *Wood-plastic composites are wood products made from recycled plastic and small wood particles. They are relatively new products compared to the long history of natural lumber or traditional wood composites such as particleboard or fiberboard. The aim of this work was to assess the influence of plastic/rubber filler (waste from the automotive and construction industries) on the mechanical and physical properties of particleboards (PBs). Plastic (painted - PBu, unpainted bumpers - UPBu, fuel tanks – FT) and rubber (tires – T, gasket and carpet mixture – GC, non-flammable – NFBC, flammable building cables - FBC) particles, at a volume of 10 %, were added to the middle layer of a three-layer particleboard made from spruce wood particles. From the mechanical properties, density, tensile strength (TS), modulus of rupture (MOR) and modulus of elasticity (MOE) were monitored according to applicable standards. Based on the results, density of PBs ranged from 0.69 g.cm-3 for PBs containing GC to 0.74 g.cm-3 for PBs containing NFBC. The higher value of TS (0.52 MPa) was obtained for PBs without plastic/rubber filler, comparable value (0.49 MPa) for PBs containing UPBu and other PBs had lower values of this characteristic. All PBs achieved the results for TS specified by the standard EN 319/2005. From point of view of MOR, all PBs reached comparable results ranged from 10.50 MPa to 12.63 MPa. The same could be state for MOE, values ranged from 2010 MPa to 2240 MPa. It can be state that PBs containing plastic/rubber filler reached very good results of mechanical properties and can be used in the construction or furniture industry.*

Keywords: *spruce wood, particleboard, recycling, plastic, rubber, tensile strength, modulus of rupture, modulus of elasticity*

Acknowledgments:

This work was supported by the Slovak Research and Development Agency under the Contract no. APVV-22-0034 and by the Ministry of Education, Research, Development and Youth of the Slovak Republic under the Contract no. VEGA 1/0027/24.

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Alternativní zdroje buničinových vláken pro přípravu nových papírenských materiálů

Michaela Filipi[1], Ida Skotnicová[2], Kateřina Hájková[3]

[1]Univerzita Pardubice, Fakulta chemicko-technologická, Ústav chemie a technologie makromolekulárních látek, Studentská 95, 532 10 Pardubice, Česká republika
[2]Slovenská technická univerzita v Bratislave, Fakulta chemickej a potravinárskej technológie, Ústav prírodných a syntetických polymérov, Katedra dreva, celulózy a papiera, Radlinského 9, 812 37 Bratislava, Slovensko
[3]Česká zemědělská univerzita v Praze, Fakulta lesnická a dřevařská, Katedra zpracování dřeva a biomateriálů, Laboratoř zpracování biomateriálů, Kamýcká 129, 165 00 Praha 6–Suchdol, Česká republika
michaela.filipi@upce.cz

Abstrakt: *In papermaking, every fiber is important. Today, the starting material for the cellulose pulp production of paper is various types of fibrous plant material. These are obtained from softwood and hardwood trees, as well as from other plants such as flax, bamboo and cotton, etc. Wood is currently the main source for the production of cellulose fibres used for papermaking. In practice, the paper industry consumes just over 10 % of the harvested wood. Non-wood fibre sources represent around 5-10 % of global pulp production, for a variety of reasons including seasonal availability and chemical recovery problems. Alternative sources of fibre for the preparation of paper materials are increasingly being explored and used to make the best and most efficient use of renewable resources. Recently, there has been an increasing focus on making the best use of agricultural waste. This paper deals with the use of wheat and barley straw for the preparation of paper material by the soda process and a comparison of its properties with conventionally produced papers. Pulp made from wheat and flax straw has half the ecological footprint of pulp made from forests.*

Klíčová slova: *Buničina, jednoleté rostliny, mechanické vlastnosti, elasticita*

1. Úvod

Jednoleté rostliny neboli jednoletky jsou označovány jako rostliny, u kterých jejich životní cyklus proběhne během jednoho roku. Mezi jednoletky řadíme rostliny, které nepřečkávají zimu, ať již celé rostliny, jejich semena nebo výtrusy. V teplejších podnebích, výjimečně v našem klimatickém pásmu mohou jednoleté rostliny vytrvat do dalšího roku. V České republice mezi nejznámější jednoleté rostliny řadíme převážně obilí, len, či konopí a rostliny s velmi krátkou vegetační dobou jako je agáve sisalové [1]. Příspěvek se zaměřuje na zpracování zemědělských odpadů, mezi které patří nejčastěji sláma, natě, znehodnocená krmiva, listí ovocných dřevin, nadzemní hmota plodin jako jsou jeteloviny, luskoviny, olejniny a byliny [2].

2. Experimentální část

2.1. Laboratorní příprava buničiny z ječmene a pšenice

Sláma z ječmene a pšenice dodané Farmou Třebešov byla zpracována v laboratorním vařáku typu VŠ-01/84 (výrobce VÚPC Bratislava). Před várkou bylo nutné stanovit vlhkost vzorku slámy. Při stanovení bylo postupováno podle normy Tappi T 210 cm – 03 [3].
Sušina vzorku vyjádřená hmotnostním zlomkem v rovnici (1)

$$x_S = \frac{m_{od}}{m_{ad}} \tag{1}$$

pro vlhkost vzorku vyjádřenou jako absolutní hmotnostní zlomek vody uvedené v rovnici (2), bude platit, že

$$x_w = 1 - x_S \tag{2}$$

Před vlastní várkou bylo také stanoveno chemické složení slámy ječmene a pšenice, viz tabulka 1.

Tab. 1: Chemické složení slámy

Surovina		Popel	Extraktivní látky (ethanol-toluen)	Celulóza	Lignin	Holocelulóza
Pšenice	průměr	4,33	3,54	42,64	28,49	75,55
	směr. odch.	0,12	0,01	0,06	0,04	0,10
Ječmen	průměr	6,09	2,25	40,77	29,58	73,14
	směr.odch.	0,07	0,00	0,03	0,02	0,06

Várka slámy pšenice a ječmenu probíhala podle zvolených parametrů, které můžeme vidět v tabulce 2.

Tab. 2: Parametry várky

H-faktor	Chemikálie	Aktivní alkálie	Hydromodul
2800 h	25% NaOH	19 %	5:1

Připravená buničina byla vyprána ve čtyřech stupních. Vypraná buničina byla kvantitativně převedena do nádoby rozvlákňovače. Vložené množství buničiny bylo zalito 1,5 l vodovodní vody a po dobu 10 minut byla rozvlákněna. U buničiny byl následně stanoven výtěžek várky a Kappa číslo, uvedené v tabulce 3.

Tab. 3: Parametry buničin

Surovina	Celkový výtěžek	Kappa Číslo
Pšenice	42,3 %	20,7
Ječmen	27,5 %	22,4

Na laboratorním archovači bylo připraveno několik zkušebních listů s různou plošnou hmotností z buničin získaných várkou slámy z pšenice a ječmene. Pro porovnání, byly připraveny i zkušební listy ze sulfátové buničiny.

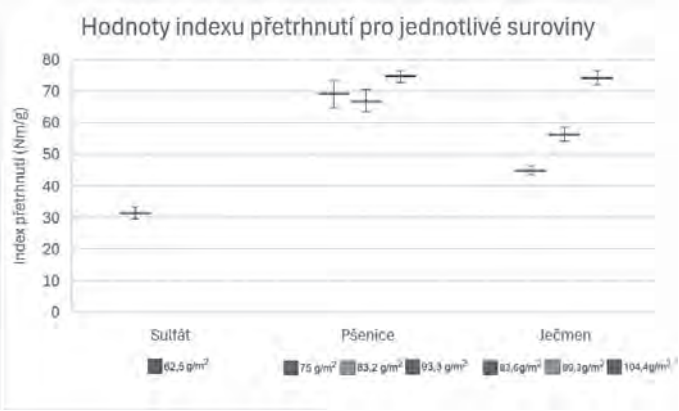
2.2. Měření mechanických vlastností zkušebních listů z buničiny z pšenice a ječmene

Zkušební listy připravené na laboratorním archovači Rapid Köthen na Univerzitě Pardubice byly podrobeny mechanickému testování na přístroji Instron 3365 na ODCP, FCHPT, STU v Bratislave. Byly proměřeny mechanické vlastnosti–pevnosti v tahu pro jednotlivé laboratorní aršíky, včetně protažení podle normy STN EN ISO 1924-2 [3]. Naměřené hodnoty jsou uvedeny v tabulce 4.

Tab. 4: Mechanické vlastnosti

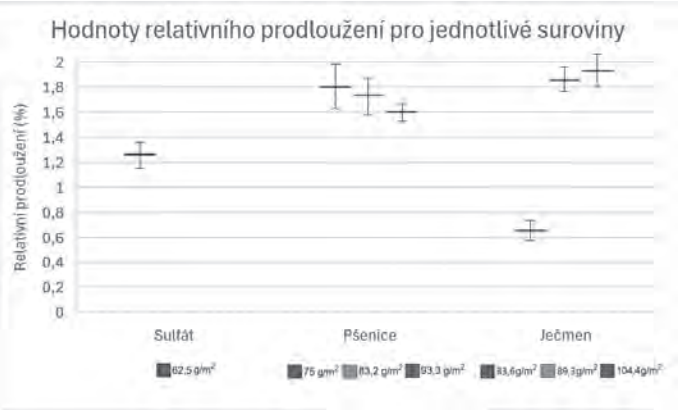
Surovina		Plošná hmotnost, g/m^2	Tloušťka, mm	F, N	Tržné zatížení, kN/m	Index přetrhnutí, Nm/g	Relatívní prodloužení, %
Sulfát	*průměr*	62,5	0,138	29,3	1,955	31,3	1,26
	směr. odch.	-	0,0042	1,4	0,093	1,5	0,10
Pšenice	*průměr*	75	0,124	78,0	5,20	69,3	1,80
	směr. odch.	-	0,0055	4,1	0,27	3,6	0,18
	průměr	83,2	0,133	83,3	5,55	66,7	1,73
	směr. odch.	-	0,015	4,6	0,31	3,7	0,15
	průměr	93,3	0,148	104,6	6,97	74,7	1,60
	směr. odch.	-	0,0084	3,1	0,21	2,2	0,070
Ječmen	*průměr*	83,6	0,124	56,1	3,75	44,7	0,65
	směr. odch.	-	0,0055	1,8	0,12	1,4	0,07
	průměr	89,3	0,174	75,4	5,02	56,3	1,86
	směr. odch.	-	*0,0055*	3,0	0,20	2,2	0,098
	průměr	104,4	0,148	116,1	7,74	74,2	1,93
	směr. odch.	-	*0,0043*	*2,9*	0,20	*1,9*	*0,13*

Laboratorní aršíky byly připraveny pouze z rozvlákněné, nemleté buničiny. Tomu odpovídají jednotlivé naměřené hodnoty.



Obr. 1: Hodnoty indexu přetrhnutí pro jednotlivé suroviny.

Jak je vidět z obr. 1, pro pšenici a ječmen dosahují hodnoty indexu přetrhnutí vyšších hodnot, než je tomu u buničiny sulfátové. Pro pšenici 66,7 Nm/g, 69,3 Nm/g a 74,7 Nm/g, pro ječmen 44,7 Nm/g, 56,3 Nm/g a 74,2 Nm/g, zatímco hodnota pro sulfát je pouze 31,3 Nm/g. Rozdíl může být samozřejmě také ovlivněn rozdílnými plošnými hmotnostmi jednotlivých vzorků. Hodnoty pro pšenici jsou pak kompaktnější, zatímco u ječmene se k těmto hodnotám přiblížila až hodnota pro aršík s nejvyšší plošnou hmotností 104,4 g/m^2.



Obr. 2: Hodnoty relativního prodloužení pro jednotlivé suroviny.

Hodnoty relativního prodloužení, které jsme také sledovali, dosahují až na vzorek ječmene s plošnou hmotností 83,6 g/m^2 pro pšenici a ječmen vyšších hodnot než pro sulfát, jak je vidět i na obr.2. Pro pšenici 1,8 %, 1,73 % a 1,6 %, pro ječmen, již zmíněná hodnota, která se vymyká ostatním měřením 0,65 %, dále pak 1,86 % a 1,93 %, a pro sulfát byla dosažena hodnota relativního prodloužení 1,26 %.

Tyto data jsou prvotními výsledky, které bude do budoucna vhodné doplnit dalšími měřeními. Také by bylo zajímavé rozšířit výsledky o hodnoty získané při výrobě laboratorních listů buničiny, která bude upravena mletím.

3. Závěr

V této práci jsme se zaměřili na zkoumání potenciálu pšeničné a ječmenné slámy jako alternativních zdrojů buničinových vláken pro přípravu nových papírenských materiálů. V laboratorních podmínkách se podařilo připravit buničinu z ječmene a pšenice s poměrně vysokým výtěžkem (42.3 % pro pšenici a 27,5 % pro ječmen). Analýzou mechanických vlastností vyrobených laboratorních listů z těchto slám je patrné, že obě suroviny nabízejí zajímavé možnosti pro výrobu papíru. Dosažené hodnoty jak pevností v tahu, tak i relativního protažení ukazují, že existuje jistý potenciál pro využití těchto surovin při hledání nových papírenských materiálů s lepšími elastickými schopnostmi.

Poděkování

Tuto práci podpořila Agentúra na podporu výskumu a vývoja SR na základe zmluvy APVV-22-0277 a projekt VEGA 1/0651/23.

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Improvement of paper elastic properties by addition of DuraPulp and mechanical modification

Lota Chrvalová, Ida Skotnicová, Štefan Šutý

Department of Wood, Pulp and Paper, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia
lota.chrvalova@stuba.sk

Abstract: *In today's world, the use of paper as a packaging material is on the rise, reflecting the demand for eco-friendly alternatives in various industries. However, there are challenges, mainly when it comes to the elastic properties of paper, which still have certain limitations. This work explores ways to improve the elasticity of paper. The aim was to study new opportunities in papermaking, specifically focused at improving elastic properties through mechanical modifications and addition of additives. One of the monitored parametres was relative elongation. The mechanical modification involved creating a relief surface on the paper using felts and pressing force on wet paper (microcrepe) and utilizing shrinkage during drying. DuraPulp was selected for modification through additive addition, applied to the suspension in two grinding stages (25 °SR and 50 °SR). By adding DuraPulp in different concentrations (2,5 % – 20 %), the strength properties of the paper were enhanced. Microcrepe increases the relative elongation while at the same time decreasing strength properties of paper. The advantage of combining these two techniques is the production of paper with elevated elongation and improved strength properties.*

Keywords: *elongation; modification in papermaking; DuraPulp; mechanical modification*

Acknowlegment:

This work was supported by the Research and Development Agency under contract APVV-22-0277 and project VEGA 1/0651/23.

Fractionation of biomass using green solvents

Veronika Jančíková, Michal Jablonský

Department of Wood, Pulp and Paper, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia
veronika.jancikova@stuba.sk

Abstract: *Hemp fibers are promising biomaterials that have many advantages, such as biodegradability, low production costs, and rapid growth. They can be used as alternatives to other cellulosic fibers that have higher environmental impacts. In this work, we used a new and green solvent, called deep eutectic solvent-like mixtures, to delignify hemp biomass [1]. Deep eutectic solvent-like mixtures are made from choline chloride and lactic acid, which are cheap, safe, and biodegradable. We tested different combinations of temperature (80–160 °C), time (60–240 min.), and solvent amount (1:10–1:60) to find the best conditions for delignification. We measured the Kappa number, which indicates how much lignin is left in the fibers, and the efficiency of delignification, which indicates how much lignin is removed. The Kappa number of delignified hemp fibers ranged from 10.7 (144 °C, 204 min, 1:30) to 21.8 (160 °C, 150 min, 1:17). The results showed that the optimal conditions to obtain the smallest Kappa number representing 6.6 are the boundary conditions of 160 °C, 240 min, and a ratio of 1:60. This method is more sustainable and environmentally friendly than the conventional methods, and it can help achieve the goal of sustainable development for mankind.*

Keywords: *DES-like mixtures, hemp fibers, choline chloride, lactic acid*

Acknowledgement

This work was supported by the Slovak Research and Development Agency under the contracts Nos. APVV-22–0277, APVV-22–0388 and APVV-22-0034, and VEGA Grant 1/0651/23 and 1/0743/24. The authors would like to thank the financial assistance from the STU Grant support schemes for Young researchers.

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Elektrochemické senzory: 3D tlačené uhlíkové elektródy povrchovo aktivované plazmou

[1]Katarína Gregová, [1]Miroslav Kováč, [2]Ľubomír Švorc, [1]Pavol Gemeiner

[1]Oddelenie polygrafie a aplikovanej fotochémie, Fakulta chemickej a potravinárskej technológie, Slovenská technická univerzita, Radlinského 9, 812 37 Bratislava
[2]Ústav analytickej chémie, Fakulta chemickej a potravinárskej technológie, Slovenská technická univerzita, Radlinského 9, 812 37 Bratislava
katarina_gregova@stuba.sk

Abstrakt: *Fused deposition modelling (FDM) is a 3D printing technology that constructs parts layer by layer by selectively depositing melted thermoplastic material along a predetermined path. This method utilizes filament-based thermoplastics to produce physical objects and is widely used across industries, including the medicinal field and electrochemical sensing, due to its versatility. In this work, two types of electrochemical sensors were fabricated using conductive polymer filaments consisting of polylactic acid (PLA) combined with carbon black (CB) and carbon nanotubes (CNTs). Following the fabrication of the electrodes, air-plasma treatment was applied to enhance the surface properties. Increasing the duration of plasma treatment led to a more significant removal of the polymer, exposing the underlying conductive carbon particles–carbon black and carbon nanotubes. This process of activation improved the electrochemical characteristics of the sensors. By prolonging the plasma treatment, the electrochemical performance of the electrodes was significantly enhanced, demonstrating the potential of this technique for creating high-performance, 3D-printed electrochemical sensors.*

Kľúčové slová: *electrochemical sensors, 3D-printed electrodes, polylactic acid, plasma, carbon black, carbon nanotubes*

1. Úvod

3D tlačové systémy využívajúce technológiu FDM fungujú na princípe extrúzie zohriateho termoplastického materiálu a následne jeho depozície vrstvy po vrstve na pracovnú podložku na základe digitálnej predlohy. Umožňujú rýchlu a nízkonákladovú výrobu finálnych produktov zo širokej škály materiálov. Vďaka ich všestrannosti nachádzajú uplatnenie v mnohých odvetviach priemyslu, v medicíne, ako aj v senzorickej analýze [1, 2].

Na produkciu elektrochemických senzorov zhotovených 3D tlačou sa využívajú aj kompozitné vodivé polymérne filamenty. Ako nosný a stavebný materiál v kompozite figuruje termoplast, najčastejšie využívaný akrylonitrilbutadiénstyrén (ABS) alebo kyselina polymliečna (PLA). Ďalšou zložkou filamentu sú vodivé uhlíkové nanočastice, menovite sadze (CB), grafén alebo uhlíkové nanorúrky (CNT). Nevodivý

termoplast bráni elektrochemickým dejom prebiehajúcim na povrchu elektródy v procese elektrochemickej analýzy. Za účelom odstránenia prebytočného nevodivého polyméru z povrchu elektród a vylepšenia ich elektrochemickej aktivity je realizovaná aktivácia povrchu. Medzi používané metódy sa radí chemická, fyzikálna, elektrochemická, mechanická a plazmová aktivácia. Vhodná elektrochemická aktivita má význam pre detekciu zlúčenín z roztoku počas senzorickej analýzy [3, 4].

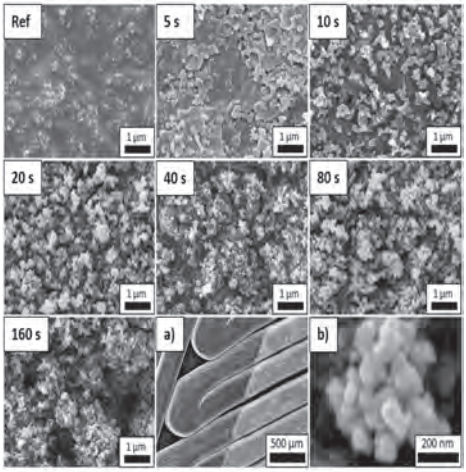
2. Experimentálna časť

Pracovné elektródy boli vytlačené 3D tlačovým systémom využívajúcim technológiu FDM z kompozitného filamentu kyseliny polymliečnej a sadzí (Protopasta Composite Conductive PLA, PLA/CB) a kyseliny polymliečnej a uhlíkových nanorúrok (FiloAlfa ALFAOHM, PLA/CNT). Zhotovené elektródy boli následne podrobené plazmovej úprave difúznym koplanárnym povrchovým bariérovým výbojom v prostredí pracovného plynu–vzduchu, z oboch strán. Na vymedzenie miesta aktivácie elektródy bola počas pôsobenia plazmového výboja aplikovaná na neaktivovaný povrch kaptónová páska. Vplyv plazmovej úpravy na povrch elektród bol skúmaný skenovacím elektrónovým mikroskopom (SEM). Meranie povrchovej energie bolo realizované metódou kontaktného uhla zmáčania a vyhodnotené Owens-Wendt metódou. Metódou cyklickej voltampérometrie (CV) boli skúmané elektrochemické vlastnosti elektród. Cyklická voltampérometria bola realizovaná v prostredí $[Fe(CN)_6]^{3-/4}$ – s podporným elektrolytom KCl.

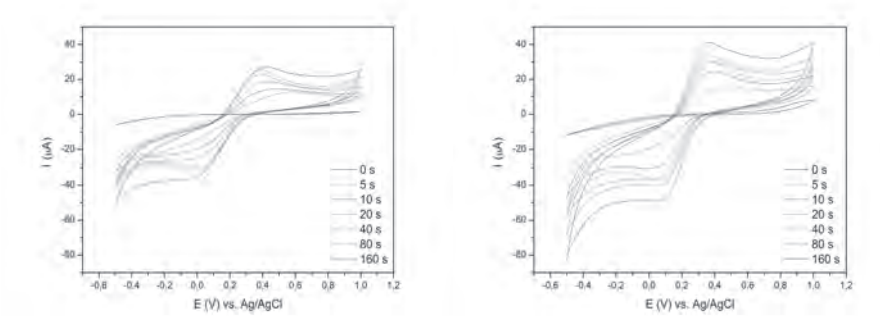
3. Výsledky a diskusia

Snímky obdržané skenovacím elektrónovým mikroskopom zachytávajú vplyv plazmovej úpravy na štruktúru povrchu elektród. Povrch elektródy bez úpravy (Obr. 1 Ref) je pokrytý vrstvou PLA, pričom sú viditeľné vyčnievacjúce nerovnosti–sadze. Predĺžením pôsobenia plazmového výboja dochádza k dôkladnejšiemu odleptaniu vrchných vrstiev PLA do väčšej hĺbky, dôsledkom čoho sú sprístupnené vodivé sadze.

Pôsobenie plazmového výboja na povrch 3D tlačených kompozitných uhlíkových elektród má významný vplyv na ich elektrochemickú aktivitu. Z cyklických voltampérogramov je možné odčítať, že neaktivované elektródy nevykazujú odozvu (Obr. 2) Elektródy, ktoré podstúpili aktiváciu disponujú priaznivejšími hodnotami píkových prúdov a veľkosťou separačného potenciálu.



Obr. 1: Povrch 3D tlačenej PLA/CB elektródy nasnímaný SEM pre neupravenú vzorku (Ref), časy úpravy od 5 s po 160 s, a) rozhranie neplazmovaného a plazmovaného povrchu, b) zhluky uhlíkových nanočastíc



Obr. 2: Cyklické voltampérogramy 3D tlačených uhlíkových elektród PLA/CB (vľavo) a PLA/CNT (vpravo) v prostredí $[Fe(CN)_6]^{3-/4}$ – bez aktivácie a aktivovaných plazmou.

4. Záver

Úprava povrchu plazmovým výbojom má pozitívny vplyv na elektrochemickú aktivitu 3D tlačených kompozitných uhlíkových elektród. Plazmová úprava je rýchla, efektívna, nevyužíva toxické chemikálie a dosahuje porovnateľné výsledky ako štandardné metódy aktivácie.

Poďakovanie

Autori by touto cestou radi poďakovali grantovým agentúram VEGA a APVV za finančnú podporu výskumu prostredníctvom projektov VEGA 2/0136/24, VEGA 1/0036/24 a APVV-23-0066.

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Lightfastness Of Kyocera Inkjet Black Water-Based Ink

Igor Majnarić, Lara Jurković, Marija Jakelić

University of Zagreb Faculty of Graphic Arts, Getaldićeva 2 Zagreb,
igor.majnaric@grf.unizg.hr

Abstract: *Among all printing inks, black is the most widely used, particularly evident in the production of achromatic halftone and monochrome images, as well as text. This paper examines the lightfastness of black-and-white prints produced with the Kyocera TASKalfa 15000c Inkjet printer, which utilizes water-based pigment ink. Designed specifically for uncoated substrates, the Kyocera TASKalfa 15000c was paired with MONDI Maestro Print paper, featuring a grammage of 120 g/m². Following the printing process, the final black-and-white halftone prints underwent accelerated aging through lightfastness testing in a xenon light chamber, the SolarBox 1500e. The simulated exposure periods for the experiment were established at 3, 6, 9, 12, 15, and 18 months. The resulting changes in black tones were quantitatively evaluated using CIE LAB ΔE values, measured with an X-Rite eXact Advanced spectrophotometer. Graphical representations of the variations in black halftones (ΔL, ΔE) over time were created using Origin 8.2 software. The findings reveal that the most pronounced changes occur within the initial 3 months, after which the prints exhibit no further color alterations. Moreover, as surface coverage increases, the deviations in achromatic tones are observed to decrease.*

Keywords: *Kyocera, Black water-based Inkjet ink, Xenon test, BW print quality, CIELABΔE color difference.*

1. Introduction

The The ancient Egyptians primarily used carbon black to make the first inks (used for writing on papyrus scrolls). Carbon black mixed with animal glue is also known as the oldest ink, used by the Chinese around 2500 BC. Intensive work on improving the process led to the invention of black ink for calligraphy and drawing. Achromatic black inks have been most commonly used since the earliest beginnings of printing. The main reason is that applying it to white paper (printing substrate) achieves the highest printing contrast and the greatest possible visual visibility and resolution of fine details. Carbon pigments formed by combustion at high temperatures are the primary substance in printing inks that gives black color tone. Although carbon blacks are most commonly used in the production of tires (pneumatics), about 6% of the total produced quantities are used in the form of pigments that serve to achieve the desired optical purpose (in the production of polymer materials, varnishes and printing inks). Depending on the applied ap-

plication unit (viscosity), the size of the black pigments and their composition can vary, whereby we distinguish between conventional inks (lithographic offset, flexo printing, gravure, screen printing) and inks for digital printing (electrophotography and inkjet). [1,2].

2. Theoretical part

2.1. Carbon black pigments

Crude carbon black is a fine powder comprised of elemental carbon, with particles that are agglomerates of graphite-like crystals. It is produced through the partial combustion of hydrocarbons and is characterized by a small particle size and a large surface area, both of which are essential for creating a deep shade of black. Its low production cost makes it the leading black pigment used in the paint industry, including in printing inks. Various methods have been developed to produce carbon black, each differing in technology and the geographical sources of raw materials utilized. Among these, the Furnace Black Process is the most efficient and widely used today. Additionally, other methods such as the Thermal Black Process and the Gas Black Process (also known as the Degussa Process) can also be employed.

The **Furnace Black Process** of carbon black utilizes petroleum and natural gas hydrocarbons as its primary raw materials. These hydrocarbons are introduced into a reactor, where they undergo thermal decomposition. Importantly, they are only partially combusted within a controlled environment of temperature and oxygen. This process leads to the formation of carbon black particles, which manifest as powdery agglomerates with primary sizes ranging from 10 to 80 nm. The conditions under which carbon black is formed can be adjusted, thereby influencing properties such as structure and surface characteristics. To facilitate handling, the powder can be compacted into grains. Modern reactors also allow for additional surface treatment of pigments, enhancing their properties for specific applications, including pigment dispersion and inkjet ink production. This particular process represents the largest segment of global carbon black production.

The **Thermal Black Process** entails the introduction of natural gas into a heated, inert furnace. Within this environment, the gas undergoes decomposition, producing carbon black and hydrogen. Due to the absence of oxygen, the resulting carbon black particles form more slowly, leading to a product that is purer, larger, and has a finer structure compared to carbon black produced in a traditional furnace. The production process utilizes two furnaces: one for preheating the gas and the other for the decomposition of natural gas into carbon black. Additionally, the hydrogen gas generated as a byproduct of this decomposition can be repurposed to preheat the second furnace, enabling the discontinuous process to continue efficiently.

Degussa carbon black process was developed in Europe using tar distillate. The oil in the tar is generally heated until it evaporates, after which the pure vapor-

ized oil is transferred to the combustion chamber using a hydrogen-rich carrier gas. Since oxygen is present, the carbon black produced has a high degree of functionality because it contains oxygen functional groups on its surface. This production process creates a high-purity, small particle-size carbon black ideal for making black printing inks and coatings. Other carbon black production processes include lamp black, channel black, and the acetylene black process.

It is estimated that during the production of 15 million tons of carbon black, between 29 and 79 million tons of carbon dioxide are emitted. There is a potential to reduce the carbon footprint by 19% if hydrogen were used instead of natural gas. Additional environmental impacts include the release of carbon monoxide, volatile organic compounds, sulfur oxides, and nitrogen oxides. However, poor recycling of carbon black also poses an environmental risk. Over the past 30 years, the introduction of high-performance filtration systems has reduced the emission of released soot particles. New trends include the production of carbon black from renewable sources (from waste materials such as tires). Living Ink produces carbon black from waste biomass in a negative carbon footprint process. Carbon black pigments derived from biomass are produced by combustion in an atmosphere with limited oxygen, like traditional carbon black. They are used in screen printing, lithographic offset, and flexographic printing inks. [3].

2.2. Black inks for industrial inkjet

For industrial Inkjet, the key physical properties of black carbon include the most accurate size of the pigment particles, their shape and tone. To achieve precise inkjet prints, the size of the carbon black particles must be less than 1 μm (only fine particle sizes will ensure flawless discharge of ink droplets through the inkjet printhead nozzles). Ultimately, this allows for the formation of high-resolution prints. For safe Inkjet printing, the golden rule is that in order to prevent nozzle clogging, the largest dimensions of the carbon black pigment particles must be at least 20 smaller than the diameter of the printhead nozzle (usually 20-25 μm). In addition, for better print quality and the formation of nano-droplets of dye, the tolerance in the variation of the size of the dispersed particles must be as small as possible. [4]

The structure of black pigments for Inkjet inks must have a large surface area to increase the ability to absorb and scatter light, which leads to deeper and richer black tones. Although the measurement in square meters per gram (m^2/g) is used in the production of printing inks, Inkjet carbon black manufacturers use the OAN number (OAN = Oil Absorption Number). If the oil absorption is higher with an absorptometer, more pigment will be absorbed and the printed area will be larger. In Inkjet inks, the OAN number can vary significantly and is important information for ink manufacturers who want to achieve high-quality black dispersion.

In Inkjet inks produced for industrial inkjet printers, carbon black must be well dispersed and remain stable throughout the entire printing process. To achieve a dispersion that will be stable over a long period of time and under different storage conditions, carefully selected dispersants and their formulation are required. Finding

the optimal ratio of carbon black pigment, dispersant and synergist will give high-density pigment dispersions that are low in viscosity and stable over time. An important property for ink manufacturers is also the Jetness or blackness of the pigment. The property refers to the depth and intensity of the black produced. High carbon black purity is desirable for creating rich and dark prints. Although the blackness of a color depends on the hue, the property manifests itself by attempting to achieve a color with an L* coordinate <1. To achieve such shades in the CIELAB space, it is possible to add cyan pigments to black Inkjet inks.

Novel black Inkjet inks are very low in viscosity and can contain various polar and non-polar solvents. Therefore, one of the most common and environmentally friendly solvents is water. Water-based inks consist of carefully selected chemicals that enable superior print quality and, in addition to water, contain alcohols, ethers, glycerol, carbon black pigment and additives. The fastest high-performance water-based Inkjet machines (which print from sheets) can achieve production speeds of 150 A4 pages/min, where the flow of black ink must be impeccable. In this paper, black prints printed on a Kyocera machine TASKalfa Pro 15000c were analyzed, whereby light fastness was analyzed, and possible use over a period of 18 months was determined. [5-8]

3. Experimental part

When evaluating the quality of printed products, various parameters are considered. Depending on the application and design, we assess attributes such as solid tone reproduction, halftones areas, line reproduction, as well as light fastness, temperature fastness, and humidity fastness. For this experiment, we investigated the light fastness of black prints produced using the TASKalfa Kyocera 15000c Inkjet printing machine. Even though it is a color Inkjet machine, we focused exclusively on a print of the black separation using Kyocera IK-7125K ink. The Kyocera IK-7125K Inkjet ink has a viscosity ranging from 5 to 10 mPa·s at 25°C. This ink consists of 40-60% demineralized water, 10-20% polyhydric alcohol, 10-20% ethers, 5-10% glycerol, 5-10% carbon black pigment, and less than 0.05% additives. The additives include preservatives formulated as 1,2-benzisothiazol-3(2H)-one and 2-methyl-2H-isothiazol-3-one. [9] For this study, we used uncoated Mondi Maestro Print paper weighing 120g/m^2.[10] The printing form utilized was the standard Fogra Media Wedge, which contains 74 fields. Measurement was conducted only on the achromatic fields printed with black ink. All files were prepared using Fiery PS50 RIP software, and a total of 50 black and white SRA3+ prints were produced.

After printing, one of the samples was set aside as a reference, while the remaining sheets were subjected to testing in the accelerated aging chamber Solar Box 1500e. The samples were exposed for six different time periods: 92 hours, 184 hours, 276 hours, 368 hours, 455 hours, and 546 hours, which approximates to ages of 3 months, 6 months, 9 months, 12 months, 15 months, and 18 months, respectively.

Once the aging process was complete, all samples were measured using an X-Rite eXact Advance colorimeter and spectrophotometer to compare them with

the reference sample. CIE LAB color values for black and gray halftones were obtained. These measurements were then processed to calculate the CIE LAB ΔE2000 color differences. Using OriginPro 8.5 software, we generated the final reproduction curves and deviations for, CIE LabΔE, and CIE LabΔL.

4. Results and Discussion

To assess the short-term durability of prints (defined as printed products with a lifespan of up to 18 months), it was necessary to produce samples promptly. Exposure to elevated temperatures and UV light accelerates the degradation of both ink and paper, which can result in a noticeable loss of image tonality. Colorimetric measurement methods are therefore useful for detecting these degradation changes. Figures 1, and 2 illustrate the observed color differences (CIE LAB DE) and brightness differences (CIE LAB DL) between unaged and aged black halftone prints.

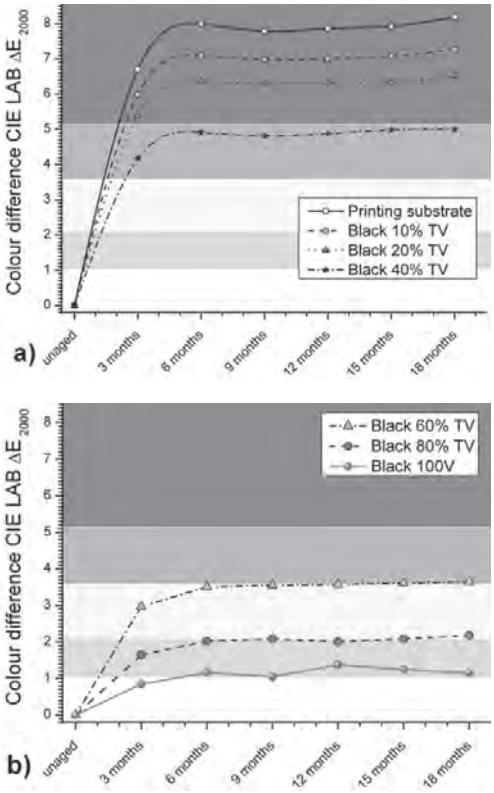

Fig. 1: The color difference is influenced by the exposure time to the xenon arc light: a) CIE LAB ΔE for light tone areas; b) CIE LAB ΔE for dark tonal areas.

Analysis of accelerated aging revealed that the most significant color differences occur within the first three months. The most notable change was observed in the unprinted paper substrate, which experienced a $\Delta E_{paper} = 6,7$, indicating that this type of paper is very unstable with respect to aging. When a small amount of black ink (10% TV) is added to the surface, there is a slight decrease in the color difference, $\Delta E_{Pap\_10\%TV} = 0,8$; compared to the unprinted paper. For the print with 10% TV, increasing the surface coverage to 20% TV further decreases the difference by $\Delta E_{20\%TV\_10\%TV} = 0,6$. When gray tones reach 40% TV, the color difference falls into the category of significant deviation, with a change amounting to $\Delta E_{40\%TV} = 4,2$. As aging continues and halftone values increase, additional changes and degradation in the quality of the black print can be observed. After six months of aging, the paper substrate shows a difference of $\Delta E_{6mount\_3mount} = 1,3$. At 10% of the raster area, the difference is $\Delta E_{6mount\_3mount} = 1,1$; at 20% TV, $\Delta E_{6mount\_3mount} = 1$; and at 40% TV, $\Delta E_{6mount\_3mount} = 0,7$.

After this period, the print stabilizes, and no further color changes occur in the black print. The print has reached its maximum change, and the results have leveled off. The average color values are as follows: $\Delta E_{paper} = 7,9$; $\Delta E_{10\%TV} = 7$; $\Delta E_{20\%TV} = 6,3$; and $\Delta E_{40\%TV} = 4,8$.

Black prints with higher surface coverage show a medium to slight change in tone. After three months, a halftone area of 60% TV experiences a color difference of $\Delta E_{60\%TV} = 2,9$, while at 80% TV, the color difference is $\Delta E_{80\%TV} = 1,6$. The full tone does not exhibit significant change compared to 80% TV, remaining imperceptible to the human eye.

With continued aging over three months (184 hours in the solar box chamber), minimal color change is noted: for the 60% TV patch, $\Delta E_{6month\ \_3month} = 0,6$, while for the full tone, the difference is $\Delta E_{6\ month\ \_3\ month} = 1,1$. Similarly to other analyzed halftone values, prints stabilize afterward and do not undergo any further changes. Black halftone fields demonstrate that greater surface coverage results in a more stable black print. Lower amounts of water-based Kyocera Inkjet ink contribute to more pronounced tone changes, with the paper substrate being responsible for the most significant degradation and subsequent color change.

The chromatic changes of achromatic black after exposure to UV light and temperature are consistent with the CIE LAB ΔE color change. After 18 months, the change trends and aging patterns are completely identical.

A detailed analysis of the lightness value (ΔL) reveals a general trend of decreasing values with accelerated aging. This results in a reduction in brightness, causing both black and gray tones to appear darker. The only exception is observed in a black surface with a 20% tonal value, which becomes slightly lighter after three months, after which it begins to darken again.

It has been noted that the black surface with a 10% TV shows almost a linear color change up to 12 months, followed by a decline in brightness. After three months of aging, the reduction in brightness is measured as $\Delta L_{0month\_3\ month} = -0,15$. After six months, $\Delta L_{0month\_6month} = -0,27$; after nine months, $\Delta L_{0month\_9month} = -0,3$; and after twelve months, $\Delta L_{0month\_12month} = -0,4$.

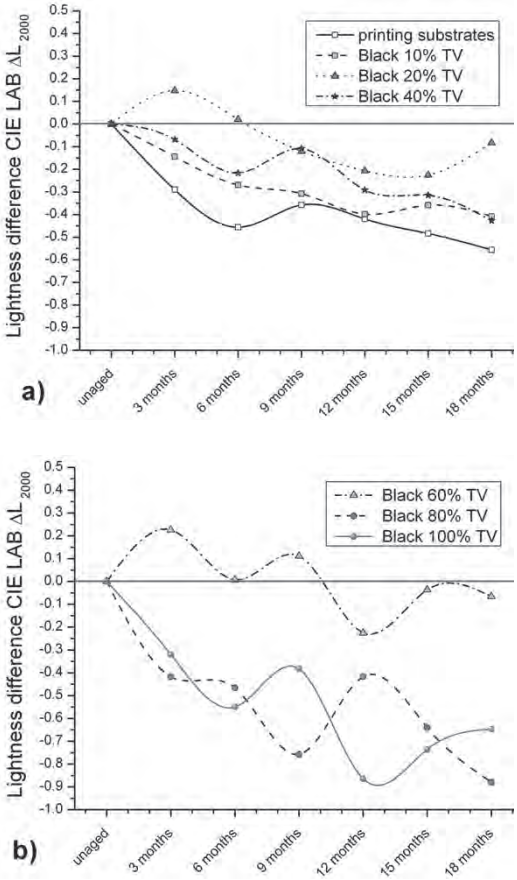

Fig. 2: The lightness difference depends on the exposure time to the xenon arc light: a) DC bright tonal areas and b) DC dark tone areas.

Following a brief stabilization period, the final measurement at 18 months indicates $\Delta L_{month\_18month} = -0,4$ compared to the unaged print. For paper substrates, the most significant color changes occur within the first six months, with $\Delta L_{0month\_6month} = -0,46$. This is followed by a linear decline in brightness that continues until the final measurement at 18 months, which shows a change of $\Delta L_{0month\_18month} = -0,5$, indicating stabilization and uniformity. As the surface coverage of black prints increases, the tones become more vibrant in brightness. It has been observed that prints experience the most significant brightness changes during the first six months, after which stabilization occurs with minimal decline.

5. Conclusion

Based on the conducted experiment, it was observed that as the surface coverage of the black Kyocera Ink increases, there is a corresponding decrease in color changes across all analyzed tones.

The unprinted paper serves as the baseline and shows the most significant deviations, which peak after six months. Following this period, the color of the black sample stabilizes.The application of black ink from Inkjet printers reveals that the most critical color changes occur within the first three months, particularly in prints with 10 % and 20 % TV, where the upper limit of apparent deviation exceeds $\Delta E > 5$. During the first six months, halftone values of 40 % and 60 % experience noticeable changes that reach the threshold of $\Delta E > 4.5$. In contrast, prints with full tonal values exhibit minimal color changes, typically ranging from ΔE 1 to 2, which are nearly insignificant.Kyocera black ink is not suited for light tonal areas and gray tones in images. However, it is recommended for use in straightforward text elements and monochrome black-and-white applications. Halftone prints can definitely be utilized for short periods, specifically within the first three months.

Additionally, it is clear that with increased exposure time to accelerated aging, brightness decreases and black prints become progressively darker. The most significant changes in the prints are related to chromaticity.

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Forensic Analysis: Steganography

Vladimír Dvonka, Barbora Dikošová, Michal Hatala

Faculty of Chemical and Food Technology,
Slovak University of Technology in Bratislava
vladimir.dvonka@stuba.sk

Abstract: *Steganography is a branch of cryptology and involves hiding secret messages within an ordinary, unclassified message so that this classified information is not normally detectable by unauthorized persons.*

Document security is a critical aspect of information protection in the digital age. In today's world, documents play a fundamental role in everyone's life. They prove our identity, enable access to education, employment, healthcare, social benefits, etc.

However, with the growing importance of documents, the problem of their alteration also increases. Altered documents are used for fraud, obtaining illegal benefits and avoiding liability. In this context, protecting documents from alteration becomes a task of paramount importance.

By comparing an unknown document with known samples, it is possible to assess whether the document is an authentic original or a copy or an altered copy. Thanks to knowledge of the unique properties of documents, altered documents can be successfully identified. Using microscopy, we can analyze in detail the properties of a document, including paper, ink, and printed information, not only in the visible range, but also in the ultraviolet range (fluorescence).

The non-destructive method of assessing the authenticity of a document is paramount, which is also assisted by various spectroscopic methods such as infrared, X-ray, and ultraviolet spectroscopy. Destructive methods can only be used in exceptional and serious cases. After all, what good would it do for the holder of Albert Einstein's signature to know that the signature on the document is genuine if we cut out part of his signature and used the dissolved ink to identify the composition and the age of the ink used at that time. Such a document would be significantly devalued and would lose its financial and historical value.

Creating document security features

There are several ways to protect documents:

– protection in the mass of the printed material: watermark, security and textile fibers, holographic and metallic strips, holographic paper, plastics…
– physical and chemical protection: infrared, luminescent (fluorescence) and magnetic protection, photochromic and thermochromic colors, optically variable colors, holograms…
– protection with special printing patterns using printing techniques: iris printing,

guilloche, line and dot screens, co-impression mark, microtext, combination of printing techniques, steganography…

Example of infrared photography of historical inks (right), first line of the picture presents atraments–iron gall (IG), sepia, IG, IG, indian ink, IG, bister. Left–photography in visible light spectrum.

Example of ball pen ink fluorescence in UV/Vis spectrum. Left–light fluorescence of ink (light red in the centre), right–ink witout fluorescence (black). You can watch light fluorescence of the paper in the background.

History of steganography

It originated before the beginning of our era, but it only got its name in the Middle Ages at the turn of the 15th and 16th centuries and became a part of computer science (mathematics) at the end of the last century. While cryptographically encrypted information can be read by anyone, but not understood, no one knows about steganographically secret information. This method of secrecy fails when someone else notices the hidden secret information.

Recent uses of steganography:

1. Use of slang words, synonyms in ordinary text–it was used mainly during the world wars, where these words expressed the positions and numbers of troops or military equipment.

2. Microdots–secret agents during and after World War II used photographically produced microdots to covertly send information. These microdots contained a microphotograph of, for example, the entire page. They were usually as small as a classic dot at the end of a sentence (about 1 mm) and were glued to the paper in the place of this dot. Given that the film material was shiny and the paper matte, they could be identified under a certain angle of incident light. A smaller microscope was sufficient for reading. Currently, the term microdots also refers to special small holograms (microholograms) with text in the size of 0.1 to 0.2 mm (or less) glued to a protected document and visually appearing as, for example, dirt from printing ink or as part of the paper.

3. Hidden messages in printed documents–this is the modification of the text to contain encrypted text–stegotext. Text encryption uses changing the size or color of letters, marking with spaces, using different fonts, introducing typos into the text, reading every other letter, for example…

4. Protection with invisible ink–which could only be read after a certain chemical change–increasing the temperature, chemical reaction with a certain agent…

Modern steganography

History of steganography used with color laser printers start in 1962 with company Fuji-Xerox.

In 2004 it was revealed that several printer manufacturers use steganography to hide information about printer serial number and the manufacturing code to track

conterfeits–Brother, Canon, Dell, Epson, HP, IBM, Konica Minolta, Lanier, Lexmark, Ricoh, Toshiba and Xerox.

Modern steganography use two selectet models, for example:

1. Hidden messages in digital images (digital audio, metadata)–this involves modifying the original tonal values of a digital image to contain encrypted text.

2. Printer steganography–some modern color laser printers integrate a dot matrix code made of small yellow dots on each printout to make the printed document traceable. The arrangement of these dots (stegogram), which are not recognizable or visible to the naked eye, contains information such as the printer model, serial number and time stamps, which allow the printed documents to be traced. The redundancy of the stegogram is important so that if the document is damaged, it still carries classified information, but on the other hand it must be sufficiently inconspicuous.

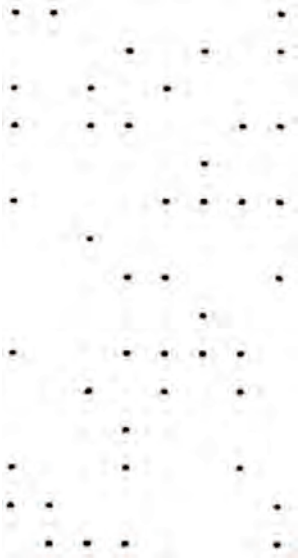
A few times we heard on television about printing or copying secret documents and even about identifying the perpetrator. However, they did not mention the method of proving the act, whether the printed materials were identified using steganography, or whether the digital trace of logging in to the printer via a computer was examined, for example.

I personally first encountered printer steganography in 2007, when I read an article in the PC REVUE magazine from the summer issue of July–August. At that time, I did not have the opportunity to verify this information, since color laser printers were used to a lesser extent.

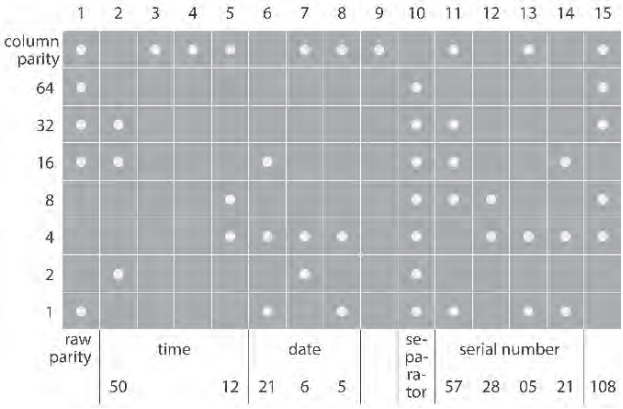
I most recently encountered steganography while working on my bachelor's thesis as a student this year, where we encountered steganography completely by chance. We originally tried to reproduce very fine details similar to raster dots on the printer and evaluated their change (deformation) or their complete loss. When scanning the thus reproduced test pattern at high resolution, we identified the disappearance of some small raster dots. Other raster dots were not placed in the correct place, which we confirmed microscopically that the raster dots did not change their place during printing, but additional raster dots were added, which we identified after examination as steganography.

Basically, we planned to simulate steganography using the created screen dots, but after scanning the printed patterns, we managed to identify the original steganography, since the yellow screen dots of our test pattern interfered with the pattern of the original steganography.

Steganography uses small dots with a diameter of less than a millimeter, which can be printed on documents using color laser printers. These dots are invisible to the naked eye and can be located in different parts of the document. Each printer has a unique set of yellow dots that can be used to identify the printer that was used to print a document. This allows the authenticity of the document to be verified and ensures that it has not been tampered with. The yellow dots can be arranged in a specific order and spaced precisely, which can provide additional information. For example, a specific pattern of yellow dots can be used to represent binary data such as text or an image.



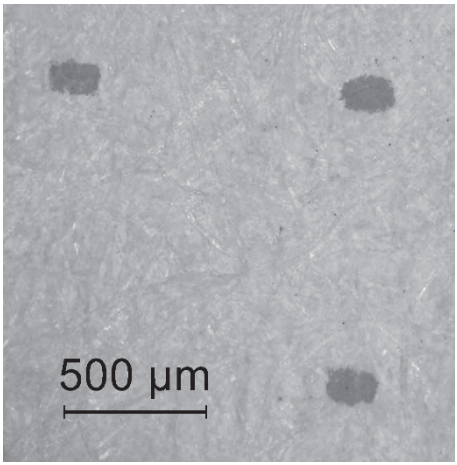
Complete steganogram from a Xerox printer (original size about 13 × 9 mm) and color-edited for readability in black.



Example of a solution to an older steganogram from Xerox. Printing time–12.50 h, date–21. 6. 2005, serial number–21052857 or 052857.

From the output of the image analysis from the microscope, we obtained the area of these dots in the range of 28000–30000 μm^2 (about 0.03 mm^2). Their width, respectively. height is in the range of 191–198 μm (about 0.2 mm), so we can fit

5 such dots in one millimeter. This means that they are so small that an ordinary observer has no chance of identifying them, they are located all over the paper and the yellow color is generally less visible.



Real image of yellow dots of steganogram from a microscope (modified image)

We managed to identify a similar steganogram on a Hewlett Packard printer. However, the steganogram here was twice as large, probably containing a larger amount of encrypted data.

Steganogram from a Hewlett Packard printer colored in black. Two identified steganograms right–light gray on the left and black on the right), left–original.

Unfortunately, we were unable to identify the steganographic recording from either printer, so we could not check our recorded data when printing with the

manufacturer's encrypted data in the steganograms. After contacting both printer manufacturers, we were informed that the data is confidential and the decryption key is available only for forensic analysis purposes. An ordinary user has no chance of accessing such information. Even the AI's response to the steganogram data decryption solution was very vague and rather evasive, with the need for further study. All AI provided was a description of the possibilities of hiding information through steganography and software tools for its identification, only finding the steganogram itself (not decrypting it).

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Využitie viacrozmernej štatistickej analýzy na stanovenie obsahu DOP v PVC

Lukáš Gál, Zuzana Bránická

Department of Graphic Arts Technology and Applied Photochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, lukas.gal@stuba.sk

Abstract: *This paper investigates the application of chemometric methods to analyze the material composition of modern cultural heritage objects containing softened polyvinyl chloride (pPVC). By integrating UV-Vis-NIR and ATR-FTIR spectroscopy with principal component analysis (PCA), the study focuses on detecting and quantifying the plasticizer di(2-ethylhexyl) phthalate (DOP) in pPVC samples. Accelerated thermal aging experiments simulated long-term degradation, and the spectro-chemometric approach reliably distinguished samples based on their DOP content. The results demonstrate that this non-destructive method can effectively monitor plasticizer content, offering a valuable tool for the conservation and preservation of polymer-based cultural heritage objects.*

Keywords: *pPVC; DOP; Chemometrics; ATR-FTIR Spectroscopy; Cultural Heritage.*

Ochrana kultúrneho dedičstva je neoddeliteľnou súčasťou konzervátorskej praxe, najmä keď ide o moderné umelecké diela, v ktorých sa často využívajú polymérne materiály. Mäkčený polyvinylchlorid (pPVC) patrí medzi najrozšírenejšie polyméry, no jeho dlhodobá stabilita je ohrozená degradáciou spôsobenou vonkajšími aj vnútornými faktormi. Degradácia pPVC je úzko spätá s migráciou pridaných zmäkčovadiel, najmä di(2-etylhexyl)ftalátu (DOP), ktoré znižujú mechanickú a chemickú odolnosť materiálu. Vzhľadom na vysoký počet umeleckých artefaktov obsahujúcich tento polymér v zbierkach pamäťových inštitúcií je kľúčové vyvinúť spoľahlivý prístup na monitorovanie a identifikáciu týchto zmien [1].

Boli pripravené modelové vzorky pPVC s rôznymi koncentráciami DOP. Tieto vzorky boli následne vystavené urýchlenému tepelnému starnutiu, čo umožnilo simulovať dlhodobé účinky environmentálnych podmienok na materiál. Spektrálne dáta boli získané pomocou ATR-FTIR spektroskopie a UV-Vis-NIR spektroskopie, pričom merania odhalili zmeny v chemickom zložení a štruktúre materiálu v závislosti od stupňa degradácie. Na spracovanie získaných údajov bola použitá analýza hlavných komponentov (PCA), ktorá umožnila rozlíšiť vzorky podľa ich spektrálnych charakteristík a získať kvantitatívne hodnotenie prítomnosti DOP.

Výsledky modelových experimentov naznačujú, že vzorky PVC obsahujúce nižšie koncentrácie zmäkčovadla DOP podliehajú dehydrochlorácii oveľa intenzívnej-

šie ako vzorky s vyšším obsahom. Tento jav sa prejavuje nielen vizuálnou farebnou zmenou, ale aj výraznými rozdielmi v ATR-FTIR spektre, čo svedčí o intenzívnejšej degradácii materiálu. Pri urýchlenom teplotnom starnutí vzorky s menším podielom DOP tmavnú oveľa výraznejšie, čo je pravdepodobne dôsledkom tvorby polyénových sekvencií. Súčasne vzorky s nižším obsahom zmäkčovadla obsahujú vyšší pomer tepelných stabilizátorov, konkrétne stearanu vápenato-zinočnatého, ktorý môže ovplyvniť proces degradácie. Zistenia naznačujú, že nižší podiel zmäkčovadla vedie k rýchlejšej degradácii polyméru, zatiaľ čo vyšší obsah DOP síce spočiatku zvyšuje flexibilitu materiálu, avšak následne podporuje migráciu zmäkčovadla, čo vedie k fyzikálnym zmenám, ako je zafarbenie a znížená mechanická pevnosť [2, 3]

Degradácia PVC prebieha v dvoch fázach. Počiatočná indukčná fáza je pomalá, no medzi 25. a 27. dňom starnutia dochádza k značne výraznejším zmenám, čo svedčí o zrýchlení degradácie. Meraním 45 FTIR-ATR spektier na každej vzorke sa preukázala nehomogenita materiálu, pričom rozdiely boli najvýraznejšie u vzoriek s nižším obsahom DOP. Tento jav potvrdzuje, že polymerné materiály môžu byť nejednotné a ich charakterizácia je komplikovanejšia.

Pri analýze UV-Vis spektier pomocou chemometrického modelu PCA bol prvý hlavný komponent zodpovedný za 52 % variability a druhý za 28 %, čím spolu vysvetľujú 80 % variability dát. Rozptýlenie dát umožnilo rozdeliť vzorky do deviatich skupín podľa koncentrácie DOP. Zistilo sa, že so zvyšovaním hodnoty prvého hlavného komponentu klesá obsah DOP vo vzorkách. Modelové vzorky sa dali rozdeliť do dvoch hlavných skupín, pričom vzorky s DOP 25, 30, 35 a 40 hm. % (s negatívnymi hodnotami PC1) boli navzájom dobre odlíšiteľné, zatiaľ čo vzorky s nižším obsahom zmäkčovadla sa rozlišovali menej jednoznačne.

Chemometrický model založený na ATR-FTIR dátach vykázal vysokú účinnosť, keďže prvý hlavný komponent pokrýva 85 % variability a druhý 9 %, čím spolu predstavujú 94 % celkovej variability. Reálna vzorka Káčera, obsahujúca DOP, sa nezaradila do žiadnej definovanej skupiny, ale umiestnila sa medzi suspensnou PVC a vzorkou s 10 hm. % DOP. Tento výsledok môže naznačovať nízky obsah zmäkčovadla v dôsledku migrácie, ako aj vplyv veku a pigmentácie vzorky. Výsledky experimentov zdôrazňujú potrebu vykonávať merania na viacerých miestach vzhľadom na inherentnú nehomogenitu polymérov a odporúčajú ďalšie štúdie pre zdokonalenie chemometrických metód, ktoré by mohli byť využité pri analýze reálnych objektov a ochrane historických materiálov. Tento prístup poskytuje dôležité poznatky pre budúci výskum v praxi.

Poďakovanie

Túto prácu podporila Agentúra na podporu výskumu a vývoja SR na základe zmluvy APVV-20-0410.

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Adsorption Treatment for Removing Yellow Flexo Printing Dye from Synthetic and Real Wastewater Using Activated Carbon: Optimization and Physicochemical Characterization

Miljana Prica*, Živko Pavlović, Sandra Dedijer, Nemanja Kašiković, Vesna Gvoić

University of Novi Sad, Faculty of Technical Sciences, Department of Graphic Engineering and Design, Trg Dositeja Obradovića 6, 21000 Novi Sad, Republic of Serbia
*corresponding author: miljana@uns.ac.rs

Abstract: *The graphic industry, especially the printing sector, contributes significantly to environmental pollution in the Republic of Serbia, through the discharge of colored wastewater, which often contains a mixture of different pollutants. Printing dyes, used from newspapers and magazines to packaging and labels, are a group of compounds that are difficult to degrade. These dyes can pose a serious threat to wastewater treatment and the environment, especially if discharged untreated into water bodies. The possibility of using an adsorption treatment to remove Yellow printing dye from synthetic solution and real wastewater was investigated. Commercially available activated carbon was used as adsorbent and yellow colored wastewater was obtained after the flexographic printing process. The optimization of the adsorption process and the physicochemical characterization of the wastewater were carried out. The results indicated that increasing dye concentration, adsorbent mass, and reaction time, along with decreasing pH, enhanced adsorption process, concurrently leading to 71 % dye removal efficiency and 36.9 % mineralization degree.*

Keywords: *adsorption, activated carbon, flexo printing dye, wastewater treatment*

Introduction

Waste generated after the printing process is the residue of dyes, varnishes, solvents, oils, lubricants and similar substances. Dyes used in the printing industry contain heavy metals and organic compounds that are difficult to degrade. Their release into the environment via wastewater leads to pollution of the aquatic ecosystem and contamination of water sources [1]. For these reasons, it is necessary to pay particular attention to the proper and most efficient treatment of wastewater in order to prevent the deposition of numerous toxic and persistent substances in the environment. By optimizing the wastewater treatment process and analyzing its physico-chemical properties, the appropriate treatment can be determined in order to achieve a satisfactory purification standard and put an end to everyday pollution and environmental threats, at least in the printing industry [2].

The subject of this work is to explore the potential of using adsorption treatment with commercially available activated carbon to remove Yellow printing dye from both synthetic solutions and printing wastewater. The aim is to optimize the adsorption process and to conduct the physicochemical characterization of the wastewater.

Materials and methods

The following chemicals were used in the experiment: activated carbon (AC, Norit Row 0.8 Supra), Yellow flexographic dye (Flint), sodium hydroxide (>98.8 % POCH, Poland) and hydrochloric acid (>96 %, J.T. Baker – Fischer Scientific, USA). Deionized water and analytical grade chemicals were used to prepare all working solutions of the desired concentrations.

The physicochemical characteristics of activated carbon as a adsobent are: iodine number 1050 mg g^{-1}, specific surface are 1150 m^2 g^{-1}, ash content 7 %, moisture content 2 %, pH 4,6 and density 390 kg m^{-3} [3].

In the adsorption tests, a sample of a synthetic solution of Yellow flexographic printing dye, which belongs to the group of azo dyes, was used as an adsorbate, as was a sample of wastewater collected after the flexographic printing process.

Concentration of the Yellow dye in the wastewater sample (121 mg l^{-1}) was carried out using the calibration curve. The absorbance of the printing dye solution was measured with a UV/VIS spectrophotometer (Genesys 10S, Thermo Fisher) at the determined maximum wavelength for Yellow dye (437 nm).

Based on the measured dye concentration in the wastewater, model systems with different dye concentrations of 20, 100 and 180 mg l^{-1} were prepared in the experimental part. In this way, a broader range of the influence of different dye concentrations in wastewater samples on the efficiency of the applied treatment was investigated.

Definitive screening design (DSD) analysis was used to investigate the influence of four process parameters: dye concentration, adsorbent mass, pH and reaction time. Jump 13 software was used for the experimental design and statistical analysis [4].

The adsorption treatment of the aqueous solution and real wastewater is described in our previous work [4].

The physico-chemical characterization of the wastewater before and after adsorption treatment included measurements of pH, electrical conductivity, temperature (AD110 Adwa device), turbidity (Turb 430 IR WTW) and total organic carbon (TOC) [5].

Results and discussion

For the four numerical factors, the Jump 13 software used for the statistical analysis of the data in this study generated a table with 15 experiments. The efficiency range was set at 1.35–94.70 %.

Figure 1 shows how the efficiency of the adsorption process changes depending on one variable, while the other variables remain constant.

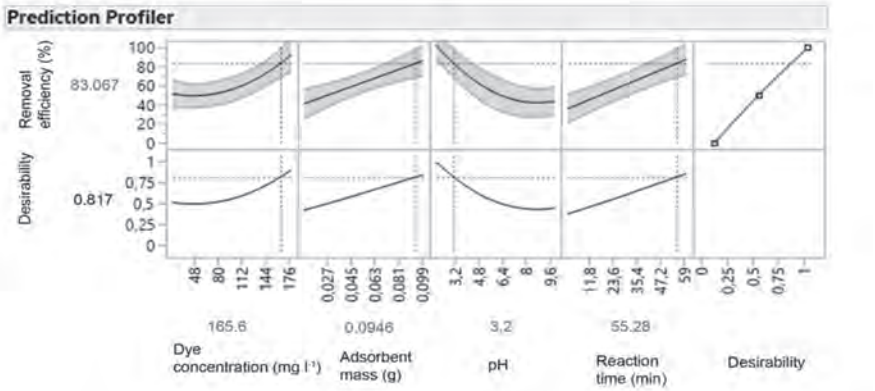

Figure 1. Optimization diagram

The optimization diagram clearly shows the pronounced influence of all variables, with the adsorption treatment being favored by high dye concentration, adsorbent mass and reaction time, as well as a lower pH value. At the same time, the highest efficiency of the applied treatment of 83 % was suggested for the removal of Yellow dye under optimal process conditions: dye concentration 166 mg l^{-1}, adsorbent mass of 0.09 g, pH 3.2 and reaction time 55 min.

In order to determine the feasibility of the optimized adsorption treatment, a real wastewater, which is produced after the printing process, was subjected to the same treatment at the determined optimum values of the process parameters (adsorbent mass 0.09 g, pH 3.2 and reaction time 55 min). The highest decolorization efficiency of 71.2 % was achieved after 90 minutes of reaction time, which confirms the lower activity of activated carbon in the treatment of real wastewater compared to a synthetic solution with pure dye. Nevertheless, the experiments conducted in this work confirm that activated carbon has a satisfactory potential to remove organic dyes in the adsorption process.

The results of the physicochemical characterization of the wastewater before and after treatment are shown in Table 1.

The pH value of the treated wastewater remained unchanged, as it was set at 3.2 as the optimum pH value at the start of the experiment. The increased conductivity after treatment indicates the formation of degradation products and the release of inorganic ions, which may also originate from the dye molecule itself. A decrease in the turbidity of the solution was also observed after treatment. The degree of dye mineralization is interpreted in terms of the determination of the TOC value. The determined degree of mineralization of 36.9 % indicates the fragmentation of the Yellow dye molecule, which is assumed to have been degraded to certain aliphatic products.

Table 1. Physicochemical characterization of the Yellow-coloured wastewater before and after treatment

Parameter	Before treatment	After treatment
pH	8.2	3.2
Conductivity (μS/cm)	423	680
Temperature (^{0}C)	22.3	23.4
Turbidity	182	220
TOC (mgC l^{-1})	120.2	75.8

Conclusion

The printing industry needs to develop effective wastewater treatment processes to remove inorganic and organic pollutants before discharging wastewater into the environment. The aim of this study was to remove Yellow flexographic dye by adsorption with activated carbon. The results showed that a higher dye concentration, adsorbent mass and reaction time together with a lower pH improved adsorption. The treatment removed 83 % of the dye from synthetic solutions and 71 % from real wastewater. Physico-chemical analyses showed a possible degradation of the Yellow dye with a mineralization rate of 36.9 %. In light of growing environmental concerns, research into efficient methods of dye removal that avoid secondary pollution and allow wastewater reuse is crucial.

Acknowledgment:

This research has been supported by the Ministry of Science, Technological Development and Innovation (Contract No. 451-03-65/2024-03/200156) and the Faculty of Technical Sciences, University of Novi Sad through project "Scientific and Artistic Research Work of Researchers in Teaching and Associate Positions at the Faculty of Technical Sciences, University of Novi Sad" (No. 01-3394/1).

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Synergia kyslého zrážania a kavitácie pre udržateľnú izoláciu lignínu

Matúš Majerčiak[1], Richard Nadányi[1], Aleš Ház[1], Sanjay Nagarajan[2]

[1]Slovenská technická univerzita v Bratislave, Fakulta chemickej a potravinárskej technológie, Ústav prírodných a syntetických polymérov, Katedra dreva, celulózy a papiera, Radlinského 9, 812 37 Bratislava, Slovensko
[2]University of Bath, Department of Chemical Engineering, Claverton Down, Bath, BA2 7AY, United Kingdom
xmajerciak@stuba.sk

Abstrakt: *Lignin, the second most abundant biopolymer on Earth, is a key component of renewable biomass, offering advantages such as lower production costs, biocompatibility, and biodegradability. This study compares two methods for isolating lignin from black Kraft liquor and alkaline lignin: acid precipitation and cavitation. A Design of Experiments (DoE) approach was used to optimize the isolation conditions (pH and temperature) and streamline the experimental process. The results were analyzed to determine the most suitable conditions for obtaining lignin with desired properties for specific applications. Acid precipitation, a traditional method, is energy-intensive, while cavitation, which involves bubble implosion, is more efficient and sustainable. The isolated lignins were characterized using UV-Vis, FTIR, TGA, and elemental analysis (C, H, N, and S). These techniques provided insights into the chemical and thermal properties of the lignins, which are critical for their potential applications in biocomposites, polymeric materials, and other biotechnological products. The study demonstrates that cavitation offers a more sustainable and efficient alternative to acid precipitation for lignin isolation, with the potential to support the development of eco-friendly materials and contribute to a more sustainable bioeconomy.*

Kľúčové slová: *Kraftový čierny lúh; alkalický lignin, lignín; izolácia lignínu; kavitácia; kyslé zrážanie*

1. Úvod

Polyméry syntetizované z lignocelulózovej biomasy sa vyznačujú ako mimoriadne životaschopná a revolučná alternatíva k tradičným polymérom získaným z fosílnych zdrojov, ponúkajúce presvedčivé výhody, ako je výrazné zníženie výrobných nákladov, vynikajúca biokompatibilita a pozoruhodná biodegradovateľnosť. Lignín, ako druhý najpočetnejší biopolymér na Zemi, zohráva kľúčovú úlohu ako základná zložka obnoviteľnej biomasy [1]. Vďaka svojej jedinečnej a komplexnej štruktúre so sieťovanými väzbami aromatických skupín má lignín výnimočné vlastnosti, ktoré ho stavajú do pozície veľmi sľubného surového materiálu pre

širokú škálu priemyselných aplikácií a otvárajú cestu k vývoju prielomových materiálov s výrazne vylepšenými charakteristikami [2]. Hoci bol historicky vnímaný prevažne ako vedľajší produkt celulózového-papierenského priemyslu, kde sa využíva v procesoch zhodnocovania energie, najnovšie pokroky ukazujú, že strategické modifikácie jeho molekulárnej štruktúry môžu výrazne zvýšiť jeho reaktivitu. Systematickými zmenami reaktívnych miest v základnej matrici lignínu, sa môže docieliť k vzniku širokého spektra produktov s pridanou hodnotou. Funkčné skupiny ako hydroxylová, karbonylová a metoxylová vykazujú výnimočnú reaktivitu a cielenou modifikáciou sa možu výrazne upraviť, čo vedie k výraznému uľahčeniu syntézy inovatívnych biodegradovateľných polymérov [3].

2. Metodológia

Táto práca skúma dve metodológie izolácie lignínu z čierneho Kraftového lúhu a alkalického lignínu: kyslé zrážanie a kavitáciu. Cieľom bolo získať ligníny s požadovanými vlastnosťami a vykonať charakterizáciu pripravených lignínov. V metóde kyslého zrážania bol lignín izolovaný modifikovaním pH pomocou kyseliny sírovej. Postup zahŕňal úpravu pH čierneho lúhu/alkalického lignínu pomocou kyseliny sírovej, následnú filtráciu cez Büchnerov lievik a sušenie lignínu na dosiahnutie konštantnej hmotnosti. Na zvýšenie efektivity experimentálneho procesu bol použitý prístup Design of Experiments (DoE). Izolované ligníny boli následne porovnané a charakterizované pomocou analytických metód. Optimalizáciou procesu boli identifikované najvýhodnejšie parametre (pH a teplota) na syntézu lignínov s optimálnymi vlastnosťami. V metóde kavitácie bola izolácia lignínu vykonaná zmenou pH a teploty a určením procesného kroku, v ktorom bola aplikovaná kavitácia (pred/po zrážaní). Kavitácia bola uskutočnená použitím dvoch zariadení: ultrazvukovej sondy a ultrazvukového kúpeľa. Čierny lúh a alkalický lignín slúžili ako východiskové materiály pre tento postup. Ligníny získané z oboch techník boli analyzované pomocou UV-Vis spektroskopie, FTIR, TGA a elementárnej analýzy (C, H, N a S).

3. Plánovaný experiment – Design of Experiments (DoE)

Plánovaný experiment bol implementovaný na zistenie optimálnych podmienok teploty a pH pre vhodnú izoláciu lignínu. V práci sa využil 5-úrovňový, 2-faktorový experiment, zameraný na teplotu a pH ako hlavné faktory záujmu. Hodnotenie bolo založené na podmienkach prípravy a kvalite výsledného produktu. Vzorky lignínu boli pripravené zrážaním vstupnej suroviny pomocou kyseliny sírovej za rôznych podmienok, pričom boli systematicky upravované pH a teplota počas procesu izolácie.

Na základe literárnej rešerše a predbežných experimentov boli stanovené rozsahy vybraných faktorov pre plánovaný experiment. Konečné hodnoty boli prepočítané z kódovaných hodnôt a následne získané pomocou experimentálneho programu implementovaného v MS Excel (ANOVA). Optimalizácia podmienok na prípravu optimálneho lignínu bola vypočítaná pomocou doplnku Solver v MS Excel.

Tab. 1: Rozpis pre plánovaný experiment.

Faktor	-alfa (-α)	-1	0	1	alfa (α)	Yi
Teplota [°C]	40,0	47,3	65,0	82,7	90,0	17,7
pH	2,0	2,4	3,3	4,1	4,5	0,9

	Matematické hodnoty		Reálne hodnoty	
Vzorka	Teplota	pH	Teplota [°C]	pH
1	-1	-1	47,32	2,37
2	1	-1	82,68	2,37
3	-1	1	47,32	4,13
4	1	1	82,68	4,13
5	-1,414	0	40,00	3,25
6	1,414	0	90,00	3,25
7	0	-1,414	65,00	2,00
8	0	1,414	65,00	4,5
9	0	0	65,00	3,25
10	0	0	65,00	3,25
11	0	0	65,00	3,25
12	0	0	65,00	3,25
13	0	0	65,00	3,25

4. Experiment – Kyslé zrážanie lignínu z alkalického lignínu a čierneho Kraftového lúhu

Lignín bol izolovaný postupom, kde sa najskôr alkalický lignín rozpustil vo vode v pomere 1:8. Výsledná suspenzia bola podrobená zrážaniu pomocou 50 % kyseliny sírovej pri neustálom miešaní. Po dosiahnutí požadovanej hodnoty pH, v rozsahu od 2 do 4,5 sa reakčná zmes zahriala na požadovanú teplotu. Keď suspenzia dosiahla požadovanú teplotu v rozmedzí od 40 °C do 90 °C, miešanie pokračovalo po dobu 1 hodiny. Následne bola suspenzia filtrovaná cez Büchnerov lievik. Výsledný filtračný koláč bol premytý horúcou vodou na neutralizáciu zvyškov kyseliny. Výsledný filtračný koláč sa sušil do konštantnej hmotnosti.

V prípade čierneho Kraftového lúhu bola na začiatku koncentrácia čierneho lúhu upravená pridaním demineralizovanej vody. Následne bola suspenzia postupne zrážaná 50 % (alebo 2 M) kyselinou sírovou, až sa dosiahlo požadované pH 4. Zmes bola potom zahrievaná na požadovanú teplotu v rozmedzí od 60 do 90 °C. Po dosiahnutí špecifikovanej teploty bola zmes ponechaná na tejto konečnej teplote po dobu 30 minút. Po uplynutí tejto doby bola suspenzia ďalej upravená na dosiahnutie požadovaného pH. Filtrácia bola vykonaná pomocou papierového filtra. Po filtrácii bol výsledný filtračný koláč suspendovaný v okyslenej destilovanej vode (pH 3) a následne podrobený filtrácii. Výsledný lignínový produkt bol sušený pri teplote v rozmedzí od 38 do 42 °C.

5. Experiment – Kavitácia

Experimenty s ultrazvukovým prístrojom (ultrazvuková sonda) boli vykonávané s roztokom kyseliny sírovej, pripraveným z demineralizovanej vody, aby sa dosiahol požadovaný objem. Lignín bol pridaný do zriedeného roztoku kyseliny v množstve v pomere 1:8. Amplitúda pre proces sonifikácie bola nastavená na 90 %. Experiment sa vykonával bez prekročenia maximálnej teploty 60 °C. Na zabezpečenie tejto teploty sa experimenty vykonávali v ľadovom kúpeli. Jediná premenná, ktorá sa menila, bol čas. Filtračné a premývacie postupy boli rovnaké ako v predchádzajúcich metódach. Podobné experimenty boli tiež vykonávané v ultrazvukovom kúpeli, bez použitia ľadového kúpeľa, pri predĺžených časoch trvajúcich od 15 do 120 minút. Experimentálne parametre, ako pH, zdroj lignínu (čierny lúh alebo alkalický lignín) a postupnosť kavitácie a úpravy pH, boli upravené podľa tabuľky uvedenej nižšie (Tab. 2).

Tab. 2: Rozpis pre experimenty s použitím metódy kavitácie.

Vzorka	Zdroj	Proces	Postup
BL1	AL	Kúpeľ	pH 4,51→Kav.
BL2	AL	Kúpeľ	pH 3,25→Kav.
BL3	AL	Kúpeľ	pH 2,01→ Kav.
BL4	ČL	Kúpeľ	pH 4,50→Kav.
BL5	ČL	Kúpeľ	pH 3,27→Kav.
BL6	ČL	Kúpeľ	pH 2,01→ Kav.
BL7	ČL	Kúpeľ	Kav.→pH 4,51
BL8	ČL	Kúpeľ	Kav.→ pH 3,26
BL9	ČL	Kúpeľ	Kav.→pH 2,00
PL1	AL	Sonda	Kav.→pH 4,52
PL2	AL	Sonda	pH 4,53→ Kav.
PL3	AL	Sonda	Kav.→ pH 3,02
PL4	AL	Sonda	pH 3,05→ Kav.
PL5	ČL	Sonda	Kav.→ pH 4,50
PL6	ČL	Sonda	pH 4,53→ Kav.
PL7	ČL	Sonda	Kav.→ pH 2,98
PL8	ČL	Sonda	pH 2,97→ Kav.
*ČL – čierny lúh, AL – alkalický lignín			

6. Záver

Merania preukázali značnú variabilitu v dôsledku rozdielnych metód izolácie. Výrazne lepšia izolácia lignínu bola dosiahnutá pomocou kavitácie, pri ktorej sa v úvodnej fáze surovina (čierny lúh/alkalický lignín) okyslila na požadované pH pred začatím kavitácie. Zhromaždené údaje boli dôkladne analyzované s cieľom určiť optimálne podmienky na prípravu lignínu s požadovanými vlastnosťami pre jeho plánované využitie v rôznych škálach priemyselných aplikácií.

Poďakovanie

Túto prácu podporila Agentúra na podporu výskumu a vývoja SR na základe zmluvy APVV-22-0388 a Vedeckou grantovou agentúrou VEGA 1/0743/24. Taktiež poďakovanie patrí Institute for Sustainability and Climate Change at University of Bath za poskytnutie financovania a podpory pri riešení tohto projektu.

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Delignification with deep eutectic solvents using oxygen as an oxidizing agent

Klára Janigová, Veronika Majová

Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Department of Wood, Pulp and Paper, Radlinského 9, 812 37 Bratislava, xjanigova@stuba.sk

Abstract: *Nowadays, it is known that many researches are focused on the substitution of fossil fuels for renewable sources. However, the same applies to chemicals used in various industries and production processes. There are ever-increasing demands to maintain environmental and health standards. Therefore, chemists and researchers around the world are looking for new greener solvents to replace conventional, toxic organic or inorganic solvents of daily use in industry [1]. In recent years, deep eutectic solvents as green solvents have shown many advantages such as high stability, economic availability, recyclability, and biodegradability [2]. They also show results in delignification, which could be used in the pulping process. A review of studies of deep eutectic solvents used for delignification is described in the literature [3]. Even the Confederation of the European Paper Industry (CEPI), according to the roadmap „2050 Road to a low-carbon bioeconomy", has chosen deep eutectic solvents (DES) as one of the most promising alternatives to carry out sustainable delignification of wood [4].*

Currently, there are already a large number of studies confirming the effectiveness of deep eutectic solvents in the delignification process. These articles investigate the effects of different solvent mixtures in different proportions, under different conditions [2], [5] or the effectiveness of their aqueous solutions [4]. So far, the delignification properties of these solvents on a raw sample of wood or other biomass have rather been investigated. Or even use in a post-delignification process, in which green solvents would replace oxygen delignification [6].

However, this work focuses on the use of deep eutectic solvents specifically in the oxygen delignification process, where the sample is unbleached pulp specifically from the Mondi SCP Ružomberok production process. The plan is to find out how solvents react in combination with oxygen as an oxidizing agent. To get the outputs, whether oxygen will increase the efficiency, will have no effect or even will decrease the efficiency of delignification. By this we want to find out the possibility of replacing the chemicals used in the oxygen delignification process with alkaline green solvents. Six solvents will be monitored at the ratios that, according to the literature, show the highest delignification efficiency on biomass.

Acknowledgement

This work was supported by the call for doctoral students and young researchers of Slovak University of Technology in Bratislava to start a research career (Grant 23-04-04-B). This work was supported by the Slovak Research and Development

Agency under the contracts Nos. APVV-22-0277, APVV-22-0388, and VEGA Grant 1/0651/23.

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Modification of the physical-mechanical properties of paper, primarily aimed at increasing elasticity

Kristína Kyseľová, Štefan Šutý, Ida Skotnicová

Department of Wood, Pulp and Paper, Faculty of Chemical and Food Technology,
Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia
xkyselovak@stuba.sk

Abstract: *Nowadays, the production of paper packaging is increasing, replacing other types of packaging materials. It is for this reason that the aim of this work is to improve the physical and mechanical properties of paper. We mainly focused on increasing the elasticity of paper, which is an important property in the production of paper packaging. In this work, we have studied the production of laboratory sheets with a high degree of grinding (31 °SR, 40 °SR, 52 °SR, 60 °SR and 71 °SR) and the characterization of their properties. With increasing degree of grinding led to changes in the physical, mechanical and surface properties of the paper. With increasing grinding degree, we observed rising in the shrinkage of the individual sheets, which reached a value of 17.92%. By increasing the degree of grinding and shrinkage, the relative elongation values developed to 13% compared to the initial 9%. In this work, we were able to enhanced the elasticity of the paper without significant changes in the strength of the paper, such as tensile strenght.*

Keywords: *elongation; increasing elasticity of paper; modification in papermaking*

Acknowlegment:

This work was supported by the Research and Development Agency under contract APVV-22-0277 and project VEGA 1/0651/23.

Use of Optimized Hydrotalcite-Based Systems for the Stabilization and Deacidification of Paper Information Carriers

Eva Guzikiewiczová, Soňa Malečková, Jana Jurišová, Radko Tiňo, and Katarína Vizárová

Slovak University of Technology, Faculty of Chemical and Food Technology, Institute of Natural and Synthetic Polymers, Department of Wood, Pulp and Paper, Radlinského 9, Bratislava SK-812 37, Slovakia, eva.guzikiewiczova@stuba.sk

Abstract: *Paper-based information carriers represent a crucial part of cultural heritage, but their longevity is threatened by cellulose degradation. The primary mechanisms responsible include acid hydrolysis, oxidation, photochemical degradation, alkaline hydrolysis, and biological degradation, with acid hydrolysis being a key factor in paper deterioration [1, 2]. To counteract this, stabilization and mass deacidification methods have been developed, though current conservation capacities remain insufficient [3, 4]. Various deacidification techniques utilize alkaline compounds, solvents, and application methods, with the Bookkeeper process being among the most widely used [5, 6]. However, challenges persist, necessitating the search for alternative deacidification agents. Hydrotalcites (HTCs), a class of anionic clays, have been widely used as stabilizers in polyolefin production and as antacids in medicine [7, 8]. Their ability to neutralize acids makes them promising candidates for paper stabilization and deacidification. This study explores the application of various HTCs in acidic paper conservation, considering differences in their synthesis, including surfactant addition, precursor materials (nitrates vs. chlorides), and Mg/Al composition. The influence of these factors on HTC effectiveness was analyzed, contributing to the development of improved paper preservation strategies [9]. The effect of modification on stabilization during accelerated aging was studied by measuring chemical (surface pH, glycosidic bond cleavage), mechanical (folding endurance – coefficient of relative increase of the lifetime), and optical (colorimetry) properties.*

Key words: *Paper; Degradation; Deacidification; Hydrotalcites; Dispersion*

Acknowledgment

This work was supported by the Slovak Research and Development Agency under Contract no. APVV-18-0155

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