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Barbara BALON[1]

MODERN TECHNOLOGIES USED IN FORENSICS AND THEIR IMPACT ON THE ACTIVITIES OF THE INVESTIGATION DEPARTMENT

1. Introduction

Security services and law enforcement agencies, in the era of dynamically advancing digitalization and the need to ensure cybersecurity of their activities, undertake a number of innovative projects supporting them in combating crime. These activities standardize the scope of activities performed within the framework of using advanced cryptographic tools, procedures, quality of expert research conducted in modern forensic laboratories, competences of their employees and forensic assessment, interpretation and review of investigative materials in order to properly identify the perpetrator of a crime or solve a detective issue. In almost every expert opinion, tools in the form of various databases, applications or research techniques [1] provide strong support for experts. The criteria for selecting tools for effective work in the area of detective and procedural projects affect each stage of the proceedings and its quality, which is why it is so important that the selection of these tools is supported by the most modern technology and hardware solutions (technical research equipment) that allow performing the tasks in question at the highest level of professionalism, thus creating a new era of forensics. In addition, due to the enormity of the ongoing socio-economic changes, the importance of implementing new solutions in modern forensics is growing, and the dynamic technological development forces law enforcement agencies to use modern IT tools. Another important aspect is the role and possibilities of forensic IT in the cloud computing environment. This topic is still insufficiently regulated by law. The growing popularity of cloud data storage services makes securing evidence located on the Internet one of the challenges of forensic IT. That is why it is so important to take care of the cybersecurity of investigative analyses.

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2. Modern forensics in practical applications

Forensics is a science of "tactical principles and methods and technical methods and means of detecting, securing, investigating and using all sources of information and information about persons and events and their circumstances" [2]. This definition helps to understand the purpose of the activities of security services and law enforcement agencies in undertaking a number of enterprises, ensuring effective protection of the life and health of citizens and property. It is important to take care of taking high-quality preventive and combating actions against crime, as well as those related to the response to crisis or terrorism-related situations. That is why it is so important to use the tools and methods of law enforcement and justice that most effectively lead to the disclosure, detection of the perpetrator and collection of evidence [3]. Moreover, due to the rapidly growing amount of information, special consideration should be given to the analysis of a number of information due to the need to use them to counter terrorism or the activities of organized crime groups [4]. Forensics is a multidisciplinary science that includes other, separate disciplines, such as:

- substantive and procedural criminal law, criminology (legal sciences);
- forensic medicine, biology, genetics, chemistry, physics, mathematics, electronics, computer science (natural and technical sciences);
- psychology, sociology (social sciences).

In the process of investigative analysis in criminal proceedings, it is important to use tools that facilitate evidentiary reasoning. In this respect, three main trends can be distinguished [5]:

- argumentative approach – confronting hypotheses with generated arguments helpful in evidential reasoning;
- narrative approach – organizing evidence by telling stories, constituting a network of causally connected events;
- hybrid approach – binding both methods in the form of a combination of arguments with narrative.

One of the innovative forensic solutions that enables effective combating of crime is the possibility of first identifying and then establishing the identity of persons suspected of committing a crime or victims of such crimes by creating a composite portrait [6]. A composite portrait is *a professional descriptive and graphic system that creates the possibility of determining a person's appearance based on third-party reports* [7]. Modern methods of preparing memory portraits are based on a memory trace, i.e. permanent changes in the nervous system caused by its momentary stimulation and constituting the basis of memory, i.e. subjective psychological traces [8].

Information about a person, including their appearance, as proven by scientific research, can also be obtained thanks to a "genetic portrait of memory" [9]. Work on DNA profiling is one of the most prestigious challenges of modern forensics, because it allows precise

individualization of evidence and even reconstruction of the genetic profile of an unknown perpetrator of a crime based on their DNA. Understanding the interactions within the genome leads to the disclosure of specific features, e.g. morphological (e.g. height, skin color, hair color, eye color) [10].

The most commonly used method of reconstructing the appearance of the deceased during their lifetime is the computer method, which allows for obtaining a three-dimensional image of the skull and the possibility of indicating the similarity of the development of the hard tissues of the head and facial features [11]. There are several methods for computer reconstruction of appearance [12]:

1. method based on the description of the analyzed skull (i.e. data obtained from anthropological research);
2. method based on a computer-scanned image of the skull, on which facial elements selected from the database are superimposed (it allows to reconstruct the appearance of representatives of the white variety, taking into account gender and age) [13, 14];
3. 3D method (Three Dimensional Facial Reconstruction) – allows to reconstruct the spatial image of the damaged skull skeleton by reconstructing the image of the resulting injuries, such as dents, crushes, cavities [15].

Other equally important methods and tools include:

1. Virtopsy – virtual autopsy – the method is based on technology using radiology, X-ray diagnostics and modern techniques for recording and processing data obtained during laser scanning of the surface of the corpse, computed tomography, magnetic resonance imaging and 3D visualization and spectroscopic technology. This method enables the image visualization of the human body's interior and its individual organs [16, 17, 18].
2. Photogrammetry with laser scanning of the body surface – a technique for imaging spatial models based on two-dimensional images [19].
3. Computed tomography in post-mortem examination provides information on:
   - analysis of bone structure for possible injuries (fractures);
   - individual characteristics, with their subsequent illustrative 3D graphic reconstruction;
   - photographic images of "bloody" preparations with soft tissues;
   - images of previously prepared and macerated bones;
   - determining spaces containing gases (air), which makes it possible to demonstrate post--traumatic changes leading to death – e.g. cardiac air embolism;
   - visualizing fluid levels – e.g. presence of blood in the pleural cavity;
   - demonstrating the presence of foreign bodies for corpse identification;
   - demonstrating the presence of bullets or small metal fragments.
4. magnetic resonance imaging – a complement to computed tomography enables imaging of changes in the soft tissues, showing the image of gunshot wounds;

5. forensic linguistics – a method that identifies authors based on the linguistic profiling of the text's sender (author/performer);
6. methods of visualizing fingerprints in finger prints – these include new methods of revealing fingerprints using nanotechnology and high-pressure technology [20];
7. electroencephalography (EEG) – this method enables verification of explanations and/or testimonies given during the trial by participants in criminal events. The purpose of EEG is to associate a specific pattern of electrical activity with the fact of telling the truth or untruth;
8. magnetoencephalography (MEG) – a method that allows the assessment of the anatomical structure of the brain in order to determine a person's truthfulness; it reaches deeper sources than EEG;
9. positron emission tomography (PET) – the method involves intravenous administration of radioactively labeled glucose, which allows for determining the locations of the greatest neuronal activity. The test checks the functioning of all parts of the central nervous system and allows for the analysis of the reaction of many of its structures as a result of the response to sensory, emotional, emotional, and even sexual stimuli;
10. functional nuclear magnetic resonance imaging – BOLD (Blood Oxygen Level Dependent) – a non-invasive method of examining the function of the human cerebral cortex using a strong magnetic field and radio waves. The method allows for verifying brain functions and assessing morphological and functional changes that underlie many diseases. Based on a comprehensive study, it is possible to trace physiological brain processes and select those that can be classified as pathological or criminal reactions.

3. Forensics in the digital space

First of all, it is necessary to mention the history of the emergence and development of computer forensics and then digital forensics. This discipline was motivated by the needs of investigative officers, who with the widespread use of computers and devices containing digital data, began to independently obtain information useful for the conducted proceedings [21]. The beginnings of research on secured computer equipment date back to the mid-1980s. Subsequently, in response to the growing demand for this type of research activities in the United States, a permanent FBI Computer Analysis Team (CART) was established.

Cyber crime is a subject of constant evolution, revealing new areas and opportunities for criminal activities – resulting from the global dissemination of Internet access and the revolution in the field of mobile technologies in the era of digitalization. The concept of cyber crime should be understood as both crimes directed against computer or access devices enabling

entry to cyberspace, as well as those committed using them (e.g. mobile access to social media). These crimes are the domain of organized crime groups with an international reach [22].
Digital forensics is related to the development of computer technologies, which have been of fundamental importance for the development of the information society and the possibility of using its achievements also for purposes inconsistent with the applicable law. Along with the dynamic digital revolution, opportunities and challenges have arisen for criminals, law enforcement agencies, governments, citizens, science and business [23].

IT tools play a key role in forensics mainly due to the amount of information that is analyzed, as they significantly increase the chance of correct verification of suspects of an offense or crime and reduce the risk of incorrect analyses performed by forensic technicians. One of the most popular electronic tools used to systematize knowledge gathered in a case, as well as to facilitate analysis and visualization of their results is i2 Analyst's Notebook2 [24]. The digital application allows for combining many elements into a coherent picture of the situation, thanks to the implemented solutions in the field of:

- importing data (telephone call records, financial transactions, wireless network login data, data collected by mobile devices);
- temporal analyses of relationships between events and people;
- social network analyses to identify people and the relationships between them.

Smartphones are another important object providing a wealth of information in preparatory proceedings. Data stored on mobile phones can achieve comparable importance to digital documents and e-mail [25], and often offer greater opportunities in the area of searching for evidentiary information than personal computers [26]. Forensic examination of mobile phones takes place as part of the examination of things and is carried out at the scene of the incident or, if they require special activities, by a forensic technician. The most popular tool used to analyze data in smartphones is Oxygen Forensic Detective [27]. With this tool, you can:

- find passwords for applications and user accounts;
- create backups of login data;
- extract data from cloud computing (iCloud, Google, Microsoft);
- sort data;
- search e-mail;
- view history in web browsers;
- restore deleted temporary files;
- recover data that has been formatted or deleted.

Another equally popular tool for searching the content of mobile phones is MOBILedit! Forensic. The use of the software provides information on the content and analysis of the phone book, contacts, calls, messages, service, analysis of data present and deleted from the SIM card and making a binary copy of the data [28]. Cloud computing technology operating within the

Internet of Things allows unlimited access to computing and data collection resources, such as servers and mass storage. Its main advantage is easy and immediate access to information from anywhere in the world where there is Internet access [29]. The growing popularity of data storage services in the cloud computing and the possibility of using these solutions for criminal purposes obliges practitioners dealing with computer forensics to pay special attention to the issue related to securing and analyzing digital evidence [30, 31]. A detailed review of the challenges and problems of computer forensics in the field of obtaining and analyzing data from cloud computing is presented in the report of the American Standardization Organization NIST [32].

There are few references in the research literature to studies on the possibility of revealing traces of cloud storage users' activity in the local device memory. Only a few researchers have addressed this topic. As found in the literature, Dehghantanha and Dargahi [33] analyzed two services: CloudMe (a service offering secure cloud storage, file synchronization, and client software for remote data management) and Qihoo 360 Yunpan (a cloud storage service offering the largest free online disk in the world). In their research, the authors analyzed the topic on three operating systems: Windows 8.1, Android KitKat 4.4.2, and Apple iOS 8.0. Their research shows that using cloud services leaves many traces in the memory of digital data carriers. This is because analyzing the contents of the disk, RAM, and internal memory of mobile devices allows reading authentication data, device names, and file names stored on virtual disks. The security of encrypted data in the case of Qihoo 360 Yunpan was determined as very low. CloudMe has been shown to be much more protective of user privacy, as confirmed by uninstalling the CloudMe client application. This action left the configuration files, but did not change the registry keys and managed to fully encrypt the data during transfer.

Mohtasebi et al. [34] conducted research on the services: SpiderOak, JustCloud and pCloud. The researchers worked using three web browsers: Internet Explorer, Mozilla Firefox and Google Chrome, as well as a client application installed on Windows 8.1 and an iPhone with iOS. The data disclosed and recovered during the research included e-mail addresses, the ID and name of the created account, and the names of uploaded and downloaded files.

In turn, researchers Teing, Dehghantanha and Choo [35] verified the possibility of revealing traces of the activity of the CloudMe online drive user in operating systems such as: Windows 8.1 Professional, Linux, Apple Mac OS and on mobile devices: iPhone 4 and HTC One. Analysis of the history of web browsing allowed the identification of unique web addresses, which allowed obtaining data on logins/logouts, accessing files/folders and downloading data. The connection of the web browser was encrypted, which did not prevent recovering the contents of the application's main directory from the browser cache, metadata from saved files and passwords to shared resources.

Ahmad et al. [36] described the existing possibilities of revealing traces of pCloud service user activity in RAM. They worked on Windows 7 Ultimate. The researchers assessed the possibility of revealing data on user interaction with the virtual disk based on the transferred data and opening and viewing its content. The results of the analyses were the demonstration of the possibility of reading authentication data and information about files stored on the virtual disk. The research confirms the results of earlier experiments performed by Dargahi, Dehghantanha, Conti (2017).

The main challenge of digital forensics is currently keeping up with the rapidly evolving research methods and processes of the digital world. The growing dependence of the information society on technological tools means that the scope of responsibilities of law enforcement agencies in controlling activities in the digital space is constantly expanding. The growing involvement of services results from the demand for forensic expertise, in particular in the field of sophisticated digital crimes, fraud, data theft, and the circulation of content prohibited by Polish and international law [37].

3.1. Cybercrime

The term cybercrime refers to the use of digital technologies or the Internet as tools for committing crimes using computer technologies or Internet networks, such as: identity theft, phishing, malware, cyberbullying, drug trafficking, etc. The International Criminal Police Organization “Interpol” divides cybercrime into attacks involving the violation of access rights to resources (e.g. hacking), fraud using a computer (e.g. ATM fraud, counterfeiting of input or output devices, fraud in telecommunications systems), program duplication, sabotage of hardware and software, storage of collections prohibited by law, crimes committed on the network [38]. In practice, cybercrime is a multi-stage and complex undertaking. As a result, cybercrime services currently constitute a professional market, characterized by high specialization and cooperation structure. It is also popular for criminals to use VPNs (Virtual Private Networks) to mask their identity and location. Charity and fundraising scams have also become widespread, with criminals using them to extort money from donors. Another threat is spoofing, a technique used to gain the trust of victims by forging caller IDs. Online fraud also involves manipulating payment systems. Malware can be installed in ATMs or tricked into mobile devices to withdraw money or take over digital payment systems or to steal card data through digital skimming. The leading area of criminal activity is the so-called Darknet. This network is used by cybercriminals for communication, trading in digital assets, trading drugs, fake documents, weapons and other illegal goods. Transactions are often carried out using cryptocurrencies, which makes it difficult to identify criminals and identify illegal activities.

The most serious cyber threats can be classified as follows:

1. Financially motivated or data theft-oriented attacks and scams:
   a) Phishing – a method in which cybercriminals attempt to obtain confidential information about individuals (usernames, passwords and credit card details). Criminals operate by impersonating trusted entities popular in electronic communications.
   b) Hacking – unauthorized access to computer systems or networks. Criminals can exploit vulnerabilities in a victim's system to steal, modify, or destroy stored data.
   c) Identity theft – theft of personal information for the purpose of committing fraud (e.g. making unauthorized purchases, opening new accounts with the victim's personal information, taking out loans).
   d) Internet fraud – crimes committed in the Internet space aimed at obtaining money or personal data. Popular crimes in this area include frauds "on a bank employee", "on a police officer", "on a prosecutor".
   e) Investment fraud – fraud that involves extorting funds by persuading the victim to participate in capital investments.
   f) Business Email Compromise (BEC) CEO Fraud – cybercriminals take control of company e-mail accounts or create the same email domain aliases to trick company employees into making unauthorized financial transfers or disclosing confidential company information.
   g) Intellectual property theft – theft or use of intellectual property without the consent of its owner (proprietary software, music, films and other digital content).
2. Attacks on infrastructure and cyberspace:
   a) Cryptojacking – unauthorized use of another person's computer to mine cryptocurrencies.
   b) Hybrid attacks – digital crimes aimed at state security. They include critical infrastructure, public and economic institutions, and cyberespionage.
   c) Denial of Service and Distributed Denial of Service – attacks that overload a system, network or website, making them unavailable to users.
   d) Malware – malicious software (e.g. computer viruses, Trojans, keyloggers, botnet) installed on computers or devices without the user's consent. It can be used for cybercriminal activities, including data theft, spying, destroying files or blocking access to the system.
   e) Ransomware – a type of malware that blocks access to data or a system and demands a ransom to unlock it. Criminals use this method to blackmail victims and extort money from them.
3. Actions detrimental to society:
   a) Cyberstalking – using the Internet or electronic means to harass or persecute individuals;
   b) Use of legally prohibited materials involving children – using the Internet to produce and distribute pornographic content involving minors.

4. Summary

Modern forensic techniques and research methods allow the correct examination of traces and identification of perpetrators, victims of crimes, and indicate how to use modern technological solutions in work for forensic and judicial purposes. Without the tools, techniques and research methods that forensics has developed to date, it would be impossible to effectively conduct detection and evidence activities. The development of information technologies largely influences the improvement of the functionality of forensic databases, collections and registers. Systematic improvement of research methods in the field of identification, interpretation and effective analysis of research results will also contribute to raising the level and efficiency of investigators' work. Preventing and combating cybercrime requires law enforcement agencies to have vast technical and interdisciplinary knowledge, including social, economic and geopolitical issues. Fighting crime requires an approach based on continuous improvement, learning and investing in appropriate modern tools and research infrastructure.

5. Direction of further research

The content of this article is an introduction and background for the development of survey research on the social awareness of issues related to cybercrime and the examination of the level of knowledge of forensic science students and candidates for studies in the scope of the issues described in this article. The survey research is planned to be conducted in three groups of respondents: candidates for studies, students of forensic science and employees of units using forensic methods and tools in their daily work. The results may be a source of multi-dimensional perception of contemporary changes in the area of forensic science, which are caused by technological progress and provide valuable information in the policy of future actions in the field of state and citizen security.

Bibliography

1. M. Zubańska: Nowe technologie w kryminalistyce. Aspekty prawne i kryminalistyczne, Wyd. ElSet, Olsztyn 2019.
2. S. Adamczyk, T. Hanausek, J. Jarosz: Kryminalistyka. Zagadnienia wybrane, cz. I, Kraków 1971, s. 8.
3. J. Gąsiorowski: Kryminalistyka w naukach o bezpieczeństwie, [w:] Elementy teorii i praktyki transdyscyplinarnych badań problemów bezpieczeństwa, t. I, M. Cieślarczyk, A. Filipek, A.W. Świderski, J. Ważniewska (red.) Monografie, Nr 139. Siedlce 2013, s. 101 nast.
4. J. Konieczny: Zagadnienia wprowadzające. W: Analiza informacji w służbach policyjnych i specjalnych, J. Konieczny (red.). Warszawa: C.H. Beck, 2012.
5. F.J. Bex, B. Verheij: Story Schemes for Argumentation about the Facts of a Crime. Computational Models of Narrative: Papers from the The AAAI Fall Symposium (FS-10-04). Menlo Park: AAAI 2010.
6. J. Gąsiorowski: Portret pamięciowy w praktyce organów ścigania, [w:] Wybrane zagadnienia służby policyjnej, A. Rosoł, J. Słobosz, K. Silska (red.), wyd. Szkoły Policji w Katowicach, Katowice 2012, s. 9-47.
7. T. Kozieł, Z. Dębiński, Portret obrazowy w identyfikacji i poszukiwaniu osób (stan i perspektywy), „Problemy Kryminalistyki" 1992, nr 197-198, s. 11.
8. Szerzej patrz: S.A. Josselyn, S. Kohler, P.W. Frankland: Finding the engram, „Neuroscience" 2015, Vol. 16, s. 521.
9. B. Sygit, E. Sadowska: Rysopis genetyczny – perspektywy predykcji wyglądu nieznanego sprawcy przestępstwa ze śladu DNA, „Prokuratura i Prawo", 2010, nr 9; także: T. Grzybowski, Genetyczny portret. O przewidywaniu cech fizycznych człowieka na podstawie analizy jego DNA rozmawiamy z doktorem Wojciechem Branickim, ekspertem w dziedzinie genetyki sądowej, „Genetyka i Prawo, Kwartalnik Naukowy Zakładu Genetyki Molekularnej i Sądowej, nr 3, 2008.].
10. P.M. Visscher, S. Macgregor, B. Benyamin, G. Zhu, S. Gordon, S. Medland, W.G. Hill, J.-J. Hottenga, G. Willemsen, D.I. Boomsma, Y.-Z. Liu, H.-W. Deng, G.W. Montgomery, N.G. Martin: Genome Partitioning of Genetic Variation for Height from 11, 214 Sibling Pairs, Am. J. Hum. Genet., 2007, nr 81, s. 1104-1110; także: T. Grzybowski: Genetyczny portret..., s. 12.
11. J. Gąsiorowski: Rekonstrukcja przyżyciowego wyglądu twarzy na podstawie czaszki, „Acta Securitatea. Wybrane zagadnienia problematyki bezpieczeństwa wewnętrznego", Nr 2, 2015, s. 103-148.
12. T. Kozieł, Z. Dębiński: Portret pamięciowy – rekonstrukcja przyżyciowego wyglądu twarzy na podstawie czaszki, „Problemy Kryminalistyki", 1993, nr 202, s. 25-32.
13. D. Lorkiewicz-Muszyńska, [w:] Kociemba, C. Żaba, A. Lemke: Badania czaszki Stanisława Papczyńskiego (1631-1701) – założyciela zgromadzenia Księży Marianów, „Archiwum Medycyny Sądowej i Kryminologii", t. 59, nr 3, 2009, s. 208-217.

14. D. Zajdel: Metody identyfikacji n/n zwłok ludzkich pośmiertnie zniekształconych z wykorzystaniem systemu komputerowego POL-SIT, „Problemy Kryminalistyki", , nr 211, 1996, s. 24-31.
15. K. Woźniak, A. Moskała, A. Urbanik, M. Kłys, Pośmiertne badania obrazowe TK z rekonstrukcją 3D u ofiar wypadków drogowych, „Archiwum Medycyny Sądowej i Kryminologii", t. 59, nr 2, 2009, s. 93-100.
16. M.J. Thali, K. Yen, W. Schweitzer, P. Vock, C. Boesch, C. Ozdoba, G. Schroth, M. Ith, M. Sonnenschein, T. Doernhoefer, E. Scheurer, T. Plattner, R. Dirnhofer: Virtopsy, a new imaging horizon in forensic pathology: virtual autopsy by postmortem multislice computed tomography (MSCT) and magnetic resonance imaging (MRI) – a feasibility study, „J. Forensic Sciences", nr 48, 2003, s. 386-403.
17. K. Woźniak, A. Urbanik, A. Moskała, R. Chrzan, B. Kamieniecka: Konfrontacja klinicznego obrazu TK złamań kości czaszki z wynikami badania sekcyjnego, „Archiwum Medycyny Sądowej i Kryminologii", LVIII, 2008, s. 188-193.
18. D. Lorkiewicz-Muszyńska, Z. Przybylski: Znaczenie porównawczych badań odontologicznych w całokształcie postępowania identyfikacyjnego na podstawie czaszki, „Archiwum Medycyny Sądowej i Kryminologii", nr 52, 2002, s. 7-19.
19. K. Woźniak, A. Moskała, A. Urbanik, P. Kopacz, M. Kłys: Pośmiertne badania obrazowe z rekonstrukcją 3D: nowa droga rozwoju klasycznej medycyny sądowej?, „Archiwum Medycyny Sądowej i Kryminologii", LIX, 2009, s. 124-130.
20. E. Rogoża, K. Drzewiecka, P. Knut: Nanodak. Ujawnianie śladów linii papilarnych nanocząsteczkami wytwarzanymi przy użyciu technologii wysokich ciśnień, „Horyzonty Kryminalistyki", nr 4, 2020, s. 29 i nast.
21. E. Casey: Handbook on Digital Forensics and Investigation, Elsevier Inc. 2010, s. 2
22. https://www.interpol.int/Crime-areas/Cybercrime
23. M. Caloyannindes, N. Memon, W. Venema: Digital Forensics – Guest Editor Introduction, "IEEE Computer", marzec-kwiecień 2009, s. 16.
24. http://www-03.ibm.com/software/products/pl/analysts-notebook
25. P. Warnke: Mobile forensics zmienia urządzenia przenośne w dowody, Magazyn Informatyki Śledczej Bezpieczeństwa IT, 2014, nr 24.
26. Encyclopedia of Forensic Science, J.A. Siegel (red.). Amsterdam: Elsevier 2013.
27. https://www.opentext.com/products/cybersecurity-cloud
28. http://www.mobiledit.pl/forensic/mobiledit-forensic/
29. P.M. Mell, T. Grance: The NIST Definition of Cloud Computing. Gaithersburg: National Institute of Standards and Technology, 2011.
30. P. Sharma, D. Arora, T. Sakthivel: Mobile cloud forensic: Legal implications and counter measures, [w:] S.C. Satapathy, A. Joshi (red.), International Conference on Information and Communication Technology for Intelligent Systems. Cham: Springer, 2018, https://doi.org/10.1007/978-3-319-63673-3_64
31. G.N. Samy, B. Shanmugam, N. Maarop, P. Magalingam, S. Perumal, S.H. Albakri:. Digital forensic challenges in the cloud computing environment, [w:] F. Saeed, N. Gazem, S. Patnaik, A.S. Saed Balaid, F. Mohammed (red.): Recent Trends in Information and Communication Technology. Cham: Springer, 2018, https://doi.org/10.1007/978-3-319-59427-9_69

32. M. Herman, M. Iorga, A.M. Salim, R.H. Jackson, M.R. Hurst, R. Leo, R. Sardinas, NIST Cloud Computing Forensic Science Challenges. Gaithersburg: National Institute of Standards and Technology, 2014.
33. A. Dehghantanha, T. Dargahi: Residual cloud forensics. W: A. Dehghantanha, K.-K.R. Choo (red.), *Contemporary Digital Forensic Investigations of Cloud and Mobile Applications*. Amsterdam–Boston i in.: Elsevier, 2017, https://doi.org/10.1016/B978-0-12-805303-4.00014-9
34. S.H. Mohtasebi, A. Dehghantanha, K.-K.R. Choo: Cloud storage forensics, [w:] A. Dehghantanha, K.-K.R. Choo (red.), Contemporary Digital Forensic Investigations of Cloud and Mobile Applications (s. 205–246). Amsterdam–Boston i in.: Elsevier, 2017, https://doi.org/10.1016/B978-0-12-805303-4.00013-7
35. Y.-Y. Teing, A. Dehghantanha, K.-K.R. Choo: CloudMe forensics: A case of big data forensic investigation. Concurrency and Computation: Practice and Experience, 30(5), 2018, https://doi.org/10.1002/ cpe.4277
36. N.H. Ahmad, A.S.S.A. Hamid, N.S.S. Shahidan, K.A.Z. Ariffin: Cloud forensic analysis on pCloud: From volatile memory perspectives. W: M.H. Miraz, P. Excell, A. Ware, S. Soomro, M. Ali (red.), *Emerging Technologies in Computing, Third EAI International Conference, iCETiC 2020*. Cham: Springer, 2020.
37. A. Rizwan, R.V. Dharaskar: Mobile Forensics: an Overview, Tools, Future Trends and Challenges from Law Enforcement Perspective, [w:] Sixth International Conference of E-governance (ICEG 08), IIT and NSIT, New Delhi 2008, s. 321.
38. M. Siwicki: Podział i definicja cyberprzestępstw, „Prokuratura i Prawo" 2012, nr 7-8, s. 241-252.

MODERN TECHNOLOGIES USED IN FORENSICS AND THEIR IMPACT ON THE ACTIVITIES OF THE INVESTIGATION DEPARTMENT

Abstract

The aim of the publication is to present issues related to modern technological solutions in the field of laboratory medicine, computer methods and cybersecurity, which influence the development of the area of forensics and which cause changes in the activities of investigative services. The latest organizational and technical solutions in the forensic aspect (forensic tactics and techniques) of the activities performed that influence the implementation of the detection process are discussed. The subject of cybercrime and its types is discussed.

Keywords: forensics, modern technologies, cybersecurity, identification, forensic expertise

NOWOCZESNE TECHNOLOGIE STOSOWANE W KRYMINALISTYCE I ICH WPŁYW NA DZIAŁANIA ORGANÓW ŚLEDCZYCH

Streszczenie

Celem publikacji jest zaprezentowanie problematyki związanej z nowoczesnymi rozwiązaniami technologicznymi z zakresu medycyny laboratoryjnej, metod informatycznych i cyberbezpieczeństwa. które wpływają na kształtowanie obszaru kryminalistyki i które powodują zmiany w działaniach służb śledczych. Omówiono najnowsze rozwiązania organizacyjno-techniczne w aspekcie kryminalistycznym (taktyki i techniki kryminalistycznej) wykonywanych czynności wpływających na realizację procesu wykrywczego. Podjęto tematykę cyberprzestępczości oraz jej rodzajów.

Słowa kluczowe: kryminalistyka, nowoczesne technologie, ceberbezpieczeństwo, identyfikacja, ekspertyza kryminalistyczna

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A REVIEW OF THE PRESENCE OF COSMETIC PRODUCTS AND PHARMACEUTICAL RESIDUES IN THE AQUATIC ENVIRONMENT AND METHODS OF THEIR REMOVAL

1. Introduction

Along with economic and social development, the degree of personal care products, called PCP for short, used in every household has increased. These mainly include cosmetic products – dermocosmetics, hair cosmetics, makeup products and perfumes [1]. However, since the primary purpose of their use is to ensure the proper level of cleanliness of the body, when talking about PCPs one should also have in mind such products as soaps, toothpastes and disinfectants [2-4]. In addition, with the use of colored cosmetics, various types of makeup removers and lotions have become an essential part of many people's daily care [4, 5].

Looking at their function from a historical perspective, primitive colored cosmetics were used to create camouflage as well as for religious and funeral ceremonies [6]. Over time, the functions of cosmetics began to broaden, with the expansion of their chemical composition, forming newer and newer groups and subgroups – it spread to the one we know today, intended to improve the appearance of people who use them, as well as perform protective functions against external factors and diseases [2, 7, 8]. Personal care products provide protection against diseases caused by various types of bacteria and viruses, and therefore in their composition must contain chemicals of an antibacterial nature, and sometimes pharmaceuticals – thus it can be said that the line between PCPs and simple, commonly available non-prescription drugs is slowly beginning to blur, so that a new group of substances called PPCPs (an acronym for Pharmaceuticals and Personal Care Products) stands out [9].

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2. Elaboration

Personal care products are a broad group of substances and cosmetics, which is growing day by day due to their wide range of applications and the companies producing them. According to Table 1, a division of personal care products into 16 groups can be adopted due to their function in daily life [4].

Table 1

Classification of personal care products (PCP) by the character of the products

Lp.	PCP group	PCP group representatives
1.	baby lotions, soaps and other baby products	wipes, diaper ointment, baby body wash, petroleum jelly
2.	general makeup and cosmetics	blush, foundation, concealer
3.	lip products	lip balm, lipstick, lip gloss
4.	eye makeup and cosmetics	eye shadow, mascara, brow liner
5.	hairstyling products	hairspray, gel, mousse, hair paste
6.	nail polish and remover	nail polish, nail polisher remover
7.	fragrance and perfumed products	perfume, bubble bath, body mist, air freshener
8.	deodorant and antiperspirants	deodorant, antiperspirant
9.	body lotions, creams and oils	body butter, belly oil, sunscreen, hand cream
10.	face lotions and creams	day cream, night lotion, acne cream, eye moisturizer
11.	body soaps	body wash, body gel, shower soap
12.	facial soaps, cleansers and washes	face cleanser, exfoliator, face masks, eye makeup remover
13.	toothpaste and mouthwash	toothpastes, dental rinse, mouthwash
14.	hand soaps, sanitizers and soap not otherwise specified (nos)	liquid soap, bar soap, waterless sanitizers, generic soap
15.	shampoo	shampoo
16.	conditioner	rinse-off conditioner, 2-in-1 shampoo and conditioner, leave-in conditioner

Source: Lang C., Fisher M., Neisa A., MacKinnon L.: Personal Care Product Use in Pregnancy and the Postpartum Period: Implications for Exposure Assessment. Int. J. Environ. Res. Public Health 2016, 13(1), 105.

The consumption of the personal care products has also changed in recent years due to the COVID-19 pandemic. This has been influenced by, in part, a forced change in daily habits, resulting from the need for a sedentary lifestyle due to restrictions on moving around in

public spaces, as well as a strong reliance on the use of disinfectants as protection against infecting with the virus [6]. There has been a change in the daily routine associated with facial care, and this phenomenon is shown in Figure 1 [10].

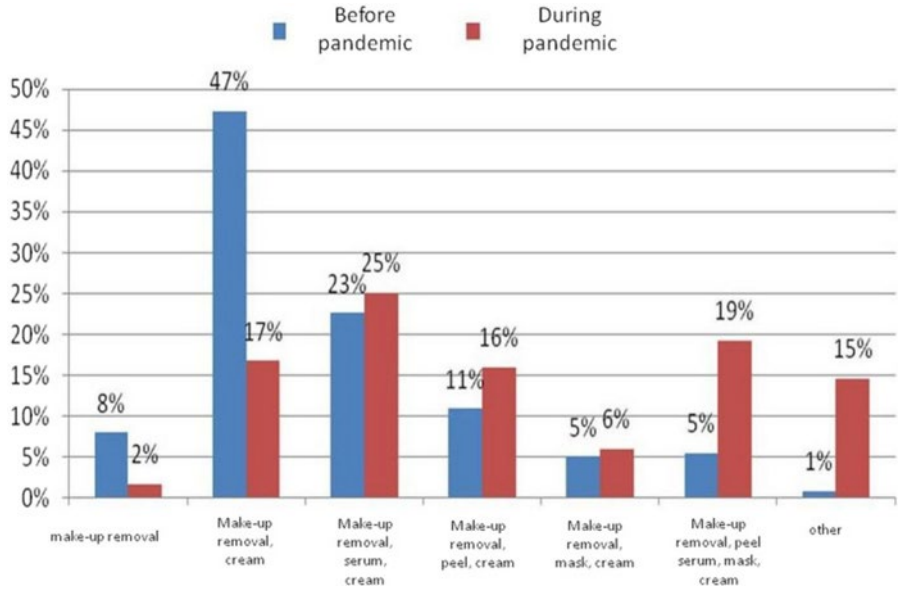

Fig. 1. The comparison of daily facial care procedure before and during the pandemic
Rys. 1. Porównanie codziennej pielęgnacji twarzy przed pandemią i w jej trakcie
Source: Ściereszko E., Budny E., Rotsztejn H., Erkiert-Polguj A.: How has the pandemic lockdown changed our daily facial skincare habits? J. Cosmet. Dermatol. 2021, 20(12), 3722-3726.

This phenomenon does not only apply to makeup cosmetics and dermocosmetics. The conducted surveys showed an increase in the use of soaps by rising frequency of hand washing during pandemics. The largest increase was shown for washing after using public transportation – the difference was more than 27% [11].

It should be noted that the different amount of personal hygiene products used is influenced not only by extreme global changes in the functioning of societies, but also by the very preferences of given social groups. A study conducted in the United States on a group of 50,000 young girls between the ages of 10 and 13 showed (Figure 2) that entire ethnic groups may have different preferences for the use of PCPs [12]. This may be influenced by genetic factors, leading, for example, to different amounts of sebum production [13].

The abovementioned shows that the consumption of PCPs, and thus their subsequent concentrations in the aquatic environment, can vary significantly not only from one region to another. Their route of entry there is the following: personal care products, most often used as creams or sprays, are washed off the surface of the skin and thus enter the wastewater and then the aquatic environment [14].

As a result of the application of PCPs on the skin and human body, not only the actual residues of personal care products enter the wastewater and aquatic environment, but also their derivatives – for example, UV filters undergo photodegradation after absorbing radiation from

sunlight [15-17]. It should be remembered that the resulting new chemical compounds or those precipitated from PCPs as their active ingredients are often very harmful and toxic in the aquatic environment, and may also bioaccumulate [2, 9, 18-20], the mechanism of which is shown in Figure 3.

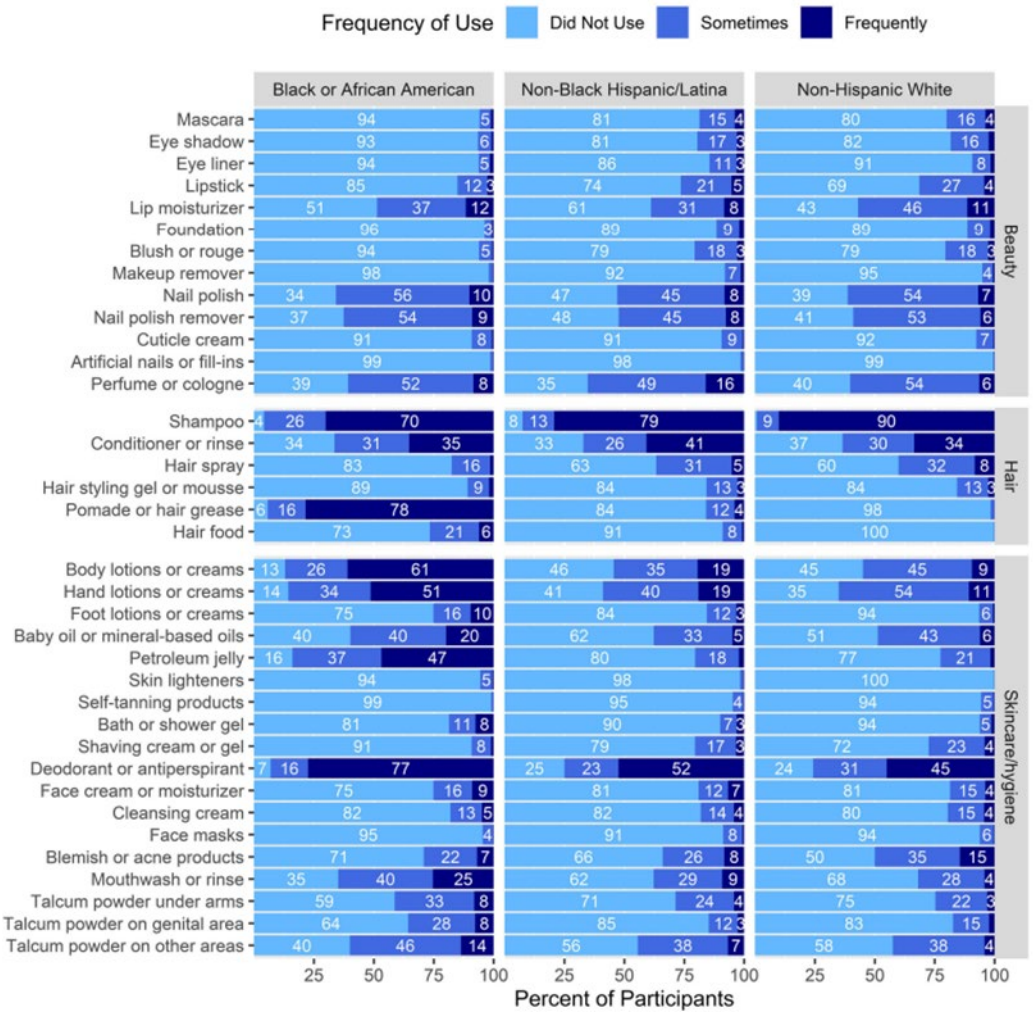

Fig. 2. Frequency of self-reported personal care product use during the ages of 10–13 years by race and ethnicity in the Sister Study

Rys. 2. Częstotliwość zgłaszanego przez pacjentów stosowania produktów do pielęgnacji osobistej w wieku 10–13 lat według rasy i pochodzenia etnicznego w badaniu Sister Study

Source: Goldberg M., Chang C.-J., Ogunsina K., O'Brien K.M., Taylor K.W., White A.J., Sandler D.P.: Personal Care Product Use during Puberty and Incident Breast Cancer among Black, Hispanic/Latina, and White Women in a Prospective US-Wide Cohort. Environ. Health Perspect. 2024, 132(2), 027001.

A particularly harmful group of substances found in PPCPs are endocrine disrupting chemicals (EDCs). They are the ones that form a direct link between pharmaceuticals and personal care products due to their occurrence in both groups as active substances (Table 2).

EDCs include substances such as benzophenone and 3-(4-methylbenzylidene)camphor (UV filters), N,N-Diethyl-m-toluamide, or DEET (repellent), and triclosan (antibacterial substance). On the other hand, EDCs that are a major component of drugs and pharmaceuticals include: carbamazepine, diethylstilbestrol, as well as the hormones – estrone or estradiol.

The endocrine system in humans and animals is affected by EDCs, most often by inhibiting or accelerating the production of hormones and interfering with their normal function [21-23]. It is important to note that endocrine disrupting chemicals show their negative effects on endocrine metabolism already at low concentrations [24].

Endocrine disrupting chemicals, like personal care products, enter the aquatic environment mainly through rinsing off the skin surface during bathing and recreational use of water [25-27]. For example, N,N-Diethyl-m-toluamide (DEET), used as an insect repellent, undergoes this process. Studies have shown the toxic properties of DEET, which can cause dermatitis of varying severity, disorientation, insomnia and even convulsions, hypotension and shortness of breath when used very frequently [28]. Analogously rinsed off can be triclosan and clotrimazole, a minimally skin-absorbed pharmaceutical substance with antifungal properties, making it widely used as an antifungal drug and fungicide in agricultural practices [29, 30].

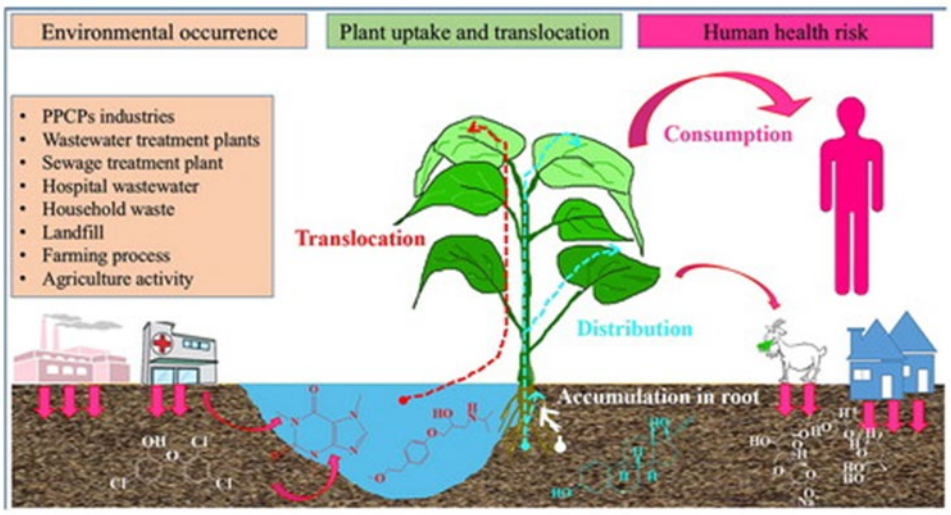

Fig. 3. The mechanism of PPCPs bioaccumulation
Rys. 3. Mechanizm bioakumulacji PPCP
Source: Keerthanan S., Jayasinghe C., Biswas J.K., Vithanage M.: Pharmaceutical and Personal Care Products (PPCPs) in the environment: Plant uptake, translocation, bioaccumulation, and human health risks. Critical Reviews in Environmental Science and Technology 2020, 51(12), 1221–1258.

Another source of PCPs and EDCs entering the water is the expulsion of substances from the body with excrement [31]. This mechanism occurs with compounds such as the previously mentioned carbamazepine. It is used as a popular antiepileptic drug, although it also helps the affliction of bipolar depression and trigeminal neuralgia, making it a psychotropic drug [32-34].

The excretion of female sex hormones, that is, estrone and estradiol [35, 36], and, in the case of veterinary medicine, diethylstilbestrol, abbreviated as DES (a synthetic estrogen, currently used as a veterinary drug and a growth promoter in animal feed), follows a similar course [37]. An obvious third possibility for chemicals of all kinds to get into water and wastewater is their migration with industrial wastewater, which, if not completely treated at wastewater treatment plants, ends up in receiving bodies along with the treated wastewater [33].

Table 2

Examples of EDCs and their sources

Name of the substance	Status of the substance as an endocrine disrupting chemical	Impact area	Main source of origin
3-(4-methylbenzylidene)camphor (4MBC)	validated by the EU	human health, natural environment	UV filters
nonylphenol	validated by the EU	natural environment	pesticides, detergents, plastic, PVC pipes, packaging products
benzophenone-2	analyzed by the EU	human health	UV filters, shampoos, lipsticks, body oils, hair sprays
triclosan	analyzed by the EU	human health	fungicides, toothpastes, antibacterial soaps, deodorants
salicylic acid	analyzed by the EU	human health	anti-acne cosmetics

Source: Own elaboration based on literature review [38-45].

The highest concentrations of PCP and EDCs are observed in raw wastewater [46]. Most of these compounds are not completely removed in traditional wastewater treatment plants based on biological chambers with activated sludge. Some of them may adsorb on activated sludge flocs [47], but most of them are passing into the treated wastewater, which is then discharged into the receiving waters – treatment plants are not adapted and designed for the removal of endocrine active compounds [48]. This results in the passage of PCPs and EDCs into the aquatic environment, where their concentrations are generally the lowest of the three environments analyzed.

The consequence of the described phenomenon is not only the pollution of rivers and lakes, but also the presence of endocrinically active compounds in drinking water [49]. The type of substances found to be present in water and their amount vary from country to country, region to region and the nature of the studied area – for example, the highest concentrations of EDCs were found in water from wells in India [50].

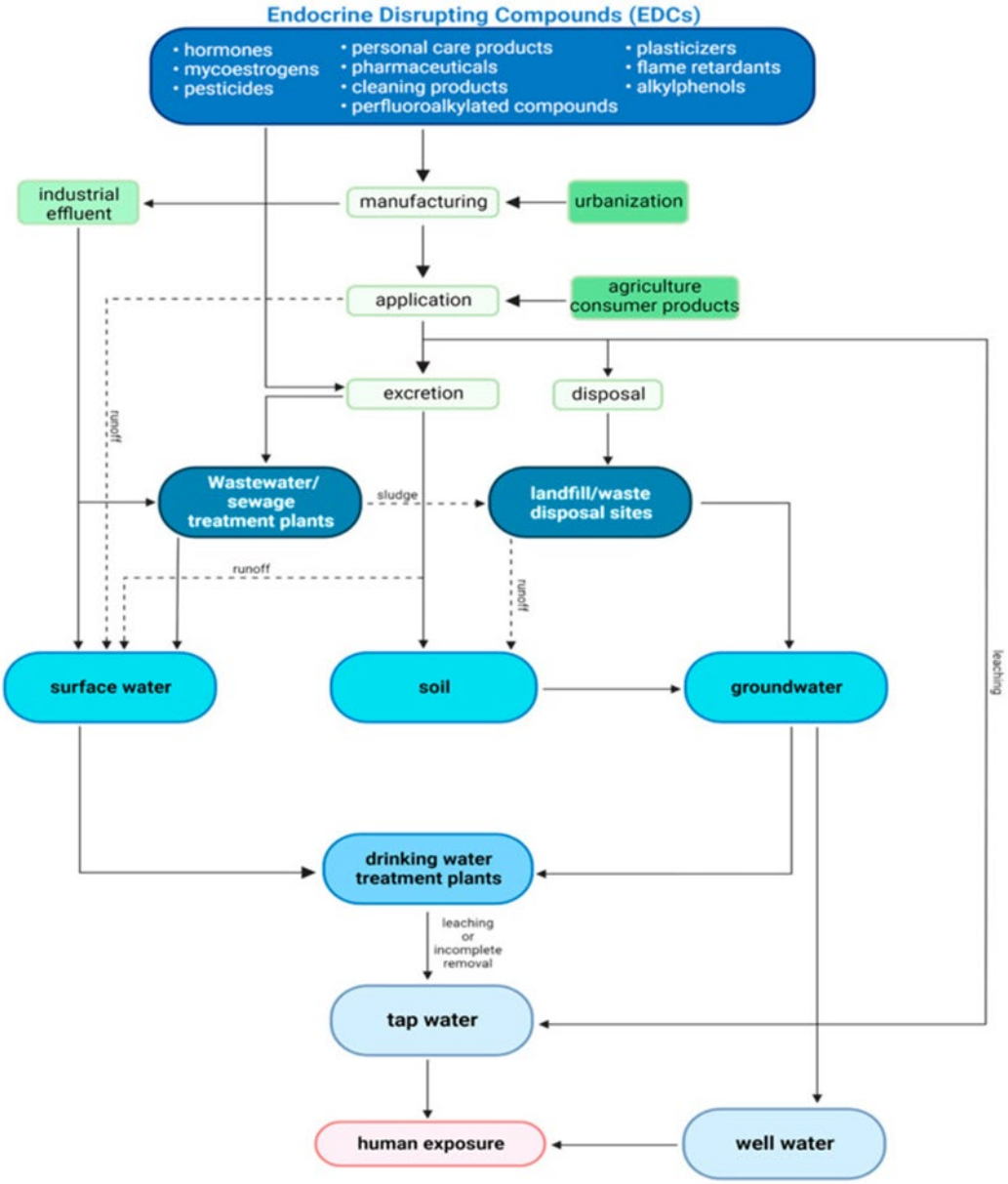

Fig. 4. Overview of human exposure to EDCs in drinking water and tap water

Rys. 4. Przegląd narażenia ludzi na substancje EDC znajdujące się w wodzie pitnej i wodzie wodociągowej

Source: Lazofsky A., Buckley B.: Recent Trends in Multiclass Analysis of Emerging Endocrine Disrupting Contaminants (EDCs) in Drinking Water. Molecules (Basel, Switzerland) 2022, 27(24), 8835.

The sources of these contaminants in drinking water (Figure 4) often vary widely. Substances that negatively affect the reproductive system and fertility in both humans and animals can be byproducts formed during water disinfection [51]. It is worth noting that disinfection byproducts, called DBPs, are formed not only in processes that use chlorine compounds, but are also demonstrated in ozonated water [52]. However, it should be remembered that endocrinically active compounds can be present in water not only because they have been transformed into oxidation byproducts, but also because oxidation simply did not remove them – the compounds remain (partially) unaffected (Table 3) [53]. For example, the most commonly used chlorination in water treatment removes only half of some EDCs at an acidic pH, while ozonation, on the other hand, is not a hundred percent effective at removing hormones [54].

Due to the presented problem of compounds that are constituents of personal care products and endocrinically active substances, it is necessary to constantly search for new, effective methods of removing them from water. The ideal situation would be to remove them without using a large amount of chemicals, as this would reduce the introduction of further foreign substances into the environment, as well as reduce the likelihood and amount of formation of the mentioned byproducts.

Table 3

Comparison of the removal of sample EDCs by two basic oxidation methods used at water treatment plants

Name of the substance	EDC removal rate [%]			
	Chlorination at pH = 6.6	Chlorination at pH = 8.6	Ozonation at pH = 6.6	Ozonation at pH = 8.6
triclosan	100	100	100	100
estrone	100	88.9	100	94.3
estriol	41.0	64.6	100	100
estradiol	50.5	68.3	100	41.7
ethynlestradiol	68.1	67.3	100	100

Source: Own elaboration based on literature sources [54, 55]

Another aspect to consider when analyzing PCP and EDC removal methods is the simplicity of the system, the ease of performing the cleanup and the uncomplicated method, as these determine the usefulness of the method – this will enable it to be used in practice.

Advanced oxidation processes (AOPs) are becoming increasingly popular. They enable the removal of contaminants through such means as the action of hydroxyl radicals·OH [56, 57]. In the case of the UV filters, promising removal results have been obtained for oxidation methods based on the use of ultraviolet radiation in several systems, including combined with oxidized water and mononadsulfates in the presence of radical scavengers – used to quench radicals to stop the oxidation reaction. Studies have shown UV filter degradation efficiencies

(using 4MBC as an example) of about 45% using UV alone. Adding hydrogen peroxide to the system improved its efficiency to 79%, and with peroxymonosulfate – to 92% [58].

Studies on the removal of endocrinically active compounds using UV light also were progressed for the more complex compounds that are bisphenol A, estradiol (E2) and ethinylestradiol (EE2). For this purpose, the UV/H_2O_2 system and the UV/Cl system were used to compare water treatment efficiencies. The study showed that both systems allow complete removal of the analyzed contaminants, however, the effect was obtained for quite different times: for UV/H_2O_2 it was 15 minutes, while for UV/Cl it was only two minutes. In addition, after the process, many substances were identified as byproducts, of which those formed after oxidation with chlorine were characterized by significant toxicity, which speaks against UV/Cl [59].

Another variation of the UV-activated system has been used in Chinese studies on the removal of steroidal estrogens – it was modified using peracetic acid [60]. In this case, peracetic acid (PAA) has the main function as an oxidant, as it is decomposed to acetic acid upon UV activation, and hydroxyl radicals are released during this process [61]. In addition, PAA is considered a stronger oxidant than hydrogen peroxide [62], and a mixture of PAA and hydrogen peroxide is able to reach a higher potential than chlorine oxidation [63]. Thus, the UV/PAA system allowed more than 90% removal of estrogens with an oxidation time of 30 minutes, while the oxidation performed with peracetic acid alone in the same time led to a removal of less than 40% [61].

Among advanced oxidation methods, iron also plays an important role, most often in the second and third oxidation state. They form the basis of many photocatalytic reactions – it is on the transition of iron from the second oxidation state to the third oxidation state under the influence of reaction with hydrogen peroxide that the Fenton reaction is based, during which active hydroxyl radicals are formed [64, 65]. A variation of it is the photo-Fenton process, which additionally utilizes the UV-induced reduction reactions of the iron(III) formed in the Fenton process back to the iron(II) [66,67]. Moreover, the photo-Fenton reaction is almost forty times faster than the classical Fenton [68].

Studies on the removal of endocrinically active phenols in the Fe(II)/Fe(III) system showed a removal effect of more than 99% after one hour of reaction. In order to obtain such high results, the Fenton process was modified by introducing a catalyst that accelerates the reduction reaction – molybdenum disulfide [69].

Studies were also conducted on the removal of endocrine disrupting chemicals in the Fe(III)/PAA system. The reduction reaction of iron(III) to iron(II) was used, with peracetic acid degrading directly leading to the formation of reactive radicals. This enabled the removal of EDCs from 87% to 94% within 90 minutes, depending on the compound analyzed and the concentration of the iron solutions. Benzophenone and endosulfan were the easiest to remove, while 4-octylphenol and diethylstilbestrol required the highest concentrations of Fe(III) [70].

To speed up the oxidation reaction in the Fe(III)/PAA system, the addition of salicylic acid (SAc) is utilized. It forms complexes with iron(III), which speeds up the oxidation of impurities. Studies conducted on bisphenols have shown that the addition of salicylic acid to the Fe(III)/PAA system achieved almost 100% removal of impurities as early as the tenth minute of oxidation, while in the base system without SAc, complete removal of bisphenols took place not until 1.5 hours of oxidation. Admittedly, this means the use of additional chemicals in the removal of EDCs and PCPs, but it should be noted that salicylic acid is a relatively gentle and naturally occurring substance [71].

3. Conclusions

The performed literature review allowed to define the following conclusions:

1) PCPs pose a growing threat especially due to their bioaccumulation ability, high toxicity and almost endless sources of their introduction into the environment.
2) Concentrations of PCPs in the environment vary and depend primarily on social conditions and the analyzed region.
3) Traditional methods of wastewater treatment and water treatment are not sufficient to remove PCPs and EDCs from water and wastewater in the majority.
4) The use of strong oxidants allows the partial removal of PCP and EDCs from water, but this produces toxic degradation products, especially when using chlorine.
5) Advanced oxidation methods (AOPs) based on ultraviolet radiation allow for better removal of EDCs from water than traditional strong oxidizers, reducing harmful residues, but this comes at the cost of the required longer oxidation time.
6) Modifications of oxidation systems with the use of peracetic acid can achieve EDC removal effects from water of more than 90%.
7) The best of the oxidation systems analyzed was the Fe(III)/PAA/SAc system, which allows almost complete (100%) removal of EDCs from water.
8) Due to the simple design of the oxidation systems, the analyzed AOPs have high potential for practical application on an industrial scale for industrial wastewater pretreatment or as upgrades to existing water treatment plants.

Bibliography

1. Shamsudin M.S., Ismail S. Din A.T.M.: Alginate-Based materials for emerging contaminants uptake. Reference Module in Materials Science and Materials Engineering, Elsevier, 2024.
2. Khalid M., Abdollahi M.: Environmental Distribution of Personal Care Products and Their Effects on Human Health. IJPR 2021, 20(1), 216-253.
3. Islam J.M., Akter T., Mokbul M., Afroz S., Mondal M.I.H.: Textiles in cosmetics and personal care. Medical Textiles from Natural Resources, Woodhead Publishing 2022, 457-497.

4. Lang C., Fisher M., Neisa A., MacKinnon L.: Personal Care Product Use in Pregnancy and the Postpartum Period: Implications for Exposure Assessment. Int. J. Environ. Res. Public Health 2016, 13(1), 105.
5. Sadeq T., Omer S.Q.: Development and Evaluation of Natural Cosmeceutical Ingredients as Makeup Remover to Prevent Hyperpigmentation. Int. J. Pharm. Res. 2019, 46(6), 145-151.
6. Ma Y., Kwon K.H.: Changes in purchasing patterns in the beauty market due to Post-COVID-19: Literature review. J. Cosmet. Dermatol. 2021, 20(10), 3074-3079.
7. Kumar S., Talwar S., Krishnan S., Kaur P., Dhir A.: Purchasing natural personal care products in the era of fake news? The moderation effect of brand trust. J. Retail. Consum. Serv. 2021, 63, 102668.
8. Shaaban H., Alhajri W.: Usage Patterns of Cosmetic and Personal Care Products among Female Population in Saudi Arabia: Important Factors for Exposure and Risk Assessment. J. Environ. Public Health 2020, 1, 8434508.
9. Osuoha J.O., Anyanwu B.O., Ejileugha C.: Pharmaceuticals and personal care products as emerging contaminants: Need for combined treatment strategy. J. Hazard. Mater. Adv. 2023, 9, 100206.
10. Ściereszko E., Budny E., Rotsztejn H., Erkiert-Polguj A.: How has the pandemic lockdown changed our daily facial skincare habits? J. Cosmet. Dermatol. 2021, 20(12), 3722-3726.
11. Mościcka P., Chróst N., Terlikowski R., Przylipiak M., Wołosik K., Przylipiak A.: Hygienic and cosmetic care habits in polish women during COVID-19 pandemic. J. Cosmet. Dermatol. 2020, 19(8), 1840-1845.
12. Goldberg M., Chang C.-J., Ogunsina K., O'Brien K.M., Taylor K.W., White A.J., Sandler D.P.: Personal Care Product Use during Puberty and Incident Breast Cancer among Black, Hispanic/Latina, and White Women in a Prospective US-Wide Cohort. Environ. Health Perspect. 2024, 132(2), 027001.
13. Shetage S.S., Traynor M.J., Brown M.B., Raji M., Graham-Kalio D., Chilcott R. P.: Effect of ethnicity, gender and age on the amount and composition of residual skin surface components derived from sebum, sweat and epidermal lipids. Skin Res. Technol. 2014, 20(1), 97-107.
14. Ray S.S., Gusain R., Kumar N.: Classification of water contaminants, [w:] Carbon Nanomaterial-Based Adsorbents for Water Purification. Fundamentals and Applications. Elsevier Inc 2020.
15. Celerio M., Facorro R., Dagnac T., Vilar V.J.P., Liompart M.: Photodegradation behavior of multiclass ultraviolet filters in the aquatic environment: Removal strategies and photoproduct identification by liquid chromatography-high resolution mass spectrometry. J. Chromatogr. A. 2019, 1596, 8-19.
16. Simetić T., Nikić J., Kuč M., Tamindžija D., Tubić A., Agbaba J., Molnar Jazić J.: New Insight into the Degradation of Sunscreen Agents in Water Treatment Using UV-Driven Advanced Oxidation Processes. Processes. 2024; 12(6), 1156.
17. Jesus A., Sousa E., Cruz M.T., Cidade H., Lobo J.M.S., Almeida I.F.: UV Filters: Challenges and Prospects. Pharmaceuticals (Basel, Switzerland) 2022, *15*(3), 263.
18. Kessler R.: More than Cosmetic Changes: Taking Stock of Personal Care Product Safety. Environ. Health Perspect. 2015, 123(5), A120-A127.
19. Balakrishnan A., Senthilkumar V., Rajan Jeyakumaran S., John J., Vinodh K., Kannan U., Paramasivam B.: Prioritization of chemicals in personal care products based on persistent, bioaccumulative and toxic (PBT) potential: An Indian perspective. Regul. Toxicol. Pharmacol. 2024, 147, 105563.
20. Keerthanan S., Jayasinghe C., Biswas J.K., Vithanage M.: Pharmaceutical and Personal Care Products (PPCPs) in the environment: Plant uptake, translocation, bioaccumulation,

and human health risks. Critical Reviews in Environmental Science and Technology 2020, 51(12), 1221-1258.
21. Bolińska M.I., Piekutin J., Kotowska U.: Selected newly emerging organic pollutants of the aquatic environment and the possibilities of their removal the water, [in:] Hubicki Z. (red.): Science and industry – challenges and opportunities. Wydawnictwo UMCS, Lublin 2024, 191-194.
22. Guarnotta V., Amodei R., Frasca F., Aversa A., Giordano C.: Impact of Chemical Endocrine Disruptors and Hormone Modulators on the Endocrine System. Int. J. Mol. Sci. 2022, 23(10), 5710.
23. Rizzo R., Bortolotti D., Rizzo, S., Schiuma, G.: Cellular Mechanisms of Endocrine Disruption, [in:] Marci, R. (red.) Environment Impact on Reproductive Health. Springer 2023.
24. Even Chorev N., Testa G.: Acting on uncertainty: real-life mixtures of endocrine disrupting chemicals. BioSocieties 2021, 16, 225-248.
25. Nendza M., Klaschka U., Berghahn R.: Suitable test substances for proof of concept regarding infochemical effects in surface waters. Environ. Sci. Eur. 2013, 25, 21.
26. Wu M.-H., Li J., Xu G., Ma L.-D., Li J.-J., Li J.-S., Tang L.: Pollution patterns and underlying relationships of benzophenone-type UV-filters in wastewater treatment plants and their receiving surface water. Ecotoxicol. Environ. Saf. 2018, 152, 98-103.
27. Marques dos Santos M., Hoppe-Jones C., Snyder S.A.: DEET occurrence in wastewaters: Seasonal, spatial and diurnal variability – mismatches between consumption data and environmental detection. Environ. Int. 2019, 132, 105038.
28. Rani R., Kumar D.: Recent advances in degradation of N,N-diethyl-3-toluamide (DEET) – an emerging environmental contaminant: a review. Environ. Monit. Assess. 2024, 196, 238.
29. Alenzi A., Hunter C., Spencer J., Roberts J., Craft J., Pahl O., Escudero A.: Pharmaceuticals effect and removal, at environmentally relevant concentrations, from sewage sludge during anaerobic digestion. Bioresour. Technol. 2021, 319, 124102.
30. de Alkmin G.D., Santos J., Soares A.M.V.M., Nunes B.: Ecotoxicological effects of the azole antifungal agent clotrimazole on the macrophyte species Lemna minor and Lemna gibba. Comp. Biochem. Physiol. C. Toxicol. Pharmacol.: CBP 2022, 237, 108835.
31. Arnold C.: Pipe Dreams: Tapping into the Health Information in Our Sewers, Environ. Health Perspect. 2016, 124, A86-A91.
32. Björlenius B., Ripszám M., Haglund P., Lindberg R.H., Tysklind M., Fick J.: Pharmaceutical residues are widespread in Baltic Sea coastal and offshore waters – Screening for pharmaceuticals and modelling of environmental concentrations of carbamazepine. Sci. Total Environ. 2018, 633, 1496-1509.
33. Lacey C., Basha S., Morrissey A., Tobin J.M.: Occurrence of pharmaceutical compounds in wastewater process streams in Dublin, Ireland. Environ. Monit. Assess. 2012, 184, 1049-1062.
34. Mula M.: Psychotropic Effects of Anticonvulsant Drugs in Patients with Epilepsy. Clin. Med. Insights Ther. 2010, 2, 285-289.
35. Heffron K.T., Gaines K.F., Novak J.M., Canam T., Collard D.A.: 17β-Estradiol influent and effluent concentrations in wastewater: demographic influences and the risk to environmental health. Environ. Monit. Assess. 2016, 188, 288.
36. Sami N., Afzal B., Rehmanji M., Naaz H., Yasin D., Jutur P.P., Fatma T.: Insight into the mechanism of estrone biodegradation by Spirulina CPCC-695. Environ. Dev. Sustain. 2023, DOI: 10.1007/s10668-023-03873-y.
37. Ma X., Chen M.: Electrochemical sensor based on graphene doped gold nanoparticles modified electrode for detection of diethylstilboestrol. Sens. Actuators B Chem. 2015, 215, 445-450.

38. Ozáez I., Aquilino M., Morcillo G., Martínez-Guitarte J.L.: UV filters induce transcriptional changes of different hormonal receptors in Chironomus riparius embryos and larvae. Environ. Pollut. 2016, 214, 239-247.
39. Broniowska Ż., Bystrowska B., Starek-Świechowicz B., Pomierny B., Krzyżanowska W., Walczak M., Budziszewska B.: Benzophenone-2 Concentration and Its Effect on Oxidative Stress and Apoptosis Markers in Rat Brain. Neurotox. Res. 2019, 36, 39-48.
40. Taştan B.E., Dönmez G.: Biodegradation of pesticide triclosan by A. versicolor in simulated wastewater and semi-synthetic media. Pestic. Biochem. Physiol. 2015, 118, 33-37.
41. Milanović M., Đurić L., Milošević N., Milić N.: Comprehensive insight into triclosan – from widespread occurrence to health outcomes. Environ. Sci. Pollut. Res. 2023, 30, 25119-25140.
42. Lotfi M., Hasanpour A.H., Moghadamnia A.A., Kazemi S.: The Investigation into Neurotoxicity Mechanisms of Nonylphenol: A Narrative Review. Curr. Neuropharmacol. 2021, 19, 1345-1353.
43. https://echa.europa.eu [dostęp: czerwiec 2024 r.]
44. https://edlists.org [dostęp: czerwiec 2024 r.]
45. Pittelkow M.R., Genebriera J.: Chapter 71 – psoriasis, [in:] Waldman S.A., Terzic A., Egan L.J. et. al. (red.), Pharmacol. Ther. 2009, 983-1005.
46. Han Y., Qi C., Niu Z., Li N., Tang, J.: Occurrence and risk assessment of endocrine-disrupting chemicals in wastewater treatment plants in the Chaohu Lake Basin. Front. Environ. Sci. 2024, 12, https://doi.org/10.3389/fenvs.2024.1409011
47. Werkneh A.A., Gebru S.B., Redae G.H., Tsige A.G.: Removal of endocrine disrupters from the contaminated environment: public health concerns, treatment strategies and future perspectives – A review. Heliyon 2024, *8*(4), e09206.
48. Abdullah M.S., Goh P.S., Ismail A.F., Hasbullah H.: The Treatment of Endocrine-Disruptive Chemicals in Wastewater through Asymmetric Reverse Osmosis Membranes: A review. Symmetry 2023, 15, 1049.
49. Thacharodi A., Hassan S., Hegde T.A., Thacharodi D.D., Brindhadevi K., Pugazhendhi A.: Water a major source of endocrine-disrupting chemicals: An overview on the occurrence, implications on human health and bioremediation strategies. Environ. Res. 2023, 231, 116097.
50. Wee S.Y., Aris A.Z.: Occurrence and public-perceived risk of endocrine disrupting compounds in drinking water. NPJ Clean Water 2019, 2, 4.
51. Gonsioroski A., Mourikes V.E., Flaws J.A.: Endocrine Disruptors in Water and Their Effects on the Reproductive System. Int. J. Mol. Sci. 2020, 21(6), 1929.
52. Sui S., Liu H., Yang X.: Research Progress of the Endocrine-Disrupting Effects of Disinfection Byproducts. J. Xenobiot.2022, 12(3), 145-157.
53. Lazofsky A., Buckley B.: Recent Trends in Multiclass Analysis of Emerging Endocrine Disrupting Contaminants (EDCs) in Drinking Water. Molecules (Basel, Switzerland) 2022, 27(24), 8835.
54. Yuniarto A., Hadibarata T.: Sources, fate, distribution, impact, and treatment of endocrine disrupting compounds (EDCs) in drinking water. Environ. Qual. Manag. 2024, 34, e22244.
55. Wu Q., Shi H., Adams C.D., Timmons T., Ma Y.: Oxidative removal of selected endocrine-disruptors and pharmaceuticals in drinking water treatment systems, and identification of degradation products of triclosan. Sci. Total Environ. 2012, 439, 18-25.
56. Kujawska A., Kiełkowska U., Atisha A., Yanful E., Kujawski W.: Comparative analysis of separation methods used for the elimination of pharmaceuticals and personal care products (PPCPs) from water – A critical review. Sep. Purif. Technol. 2022, 290, 120797.

57. Deng Y., Zhao R.: Advanced Oxidation Processes (AOPs) in Wastewater Treatment. Curr. Pollution. Rep. 2015, 1, 167-176.
58. Simetić T., Nikić J., Kuč M., Tamindžija D., Tubić A., Agbaba J., Molnar Jazić J.: New Insight into the Degradation of Sunscreen Agents in Water Treatment Using UV-Driven Advanced Oxidation Processes. Processes 2024, 12, 1156.
59. Chaves F.P., Gomes G., Della-Flora A., Dallegrave A., Sirtori C., Saggioro E.M., Bila D.M.: Comparative endocrine disrupting compound removal from real wastewater by UV/Cl and UV/H_2O_2: Effect of pH, estrogenic activity, transformation products and toxicity. Sci. Total Environ. 2020, 746, 141041.
60. Hu J., Li T., Zhang X., Ren H., Huang H.: Degradation of steroid estrogens by UV/peracetic acid: Influencing factors, free radical contribution and toxicity analysis. Chemosphere 2022, 287(Pt 3), 132261.
61. Kiejza D., Kotowska U., Polińska W., Karpińska J.: Peracids – New oxidants in advanced oxidation processes: The use of peracetic acid, peroxymonosulfate, and persulfate salts in the removal of organic micropollutants of emerging concern − A review. Sci. Total Environ. 2021, 790, 148195.
62. Stearns R., Freshour A., Shen C.: Literature review for applying peroxyacetic acid and/or hydrogen peroxide to control foodborne pathogens on food products. J. Agric. Food Res. 2022, 10, 100442.
63. Popescu E.M., Pantea O., Gologan D., Doukeh R.A.: Hydrogen Peroxide and Peracetic Acid Oxidizing Potential in the Treatment of Water. Revista de Chimie 2019, 70(6/2019), 2036-2039.
64. O'Shea K.E., Dionysiou D.D.: Advanced Oxidation Processes for Water Treatment. J. Phys. Chem. Lett. 2012, 3(15), 2112-2113.
65. Barrera-Salgado K.E., Ramírez-Robledo G., Álvarez-Gallegos A., Pineda-Arellano C.A., Sierra-Espinosa F.Z., Hernández-Pérez J.A., Silva-Martínez S.: Fenton Process Coupled to Ultrasound and UV Light Irradiation for the Oxidation of a Model Pollutant, J. Chem. 2016, 4262530.
66. Garrido-Cardenas J.A., Esteban-García B., Agüera A., Sánchez-Pérez J.A., Manzano-Agugliaro F.: Wastewater Treatment by Advanced Oxidation Process and Their Worldwide Research Trends. Int. J. Environ. Res. Public Health 2019, 17(1), 170.
67. Napoleão D.C., Mendes Carneiro Zaidan L.E., Rodríguez-Díaz J.M., da Rocha Santana R.M., Branco da Silva de Mendonça Montenegro M.C., da Nova Araújo A., Benachour M., Lins da Silva V., Use of the photo-Fenton process to discover the degradation of drugs present in water from the Wastewater Treatment Plants of the pharmaceutical industry. AFINIDAD. J. Chem. Eng. Theor. Appl. Chem. 2018, 75, 581.
68. O'Dowd K., Pillai S.C.: Photo-Fenton disinfection at near neutral pH: Process, parameter optimization and recent advances. J. Environ. Chem. Eng. 2020, 8(5), 104063.
69. You Y., He Z.: Phenol degradation in iron-based advanced oxidation processes through ferric reduction assisted by molybdenum disulfide. Chemosphere 2023, 312(1), 137278.
70. Kotowska U., Karpińska J., Kiejza D., Ratkiewicz A., Piekutin J., Makarova K., Olchowik--Grabarek E.: Oxidation of contaminants of emerging concern by combination of peracetic acid with iron ions and various types of light radiation – Optimization, kinetics, removal efficiency and mechanism investigation. J. Mol. Liq. 2023, 369, 120859.
71. Kiejza D., Karpińska J., Lesczyńska A., Olchowik-Grabarek E., Makarova K., Kotowska U.: Acceleration of the bisphenols oxidation in the Fe(III)/peracetic acid system with salicylic acid. J. Mol. Liq. 2024, 411, 125697.
72. Mukherjee S., Das A., Chowdhury A., Biswas A., Roy S., Majumdar S., Paul S.: Harmful effect of personal care products on ecosystem and the possible alternative approach. Biocatal. Agric. Biotechnol. 2024, 57, 103065.

A REVIEW OF THE PRESENCE OF COSMETIC PRODUCTS AND PHARMACEUTICAL RESIDUES IN THE AQUATIC ENVIRONMENT AND METHODS OF THEIR REMOVAL

Abstract

Personal care products are a new source of pollution in the environment. Some of them decompose on the skin when exposed to natural factors, resulting in toxic derivative products. Nevertheless, their use is increasing day by day, and so is their concentration in the aquatic environment. The active ingredients of personal care products, which belong to the group of endocrinically active compounds, pose a real threat to the health and life of humans and animals, despite their common use as weather protection, antibacterial or beautifying functions. Their bioaccumulation ability and resistance to removal by traditional wastewater and water treatment processes make them a real threat to the environment. This paper presents the genesis of personal care products, necessary to understand the nature of the currently emerging issue, as well as an analysis of their removal methods, based on strong oxidants.

Keywords: Personal care products, endocrine disrupting chemicals, advanced oxidation processes, peracetic acid

OBECNOŚĆ PRODUKTÓW KOSMETYCZNYCH I POZOSTAŁOŚCI FARMACEUTYCZNYCH W ŚRODOWISKU WODNYM ORAZ METODY ICH USUWANIA

Streszczenie

Produkty do pielęgnacji ciała są nowym źródłem zanieczyszczeń w środowisku. Część z nich rozkłada się na skórze pod wpływem czynników naturalnych, co skutkuje powstaniem toksycznych produktów pochodnych. Niemniej jednak ich stosowanie z dnia na dzień wzrasta, podobnie jak ich stężenie w środowisku wodnym. Składniki aktywne produktów do pielęgnacji ciała, należące do grupy związków endokrynnie czynnych, stanowią realne zagrożenie dla zdrowia i życia ludzi i zwierząt, pomimo ich powszechnego stosowania jako ochrony przed warunkami atmosferycznymi, funkcji antybakteryjnych czy upiększających. Ich zdolność do bioakumulacji i odporność na usuwanie tradycyjnymi procesami oczyszczania ścieków i wody sprawiają, że stanowią realne zagrożenie dla środowiska. W artykule przedstawiono genezę produktów do pielęgnacji ciała, niezbędną do zrozumienia natury obecnie narastającego problemu. Przeprowadzona analiza metod usuwania produktów do pielęgnacji ciała wykazała, że metody oparte na silnych utleniaczach są skuteczną metodą degradacji nowo powstających zanieczyszczeń organicznych. Przedstawiono również, że do utleniania problematycznych zanieczyszczeń możliwe jest wykorzystanie takich związków chemicznych, które nie będą obciążać środowiska i częściowo ograniczą powstawanie szkodliwych produktów ubocznych. Okazało się, że warto rozwijać i zgłębiać badania nad zaawansowanym utlenianiem, zwłaszcza pracując z systemami bazującymi na promieniowaniu ultrafioletowym i kwasie nadoctowym.

Słowa kluczowe: Produkty do pielęgnacji osobistej, substancje zaburzające gospodarkę hormonalną, zaawansowane procesy utleniania, kwas nadoctowy

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DEVICE FOR THE INTRAOPERATIVE INTESTINE VITALITY ASSESSMENT

1. Introduction

Resections of a fragment of the intestine, stomach, or oesophagus are life-saving operations after neoplastic changes in the gastric tract are detected. The surgical intervention consists of removing the pathologically changed fragment of the intestine, oesophagus or stomach and anastomosis of the healthy parts. Anastomosis of tissues characterised by sufficient blood perfusion is crucial in terms of successful gastrointestinal tract resection surgery. Poor local tissue oxygenation secondary to inadequate anastomotic vascular perfusion seems to play a key role in the determination of anastomotic viability [1, 2]. Anastomotic leakage (AL) represents a serious complication that may occur following resection surgery, especially when suboptimally perfused tissues are anastomosed. AL can lead to increased morbidity, mortality, hospital stay duration, costs, and the risk of cancer recurrence [3-6]. The reported incidence of AL after colorectal surgery varies from 1% to 19% depending on the anatomic location of the anastomosis: ileocolic (1-8)%; colocolic (2-3)%; ileorectal (3-7)%; colorectal or coloanal (5-19)% [7-9].

According to chart review by Turrentine et al. [10] among patients with an anastomotic leak, 8.4% died within 30 days of surgery compared with 2.5% of thosewho did not have an anastomotic leak. Anastomotic leak incidence rates with associated 30-day mortality rates with

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various locations of gastrointestinal anastomoses based on Turrentine et al. findings have been presented in Fig. 1. In Poland, approximately 6,000 stomach resections, and 10,000 extensive intestinal resections are performed yearly, which indicates a substantial need for development of an accurate, low-cost system for blood circulation measurements of gastrointestinal tract during resection surgery.

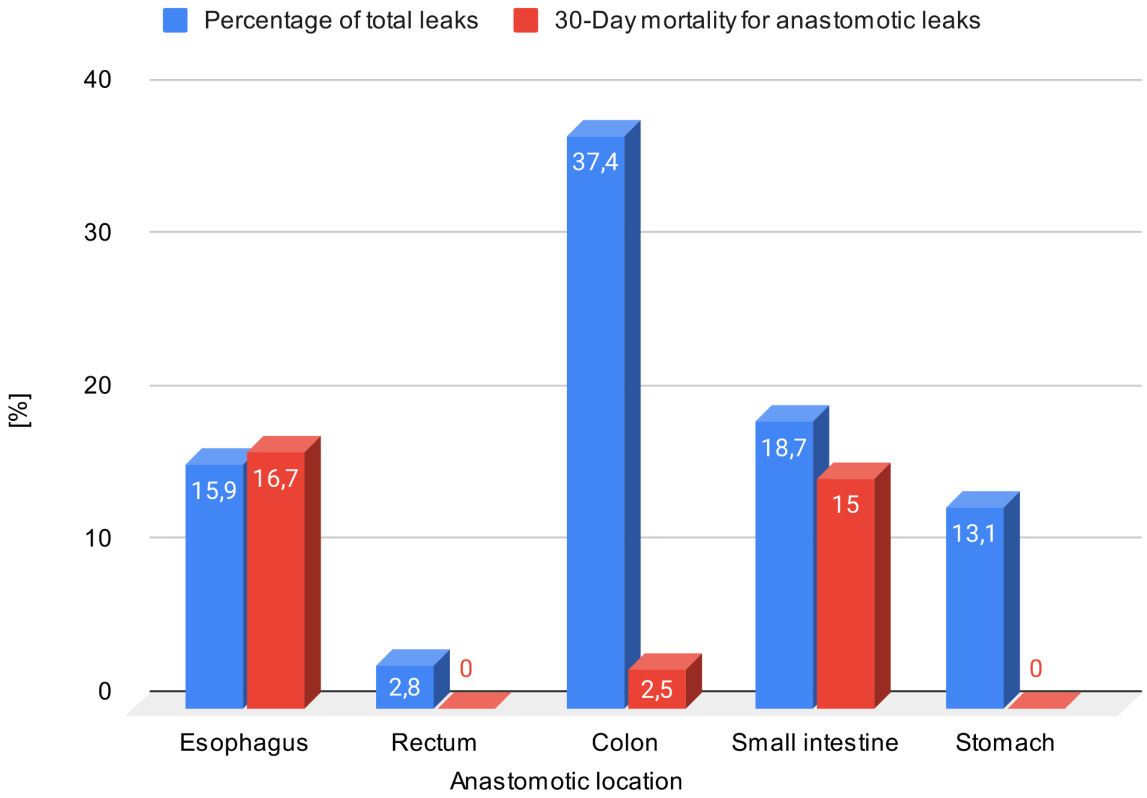


Fig. 1. Anastomotic leak incidence rates with associated 30-day mortality rates with various locations of gastrointestinal anastomoses. Adapted from Turrentine et al. [10]

Rys. 1. Wskaźniki częstości występowania nieszczelności zespolenia ze związanymi z nimi 30-dniowymi wskaź. nikami śmiertelności w różnych miejscach zespoleń żołądkowo-jelitowych. Adaptacja z Turrentine i in. [10]

2. Measurement setup

Currently there are no methods that are easily applicable as an intraoperative scan. For that purpose, a dedicated, scissor-like device for the sensor's application in the body was developed. It is a clamp equipped with integrated impedance electrodes, all the pressure gauges, and the optical sensors (Fig. 2).

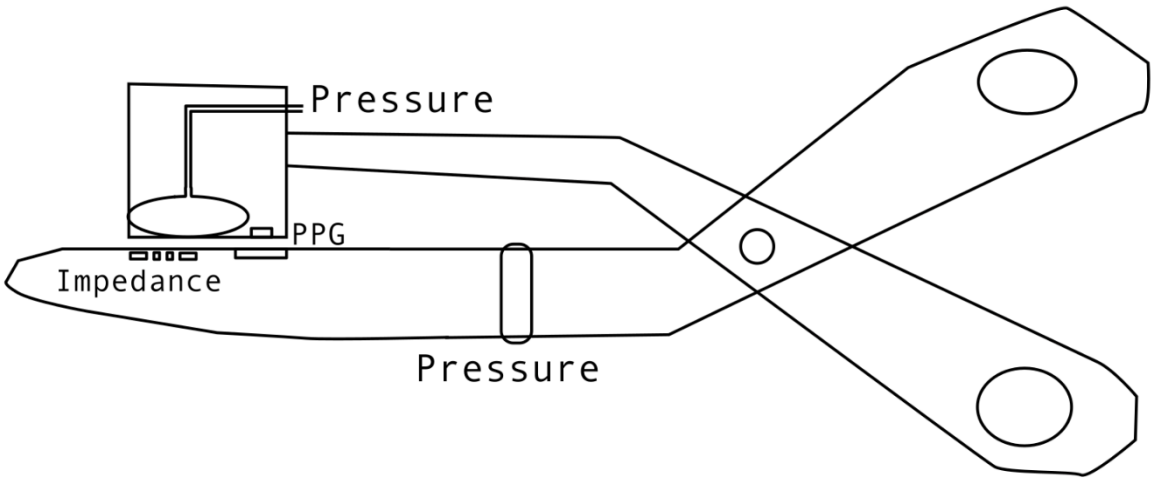


Fig. 2. A measurement device in a scissors-like form to hold a sample tissue
Rys. 2. Urządzenie pomiarowe w formie nożyczek do trzymania próbki tkanki

A main control and measurement unit is made using the STM32F373 microcontroller. The measurement device allows the measurement of impedance changes, pressure changes and optical plethysmography in both transmittance and reflection channels. As expected, changes are unknown as a time reference for the ECG channel that has been added. The block diagram of the device is shown in Fig. 3 It is an ARM-based microcontroller with two multi-input sigma-delta analogue-to-digital converters (ADC) and one multiple-input successive approximation ADC. Moreover, it has incorporated two DAC channels, which simplifies design. An ECG is measured utilising the AD8232 (Analog Devices). This approach gives reasonable results and saves space on the PCB.

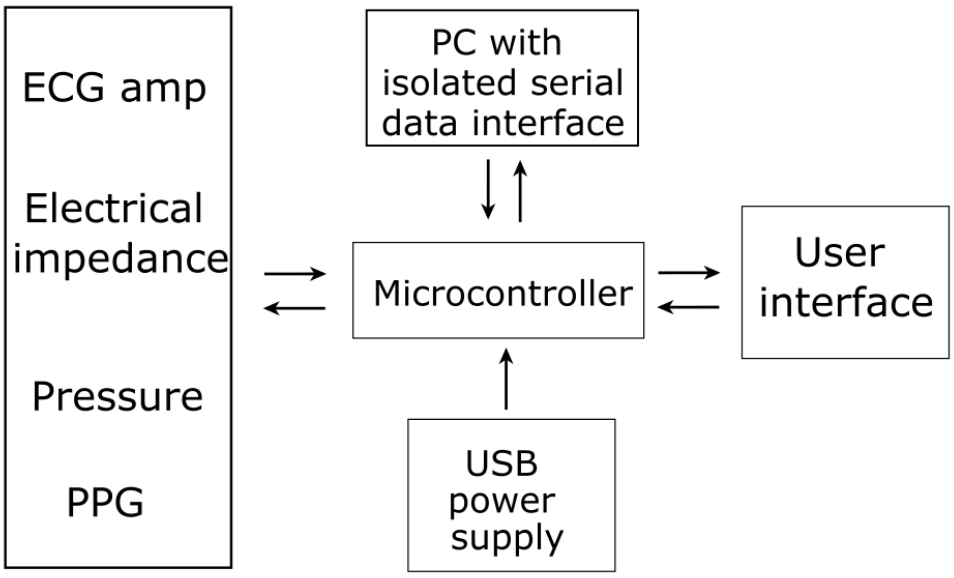


Fig. 3. A block diagram of developed device: Z/dZ – impedance and its changes measurement unit, P1, P2 pressure measurements units
Rys. 3. Schemat blokowy opracowanego urządzenia: Z/dZ – jednostka pomiaru impedancji i jej zmian, P1, P2 jednostki pomiaru ciśnienia

The impedance measurement channel is designed as a 4-electrode measurement setup where current and voltage channels are separated. In the current channel, a Howland current source is used to produce a 0.1 mA current, meeting safety regulations. The current source is controlled using a digital-to-analog converter and tabularized sine-wave signal, generating a regulated amplitude 20 kHz sine wave. The signal is received by an instrumentation amplifier (MAX333), then band-pass filtered, amplified by the programmable gain amplifier (PGA), and synchronously demodulated by the SA612 analogue multiplier. Following low-pass filtration, an impedance signal is obtained. The impedance value is determined by aligning the phase of the reference and current signals. Next, a 0.02 Hz high-pass filter is used to generate a dZ signal, which can be further amplified before being sent to the ADC.

The MAX30105 reflective pulse-oximeter containing three electromagnetic radiation sources: infrared, red, and green was used in photoplethysmographic (PPG) setup. Additionally, second photodiode with an amplifier was added to enable transmitted radiation detection.

In the post-resection interstitial segment, circulation can be influenced by pressure changes, which can be measured using a pressure gauge. To expand the search range, a pneumatic obturation system was added to the device. The measurement concept is similar to the Korotkov method used in non-invasive blood pressure monitoring. The focus is on detecting pulsations rather than obtaining the exact pressure value. Two identical pneumatic systems were implemented – one for precise measurement and the other for controlled obturation to enhance measurement sensitivity.

The device was designed, assembled, and programmed. A PCB of the unit can be seen in Fig. 4, while the assembled and working unit is shown in Fig. 5. In addition, a few application units were produced by means of rapid prototyping – see Fig. 6. For safety purposes, the measuring unit is operated using a rechargeable battery. Additionally, a serial interface has been implemented to send the data to potentially un-isolated hosts. A safety barrier was kept at approximately 4000 V, and high-speed digital optocouplers were used. The operating algorithm provides a timer-based sampling of all measured signals – ECG, Z, dZ, P1, P2 and PPG. Measured data are sent out to the host via UART or USB CDC, depending on the latter's availability.

Additionally, the device can retrieve single-character commands for changing the PGA gains, DAC amplitude, MAX30105 configuration, etc. In parallel, selected channels are shown on the associated display. The keypad is not utilized and is left for future development.

To communicate with the device, a SerialPlot application has been used. It is an application for plotting data received via the serial port. The application allows specifying almost any data format, including text and binary, to produce multi-plots. Moreover, it allows storing data in a file for future processing and provides a simple interface for feeding commands to the device. Data is stored in the so-called CSV format.

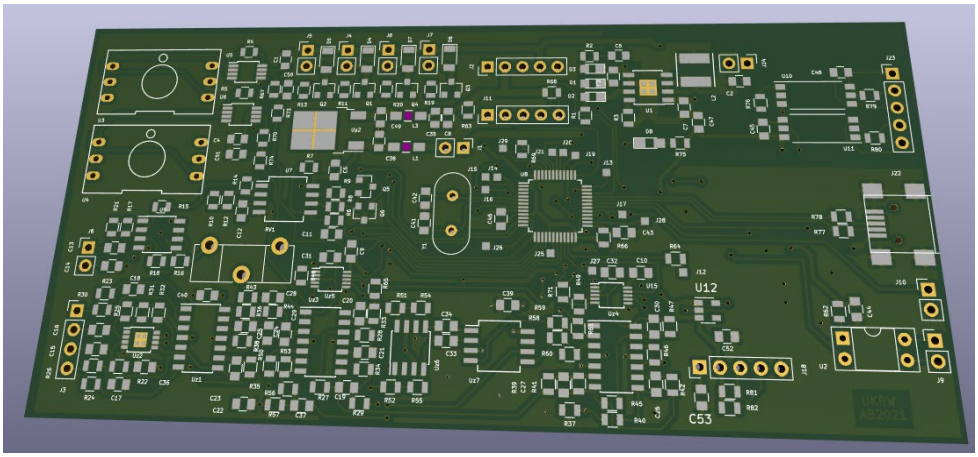


Fig. 4. Designed measurement system motherboard
Rys. 4. Płyta główna zaprojektowanego układu pomiarowego

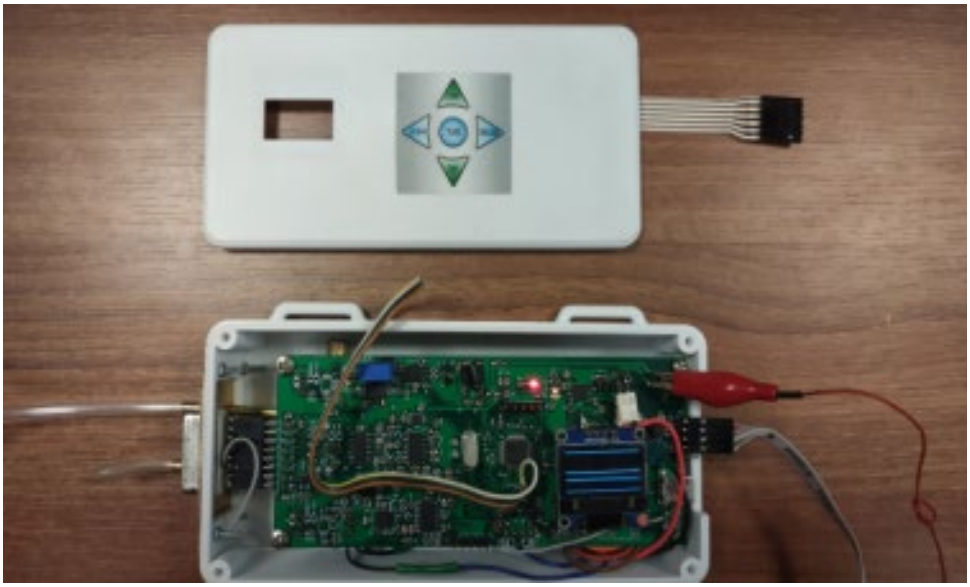


Fig. 5. Assembled unit with 3D printed case
Rys. 5. Zmontowany układ z obudową drukowaną w technologii 3D

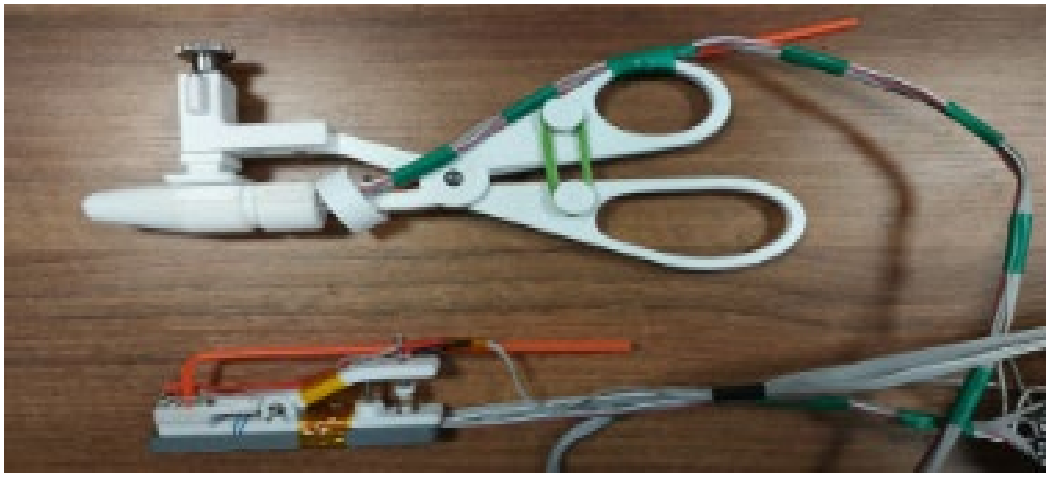


Fig. 6. Two versions of application system – prototyped with use of 3D printing technique
Rys. 6. Dwie wersje układu aplikacyjnego – prototyp wykonany techniką druku 3D

3. Results

A domestic pig, approximately six weeks old, was used for the experiments. All the experiments were performed under the approval of the ethical committee. The experiments were conducted in the following scenario: After anaesthesia, the animals were connected to the vital sign monitoring system. A body was opened to access the small intestine. Then, a probe was connected to the intestine, and data were collected without cutting the intestine. After all, resection was conducted following the joining of the intestine. The animal was closed and left for observation for a week. After a week, an inspection following euthanasia was conducted.

During the measurement session, a considerable dataset was collected. First, an impedance measurement of the intestine tissue was conducted to set the measurement unit for the correct range. For this, a battery-powered RLC bridge was used. Sample data are summarised in Table 1. Although presented data were not corrected according to the measurement probe constant, their behaviour is typical for biological tissues.

Table 1

Parameters of the intestine tissue for domestic pig vs frequency

frequency	C	D	R
120 Hz	1340 nF	2.76	2.99 kΩ
1 kHz	370 nF	5.15	2.34 kΩ
10 kHz	73.4 nF	8.78	1.99 kΩ
100 kHz	5.0 nF	5.06	1.67 kΩ

D – The dissipation factor. A measure of loss-rate of energy of a mode of oscillation.

Following that, we started to examine different parameters over time. As one of the first signals, the ECG was measured. Despite motion artefacts, the ECG signal exhibits additional anomalies caused by atypical lead configuration and completely non-physiological animal body positioning. In Fig. 7, an example of a recorded signal with marked specific points is shown. For such signal analysis, a custom signal detector was written and implemented.

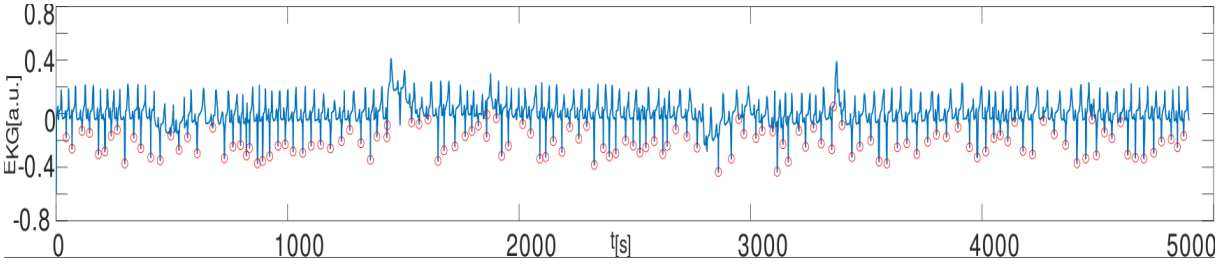


Fig. 7. An example of the ECG signal with non-standard R-wave detector applied
Rys. 7. Przykład sygnału EKG z zastosowanym niestandardowym detektorem fali R

In the experiment, an ECG and dZ signals were analyzed, and an example of the reading is shown in Fig. 8. With the same experiment with knowledge about perfusion. Following this, pressure measurements by applying various pressures to the intestine tissue and trying to locate the pulsation component were conducted. In Fig. 9, an example of such data is shown. Since the blood pressure in capillaries very close to atmospheric inflation of the cuff cause retraction of the blood from the measured segments. In Figure 10, PPG measurements of the intestine, synchronized with the ECG were presented. There is a large amount of noise present in all of these measurements, except for the ECG signal. In fact, it is difficult to objectively determine whether the pulsatile component is present in the measurements or not. The noise can be caused by various factors, e,g, spontaneous movements of the animal during anesthesia period etc. To improve data reliability a more statistical approach has been used. The entire data record was analyzed, and areas without any significant motion artifacts were manually chosen. For these areas, the ECG signal was analyzed to detect individual heartbeats (using modified QRS detection and analysis). The remaining recordings were segmented based on the detected QRS complexes. Each segment was then resampled to display physiological activity rather than exact timing. The resampled segments were then averaged to obtain more in-depth statistical information about the records. The data processing procedure is illustrated in Fig. 11 for dZ. The same approach was applied to other signals as well.

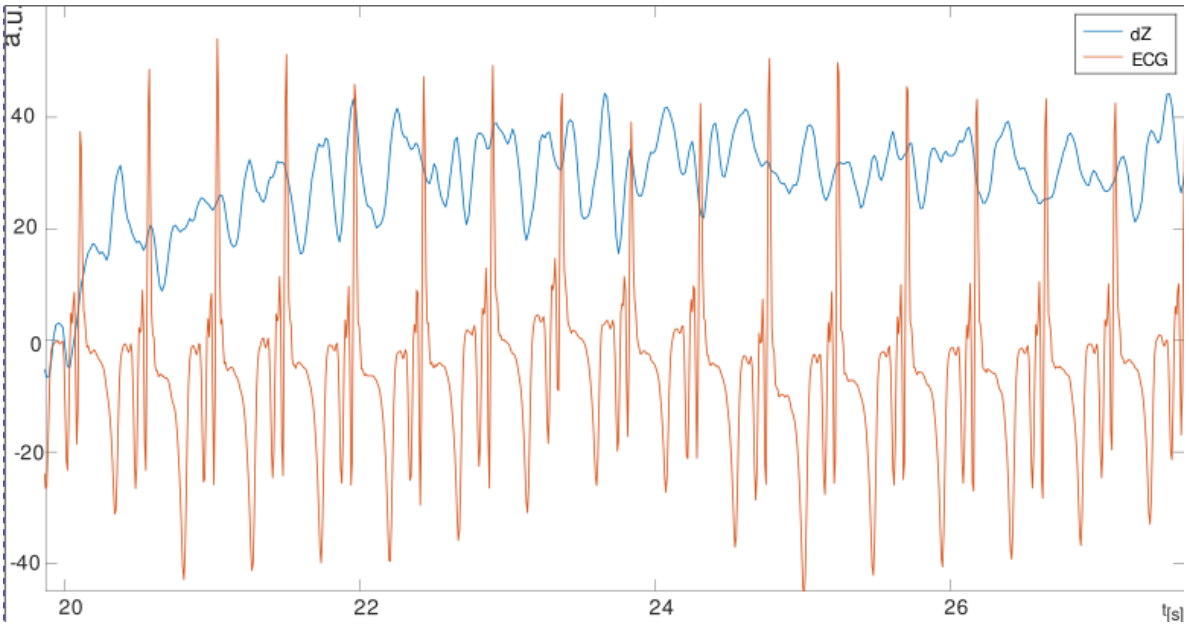


Fig. 8. Simultaneous ECG and dZ signals measurement
Rys. 8. Simultaneous ECG and dZ signals measurement

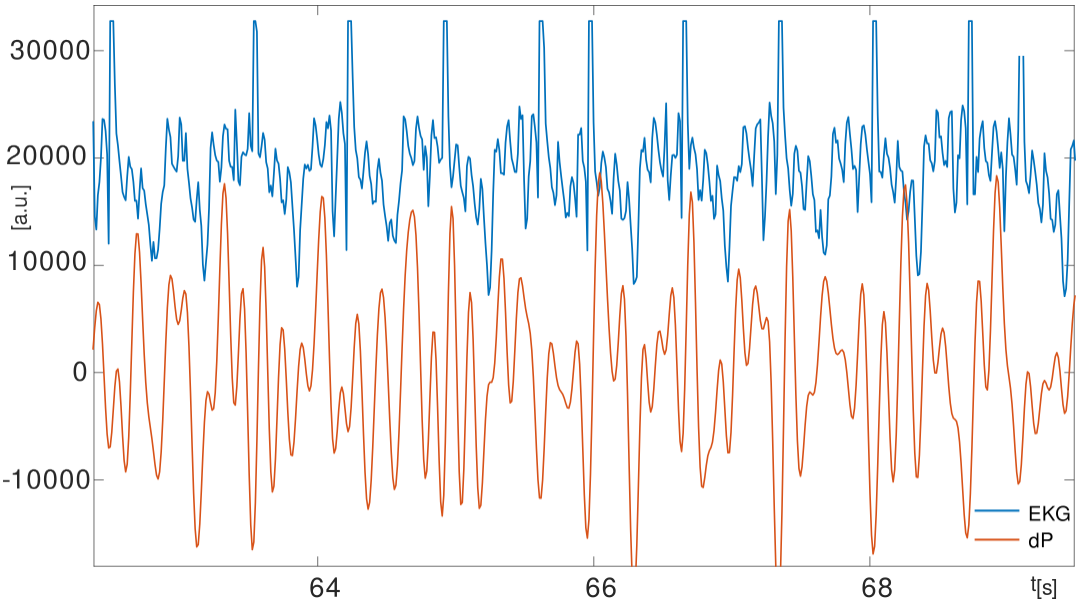


Fig. 9. Pressure changes in the tissue synchronous with the ECG as measured using cuff 1
Rys. 9. Zmiany ciśnienia w tkance synchroniczne z EKG mierzone za pomocą mankietu 1

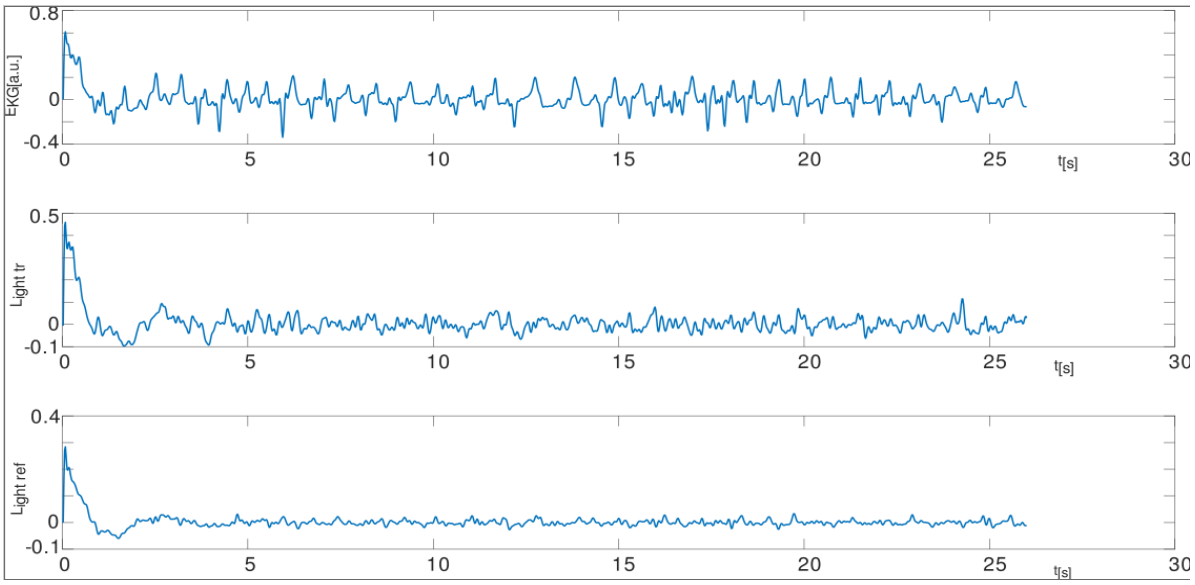


Fig. 10. A measurement of transilluminated and reflected light on the intestine – green LED as the light source, synchronous with the ECG
Rys. 10. Pomiar światła prześwietlonego i odbitego na jelicie – zielona dioda LED jako źródło światła, synchronicznie z EKG

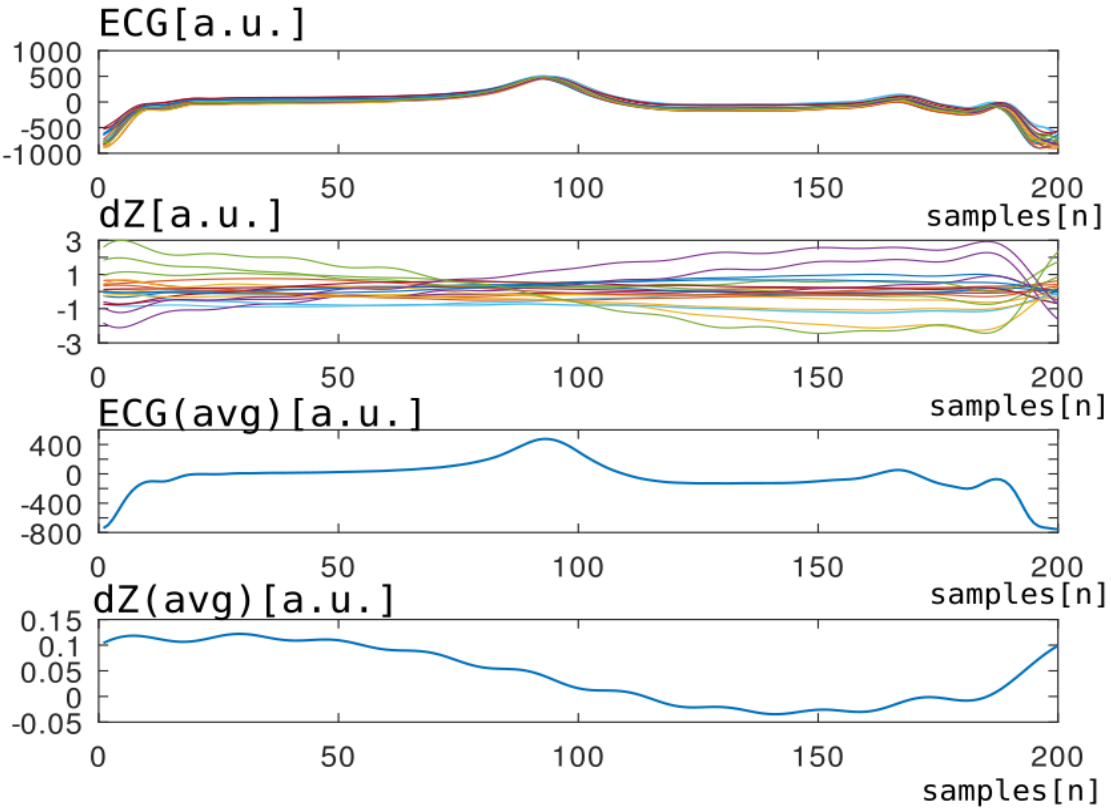


Fig. 11. dZ signal averaging on the basis of the ECG period
Rys. 11. Uśrednianie sygnału dZ na podstawie okresu EKG

4. Discussion and Conclusion

In the surgical treatment of the small intestine, there is a risk associated with incorrectly classifying the circulation of anastomosed fragments, which can lead to post-surgical complications, including patient death. We conducted a study to investigate methods for performing quick tests intraoperatively.

One of the major challenges was the lack of information about the physiology of the intestine, including electrical parameters of tissue, blood pressure within capillaries, and the nature of blood circulation in the smallest arteries. The proposed prototype of a device has allowed us to investigate the problem. We started with testing animal tissues using young domestic pigs as a preliminary subject. The tissue parameters were measured, and we observed the fundamental behaviour of the intestine in relation to impedance, pressure, and light transmission using the developed device. The initial experiments helped us refine the device's design and determine the expected parameter value ranges. During the experiments, we found that the pressure measured by the device we designed was close to the atmospheric level.

Additionally, pumping the cuff caused the blood to retreat from the bowel. Those observations were caused by low blood pressure within the capillaries (as low as 10 mmHg).

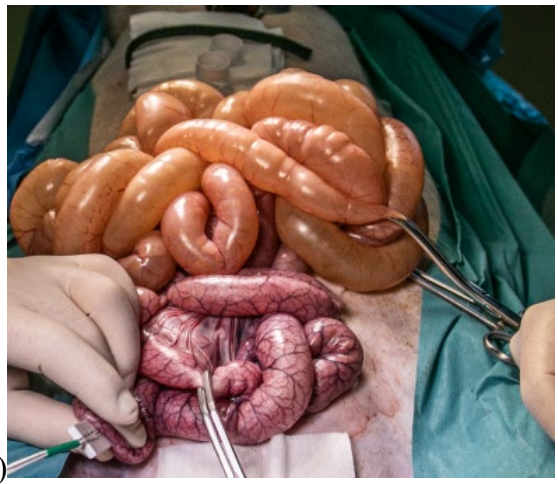
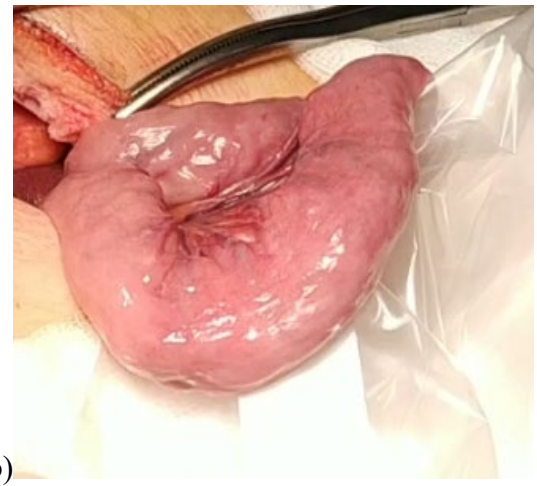
a)  b) 

Fig. 12. Comparison of the pig and human small intestine: a) young pig, b) human (approximately 80-year-old)
Rys. 12. Porównanie jelita cienkiego świni i człowieka: a) młoda świnia, b) człowiek (około 80 lat

Initially the observed changes were too small to make valuable decisions based on a simple measurement. Therefore, an ECG-triggered mechanism for data averaging has been adopted. Statistical data analysis can bring more relevant information, but after analysis of all collected data, more research is needed, especially when comparing human intestine tissue with pig tissue. In Fig. 12, an optical comparison of the pig (a) with the human tissue is made. It is a clear difference, especially regarding the thickness of the tissue. After completion of experiments with the use of the animals, the device needs to be re-designed to achieve a septic and sterilisable form. It would allow us to begin experiments on humans.

Bibliography

1. Frasson M., Flor-Lorente B., Rodríguez J.L.R., Granero-Castro P., Hervás D., Rico M.A.A., ... ANACO Study Group (2015): Risk factors for anastomotic leak after colon resection for cancer: multivariate analysis and nomogram from a multicentric, prospective, national study with 3193 patients. *Annals of surgery*, 262(2), 321-330.
2. Kingham TP, Pachter HL (2009): Colonic anastomotic leak: risk factors, diagnosis, and treatment. J Am Coll Surg 208(2):269-278.
3. Mirnezami A., Mirnezami R., Chandrakumaran K., Sasapu K., Sagar P., Finan P. (2011): Increased local recurrence and reduced survival from colorectal cancer following anastomotic leak: systematic review and meta-analysis. *Annals of surgery*, 253(5), 890-899.
4. Kang C.Y., Halabi W.J., Chaudhry O.O., Nguyen V., Pigazzi A., Carmichael J.C., Stamos M.J. (2013): Risk factors for anastomotic leakage after anterior resection for rectal cancer. *JAMA surgery*, 148(1), 65-71.

5. Chiarello M.M., Fransvea P., Cariati M., Adams N.J., Bianchi V., Brisinda G. (2022): Anastomotic leakage in colorectal cancer surgery. *Surgical oncology*, 40, 101708.
6. Kingham P.T., Pachter L.H. (2009): Colonic anastomotic leak: risk factors, diagnosis, and treatment. *Journal of the American College of Surgeons*, 208(2), 269-278.
7. McDermott F.D., Heeney A., Kelly M.E., Steele R.J., Carlson G.L., Winter D.C. (2015): Systematic review of preoperative, intraoperative and postoperative risk factors for colorectal anastomotic leaks. *Journal of British Surgery*, 102(5), 462-479.
8. Phitayakorn R., Delaney C.P., Reynolds H.L., Champagne B.J., Heriot A.G., Neary P., ... International Anastomotic Leak Study Group. (2008): Standardized algorithms for management of anastomotic leaks and related abdominal and pelvic abscesses after colorectal surgery. *World journal of surgery*, 32, 1147-1156.
9. Yılmazlar T. (2017): Relationship between method of anastomosis and anastomotic failure after right hemicolectomy and ileo-caecal resection: An international snapshot audit.
10. Turrentine F.E., Denlinger C.E., Simpson V.B., Garwood R.A., Guerlain S., Agrawal A., ... Jones R.S. (2015): Morbidity, mortality, cost, and survival estimates of gastrointestinal anastomotic leaks. *Journal of the American College of Surgeons*, 220(2), 195-206.

DEVICE FOR THE INTRAOPERATIVE INTESTINE VITALITY ASSESSMENT

Abstract: Determination of the regions of proper blood perfusion is crucial for a successful gastrointestinal tract resection surgery. Anastomotic leakage can lead to severe complications, prolonged hospitalisation, increased costs, and the risk of cancer recurrence. This study delves into innovative methods for enhancing surgical decision-making during small intestine surgeries. Existing techniques for intraoperative evaluation of the gastrointestinal tract are not without drawbacks, mainly due to the difficulty of application and considerable measurement uncertainty. Recognizing the high-risk factors associated with the misclassification of circulatory segments in joined intestinal fragments, we aimed to refine intraoperative strategies to mitigate post-surgical complications. A prototype of a device combining ECG, electrical impedance, pressure modules and a three-wavelength optical sensor working both in reflection and transmission modes has been developed. Preliminary findings include a comparison of human and pig tissues. This research sets a pivotal foundation for future studies to improve small intestine resection surgery outcomes significantly.

Keywords: Anastomotic leakage, Resection surgery, Intestinal Vascularization, Photoplethysmography, Electric Impedance

URZĄDZENIE DO ŚRÓDOPERACYJNEJ OCENY UKRWIENIA SEGMENTÓW JELIT

Streszczenie

Określenie obszarów prawidłowego ukrwienia ma kluczowe znaczenie dla powodzenia operacji resekcji przewodu pokarmowego. Nieszczelność zespolenia może prowadzić do poważnych powikłań, przedłużonej hospitalizacji, zwiększonych kosztów i ryzyka nawrotu nowotworu. W niniejszym badaniu zagłębiono się w innowacyjne metody usprawniające podejmowanie decyzji chirurgicznych podczas operacji jelita cienkiego. Istniejące techniki śródoperacyjnej oceny przewodu pokarmowego nie są pozbawione wad, głównie ze względu na trudności w stosowaniu i znaczną niepewność pomiaru. Rozpoznając czynniki wysokiego ryzyka związane z błędną klasyfikacją segmentów krążeniowych w połączonych fragmentach jelit, postanowiliśmy udoskonalić strategie śródoperacyjne w celu złagodzenia powikłań pooperacyjnych. Opracowano prototyp urządzenia łączącego pomiary EKG, impedancji elektrycznej, ciśnienia i trójzakresowy czujnik optyczny działający zarówno w trybie odbicia, jak i transmisji. Wstępne wyniki obejmują porównanie tkanek ludzkich i świńskich. Badania te stanowią podstawę dla przyszłych badań mających na celu znaczną poprawę wyników operacji resekcji jelita cienkiego.

Słowa kluczowe: Nieszczelność zespolenia, chirurgia resekcji, unaczynienie jelit, fotopletyzmografia, impedancja elektryczna

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Bujnarowski KEVIN[1]

KRUSZYWO Z ODPADÓW TWORZYW SZTUCZNYCH DO ZASTOSOWAŃ W BETONACH LEKKICH

1. Wprowadzenie

W kontekście dynamicznie rozwijającego się stylu życia w krajach rozwijających się, kluczowym aspektem pozostaje jego wpływ na rosnącą produkcję odpadów z tworzyw sztucznych, które co roku generowane są w znacznych ilościach [4, 16]. Obecna gospodarka odpadami opiera się głównie na składowaniu odpadów na otwartych wysypiskach, co stanowi powszechną praktykę, lecz wiąże się z istotnymi wyzwaniami. Składowanie odpadów na wysypiskach jest kosztowne i wymaga znacznych powierzchni gruntów, które mogłyby być przeznaczone na inne cele. Co więcej, mimo wzrostu ilości produkowanych odpadów, jedynie niewielka ich część jest poddawana recyklingowi, podczas gdy pozostałe materiały trafiają na wysypiska bez wcześniejszego przetworzenia, co skutkuje znacznym obciążeniem środowiska i jego skażeniem [2, 15, 17].

Według danych zawartych w raporcie „Plastics Europe – Tworzywa sztuczne w obiegu zamkniętym. Analiza sytuacji w Europie", zagospodarowanie pokonsumenckich odpadów tworzyw sztucznych w 2022 roku, jedynie 26,9% odpadów z tworzyw sztucznych jest poddawanych procesom recyklingu, 49,6% odpadów trafia do spalania w celu odzysku energii, podczas gdy 23,5% ulega składowaniu na wysypiskach [10]. Problem ten jest dodatkowo potęgowany przez fakt, że tworzywa sztuczne nie ulegają biodegradacji, co czyni je trwałym zagrożeniem dla środowiska. W kontekście zrównoważonego rozwoju, przekształcenie tych odpadów w surowiec wtórny i ich ponowne wykorzystanie stanowią jedno z najbardziej efektywnych i opłacalnych rozwiązań zarówno pod względem ekonomicznym, jak i energetycznym [1]. Recykling staje się kluczowym narzędziem w ograniczeniu ilości odpadów, redukując potrzebę składowania i pozytywnie wpływając na równowagę ekologiczną.

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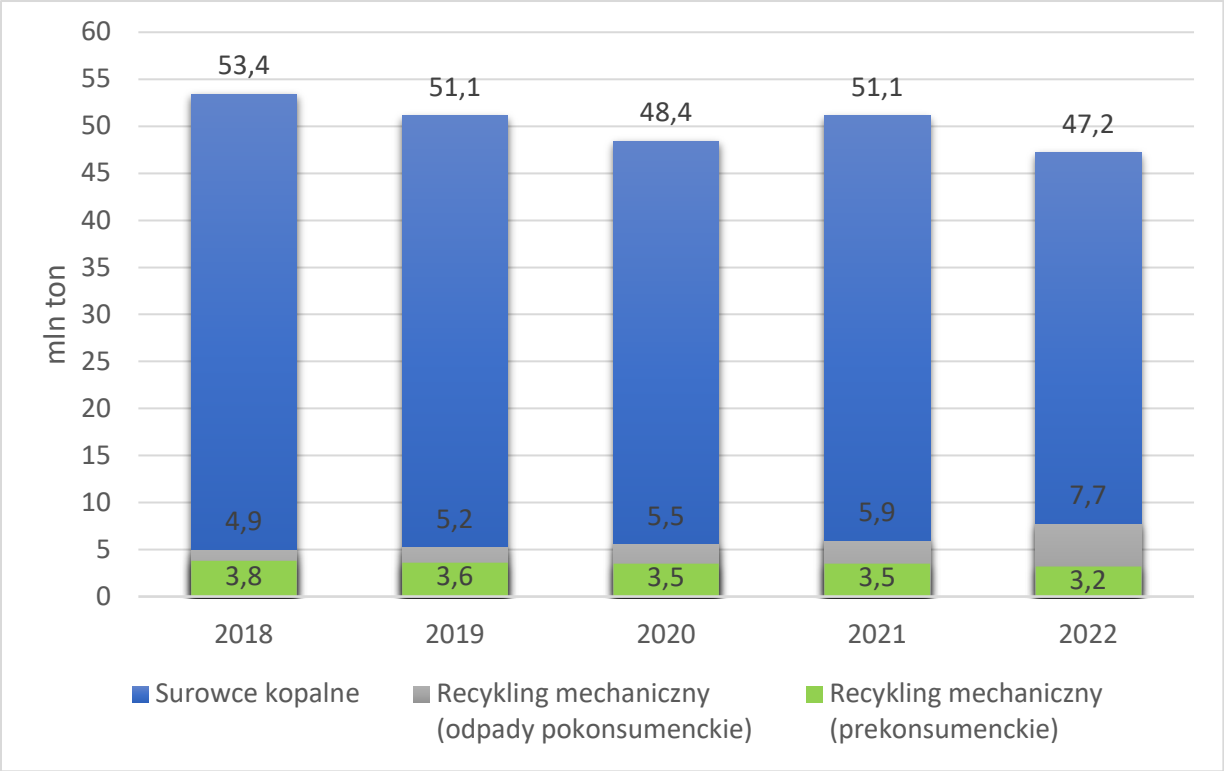
W sektorze budowlanym, z uwagi na rosnący popyt i malejące zasoby naturalne, coraz większego znaczenia nabierają zrównoważone alternatywy dla tradycyjnych materiałów budowlanych. Produkcja betonu, który w dużej mierze opiera się na zużyciu zarówno grubych, jak i drobnych kruszyw, jest szczególnie wymagająca pod względem surowców. Kruszywa te, stanowiące około 60-80% objętości betonu, mają decydujący wpływ na jego właściwości fizyczne i mechaniczne, a także na koszty produkcji [8, 13]. Jednakże ciągła eksploatacja nieodnawialnych surowców, takich jak kruszony kamień i piasek rzeczny, prowadzi do ich szybkiego wyczerpywania. Aby sprostać rosnącym potrzebom branży budowlanej i jednocześnie chronić zasoby naturalne dla przyszłych pokoleń, konieczne jest wprowadzenie odnawialnych, zrównoważonych kruszyw. W tym kontekście odpady z tworzyw sztucznych stanowią realną alternatywę dla kruszyw naturalnych, umożliwiając produkcję ekologicznego betonu i redukcję negatywnego wpływu na środowisko [9].

Zastosowanie materiałów z recyklingu w produkcji betonu nie tylko przyczynia się do oszczędności surowców, ale także pozwala na znaczną redukcję kosztów budowlanych. W obliczu postępującej degradacji środowiska, branża budowlana dąży do wdrażania rozwiązań technologicznych i architektonicznych, które ograniczają zużycie energii oraz minimalizują koszty i negatywne skutki ekologiczne. Poszukiwanie przyjaznych dla środowiska materiałów budowlanych staje się priorytetem, gdyż warunki wewnętrzne w budynkach mają bezpośredni wpływ na zdrowie użytkowników [14].

Tworzywa sztuczne, ze względu na swoje właściwości, takie jak niska przewodność elektryczna i cieplna, trwałość oraz odporność na korozję, mają szerokie zastosowanie w różnych sektorach przemysłu. Jednak kluczowe wyzwanie dla przyszłości budownictwa to wytwarzanie materiałów budowlanych o wysokich parametrach technicznych i mechanicznych, z jednoczesnym ograniczeniem ilości odpadów i minimalizacją negatywnego wpływu na środowisko naturalne. Przekształcenie odpadów z tworzyw sztucznych w surowiec do produkcji betonu stanowi zatem istotny krok w kierunku zrównoważonej przyszłości budownictwa [14].



Rys. 1. Europejska produkcja tworzyw sztucznych w latach 2018-2022
Fig. 1. European plastic production 2018-2022

W 2022 roku produkcja cyrkularnych tworzyw sztucznych wzrosła o ponad 30%, mimo że całkowita produkcja tworzyw sztucznych spadła o ponad 5%. W zestawieniu z 2018 rokiem należy zauważyć spadek produkcji tworzyw sztucznych z surowców kopalnych o 11,6%, oraz wzrost produkcji tworzyw cyrkularnych o 25,3%. Zwiększenie udziału tworzyw cyrkularnych oraz redukcja zależności od surowców kopalnych zaliczają się do gospodarki o obiegu zamkniętym. Jednak wciąż istnieje potrzeba dalszej poprawy w zakresie recyklingu odpadów prekonsumenckich i jeszcze większej redukcji zużycia surowców pierwotnych.

W niniejszej pracy omówiono zastosowanie mieszanych tworzyw sztucznych do produkcji kruszyw dla betonu lekkiego, co w znaczący sposób przyczyni się do ochrony środowiska oraz redukcji ilości odpadów trafiających na składowiska. Odwołując się do zagadnień omówionych w artykułach 3, 5, 6 oraz 11, niniejsza praca podejmuje analizę chropowatości kruszywa pochodzącego z odpadów tworzyw sztucznych, jak również występowania porów w stwardniałym betonie, uwzględniając przy tym pomiary ich wielkości.

2. Właściwości kruszywa z odpadów tworzyw sztucznych

Do produkcji lekkiego kruszywa betonowego zastosowano mieszankę odpadów tworzyw sztucznych, w tym PET, PVC i OPS, pochodzących z poprodukcyjnych odpadów folii wykorzystywanej w produkcji etykiet (rys. 2).

Rys. 2. Kruszywo lekkie z tworzyw sztucznych PET/PVC/OPS
Fig. 2. PET/PVC/OPS lightweight plastic aggregate

W celu zbadania właściwości kruszywa pochodzącego z odpadów tworzyw sztucznych, przygotowano trzy próbki materiału, które przed przystąpieniem do procedury badawczej zostały poddane suszeniu w temperaturze 110±5°C do uzyskania stałej masy. Zgodnie z wymaganiami norm PN-EN 1097-3:2000 [18] oraz PN-EN 932-5:2012 [20], przeprowadzono analizę gęstości nasypowej ekologicznego kruszywa lekkiego. W porównaniu z kruszywem popiołoporytowym Certyd, którego gęstość nasypowa wynosi 725 kg/m³, proekologiczne kruszywo z tworzyw sztucznych wykazuje gęstość nasypową mniejszą o 18%. Wyniki badań własnych dotyczących innych kruszyw lekkich, takich jak certyd, keramzyt, perlit, gransil oraz Penostek, zostały szczegółowo opisane w literaturze [3, 5, 6].

Wartości gęstości nasypowej prezentują się następująco:

- PET (frakcja 2-4 mm) osiąga wartość 612 kg/m³,
- PET (frakcja 4-8 mm) ma gęstość 598 kg/m³,
- certyd charakteryzuje się największą gęstością nasypową, wynoszącą 725 kg/m³,
- keramzyt ma najmniejszą gęstość spośród analizowanych materiałów, wynoszącą 290 kg/m³.

Dodatkowo, przeprowadzono badania nasiąkliwości zgodnie z normą PN-EN 1097-6:2013-11 [19], przy użyciu piknometru, a uzyskane rezultaty klasyfikują się następująco:

- PET (frakcja 2-4 mm) osiąga wartość 1,56%,
- PET (frakcja 4-8 mm) na poziomie 1,12%,
- certyd charakteryzuje się nasiąkliwością na poziomie 18%,
- keramzyt posiada największą nasiąkliwość na poziomie 35%.

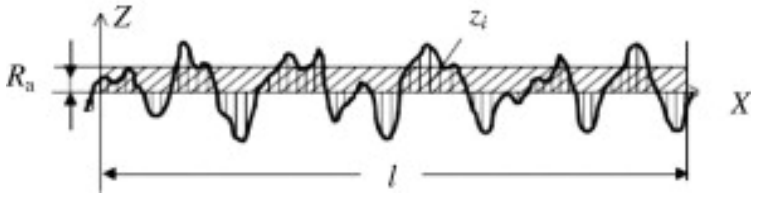
Z powyższych wyników należy zaobserwować znaczną różnicę pomiędzy kruszywem popiołoporytowym i ceramicznym a kruszywem z odpadów tworzyw sztucznych, która wynosi kolejno 94% i 97%.

W ramach dalszych badań wykonano pomiary chropowatości kruszywa lekkiego z odpadów tworzyw sztucznych, porównując wyniki z chropowatością innych, dostępnych na rynku kruszyw (rys. 4). Badania chropowatości kruszywa lekkiego PET o frakcji 4-8 mm przeprowadzono z wykorzystaniem mikroskopu optycznego KEYENCE VHX 7000N.

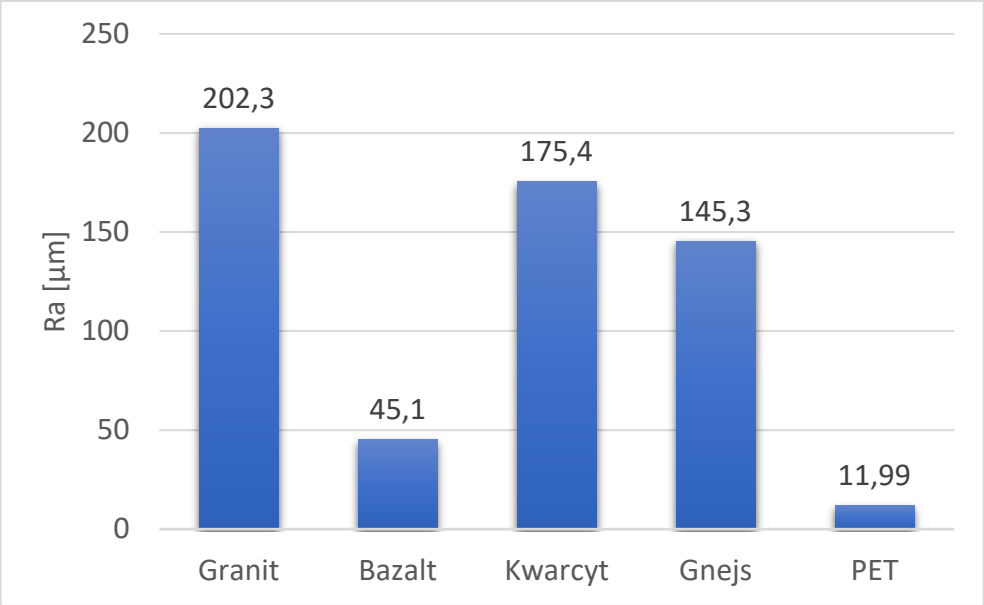
Badania chropowatości powierzchni pozostałych kruszyw przeprowadzono z zastosowaniem profilometru powierzchni Form Talysurf serii PGI, produkowanego przez firmę Taylor Hobson, wyposażonego w precyzyjny, diamentowy rysik pomiarowy. Pomiary chropowatości powierzchni (parametr *Ra* – średnia arytmetyczna odchyleń od linii średniej) wykonano na pięciu próbkach kruszywa o nominalnym rozmiarze przekraczającym 40 mm, pobranych z każdego z analizowanych źródeł. Każda próbka została odpowiednio zamocowana, zapewniając niemal prostopadłe ułożenie powierzchni pomiarowej względem rysika profilometru. Proces pomiarowy polegał na precyzyjnym przesuwaniu rysika po powierzchni próbki, w celu rejestracji jej chropowatości. Minimalna długość toru pomiarowego została ustalona na 10 mm [12]. W przypadku kruszywa lekkiego z tworzywa PET długość pomiaru wynosiła 225 μm.

Chropowatość badanej powierzchni została określona za pomocą parametru *Ra*, który obliczono zgodnie z poniższym równaniem (1). Wzór ten uwzględnia długość odcinka próbkowania l na powierzchni oraz całkowitą liczbę punktów próbkowania n. Współrzędna z_i reprezentuje wartość odchylenia punktu próbkowania i w kierunku osi Z, jak przedstawiono na rysunku 3 [7].

$$R_a = \frac{1}{n}\sum_{i=1}^{n} |z_i| \tag{1}$$



Rys. 3. Profil powierzchni i Ra [7]
Fig. 3. Surface profile and Ra [7]

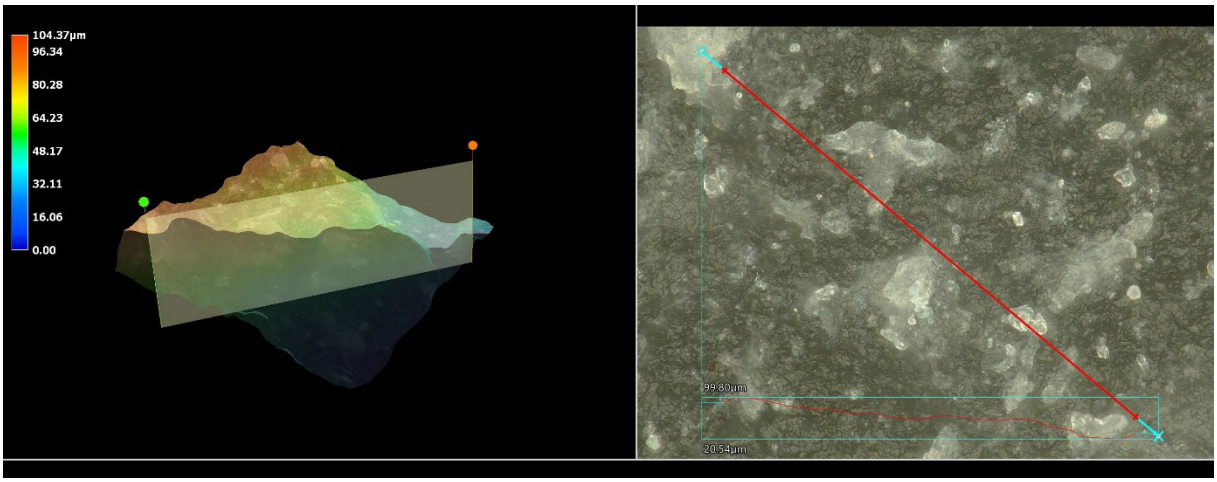


Rys. 4. Wyniki pomiaru chropowatości „Ra" kruszyw do betonu [12]
Fig. 4. Results of measurement of roughness "Ra" of aggregates for concrete [12]

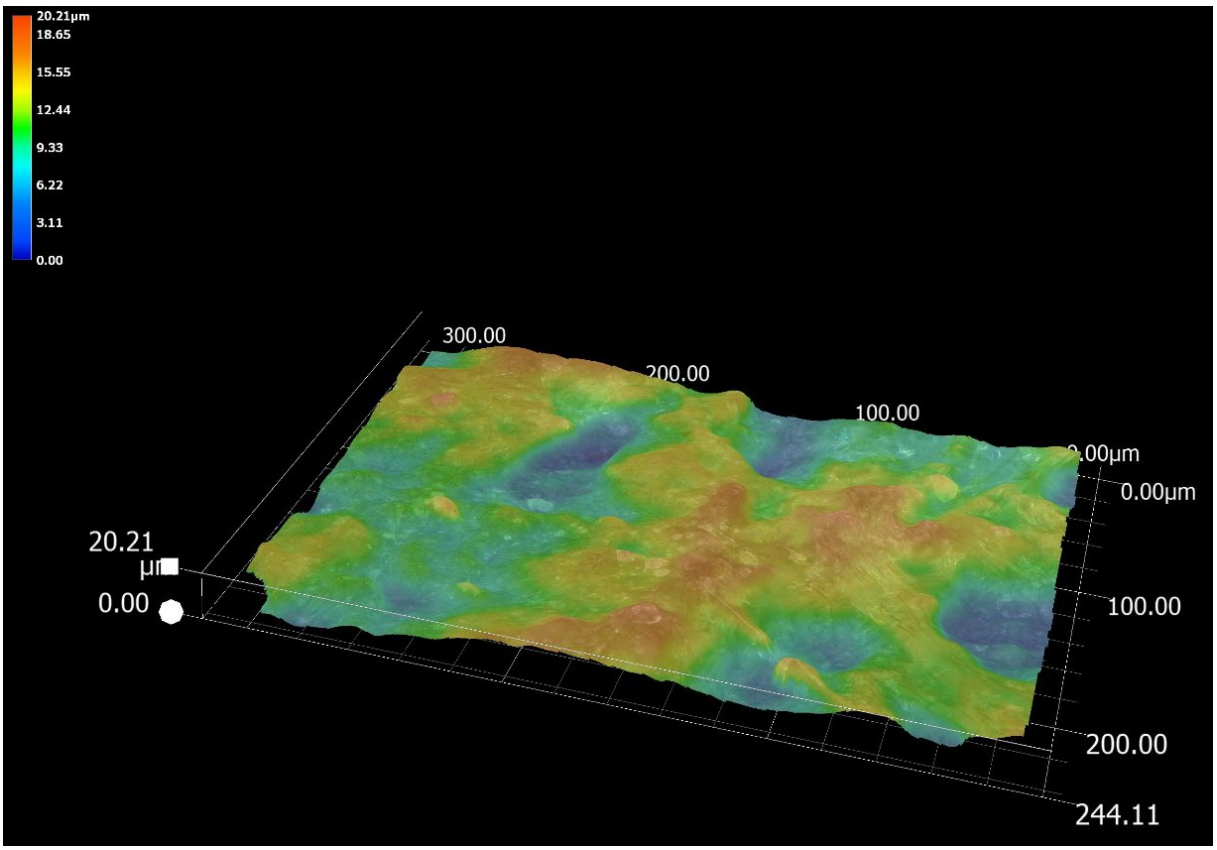
Przeprowadzona analiza zestawia wartości parametru Ra (średnia chropowatość) pięciu różnych kruszyw: granitu, bazaltu, kwarcytu, gnejsu oraz kruszywa z tworzywa sztucznego (PET). Wartość Ra jest istotnym parametrem, charakteryzującym powierzchniową chropowatość materiału i ma bezpośredni wpływ na przyczepność zaczynu cementowego do kruszywa, co przekłada się na wytrzymałość betonu.

Wartość Ra w przypadku granitu jest na poziomie 202,3 µm, co stanowi o wysokiej przyczepności do zaczynu cementowego, a w efekcie, wyższych wytrzymałości na ściskanie betonu wykonanego z tym kruszywem, o czym świadczy stosowanie granitu w betonach wysokowytrzymałych. Kwarcyt charakteryzuje się również znaczną chropowatością, jednak mniejszą od granitu o nieco ponad 13%, a większą od gnejsu o prawie 21%.

Bazalt i PET mają najmniejsze wartości chropowatości powierzchni, kolejno 45,1 µm i 11,99 µm, przy czym należy zauważyć, że kruszywo z odpadów tworzyw sztucznych ma mniejszą wartość od bazaltu o 73,4%.



Rys. 5. Zrzut pomiaru chropowatości kruszywa z urządzenia KEYENCE VHX 7000N
Fig. 5. A snapshot of aggregate roughness measurement from the KEYENCE VHX 7000N

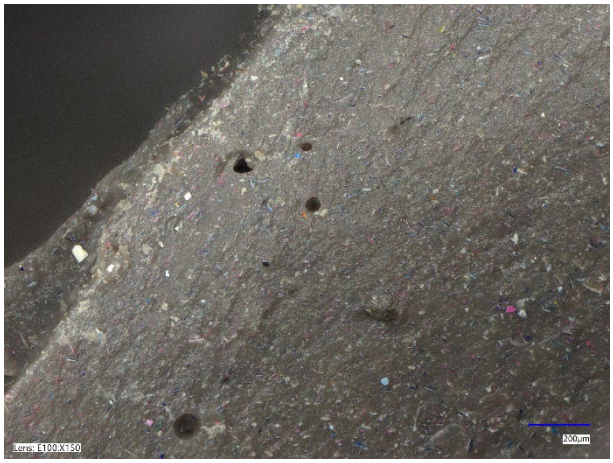


Rys. 6. Mapa obrazująca powierzchnię kruszywa lekkiego PET, wykonana mikroskopem optycznym KEYENCE VHX 7000N
Fig. 6. Map showing the surface of the PET light aggregate, taken with the KEYENCE VHX 7000N optical microscope

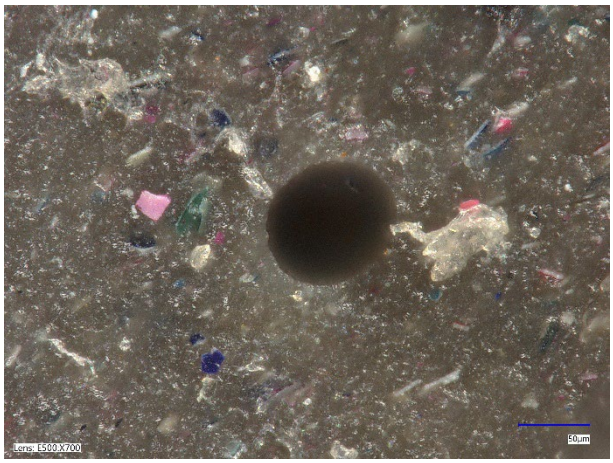
Z mapy przedstawionej na rysunku 6, można odczytać, że największa różnica pomiędzy najwyższym a najniższym punktami wynosi 20,21 µm.

W trakcie badań właściwości kruszywa lekkiego pochodzącego z odpadów tworzyw sztucznych wykonano również zdjęcia przy użyciu mikroskopu optycznego KEYENCE VHX 7000N. Szczegółowy opis wyników uzyskanych z analizy mikroskopowej przedstawiono w literaturze własnej [11].

Rys. 7. Kruszywo uzyskane z odpadów tworzyw sztucznych – skala 2000 µm
Fig. 7. Kruszywo uzyskane z odpadów tworzyw sztucznych – skala 2000 µm



Rys. 8. Kruszywo z tworzyw PET/PVC/OPS – skala 200 µm
Fig. 8. PET/PVC/OPS plastic aggregate – 200 µm scale



Rys. 9. Zdjęcie kruszywa lekkiego z mikroskopu KEYENCE VHX 7000N – skala 50 µm
Fig. 9. Photo of lightweight aggregate from KEYENCE VHX 7000N microscope – 50 µm scale

Zdjęcie w skali 2000 µm (rys. 7) przedstawia kruszywo lekkie o nieregularnym kształcie, otrzymane w wyniku kruszenia materiału uzyskanego z przetwarzania odpadów tworzyw sztucznych. Ponadto w efekcie kruszenia otrzymano chropowatą powierzchnię oraz odstające ostre części kruszywa, wpływające pozytywnie na przyczepność do matrycy cementowej. W strukturze kruszywa widoczne są również pojedyncze mikropory (rys. 8), wynikające z minimalnej zawartości wilgoci w surowcu odpadowym lub też ze zbyt słabego odgazowania w procesie przetwarzania. Przełam powierzchni ukazał również kolorowe zabarwienia, które stanowią pozostałości farb na etykietach, jednak równomierne ich rozmieszczenie świadczy o prawidłowym przetopieniu oraz wymieszaniu odpadów w procesie produkcji. Jak widać na rysunku 9, farba nie uległa całkowitemu rozpuszczeniu w mieszance tworzyw termoplastycznych – pozostałości w postaci cząstek. Powiększenie w skali 50 µm uwidoczniło również (omawiane wcześniej) pory powietrzne, które mają średnicę na poziomie 30-50 µm.

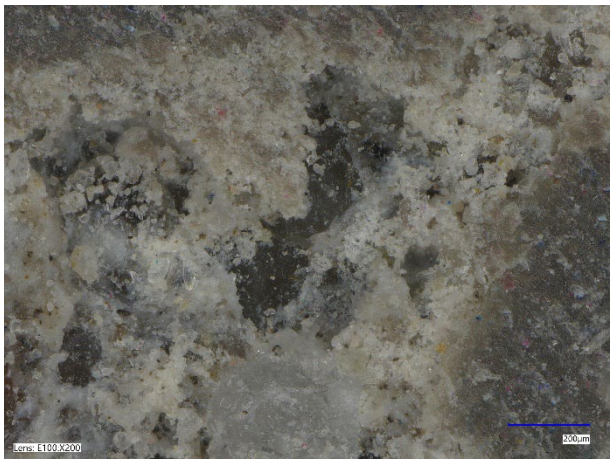
3. Analiza mikroskopowa ekologicznego betonu lekkiego

W celu oznaczenia właściwości betonu lekkiego na kruszywie z odpadów tworzyw sztucznych opracowano recepturę mieszanki betonowej ze stosunkiem woda-cement na poziomie 0,55. Próbki betonu poddano dojrzewaniu przez 28 dni, po czym wykonano badania właściwości, które zostały opisane w pracach [5, 6, 11].

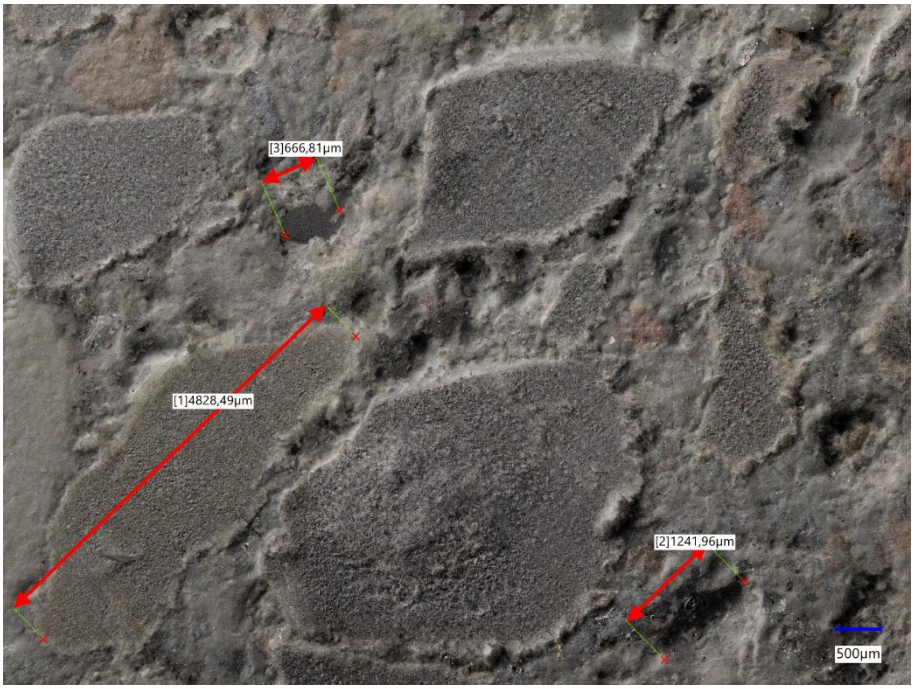
Próbkę betonu, w której zastosowano kruszywo sztuczne, poddano szczegółowej analizie za pomocą mikroskopu optycznego KEYENCE VHX 7000N. Badanie przekroju próbki betonowej ujawniło obecność porów w bezpośredniej strefie kontaktu z kruszywem. Pory te powstały na skutek odparowania niezwiązanej wody zarobowej, co istotnie wpływa na jakość i trwałość połączenia między zaczynem cementowym a kruszywem (rys. 10, 12).

Pomiar porów przeprowadzono z wykorzystaniem dedykowanego oprogramowania do mikroskopu KEYENCE VHX 7000N. Wyniki analizy wykazały, że pory w badanej próbce betonu osiągają rozmiary przekraczające 1200 µm (rys. 11). Rysunek 11 przedstawia również pomiar wielkości kruszywa, który zgodnie z wynikami przedstawionymi w punkcie 2. niniejszej pracy, mieści się w zakresie frakcji: od 2 do 4 mm oraz od 4 do 8 mm.

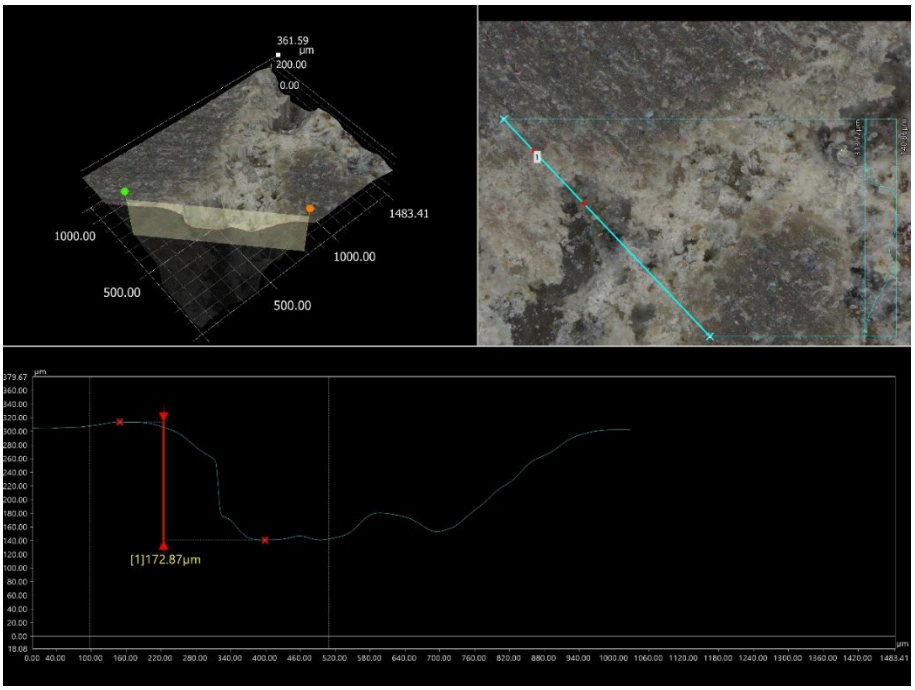
Ponadto pomiar głębokości w strefie kontaktu, przedstawiony na rysunku 12, wykazał wartość 172,87 µm, co ma istotne znaczenie dla oceny mikrostruktury i właściwości mechanicznych betonu w miejscu styku kruszywa z zaczynem cementowym.



Rys. 10. Przekrój próbki betonowej z kruszywem lekkim PET – skala 200 µm
Fig. 10. Cross-section of concrete sample with PET lightweight aggregate – 200 µm scale



Rys. 11. Przekrój próbki z pomiarem porów oraz kruszywa lekkiego – skala 500 µm
Fig. 11. Sample cross-section with pore measurement and lightweight aggregate – 500 µm scale



Rys. 12. Analiza przekroju próbki z wykorzystaniem zdjęć 3D
Fig. 12. Sample cross-section analysis using 3D images

4. Podsumowanie

Analiza kruszywa lekkiego z zastosowaniem mikroskopu wykazała, że największą chropowatość ma granit z wartością na poziomie 202,3 µm, a następnie kwarcyt i gnejs. Znaczna chropowatość tych kruszyw świadczy o dobrej adhezji do zaczynu cementowego, co przekłada się na wytrzymałość betonu. Świadczy o tym stosowanie na przykład granitu w betonach wysokowytrzymałych. Kruszywo z odpadów tworzyw sztucznych ma najmniejszą chropowatość – na poziomie 11,99 µm, jest to wartość mniejsza o 94% w porównaniu z chropowatością granitu. W związku z tym, jego zastosowanie w betonach skutkuje obniżeniem wytrzymałości kompozytu w miejscach styku z kruszywem. Niemniej jednak, kruszywa z PET mogą znaleźć zastosowanie w betonach lekkich lub betonach izolacyjnych, gdzie priorytetem jest redukcja ciężaru, a nie osiągnięcie maksymalnej wytrzymałości.

Na podstawie przedstawionych badań i analiz można stwierdzić, że zastosowanie kruszywa z odpadów tworzyw sztucznych stanowi innowacyjne i zrównoważone rozwiązanie w kontekście współczesnych wyzwań środowiskowych i gospodarczych. W dobie rosnącej produkcji odpadów plastikowych, szczególnie w krajach rozwijających się, przetworzenie tych odpadów w kruszywo do betonu lekkiego pozwala nie tylko na zmniejszenie obciążenia wysypisk i ograniczenie emisji CO_2, ale także na efektywne wykorzystanie surowców wtórnych, wspierając gospodarkę o obiegu zamkniętym i promując zrównoważony rozwój.

W związku z tym, wdrożenie tej technologii w szerszej skali może stanowić kluczowy krok w kierunku bardziej ekologicznego i zasobooszczędnego budownictwa przyszłości.

Kruszywo z tworzyw sztucznych może stać się alternatywą dla naturalnych kruszyw, takich jak żwir czy piasek, które są surowcami nieodnawialnymi. Dodatkowo, niska przewodność cieplna oraz lekkość kruszywa z tworzyw sztucznych mogą znacząco poprawić właściwości izolacyjne i akustyczne betonu, co czyni go atrakcyjnym materiałem budowlanym dla takich zastosowań jak: modernizacja istniejących konstrukcji, produkcja ekranów akustycznych czy podłóg przemysłowych.

Badania zostały zrealizowane w ramach prac WZ/WB-IIL/6/2023, WI/WB-IIL/1/2021 i WI/WB-IIL/2/2024 na Politechnice Białostockiej i sfinansowane z subwencji badawczej przekazanej przez MEiN.

Bibliografia

1. Balcom P., Cabrera J.M., Carey V.P.: Extended exergy sustainability analysis comparing environmental impacts of disposal methods for waste plastic roof tiles in Uganda. Develop. Eng., 6 (2021). DOI: 10.1016/j.deveng.2021.100068
2. Bernardo B., Candeias C., Rocha F.: Characterization of the dynamics of leachate contamination plumes in the surroundings of the Hulene-B waste dump in Maputo, Mozambique. Environments, 9 (2022), p. 19. DOI: 10.3390/environments9020019
3. Bujnarowski K., Grygo R.: Właściwości kruszyw lekkich do zastosowania w budownictwie, Instal, 2022, nr 7/8, s. 71-75, DOI: 10.36119/15.2022.7-8.10
4. Chaturvedi V., Mahajan T., Singh R.P., Kaur P., Arora A.: Industrial Waste Management in Portugal for Environmental Development, Proceedings of the International Conference on Industrial and Manufacturing Systems (CIMS-2020) (2022), pp. 519-534, DOI: 10.1016/j.susmat.2024.e00877
5. Grygo R., Bujnarowski K., Prusiel J.A.: Analysis of the possibility of using plastic post-production waste in construction, Ekonomia i Środowisko, 2022, vol. 81, no. 2, p. 241-256, DOI: 10.34659/eis.2022.81.2.467
6. Grygo R., Prusiel J.A., Bujnarowski K.: Use of ecological lightweight aggregates in reinforced concrete structures, Ekonomia i Środowisko, 2021, no. 4, p. 112-132.
7. Hong L., Gu X., Lin F.: Influence of aggregate surface roughness on mechanical properties of interface and concrete, Construction and Building Materials, vol. 65, p. 338-349, 2014, DOI: 10.1016/j.conbuildmat.2014.04.131
8. Kobayashi S., Kawano H.: Properties and usage of recycled aggregate concrete. Demoli. Reuse of Concrete and Masonry, 2 (2023), pp. 547-556.
9. Liu T., Nafees A., Javed M.F., Aslam F., Alabduljabbar H., Xiong J.-J., et al.: Comparative study of mechanical properties between irradiated and regular plastic waste as a replacement of cement and fine aggregate for manufacturing of green concrete. Ain Shams Eng. J., 13 (2022), DOI: 10.1016/j.asej.2021.08.006
10. Plastics Europe. Tworzywa sztuczne w obiegu zamkniętym. Analiza sytuacji w Europie. Belgia, 2024.
11. Prusiel J.A., Bujnarowski K.: Proekologiczne kruszywo z odpadów tworzyw sztucznych jako alternatywa kruszywa naturalnego do betonów lekkich, Przegląd Budowlany, Art. nr 11-12, 2023, DOI: 10.5604/01.3001.0054.1329

12. Qudoos A., Atta-ur-Rehman, Kim H.G., Ryou J.-S.: Influence of the surface roughness of crushed natural aggregates on the microhardness of the interfacial transition zone of concrete with mineral admixtures and polymer latex, Construction and Building Materials, vol. 168, p. 946-957, 2018, DOI: 10.1016/j.conbuildmat.2018.02.205
13. Rashid K., Rehman M.U., de Brito J., Ghafoor H.: Multi-criteria optimization of recycled aggregate concrete mixes. J. Clean. Prod., 276 (2020).
14. Sau D., Shiuly A., Hazra T.: Study on green concrete replacing natural fine and coarse aggregate by plastic waste – An experimental and machine learning approach, Materials Today: Proceedings, 2023, DOI: 10.1016/j.matpr.2023.04.207
15. Siddiqua A., Hahladakis J.N., Al-Attiya W.A.K.: An overview of the environmental pollution and health effects associated with waste landfilling and open dumping. Environ. Sci. Pollut. Res., 29 (2022), pp. 58514-58536, DOI: 10.1007/s11356-022-21578-z
16. Srivastav A.L., Kumar A.: An endeavor to achieve sustainable development goals through floral waste management: a short review. J. Clean. Prod., 283 (2021), DOI: 10.1016/j.jclepro.2020.124669
17. Tejaswini M., Pathak P., Gupta D.: Sustainable approach for valorization of solid wastes as a secondary resource through urban mining. J. Environ. Manag., 319 (2022), DOI: 10.1016/j.jenvman.2022.115727
18. PN-EN 1097-3:2000 Badania mechanicznych i fizycznych właściwości kruszyw – Oznaczanie gęstości nasypowej i jamistości.
19. PN-EN 1097-6:2013-11 Badania mechanicznych i fizycznych właściwości kruszyw – Część 6: Oznaczanie gęstości ziarn i nasiąkliwości.
20. PN-EN 932-5:2012 Badania podstawowych właściwości kruszyw – Część 5: Wyposażenie podstawowe i wzorcowanie.

KRUSZYWO Z ODPADÓW TWORZYW SZTUCZNYCH DO ZASTOSOWAŃ W BETONACH LEKKICH

Streszczenie

W artykule przedstawiono kruszywo lekkie z poprodukcyjnych odpadów tworzyw sztucznych, wraz z jego zastosowaniem do betonu. Kruszywo lekkie wytworzono w formie łamanej o frakcji do 8 mm z tworzyw, tj. PET − Poli(tereftalan etylenu), PVC − Poli(chlorek winylu) i OPS − Orientowany Polistyren.. W artykule przedstawiono wyniki badania właściwości kruszywa z recyklingu tworzyw sztucznych, takich jak gęstość nasypowa, nasiąkliwość i chropowatość. Ponadto przedstawiono zdjęcia z mikroskopu optycznego dla kruszywa z odpadów tworzyw sztucznych oraz przeprowadzono analizę mikroskopową przekroju próbki betonu z zawartością tego kruszywa lekkiego. Zastosowanie ekologicznego kruszywa do betonu lekkiego wspiera gospodarkę o obiegu zamkniętym i promuje zrównoważony rozwój.

Słowa kluczowe: odpady poprodukcyjne, lekkie kruszywa sztuczne, recykling, mikroskopia optyczna, gospodarka obiegu zamkniętego

WASTE PLASTIC AGGREGATE FOR LIGHTWEIGHT CONCRETE APPLICATIONS

Abstract

This article presents lightweight aggregate from post-production plastic waste, along with its application to concrete. The lightweight aggregate was produced in broken form with a fraction of up to 8 mm from plastics, i.e. PET – Poly(ethylene terephthalate), PVC – Poly(vinyl chloride) and OPS – Oriented Polystyrene. The article presents the results of testing the properties of recycled plastic aggregate, such as bulk density, absorbability and roughness. In addition, optical microscope images for the waste plastic aggregate are presented, and a microscopic analysis of the cross-section of a concrete sample containing this lightweight aggregate is carried out. The use of environmentally friendly aggregate for lightweight concrete supporting a closed-loop economy and promoting sustainable development.

Keywords: post-production waste, lightweight plastic aggregate, recycling, optical microscopy, circular economy

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THERMAL PROPERTIES OF L-ARGININE AND ITS POTENTIAL INFLUENCE ON THE FLAMMABILITY OF UNSATURATED POLYESTER RESIN

1. Introduction

Flame retardants (FRs) are structurally diverse compounds that influence materials' flammability. Their incorporation into materials allows them to meet the fire safety requirements for materials exhibiting poor fire performance. FRs are applied in materials used in many fields of industry, e.g. construction, shipbuilding, or rail, where it is essential to ensure an adequate safety level [1].

The reduction of the flammability of materials is still an ongoing issue due to the escalating significance of fire safety. An example of a material in which flame retardancy is crucial in terms of its use in the mentioned industry areas is unsaturated polyester resin (UPR). Although it exhibits good mechanical performance, chemical resistance, and dimension stability, it may be a huge threat to people and the environment during a fire due to the high calorific value and large amount of toxic gases produced during combustion [2].

There are several groups of FRs used for UPR, including inorganic hydroxides, phosphorus, nitrogen, boron or tin, and zinc FRs [3]. The recent increase in interest in nanotechnology has also led to the study of the effects of nano-sized particles on the flammability of UPR [4]. Although FRs vary in structure, they should exhibit certain characteristics desired for them (Fig. 1). Novel FRs should meet as many of the outlined features as possible.

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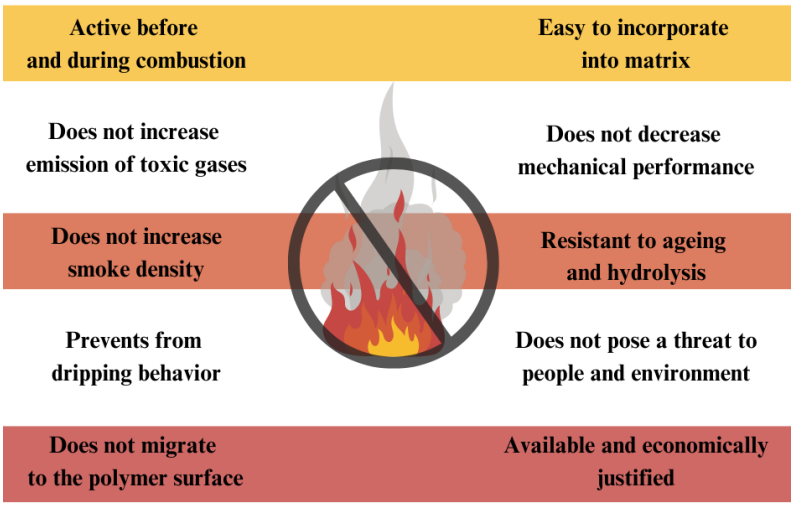

Fig. 1. Features of FRs [Source: own study based on [5]]
Rys. 1. Cechy FR [Źródło: opracowanie własne na podstawie [5]]

Nitrogen FRs are a group of compounds exhibiting flame retardant mechanism in the vapor or condensed phases. The most common subgroups are ammonium and melamine-based FRs. However, amines, azoalkanes, and phosphorus-nitrogen compounds are also considered as a part of that group [6].

Nitrogen FRs' efficiency is relatively high, and their performance in decreasing the flammability of materials is greater than inorganic hydroxides (e.g. aluminum or magnesium), but lower compared to halogenated FRs. Although that group of FRs was ascribed as environmentally friendly in the past [7], nowadays, literature reports indicate the need for thorough verification. For example, melamine is suspected of fertility and unborn children damage and is under evaluation for being persistent and toxic [3].

One of the most commonly used FR for UPR is ammonium polyphosphate (APP), which contains polyphosphoric acid and ammonia in its chain [8]. The effectiveness of nitrogen and phosphorus-containing FRs is due to their synergistic effect.

Due to the continuous development of flame retardant technology, increasing concern for the environment and awareness of the risks that selected FRs can pose to human health, the search for new FRs is now largely focused on compounds of natural origin. The aim of this study is to assess the thermal properties of L-arginine, an amino acid containing the greatest content of nitrogen in its structure, including thermal effects during decomposition and gross heat of combustion, in order to determine its potential influence on the flammability of unsaturated polyester resin, and its application as a precursor for the synthesis of bio-based FRs.

2. Materials and methods

L-arginine and benzoic acid were purchased from Sigma-Aldrich Co. and used without further purification.

Analysis of carbon, hydrogen, and nitrogen content was performed with the use of Elemental Analyzer 2400 Series II CHNS (PerkinElmer, Waltham, USA). The analysis was performed in the CHN mode in helium atmosphere. Complete combustion of samples of 2.5 ± 0.1 mg was performed at 905°C. The measurements were performed in three repetitions.

Thermal effects of L-arginine decomposition were examined using a STA 6000 Simultaneous Thermal Analyzer (PerkinElmer, Waltham, USA). Samples of 5 ± 0.1 mg in a ceramic crucible were heated from 25°C to 300°C in a nitrogen atmosphere with a heating range of 10°C/min.

The gross heat of combustion of L-arginine was assessed with the use of bomb calorimeter C6000 (IKA, Poland). The calorimeter was firstly calibrated with certified benzoic acid with a heat of combustion of 26460 J/g. The pellets consisting of 0.5 g of certified benzoic acid and 0.5 g of L-arginine were prepared in a press and placed in the steel crucible. The specimens were linked to the cotton wire and placed in the vessel. The measurements were performed in an oxygen atmosphere in three repetitions. The gross heat of combustion H_o was calculated according to the equation (1):

$$H_o = \frac{CV * dt - Q_{ext}}{m} \quad (1)$$

Where: CV is the calorific value [J], dt is the measured and corrected increase in temperature [-], Q_{ext} is the external energy from the wire [J], and m is the sample mass [g]. The results were recalculated based on the known value of heat of combustion of benzoic acid.

3. Results and discussion

The L-arginine elemental analysis results compared with calculated values are presented in Table 1. The carbon and nitrogen content results are consistent with the calculated values and are within the standard deviation. The hydrogen content is slightly higher than calculated, which may be ascribed to its hygroscopic nature [9]. All the results are within the standard requirement (± 0.4 wt.%) according to [10].

Table 1

Elemental analysis results

Element content [wt. %]	Experimental	Calculated
C	41.41 ± 0.31	41.37
H	8.49 ± 0.10	8.10
N	32.00 ± 0.24	32.16

Source: own study.

On the one hand, compared to the nitrogen content of APP (14-16 wt.% depending on the producer), L-arginine contains twice as much nitrogen in its structure. However, APP contains also a significant amount of phosphorus, which enhances its flame retardant properties. On the other hand, compared to melamine (66.6 wt.% of nitrogen) characterized by three amino groups [11], the nitrogen content of L-arginine is significantly lower (by 52 %).

Due to the fact that amino acids do not melt, but rather decompose at higher temperatures, thermal analysis was performed in a temperature range of 25-500°C in order to maintain safe conditions [12]. The thermogravimetric curve of L-arginine and its derivative are presented in Figure 2a, whereas the differential scanning calorimetric curve is presented in Figure 2b.

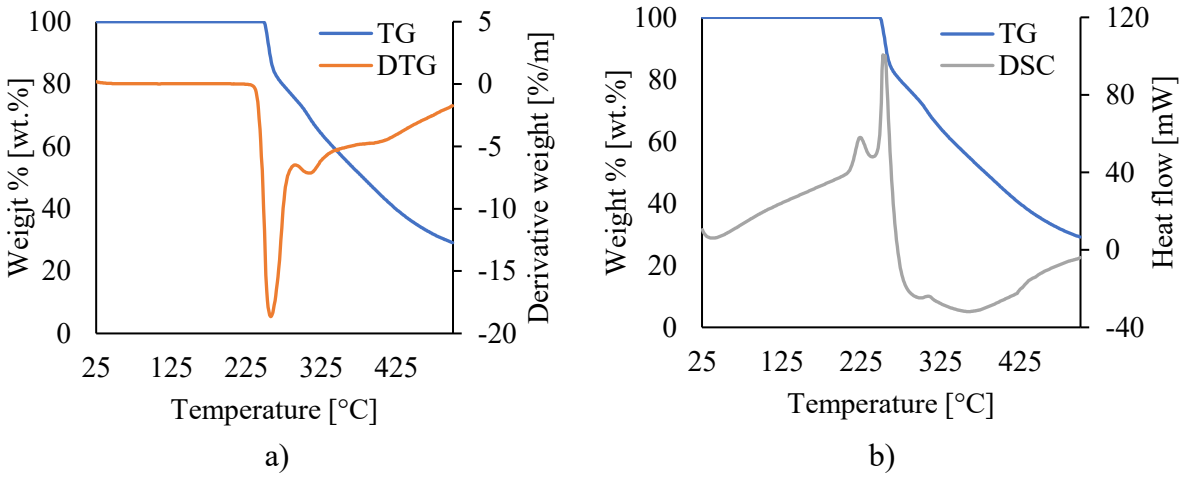

Fig. 2. Thermal analysis results of L-arginine: a) thermogravimetric (TG) and derivative TG (DTG) curves; b) TG and differential scanning calorimetry (DSC) curves [Source: own study]

Rys. 2. Wyniki analizy termicznej L-argininy: a) krzywe termograwimetryczne (TG) i pochodne TG (DTG); b) krzywe TG i różnicowej kalorymetrii skaningowej (DSC) [Źródło: opracowanie własne]

The endothermic peak at 204 °C which is not associated with mass loss (Fig. 2b) is ascribed to the crystal-crystal transition [12]. For the L-arginine, the mass loss starts at 226°C (Fig. 2a), which is in good agreement with previous literature findings (217 °C according to [13], 220°C according to [14], and 233°C according to [12]). The maximum mass loss rate based on the peak on the DTG curve is at 258°C. The temperature at the 5 wt. % mass loss is 253°C. The first degradation step (226-265°C) is ascribed to the release of one mole of water and one mole

of ammonia [14]. The mass loss at the first decomposition stage is 17.82 wt.%, which is similar to the calculated value (20.12 wt.%). The residue after that stage of decomposition contains double internal cyclization products [14]. The second decomposition stage is slower compared to the first one. The final residue at 500°C is 29.12 wt. %.

According to previous studies conducted by the authors [15], UPR thermal degradation is a one-stage process and occurs in a temperature range of 200-450°C. Therefore, the addition of L-arginine, as its decomposition starts at a similar temperature, may influence the decomposition process of UPR. The release of ammonia and water may decrease the combustible gases concentration and decrease the temperature in the combustion area.

The thermal degradation of APP occurs also in a similar temperature range as for the UPR (200-450°C), but the temperature of 5 wt. % mass loss is higher (311°C). In the first stages, it also releases water and ammonia. Further degradation steps are related to phosphate anions in its structure [16, 17].

The temperature-time curve for L-arginine gross heat of combustion measurement is presented in Figure 3.

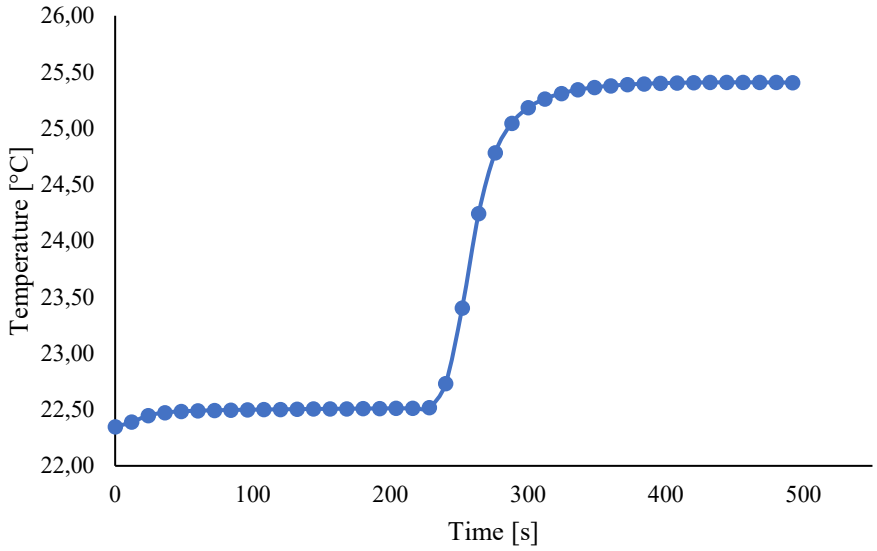

Fig. 3. Temperature-time curve for the L-arginine combustion in the bomb calorimeter
Source: own study.
Rys. 3. Krzywa temperatura-czas spalania L-argininy w bombie kalorymetrycznej

The gross heat of combustion of L-arginine was calculated as 21779.49 ± 243.56 J/g, which is in good agreement with previous literature findings (21371.54 ± 17.75 J/g according to [18]). Minor differences may be ascribed to the different type of calorimeter used for the study conducted by Wu Yang et al. The ignition started at 228 s of the measurement, and the increase in the water temperature after ignition was 2.86°C.

The gross heat of combustion of resins is typically in a range of 30000-40 000 J/g, (e.g. epoxy resin 35360 J/g [19], for UPR up to 40000 J/g [3]). The addition of L-arginine, with significantly lower gross heat of combustion, will result in the decrease of the total gross heat of combustion of material.

The gross heat of combustion of APP alone was not found in the literature. The addition of APP or other compounds that exhibit lower gross heat of combustion results in decreasing the gross heat of combustion of material. An interesting phenomenon was observed by Khalili et al. [19], that there is an optimum amount of APP additive. The addition of 5 wt. % and 10 wt.% of APP to a composite of epoxy resin resulted in a decreasing gross heat of combustion. However, the gross heat of combustion of the composite containing 15 wt. % of APP was only slightly lower than for the non-modified composite.

4. Conclusions

Due to its relatively high nitrogen content (32.00 ± 0.24), L-arginine could stand as a precursor for bio-based FR synthesis. Thermal analysis revealed that the decomposition of L-arginine is within the UPR thermal degradation temperature range (200-450°C) which confirms its ability to influence the course and rate of the UPR decomposition process. The L-arginine gross heat of combustion was calculated as 21779.49 ± 243.56 J/g, which is significantly lower compared to pure UPR. That indicated that the addition of L-arginine to UPR will result in the decrease of the gross heat of combustion of a material.

Although in comparison to APP, L-arginine has a higher nitrogen content, it does not contain any phosphorus in its structure. The presence of phosphorus and nitrogen compounds in the APP molecule is largely responsible for its high activity, due to the synergistic effect.

The incorporation of phosphate or borate anions into the L-arginine structure may further improve their flame retardant properties, due to the synergistic effects between nitrogen and phosphorus and nitrogen and boron elements.

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Bibliography

1. Purser D.A.: Fire Safety Performance of Flame Retardants Compared with Toxic and Environmental Hazards. [In:] *Polymer Green Flame Retardants*; Papaspyrides C.D., Kiliaris P., (eds.); 2; Elsevier: Amsterdam, 2014; pp. 45–86 ISBN 978-0-444-53808-6.
2. Dowbysz A., Samsonowicz M., Kukfisz B.: Recent Advances in Bio-Based Additive Flame Retardants for Thermosetting Resins. *International Journal of Environmental Research and Public Health* 2022, 19, DOI:10.3390/ijerph19084828.
3. Dowbysz A., Samsonowicz M., Kukfisz B.: Modification of Glass/Polyester Laminates with Flame Retardants. *Materials*, 2021, 14, DOI:10.3390/ma14247901.
4. Dowbysz A., Samsonowicz M., Kukfisz B., Koperniak P.: Recent Developments of Nano Flame Retardants for Unsaturated Polyester Resin. *Materials*, 2024, 17, DOI:10.3390/ma17040852.
5. Tawfik S.Y.: Flame Retardants: Additives in Plastic Technology. In *Polymers and Polymeric Composites: A Reference Series*; Palsule S. (ed.); Springer Berlin Heidelberg: Berlin, Heidelberg, 2016; pp. 1-27, ISBN 978-3-642-37179-0.
6. Morgan A.B., Klatt M.: Nitrogen-Based Flame Retardants. In *Non-Halogenated Flame Retardant Handbook*; 2021; pp. 236-270, ISBN 978-1-119-75224-0.
7. Horacek H., Grabner R.: Advantages of Flame Retardants Based on Nitrogen Compounds. *Polym Degrad Stab*, 1996, 54, 205-215, DOI:10.1016/S0141-3910(96)00045-6.
8. Yang X., Zhang W.: Flame Retardancy of Wood-Polymeric Composites. [In:] *Polymer-Based Multifunctional Nanocomposites and Their Applications*; Song K., Liu C., Guo J.Z., (eds.); Elsevier, 2019; pp. 285-317, ISBN 978-0-12-815067-2.
9. Hackl E., Darkwah J., Smith G., Ermolina I.: Effect of Arginine on the Aggregation of Protein in Freeze-Dried Formulations Containing Sugars and Polyol: 1-Formulation Development. *AAPS PharmSciTech*, 2018, 19, 896-911, DOI:10.1208/s12249-017-0884-0.
10. Kuveke R.E.H., Barwise L., van Ingen Y., Vashisth K., Roberts N., Chitnis S.S., Dutton J.L., Martin C.D., Melen R.L.: An International Study Evaluating Elemental Analysis. *ACS Cent Sci*, 2022, 8, 855-863, DOI:10.1021/acscentsci.2c00325.
11. Melamine. In *Synthetic Nitrogen Products: A Practical Guide to the Products and Processes*; Maxwell G.R., (ed.), Springer US: Boston, MA, 2004; pp. 299-306 ISBN 978-0-306-48639-5.
12. Pokorný V., Lieberzeitová E., Štejfa V., Havlín J., Fulem M., Růžička K.: Heat Capacities of L-Arginine, l-Aspartic Acid, l-Glutamic Acid, l-Glutamine, and l-Asparagine. *Int J Thermophys*, 2021, 42, 160, DOI:10.1007/s10765-021-02911-z.
13. Goel D., Santhiya D., Kumar S., Kumar Mahapatro: A. Synthesis of Mesoporous Core Shell Magnetite Bioactive Glass Nanoparticles for Magnetic Hyperthermia Treatment of Cancer. *Chemistry Select*, 2024, 9, e202302119, DOI:10.1002/slct.202302119.
14. Weis I.M.; ‚Muth C., Drumm R., Kirchner H.O.K.: Thermal Decomposition of the Amino Acids Glycine, Cysteine, Aspartic Acid, Asparagine, Glutamic Acid, Glutamine, Arginine and Histidine. *BMC Biophysics*, 2018, 11, 2, DOI:10.1186/s13628-018-0042-4.
15. Dowbysz A., Samsonowicz M., Kukfisz B.: Analiza Wpływu Ligniny Na Rozkład Termiczny Nienasyconej Żywicy Poliestrowej (Ang. Analysis of the Effect of Lignin on the Thermal Decomposition of Unsaturated Polyester Resin). [In:] *Nauka i przemysł: lubelskie spotkania studenckie*; Kołodyńska D., (ed.); Uniwersytet Marii Skłodowskiej-Curie: Lublin, Poland, 2022; pp. 266-269 ISBN 978-83-227-9603-0.
16. Cayla A., Rault F., Giraud S., Salaün F., Sonnier R., Dumazert L.: Influence of Ammonium Polyphosphate/Lignin Ratio on Thermal and Fire Behavior of Biobased Thermoplastic: The Case of Polyamide 11. *Materials*, 2019, 12, DOI:10.3390/ma12071146.

17. Dong T., Wang G., Li Z., Li D., Liu Y., Zhou P., Guo S.: Preparation and Properties of Modified Ammonium Polyphosphate Synergistic with Tris(2-Hydroxyethyl) Isocynurate for Flame-Retardant LDPE. 2023, 23, DOI:10.1515/epoly-2023-0023.
18. Wu Yang X., Rui Liu J., Li Gao S., Dong Hou Y., Zhen Shi Q.: Determination of Combustion Energies of Thirteen Amino Acids. *Thermochim Acta*, 1999, 329, 109-115, DOI:10.1016/S0040-6031(99)00002-7.
19. Khalili, P.; Tshai, K.Y.; Hui, D.; Kong, I. Synergistic of Ammonium Polyphosphate and Alumina Trihydrate as Fire Retardants for Natural Fiber Reinforced Epoxy Composite. *Compos B Eng* 2017, 114, 101–110, doi:10.1016/j.compositesb.2017.01.049.

THERMAL PROPERTIES OF L-ARGININE AND ITS POTENTIAL INFLUENCE ON THE FLAMMABILITY OF UNSATURATED POLYESTER RESIN

Abstract

Unsaturated polyester resins, among their many advantages, pose a high fire hazard. The reduction of their flammability is still an on-going issue. As many of the most effective flame retardants have been discontinued due to their negative impact on people and the environment at various stages of the finished product's life cycle, new flame retardants that are both effective and safe are constantly being sought. Flame retardants of natural origin are the focus of contemporary research. The aim of this study is to evaluate the properties of L-arginine, including gross heat of combustion and thermal properties, which may provide a basis for considering L-arginine as a compound for the synthesis of bio-based flame retardants. Analysis of the thermal decomposition of L-arginine showed that it occurs in two stages in the temperature range 250-400°C corresponding to the decomposition temperature of unsaturated polyester resin. The release of water and ammonia can reduce the concentration of combustible gases and lower the temperature in the combustion zone. The gross heat of combustion of L-arginine is almost twice as low as that of unsaturated polyester resin, indicating a potential decrease in the value of the total gross heat of combustion of the material produced from L-arginine addition. The studies conducted in this work indicate the possibility of reducing the flammability of unsaturated polyester resin by the addition of L-arginine.

Keywords: L-arginine; thermal analysis; heat of combustion; flammability; unsaturated polyester resin

WŁAŚCIWOŚCI TERMICZNE L-ARGININY I JEJ POTENCJALNY WPŁYW NA PALNOŚĆ NIENASYCONEJ ŻYWICY POLIESTROWEJ

Streszczenie

Nienasycone żywice poliestrowe, oprócz wielu zalet, stwarzają wysokie zagrożenie pożarowe. Zmniejszenie ich palności jest wciąż aktualnym zagadnieniem badanym przez wielu naukowców. W związku z tym, że wiele grup najskuteczniejszych środków zmniejszających palność zostało wycofanych z użytku ze względu na ich negatywny wpływ na ludzi i środowisko na różnych etapach cyklu życia gotowego produktu, stale poszukuje się nowych środków zmniejszających palność, które są zarówno skuteczne, jak i bezpieczne dla środowiska i ludzi. Przedmiotem współczesnych badań są więc środki zmniejszające palność pochodzenia naturalnego. Celem pracy jest ocena właściwości L-argininy, w tym ciepła spalania brutto i właściwości termicznych, które mogą stanowić podstawę do rozważenia L-argininy jako związku do syntezy środków uniepalniających pochodzenia naturalnego. Analiza procesu rozkładu termicznego L-argininy wykazała, że następuje on dwuetapowo w zakresie temperatur 250-400 °C odpowiadającym rozkładowi nienasyconej żywicy poliestrowej. Wydzielanie wody oraz amoniaku może wpłynąć na zmniejszenie stężenia gazów palnych i obniżenie temperatury w strefie spalania. Ciepło spalania brutto L-argininy jest niemal dwukrotnie niższe od nienasyconej żywicy poliestrowej, co wskazuje na potencjalne zmniejszenie wartości całkowitego ciepła spalania brutto wytworzonego z nich materiału. Badania przeprowadzone w ramach pracy wskazują na możliwość zmniejszania palności nienasyconej żywicy poliestrowej poprzez dodatek L-argininy.

Słowa kluczowe: L-arginina; analiza termiczna; ciepło spalania; palność; nienasycona żywica poliestrowa

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PLOMBA MIEJSKA. PROGRAM ADAPTACJI HISTORYCZNEJ STRUKTURY W TRUDNYM KONTEKŚCIE URBANISTYCZNYM. GALERIA SZTUKI U ZBIEGU ULIC KIJOWSKIEJ I MŁYNOWEJ W BIAŁYMSTOKU

1. Wprowadzenie

1.1. Cel i zakres

Temat galerii sztuki w zabudowie plombowej przy ul. Kijowskiej w Białymstoku łączy w sobie różnorodne aspekty w zakresie urbanistyki, architektury oraz ochrony zabytków, co czyni go interesującym i wartościowym z perspektywy akademickiej. Projektowana galeria ma za zadanie wzbogacić ofertę kulturalną miasta oraz stać się ważnym elementem przestrzeni publicznej. Bliskość innych instytucji kulturalnych, takich jak Opera i Filharmonia Podlaska oraz Teatr Lalek, stwarza możliwość integracji projektowanego obiektu z istniejącą infrastrukturą kulturalną Białegostoku.

Projekt zakłada, że odpowiednio zaplanowane i wykonane prace adaptacyjne mogą skutecznie zintegrować nowoczesne funkcje z historycznym charakterem obiektu, przyczyniając się do zachowania cennego dziedzictwa architektury i staną się katalizatorem rewitalizacji otaczającego obszaru miejskiego (ul. Młynowa), wspierając rozwój kulturalny i społeczny miasta. Badania prowadzone w ramach pracy inżynierskiej mogą dostarczyć cennych wniosków i rekomendacji, które będą mogły być wykorzystane w praktyce, zarówno w kontekście Białegostoku, jak i innych miast o podobnych wyzwaniach.

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1.2. Podstawowe założenia metodologiczne

Postawiono wiele pytań dotyczących ochrony i konserwacji zabytków, w zakresie technicznych i logistycznych wyzwań przy adaptacji historycznego budynku, a także optymalnego wykorzystania przestrzeni. Rozwiązanie przedstawionych problemów przyczyniło się do stworzenia kompleksowego i dobrze zintegrowanego projektu, który nie tylko zachowuje historyczne dziedzictwo, ale także wzbogaca kulturalne i społeczne życie Białegostoku.

Podczas badań przeprowadzono dogłębną analizę literatury przedmiotu, dokumentacji architektonicznej oraz map historycznych. Kluczowe dokumenty archiwalne zostały uzyskane dzięki współpracy z instytucjami miejskimi, takimi jak Biuro Miejskiego Konserwatora Zabytków w Białymstoku, Zarząd Mienia Komunalnego oraz Wojewódzki Urząd Ochrony i Konserwacji Zabytków. Uzyskana dokumentacja była kluczowa przy podejmowaniu decyzji projektowych. Stan faktyczny wybranej lokalizacji został szczegółowo udokumentowany przez rysunki, zdjęcia i opisy. W ramach studium przypadków przeanalizowano przykłady udanych rewitalizacji podobnych przestrzeni miejskich w innych miastach, w celu zidentyfikowania najlepszych praktyk i rozwiązań. Opracowane zostały modele 3D i wizualizacje, pozwalające na lepsze zrozumienie potencjalnego wpływu projektu na otoczenie miejskie oraz relacje z nim.

1.3. Historia i geneza

W celu lepszego zrozumienia kontekstu projektu, prześledzono genezę muzeów sztuki, od starożytnego museionu[15], przez kolekcje prywatne przy rezydencjach, po współczesne instytucje muzealne. W XX wieku muzea sztuki stały się integralną częścią krajobrazu kulturalnego, odgrywając kluczową rolę w edukacji, badaniach naukowych oraz ochronie dziedzictwa kulturowego. Muzea stają się coraz bardziej dostępne dla różnych grup społecznych, a ich zadania obejmują także działania społeczne i aktywne zaangażowanie społeczności. Współczesna sztuka odznacza się zdolnością do refleksji nad bieżącymi problemami społecznymi, politycznymi i ekologicznymi. Sztuka współczesna nie tylko wspiera aktywizm, ale także promuje zmiany społeczne i prowokuje do dyskusji na ważne tematy.

[15] Miejsce kultu muz, pierwowzór muzeum. W starożytności musejony nie zajmowały się sztukami plastycznymi, które były traktowane jako rzemiosło. Zamiast tego skupiały się na literaturze, historii, muzyce, matematyce, astronomii i medycynie.

1.4. Ochrona i konserwacja zabytków

Zbadano dokumenty doktrynalne oraz formy ochrony i konserwacji zabytków. Przyjęta w 1931 r., w ramach Międzynarodowego Kongresu Historyków Sztuki w Atenach, Karta Ateńska jest jednym z pierwszych dokumentów, uwzględniających pytanie ochrony dziedzictwa kulturowego. Stanowi ona podstawę wielu międzynarodowych standardów i zasad praktyki konserwatorskiej.

Karta Wenecka, zwana również „Międzynarodową Kartą Konserwacji i Restauracji Zabytków i Miejsc Zabytkowych", przyjęta w 1964 r. przez Międzynarodową Radę ICOMOS[16], jest fundamentalnym dokumentem w zakresie konserwacji i restauracji obiektów zabytkowych, uznawanym na całym świecie. Określa zasady, mające na celu ochronne autentyczności
i integralności zabytków architektury. Można wyróżnić kluczowe zasady Karty Weneckiej:

a) Zachowanie autentyczności i integralności, minimalizacja ingerencji i ochrona oryginalnych materiałów oraz struktury.
b) Jak najmniejsze zmiany w strukturze zabytku.
c) Dokładne dokumentowanie stanu przed, w trakcie i po pracach konserwatorskich.
d) Poszanowanie dla dzieł sztuki i zabytków historycznych, prace muszą uwzględniać wartości artystyczne i historyczne.
e) Użycie odpowiednich materiałów i technik. Preferowanie oryginalnych materiałów lub ich odpowiedników.
f) Współpraca międzynarodowa, wymiana wiedzy i doświadczeń[17].

Karta Wenecka nie może być traktowana jako źródło uniwersalnych zasad postępowania konserwatorskiego. Zachowuje jednak ważność jako podstawowy punkt odniesienia dla działalności konserwatorskiej, wynikającej z poszanowania tradycji kultury europejskiej. Zwrot ku postanowieniom Karty Weneckiej w epoce globalizacji jest wyrazem dążeń do zachowania ciągłości europejskiego dziedzictwa kulturowego[18].

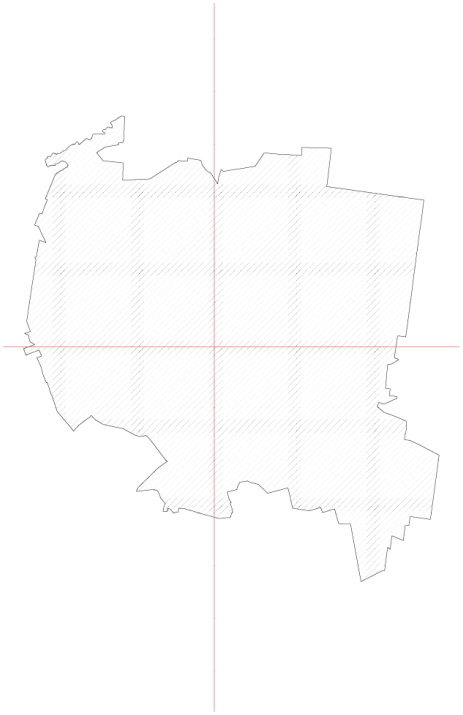
Przy pracach nad zabytkiem niedopuszczalne są domyły. Oznacza to, że nie należy wprowadzać elementów, które nie są oparte na dokładnych badaniach i dowodach historycznych. W przypadku gdy wprowadzane są nowe elementy (prace uzupełniające), wówczas muszą się one wywodzić z kompozycji architektonicznej zabytku i nosić znamiona

[16] ICOMOS (ang. International Council on Monuments and Sites) – międzynarodowa organizacja pozarządowa zajmująca się ochroną zabytków i miejsc na świecie.
[17] *Międzynarodowa Karta Konserwacji i Restauracji Zabytków i Miejsc Zabytkowych (Karta Wenecka), postanowienia i uchwały II Międzynarodowego Kongresu Architektów i Techników Zabytków*, Wenecja 1964, http://www.icomos-poland.org/pl/dokumenty-doktrynalne.html [dostęp: 26.05.2024].
[18] W. Bukowska, J. Krawczyk, *Karta Wenecka 1964-2014. Karta wenecka i spór o zasady postępowania konserwatorskiego*, Wydział Sztuk Pięknych Uniwersytetu Mikołaja Kopernika w Toruniu, Toruń 2015, s. 101.

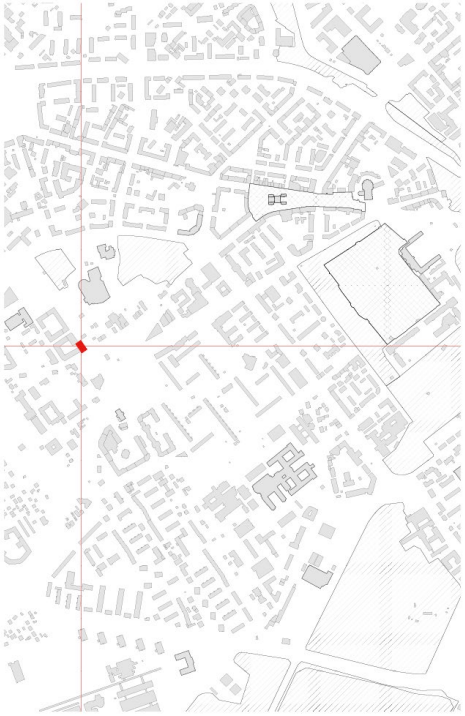
współczesności. Powinny być wyraźnie odróżnialne od oryginału, aby nie zacierać granicy między nowym a starym. Rekonstrukcja zabytku jest zabiegiem dopuszczalnym, ale powinna być stosowana w ograniczonym i niezbędnym zakresie dla zachowania lub przywrócenia wartości zabytku.

2. Charakterystyka lokalizacji projektu

Projektowany budynek galerii sztuki zlokalizowany jest w stolicy województwa podlaskiego – Białymstoku, przy skrzyżowaniu ul. Młynowej i Kijowskiej, obręb Śródmieście, nieopodal centralnego punktu miasta – Rynku Kościuszki. W bezpośrednim otoczeniu znajdują się takie ośrodki kulturowe, jak Opera i Filharmonia Podlaska – Europejskie Centrum Sztuki w Białymstoku imienia Stanisława Moniuszki oraz Białostocki Teatr Lalek.



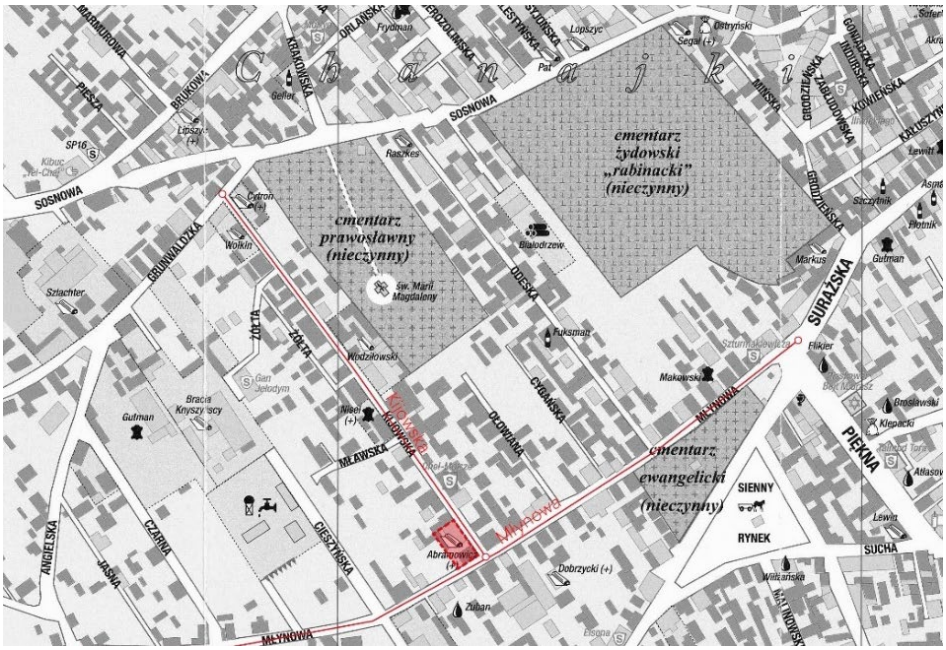
Rys. 1. Orientacja w skali miasta Białystok
Fig. 1. Orientation on the city scale of Białystok
Źródło: opracowanie własne na podstawie podkładu z serwisu Q-GIS.



Rys. 2. Sytuacja w strukturze miasta Białystok.
Fig. 2. Situation in the urban structure
Źródło: opracowanie własne na podstawie podkładu z serwisu Q-GIS.

2.1. Kontekst historyczny. Osiedle Chanajki w Białymstoku

Ulice Kijowska i Młynowa były częścią przedwojennej dzielnicy Chanajki – biednej i ubogiej żydowskiej dzielnicy w Białymstoku. Historia domów, typowych dla ówczesnej zabudowy wiejskiej na tym obszarze, sięga jeszcze XVIII i XIX wieków. W tym okresie tereny te stanowiły część wiejskiego krajobrazu otaczającego miasto. Na przełomie wieków XIX i XX, w wyniku dynamicznego rozwoju i ekspansji terytorialnej, tereny dawnej wsi zostały wcielone do granic administracyjnych Białegostoku[19]. W kontekście dynamicznego rozwoju miasta, ochrona nielicznie zachowanych domów i kamienic staje się coraz ważniejsza. Ulica Młynowa, jako fragment dawnego Białegostoku, przypomina mieszkańcom i turystom o bogatej przeszłości i wielokulturowym dziedzictwie tego miejsca, a do współczesnego krajobrazu miejskiego dodaje głębię i autentyczność.



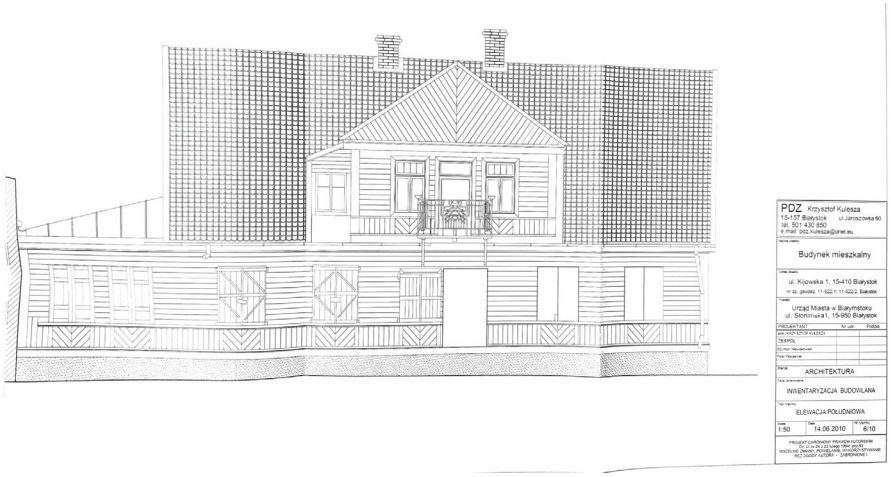
Rys. 3. Fragment dzielnicy Chanajki
Fig. 3. Fragment of the Chanajki district
Podkład: Historyczny plan miasta Białystok lata 30. XX wieku, opracowanie Tomasza Popławskiego.

[19] A. Kłopotowska, *Spacerem po Młynowej. W poszukiwaniu tożsamości dzielnicy,* Czasopismo techniczne z.12. Architektura z. 3-A, Wydawnictwo Politechniki Krakowskiej im. Tadeusza Kościuszki, 2012

2.2. Historia posesji przy ul. Kijowskiej 1

Przed 1939 r. właścicielem posesji była rodzina Leszec. Posesja graniczyła z ul. Młynową i Kijowską oraz z posesjami Cabana i Ałkona[20]. Na posesji znajdowały się:

– dom drewniany (z dużą facjatą oraz użytkowym poddaszem), usytuowany w narożniku ulic, wzdłuż ul. Młynowej, zbudowany w ok. 1893 r., rozbudowany w 1922 r.[21];



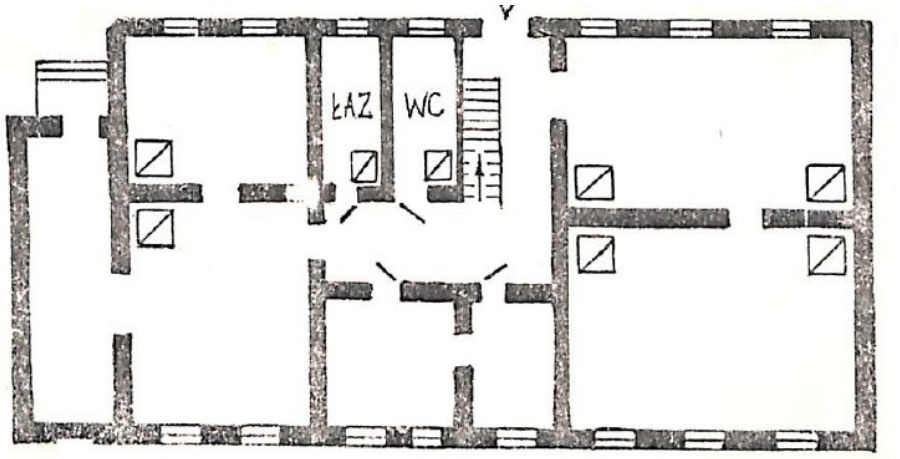
Rys. 4. Elewacja frontowa domu Leszeców
Fig. 4. Front elevation of the Leszec family house
Źródło: ałącznik do Ekspertyzy architektoniczno-konserwatorskiej drewnianego budynku mieszkalnego przy ul. Kijowskiej 1, w Białymstoku, sygn. 9015-PWKZ, Wojewódzki Urząd Ochrony Zabytków w Białymstoku, Białystok 2010.

– drewniany chlew;
– dwupiętrowy budynek murowany, usytuowany wzdłuż granicy z ul. Kijowską.

Obiekt zbudowany został w 1930 r. (...) W domu murowanym na piętrze znajdowały się warsztaty, całe piętro zajmowała hala, Leszec był właścicielem domu do 1939 posesja liczyła 166 sążni kwadratowych. W latach 1941-44 dom zamieszkiwali Niemcy, którzy przeprowadzili w nim remont. Na piętrze wydzielono nowe izby. Budynek pierwotnie pokryty był dachówką ceramiczną. Szai i Sorie Leszec zginęli w gettcie. Ich syn wyjechał do Ameryki, córka w 1946 r. wystąpiła do Okręgowej Komisji Likwidacyjnej o przywrócenie jej posesji będącej spadkiem po zmarłych rodzicach. W tym czasie budynek został zaadaptowany do potrzeb Szkoły Podstawowej Nr 9. Przeprowadzono w nim remont na koszt Skarbu Państwa. 5 XII 1946 r. decyzją Sądu przywrócono Sarze Szwedzkie posesję na własność, zatrzymując budynek

[20] *Karta ewidencyjna zabytków architektury i budownictwa, ul. Kijowska 1*., sygn. 2449, Biuro Miejskiego Konserwatora Zabytków w Białymstoku, Białystok 1989, s. 2.
[21] W. Wróbel, *Historia ulicy Kijowskiej. Studia z dziejów Białegostoku,* Białystok 2011, s. 131.

murowany będący w użytkowaniu Szkoły, do czasu opłacenia przez właścicielkę kosztów remontu. Kolejnymi właścicielami posesji zostali Helena i Wacław Kołakowscy. W budynku murowanym nadal funkcjonowała Szkoła, a następnie mieścił się tu Ośrodek Zdrowia, Warsztaty mechaniczne PAN, Magazyn CEFARMU. W 1989 r. obiekt zakupiony został przez spółkę "Maritex". (...)[22].



Rys. 5. Układ funkcjonalny parteru fabryki, stan na 1989 r.
Fig. 5. Functional layout of the factory's ground floor, as of 1989.
Źródło: Karta ewidencyjna zabytków architektury i budownictwa, ul. Kijowska 1. Sygn. 2449, Biuro Miejskiego Konserwatora Zabytków w Białymstoku, Białystok 1989, s. 1.

W 1990 r. budynek fabryki został wpisany do rejestru zabytków województwa podlaskiego, decyzją Wojewódzkiego Konserwatora Zabytków nr Kl.WKZ-5340/1/90 z dn. 14.03.1990 r., nr rej. 734[23]. Budynek zachował się po dziś, obecnie nieużytkowany ze względu na stan techniczny. Drewniany dom Leszeców nie był objęty żadną formą ochrony konserwatorskiej. W czerwcu 2010 r. przeprowadzona została ekspertyza architektoniczno-konserwatorska budynku, niezbędna do opracowania projektu jego rozbiórki[24]. Budynek został rozebrany ze względu na awaryjny stan techniczny.

2.3. Stan obecny budynku fabryki

Ekspertyza techniczna (z dn. 5 czerwca 2023 r.), w której dokonano oceny stanu technicznego poszczególnych elementów konstrukcyjnych pod kątem możliwości wykonania

[22] *Karta ewidencyjna zabytków architektury i budownictwa, ul. Kijowska 1*, sygn. 2449, Biuro Miejskiego Konserwatora Zabytków w Białymstoku, Białystok 1989, s. 2.
[23] Karta adresowa gminnej ewidencji zabytków, Dawna fabryka, ul. Kijowska 1, Biuro Miejskiego Konserwatora Zabytków w Białymstoku, Białystok 2016.
[24] Ekspertyza architektoniczno-konserwatorska drewnianego budynku mieszkalnego przy ul. Kijowskiej 1 w Białymstoku, sygn. 9015-PWKZ, Wojewódzki Urząd Ochrony Zabytków w Białymstoku, Białystok 2010

remontu, przebudowy oraz zmiany sposobu użytkowania budynku, wykazała, że liczne zniszczenia i brak bieżącej konserwacji sprawiły, że budynek jest w stanie awaryjnym[25].

Tabela 1

Stan techniczny elementów konstrukcyjnych budynku przy ul. Kijowskiej 3

Element konstrukcyjny	**Stan techniczny**	**Uwagi**
Fundamenty murowane kamienno-ceglane	zły	Ze względu na nieszczelną izolację fundamenty narażone są na niszczące działanie wilgoci przesiąkającej z gruntu.
Ściany zewnętrzne murowane	awaryjny	Widoczny rozpad struktury materiału oraz znaczne zarysowania świadczą o przekroczeniu ich nośności oraz odkształceniach fundamentów. W ścianach brak wieńców do przeniesienia sił poziomych oraz brak usztywnienia przez uszkodzone stropy drewniane.
Nadproża murowane z cegły pełnej	średni	Miejscami widoczne uszkodzenia.
Stropy z belek drewnianych wypełnione piaskiem z gliną	awaryjny	Wyraźne zniszczenia korozją biologiczną.
Więźba dachowa drewniana krokwiowo-jętkowa	zły	Wyraźne zniszczenia pod względami fizycznym i biologicznym. Nieszczelności pokrycia. Uszkodzenia kwalifikują konstrukcję do całkowitej rozbiórki. Konieczne jest wykonanie nowej więźby dachowej.

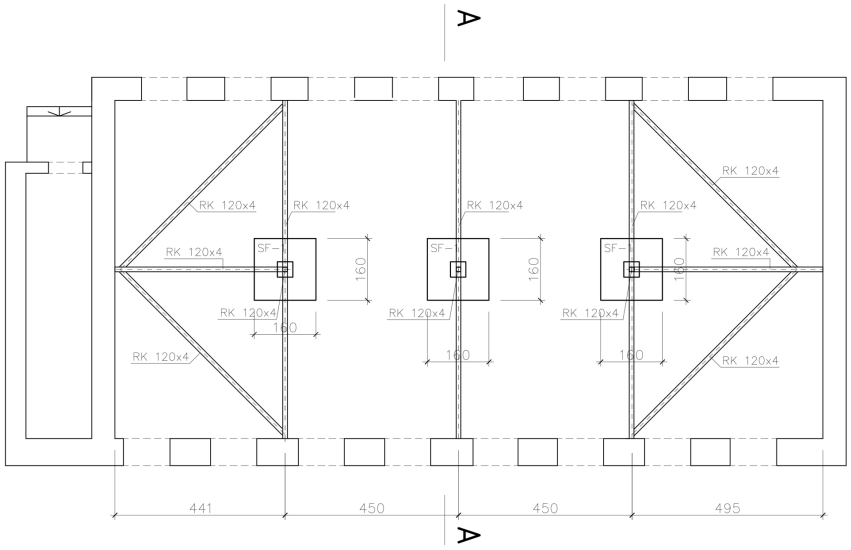
Źródło: Opracowanie własne na podstawie Ekspertyzy technicznej do projektu remontu, przebudowy i zmiany sposobu użytkowania budynku dawnej fabryki przy ulicy Kijowskiej 3 w Białymstoku z dn. 5 czerwca 2023.

W ramach remontu zabezpieczającego zlikwidowano oryginalne stropy drewniane, schody, ściany wewnętrzne, więźbę dachową oraz kaflowe piece. Wewnątrz została wybudowana tymczasowa konstrukcja wsporcza z belek i słupów stalowych o przekroju 120x120 mm, posadowiona na stopach fundamentowych. Oryginalne ściany połączono z konstrukcją wsporczą za pomocą kotw stalowych, widocznych w elewacjach. Wykonano stężające wieńce żelbetowe u szczytu oryginalnych ścian murowanych, nową drewnianą więźbę dachową krokwiowo-jętkową. Ubytki tynków wypełniono zaprawą cementową.

[25] Ekspertyza techniczna do projektu remontu, przebudowy i zmiany sposobu użytkowania budynku dawnej fabryki przy ulicy Kijowskiej 3 w Białymstoku, Zarząd Mienia Komunalnego w Białymstoku, Białystok 2023.

Rys. 6. Wnętrze zabytkowego budynku, stan obecny z 2023 r.
Fig. 6. Interior of the historic building, current condition as of 2023
Źródło: ze zbiorów Biura Miejskiego Konserwatora Zabytków w Białymstoku.

Rys. 7. Wnętrze zabytkowego budynku, stan obecny z 2023 r.
Fig. 7. Interior of the historic building, current condition as of 2023
Źródło: ze zbiorów Biura Miejskiego Konserwatora Zabytków w Białymstoku.

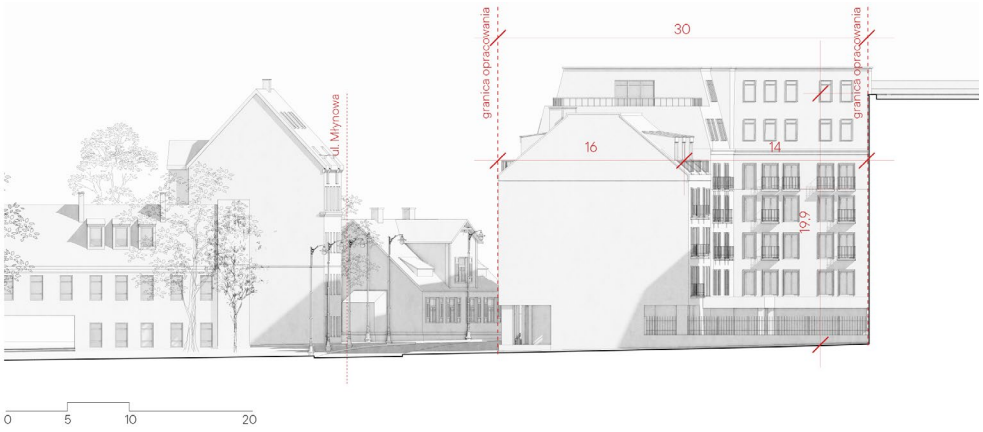


Rys. 8. Rzut parteru do projektu remontu zabezpieczającego budynek dawnej fabryki.
Fig. 8. Ground floor plan for the renovation project of the former factory building.
Źródło: załącznik do Ekspertyzy technicznej do projektu remontu, przebudowy i zmiany sposobu użytkowania budynku dawnej fabryki przy ulicy Kijowskiej 3 w Białymstoku, Zarząd Mienia Komunalnego w Białymstoku, Białystok 2023.

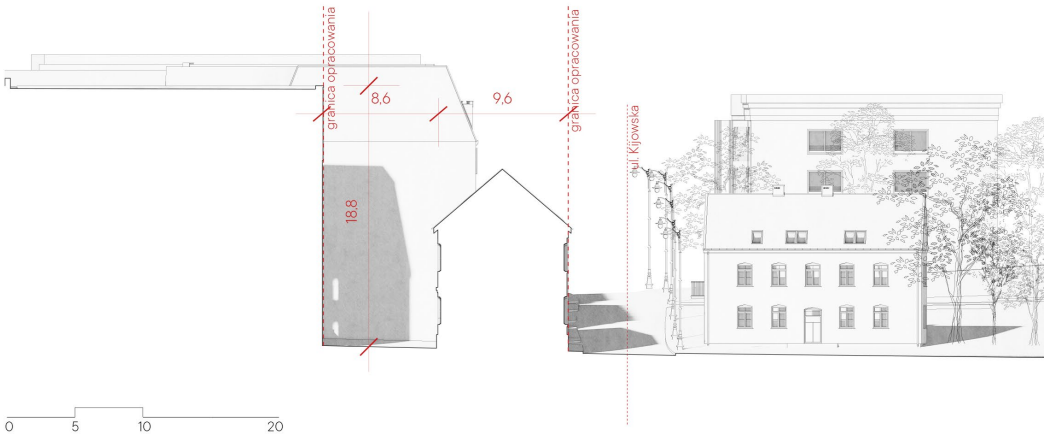
2.4. Inwentaryzacja

Teren opracowania położony jest na działkach o nr ewid. 522/1, 522/2 obręb 11, Śródmieście. Od strony północnej teren graniczy ze ścianą szczytową budynku hotelu Opera (ul. Kijowska 5), a od strony zachodniej ze ścianą budynku mieszkalnego wielorodzinnego z usługami w parterze (ul. Młynowa 38). Na terenie opracowania znajduje się dwukondygnacyjny budynek murowany, wpisany do rejestru zabytków, będący przedmiotem opracowania.

Topografia nierównomierna, najniższa rzędna terenu od strony ul. Młynowej – 148,6 m n.p.m., najwyższa – 149,6 m, różnica wysokości na długości całego terenu opracowania wynosi ok. 1,0 m. W najwęższym miejscu (pomiędzy tylną elewacją istniejącego budynku a granicą sąsiedniej nieruchomości) szerokość dla nowo projektowanej zabudowy wynosi ok. 8,60 m.



Rys. 9. Przekrój urbanistyczny 1
Fig. 9. Urban section 1
Źródło: opracowanie Autora.



Rys. 10. Przekrój urbanistyczny 2
Fig. 10. Urban section 2
Źródło: opracowanie Autora.

Rys. 11. Widok od strony skrzyżowania ulic
Fig. 11. View from the street intersection
Źródło: archiwum autora, Maj 2024.

2.5. Uwarunkowania urbanistyczne

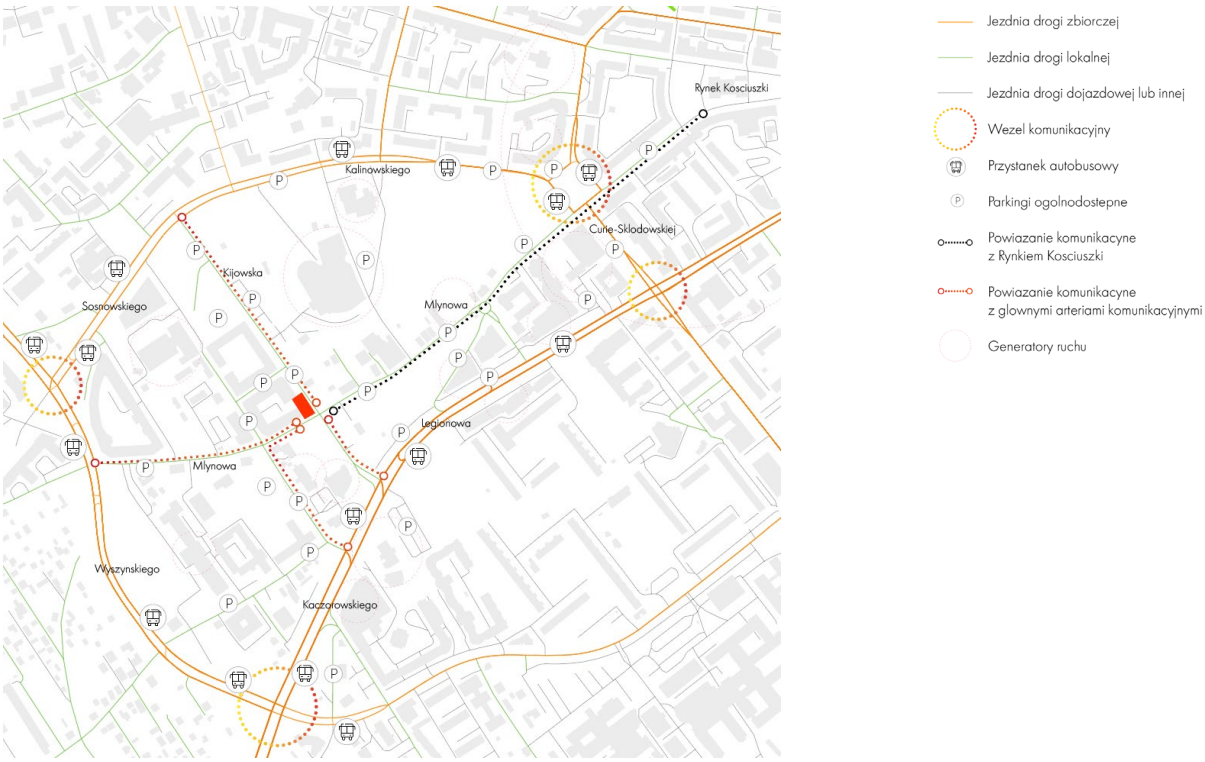
a) powiązania funkcjonalno-przestrzenne

Wybrana lokalizacja dla inwestycji celu publicznego w centrum Białegostoku pozwala na integrację projektowanej galerii z innymi funkcjami miejskimi, wspierając różne scenariusze użytkowe. Dzięki swojemu strategicznemu położeniu, projektowany obiekt ma potencjał, aby stać się ważnym elementem miejskiej przestrzeni kulturalnej, służąc zarówno mieszkańcom, jak i turystom.

Rys. 12. Schemat powiązań funkcjonalnych
Fig. 12. Diagram of functional relationships
Źródło: opracowanie Autora na podstawie podkładu z serwisu Q-GIS.

b) analiza komunikacji

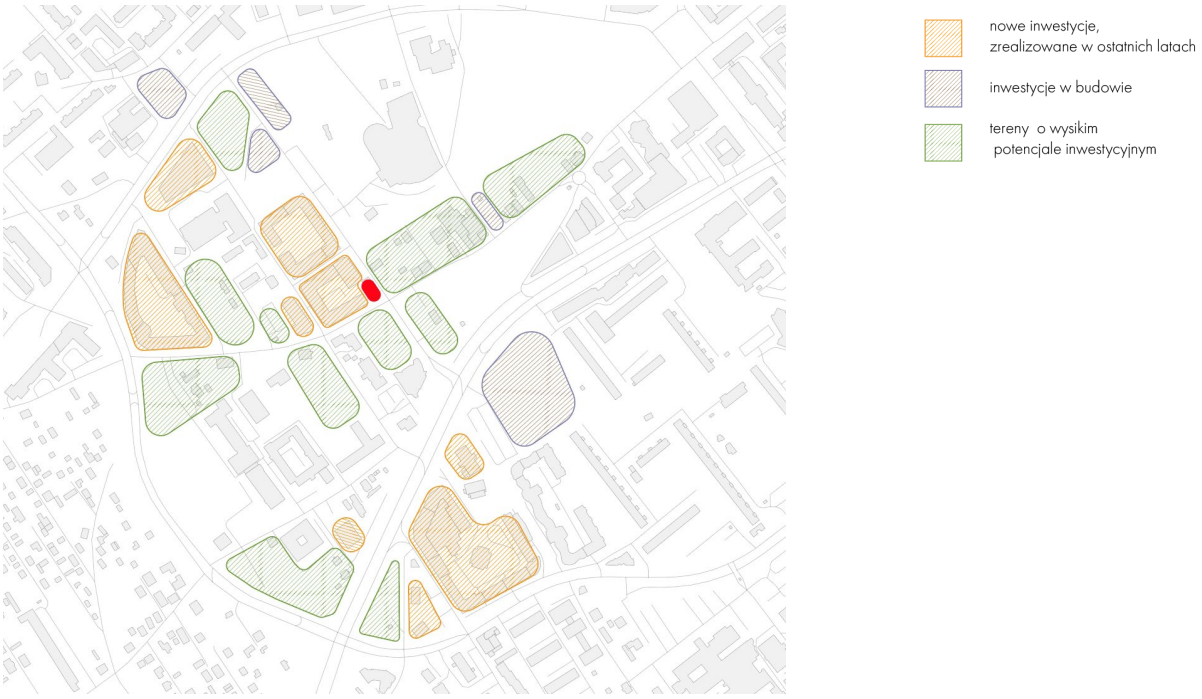
Projektowany budynek jest zlokalizowany w miejscu o doskonałej dostępności komunikacyjnej. W sąsiedztwie znajdują się kluczowe węzły komunikacyjne oraz główne arterie miejskie, takie jak ulice Legionowa, Kaczorowskiego, Wyszyńskiego i Sosnowskiego, co zapewnia łatwy dostęp zarówno dla osób poruszających się samochodami, jak i korzystających z komunikacji miejskiej, pieszych oraz rowerzystów. Na analizowanym obszarze znajdują się liczne parkingi miejskie, dostępne z dróg publicznych, co dodatkowo ułatwia dojazd.



Rys. 13. Analiza komunikacji
Fig. 13. Communication analysis
Źródło: opracowanie Autora na podstawie podkładu i danych z serwisu Q-GIS

c) analiza inwestycyjna

Położenie w samym sercu rozwijającej się dzielnicy Białegostoku stwarza korzystne możliwości dla przyszłych inwestycji. W ostatnich latach zauważalny jest tu znaczny wzrost liczby nowo powstających budynków mieszkalnych, co świadczy o zainteresowaniu inwestorów daną lokalizacją. Ten trend sprawia, że teren staje się atrakcyjniejszy dla różnorodnych przedsięwzięć, w tym inwestycji o charakterze publicznym.



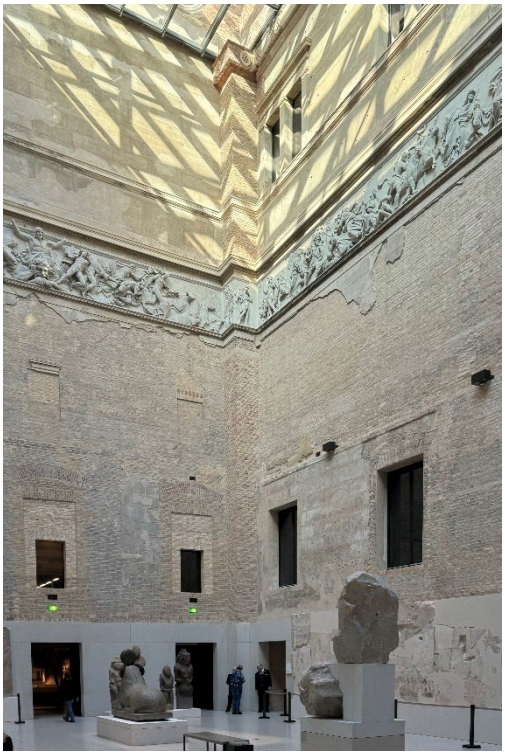
Rys. 14. Analiza inwestycyjna.
Fig. 14. Investment analysis
Źródło: opracowanie Autora na podstawie podkładu z serwisu Q-GIS

Wprowadzenie do tego obszaru nowoczesnej galerii sztuki miałoby duży potencjał. Przede wszystkim, znajdując się w centrum dynamicznie rozwijającej się dzielnicy, mieszkańcy oraz osoby z zewnątrz miieliby łatwy dostęp do galerii, co mogłoby przyczynić się do zwiększenia zainteresowania kulturą w mieście. Inwestycja byłaby nie tylko miejscem prezentacji dzieł sztuki, ale również przestrzenią spotkań i wymiany myśli dla społeczności lokalnej. Organizacja wystaw, warsztatów czy wykładów mogłaby przyczynić się do budowy więzi społecznych oraz integracji mieszkańców różnych grup wiekowych i społecznych.

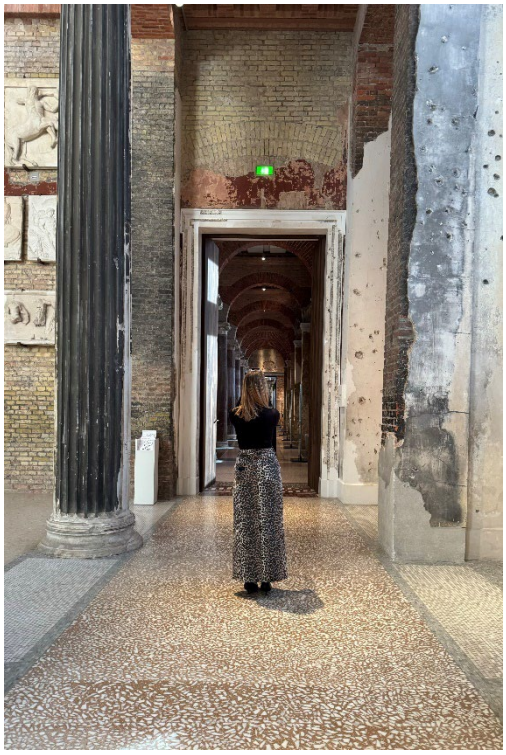
3. Studium przypadków

Studium przypadków było istotnym elementem metodologii, ponieważ pozwoliło na zidentyfikowanie praktyk i podejścia architektów do kształtowania założeń łączących nowoczesną architekturę z historycznym dziedzictwem (James-Simon-Galerie, David Chipperfield; La Bourse de Commerce, Tadao Ando) oraz tworzenie budynków o funkcji muzealnej na ograniczonej powierzchni (Gotoh Museum, David Chipperfield); wykorzystanie nowoczesnych techniki i materiałów, przy jednoczesnym poszanowaniu historycznego kontekstu, tworząc przestrzenie, które są zarówno funkcjonalne, jak i estetyczne (Olivetti Showroom, Carlo Scarpa).

Stanowiło to inspirację do projektu galerii w Białymstoku zarówno w zakresie konceptualnym, jak i projektu wnętrza, które w przypadku budynku o funkcji reprezentacyjnej jest bardzo istotnym elementem.



Rys. 15. Wnętrze Neues Museum w Berlinie
Fig. 15. Interior of the Neues Museum in Berlin
Źródło: archiwum Autora, Luty 2024.



Rys. 16. Wnętrze Neues Museum w Berlinie
Fig. 16. Interior of the Neues Museum in Berlin
Źródło: archiwum Autora, Luty 2024.

Rys. 17. Wnętrze rotundy La Bourse de Commerce w Paryżu
Fig. 17. Interior of the rotunda of La Bourse de Commerce in Paris
Źródło: archiwum Autora, Maj 2024.

Rys. 18. Wnętrze rotundy La Bourse de Commerce w Paryżu
Fig. 18. Interior of the rotunda of La Bourse de Commerce in Paris
Źródło: archiwum Autora, Maj 2024.

a) Część projektowa

4. Założenia projektowe

Rys. 19. Schemat założeń projektowych
Fig. 19. Diagram of planning principles
Źródło: opracowanie Autora na podstawie podkładu z serwisu Q-GIS.

Przez kompleksowe podejście do projektowania, uwzględniające zarówno nowoczesne potrzeby, jak i historyczny kontekst, nowa galeria sztuki w Białymstoku będzie stanowić harmonijne i funkcjonalne uzupełnienie miejskiej przestrzeni kulturalnej:

a) Uzupełnienie pierzei i akcent narożnika

Projektowany budynek, będący nową częścią galerii sztuki w Białymstoku, został zaplanowany jako uzupełnienie pierzei i narożnika ulic Kijowskiej i Młynowej, wzbogacając i dopełniając przestrzeń miejską. Budynek wypełnia lukę w zabudowie, jednocześnie podkreślając narożnik, co nadaje całemu kwartałowi dynamiczny i reprezentacyjny charakter.

b) Skwer Sztuki i Integracja Przestrzeni Kultury

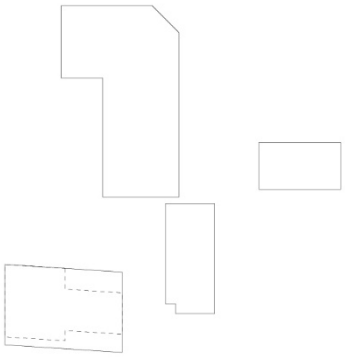
Po drugiej stronie ulicy Kijowskiej znajduje się teren, na którym możliwe jest stworzenie skweru sztuki, który miałby kluczowe znaczenie dla połączenia galerii z innymi ważnymi instytucjami kulturalnymi miasta, takimi jak Opera i Filharmonia Podlaska oraz Teatr Lalek, tworząc jeden ciąg przestrzeni kultury. Ta integracja wzbogaciłaby ofertę kulturalną miasta i stworzyłaby przestrzeń, która będzie sprzyjać interakcji społecznej oraz wymianie kulturalnej.

Powiązanie galerii z Parkiem Centralnym przez skwer sztuki tworzyłoby spójny ciąg spacerowy, który sięga Rynku Kościuszki, Pałacu Branickich oraz parku Planty. Taki ciąg spacerowy może być nie tylko atrakcyjny dla mieszkańców i turystów, ale również może przyczynić się do zwiększenia dostępności i funkcjonalności przestrzeni miejskich Białegostoku.

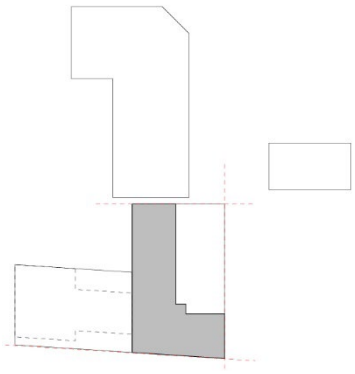
c) Rewitalizacja pozostałości przedwojennej zabudowy

Ulica Młynowa jest obecnie terenem zdegradowanym w centrum miasta, który wymaga kompleksowych działań rewitalizacyjnych. Zakłada się, że projektowana galeria przyczyni się do tych procesów, m.in. pozytywnie wpływając na wartość nieruchomości, przyciągając potencjalnych inwestorów, stymulując rozwój lokalnej gospodarki.

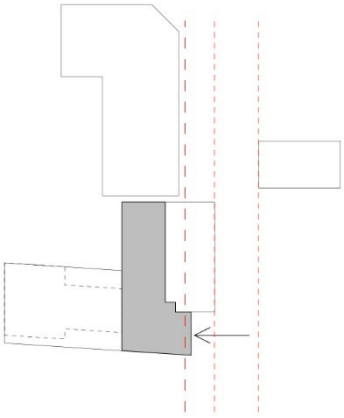
5. Określenie gabarytu



1. Sytuacja obecna

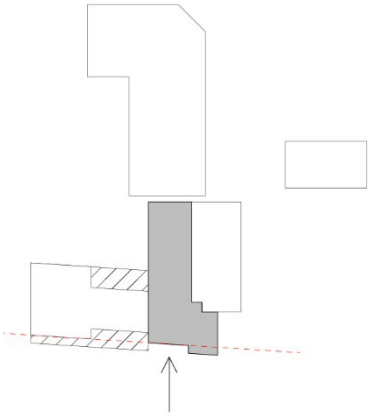


2. Określenie wstępnego gabarytu



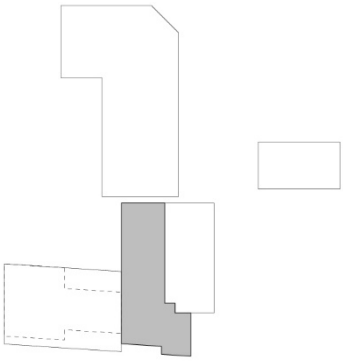
3. Pierzeje stara i nowa

Nowa część galerii od strony ul. Kijowskiej została cofnięta względem linii frontu zabytkowej kamienicy. Celem tego zabiegu było wizualne zróżnicowanie nowej linii zabudowy ul. Kijowskiej od jej dawnego przebiegu, na który wskazują dwa, zachowane na tej ulicy, zabytkowe budynki.



4. Podcienie usługowe ul. Młynowej

Fragment fasady nowej części galerii od strony ul. Młynowej został cofnięty w głąb, nawiązując do podcieni usługowych istniejącej zabudowy przy ul. Młynowej. Zabieg ten pozwolił również na zaakcentowanie głównego wejścia do galerii sztuki.



5. Ostateczny gabaryt

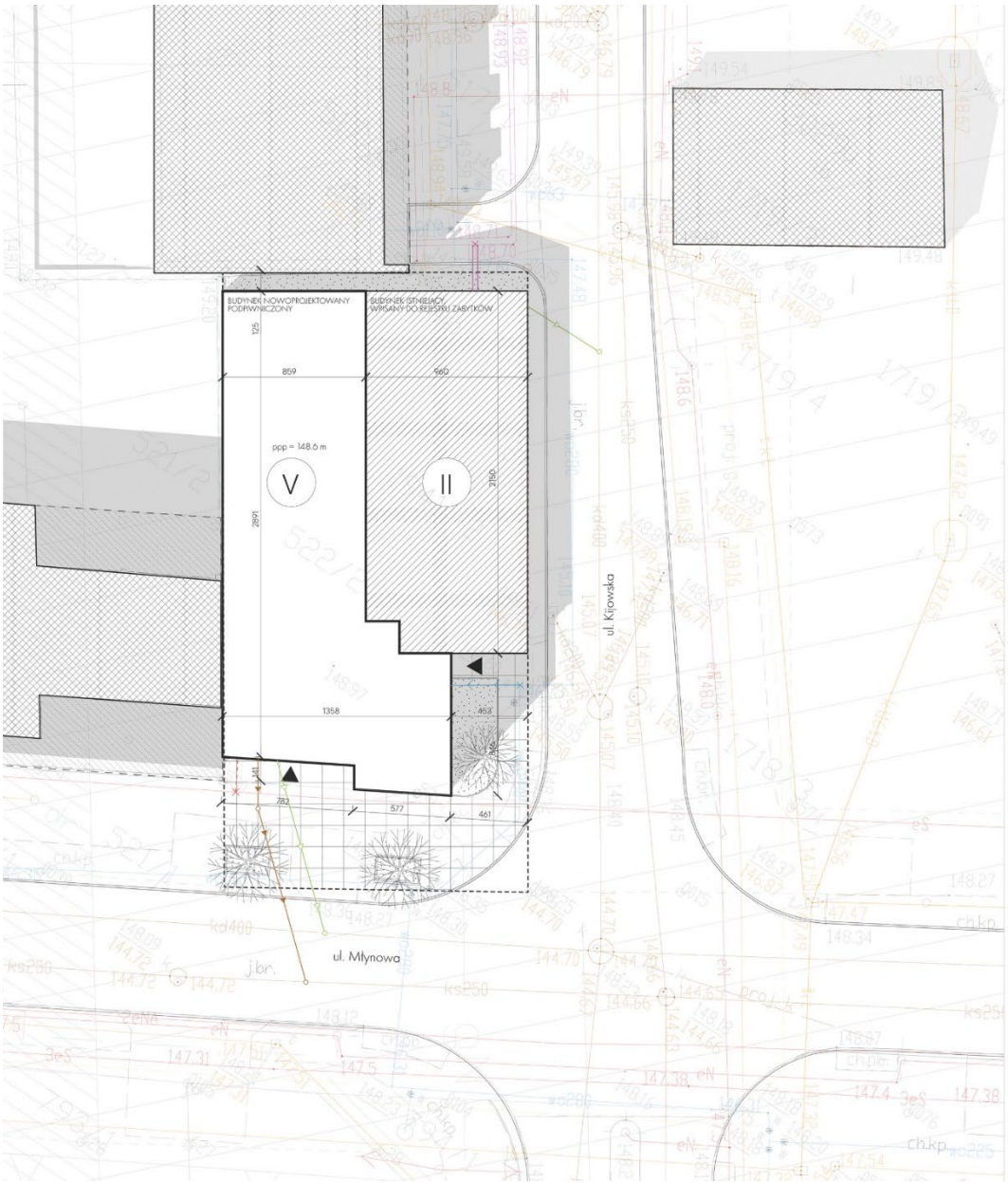
Rys. 20. Zasady kształtowania gabarytu nowej zabudowy
Fig. 20. Principles of shaping of new development
Źródło: opracowanie Autora.

6. Rozwiązania projektowe

Rys. 21. Widok projektowanego budynku od strony skrzyżowania
Fig. 21. View of the proposed building
Źródło: opracowanie Autora.

Nowa zabudowa wywodzi się z logiki sąsiadującej, jednocześnie wyróżniając się na jej tle, aby podkreślić unikalną funkcję budynku. Forma budynku akcentuje narożnik, zwłaszcza kierunek prowadzący z centralnego punktu miasta – Rynku Kościuszki. Zabieg cofnięcia, minimalistyczna architektura nowo projektowanej części budynku oraz materiały zostały zastosowane w celu wyeksponowania zabytkowej fasady dawnej fabryki. Projekt ten koncentruje się na subtelnym połączeniu nowoczesnych i historycznych elementów, umożliwiając jednoczesne zachowanie i uwydatnienie wartości architektonicznych obu części.

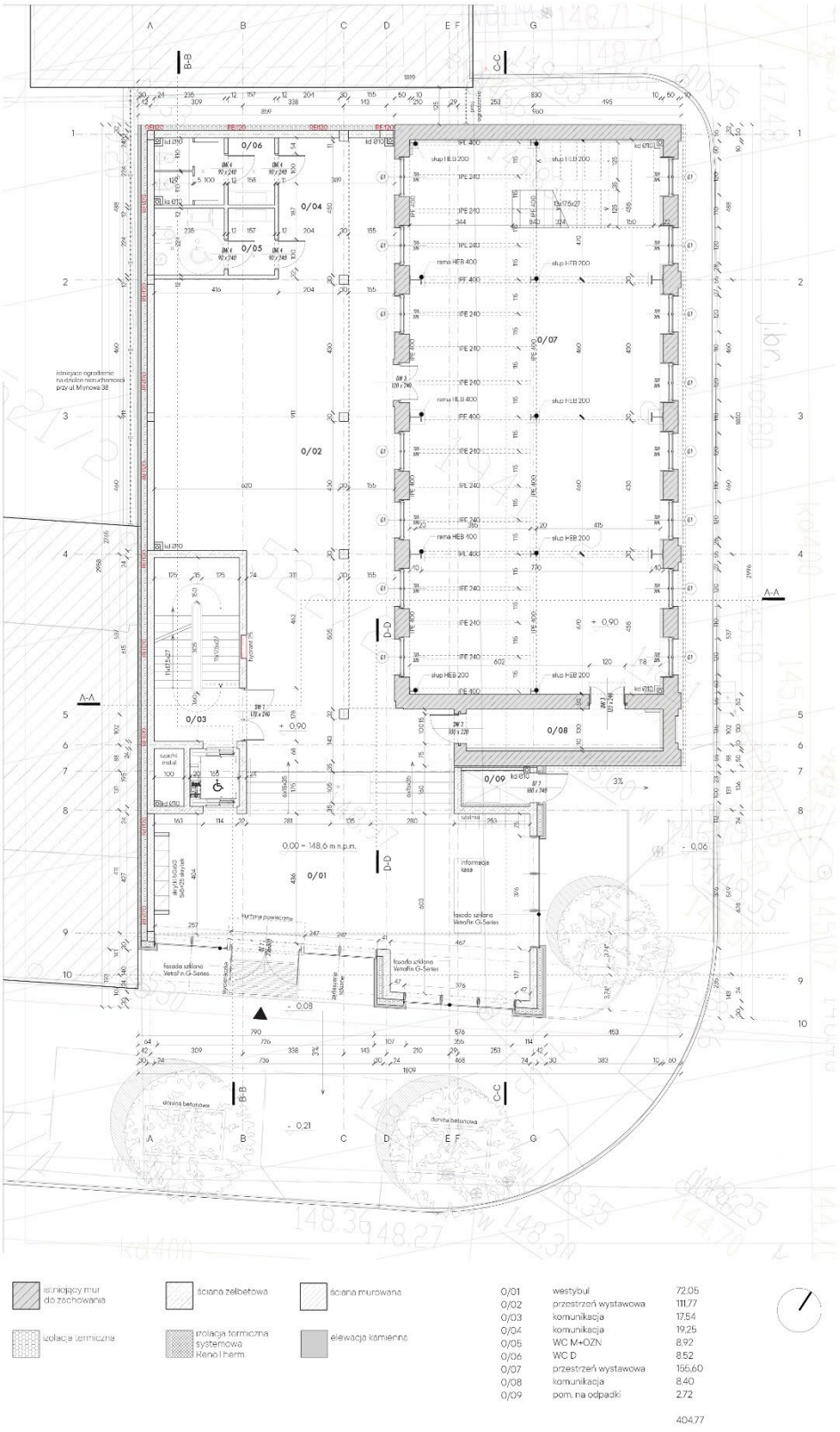
Zaprojektowano lekką ażurową fasadę zacieniającą, składającą się ze stalowych profili spiralnych, tworzących ciekawy efekt po odbiciu promieni słonecznych, dodając elewacji całego budynku lekkości i elegancji.



Rys. 22. Zagospodarowanie terenu
Fig. 22. Masterplan
Źródło: opracowanie Autora.

Projekt obejmuje remont, adaptację i rozbudowę budynku dawnej fabryki.

Projektowany budynek zajmuje większość terenu opracowania: od strony północnej do linii ściany szczytowej zabytkowego budynku, od strony ul. Młynowej do linii ściany budynku wielorodzinnego, a od strony ul. Kijowskiej jest lekko wycofany względem linii ściany frontowej historycznego budynku. Nowo projektowana część łączy się ze ścianami zachodnią i południową zabytkowego budynku, tworząc jedną formę architektoniczną. Główne wejście do budynku dostępne jest z ul. Młynowej. Zaprojektowano miejsce na gromadzenie odpadów wewnątrz budynku, dostępne z ul. Kijowskiej.



Rys. 23. Rzut parteru.
Fig. 23. Ground floor plan
Źródło: opracowanie Autora.

Rys. 24. Widok aksonometryczny
Fig. 24. Axonometric view
Źródło: opracowanie Autora.

Rys. 25. Grupa wejściowa
Fig. 25. Entrance group
Źródło: opracowanie Autora.

Istotnym elementem projektu jest grupa wejściowa od strony ulicy Młynowej. Witryna została zaprojektowana w sposób, który jest zarówno prosty, jak i elegancki, aby harmonijnie współgrać z charakterem dzielnicy. Zastosowanie dużych przeszkleń okazało się skutecznym sposobem na maksymalne wprowadzenie naturalnego światła do wnętrza galerii, jednocześnie umożliwiając widok na reprezentacyjną przestrzeń dla przechodniów, a w konsekwencji – dialog budynku z przestrzenią miejską oraz promowanie sztuki i kultury jako części życia miejskiego.

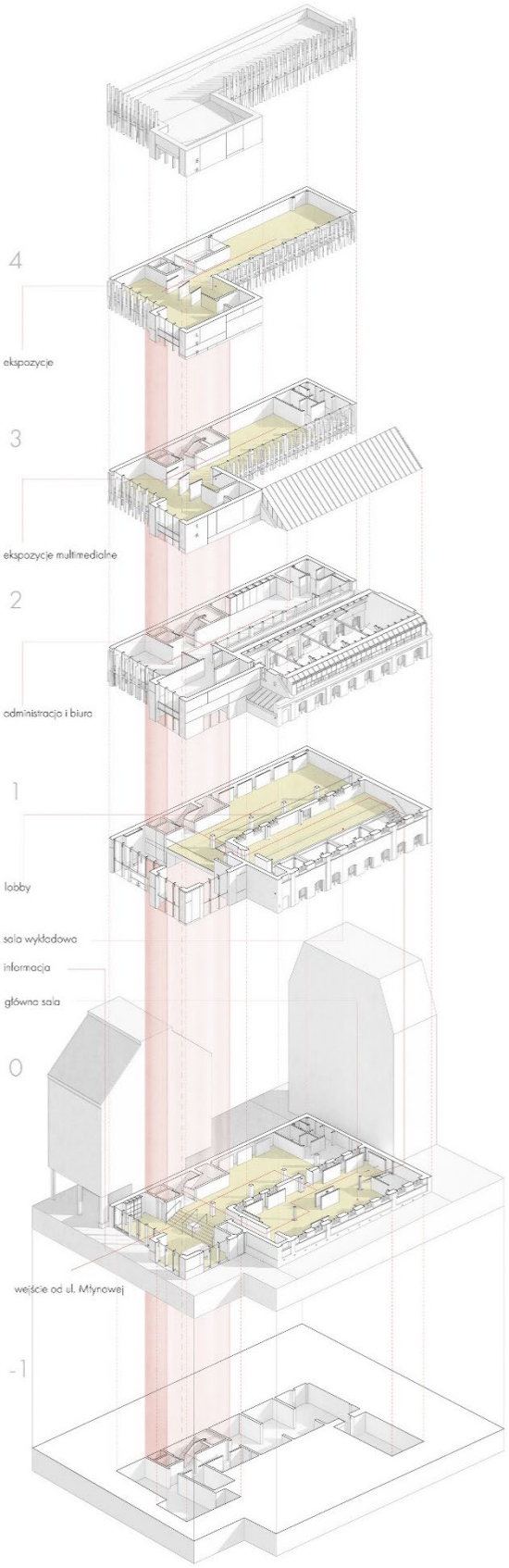
Rys. 26. Westybul
Fig. 26. Vestibule
Źródło: opracowanie Autora

Główne wejście prowadzi do reprezentacyjnego westybulu, z którego można dostać się do części budynku – dawnej fabryki lub na wyższe piętra. Wejście do istniejącego budynku zostało zapewnione przez istniejące otwory w murach, dostępne z nowo projektowanej części. Ze względu na różnicę poziomów między wejściem do budynku a podłogą starej kamienicy zaprojektowano dwutraktowe schody, umożliwiające pokonanie tej różnicy oraz wzbogacające reprezentacyjny charakter przestrzeni westybulu i dzielące go na dwie części, tj. wejściową z punktem informacyjnym oraz wystawową, znajdującą się za schodami.

Serce całego zespołu stanowi jednoprzestrzenna, wielofunkcyjna przestrzeń, znajdująca się w murach zabytkowego budynku. Nowa konstrukcja wsporcza została wyeksponowana w sposób, który podkreśla industrialny charakter budynku. Miejscami wyeksponowane zostały oryginalne elementy zabytkowe struktury, takie jak ceglane ściany oraz drewniane okna skrzynkowe, które dodają autentyczności i charakteru przestrzeni:

Rys. 27. Przestrzeń w budynku dawnej fabryki
Fig. 27. The space inside the old factory building
Źródło: opracowanie Autora

Rys. 28. Antresola
Fig. 28. Intermediate level
Źródło: opracowanie Autora.



Rys. 29. Schemat strukturalny
Fig. 29. Structural Diagram
Źródło: opracowanie Autora.

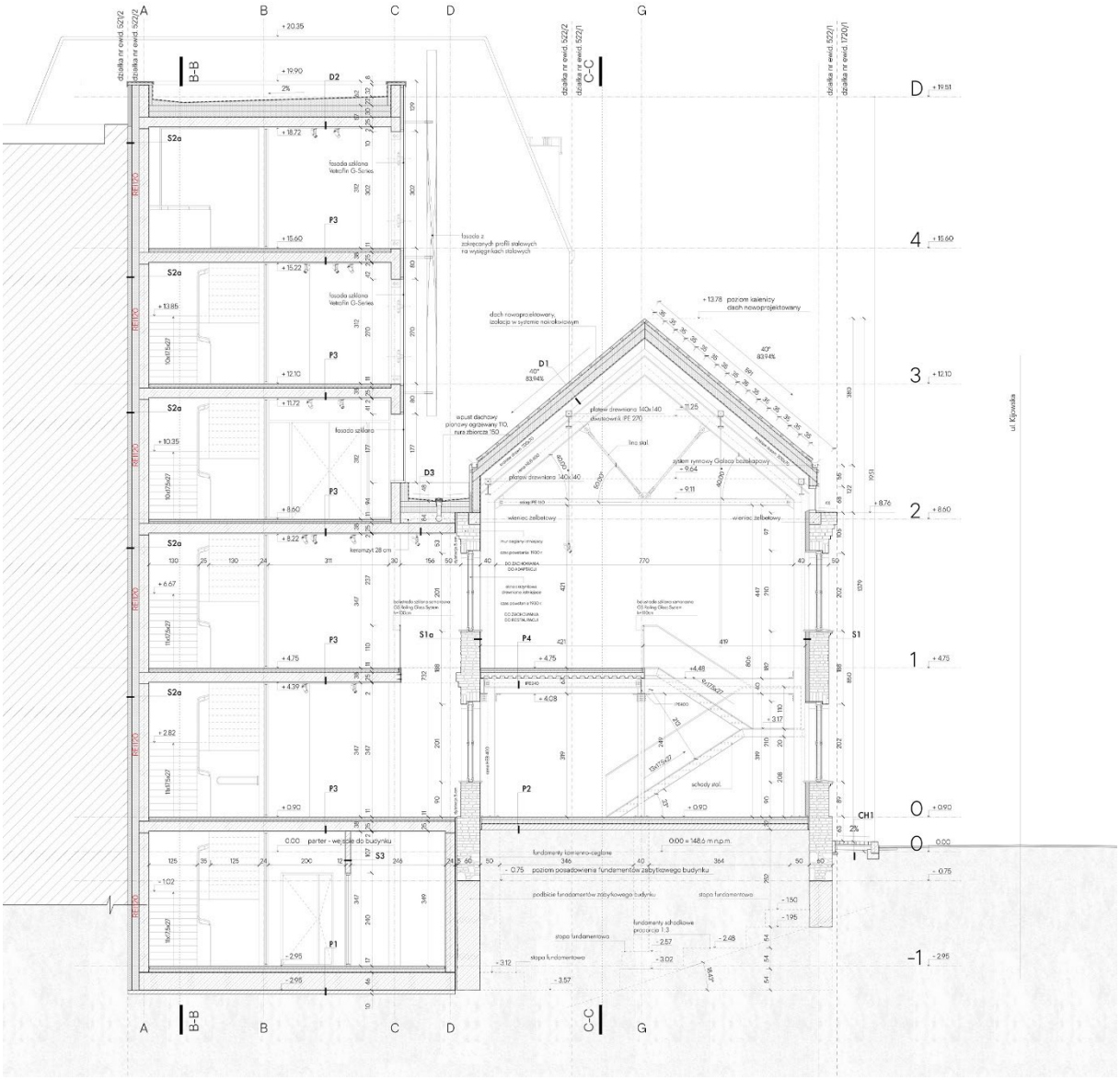
Na piętrze znajduje się lobby połączone z antresolą w zabytkowym budynku.

Drugie piętro przeznaczone jest na część administracyjną i biurową.

Na piętrach trzecim i czwartym znajdują się przestrzenie wystawowe, w tym przeznaczone dla ekspozycji multimedialnych.

Ze względu na rozmiar projektowanego obiektu, ogólnodostępne toalety zostały zapewnione na parterze oraz na trzeciej kondygnacji budynku.

Ze względu na funkcję budynku pomieszczenia magazynowe przewidziane zostały w piwnicy pod nowo projektowaną częścią galerii o łącznej powierzchni 168,56 m^2.



Rys. 30. Przekrój A-A
Fig. 30. Section A-A
Źródło: opracowanie Autora.

Posadowienie nowej części budynku zaprojektowano jako bezpośrednie w postaci płyty żelbetowej monolitycznej o grubości 45 cm, posadowionej na głębokości 2,95 cm od poziomu parteru. W budynku zabytkowym należy wykonać podbicie istniejących kamienno-ceglanych fundamentów do poziomu posadowienia płyty żelbetowej w nowo projektowanej części.

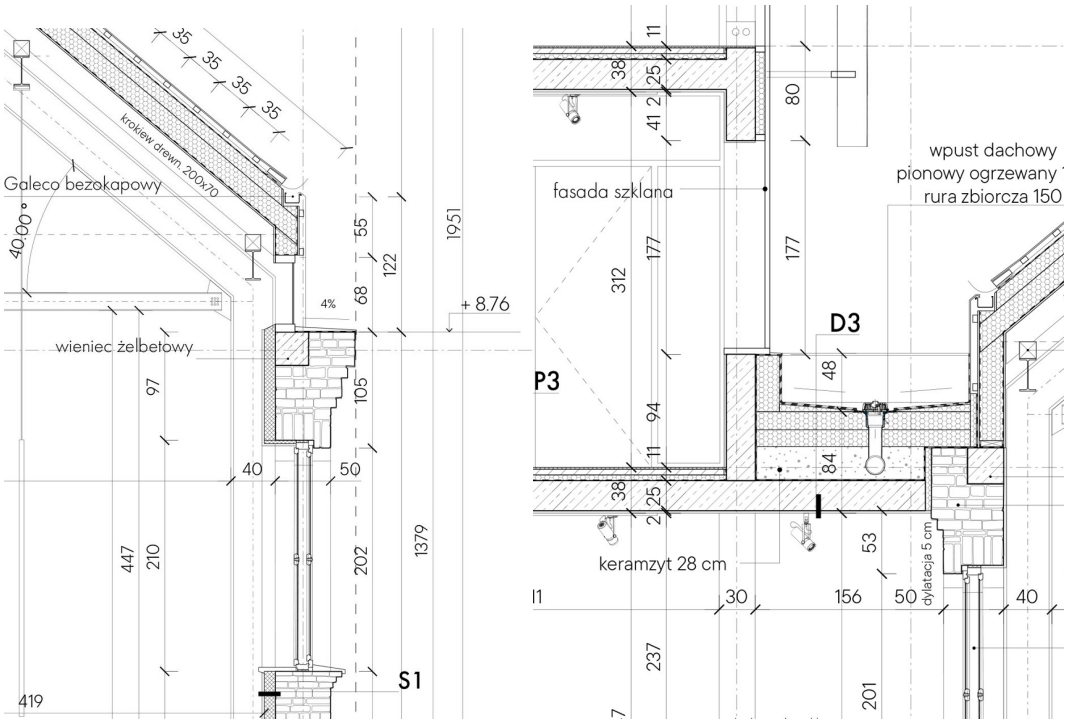
W zabytkowym budynku zaprojektowano stalową konstrukcje wsporczą. Główny element nośny stanowi ramy stalowe z dwuteowników HEB400 w rozstawie 360 cm, posadowione na żelbetowych stopach fundamentowych. Ściany zabytkowego budynku będą połączone z ramami za pomocą kotw stalowych. Konstrukcja służy również jako podparcie dla projektowanej antresoli oraz projektowanego dwuspadowego dachu nad budynkiem.

Nowo projektowany budynek traktuje się jako oddylatowany konstrukcyjnie. Na etapie projektowania wstępnego konstrukcji przyjęto dylatację 5 cm pomiędzy fundamentami i murem istniejącego budynku a nowo projektowanymi elementami konstrukcji.

Od strony wewnętrznej budynku przewidziano wykonanie izolacji termicznej z mineralnej płyty wysokoparoprzepuszczalnej w systemie RenoTherm.

W zabytkowym budynku strop antresoli zaprojektowano jako zespolony na blasze trapezowej Cofraplus 60 ArcelorMittal Construction. Element nośny stanowią dwuteowniki stalowe IPE400 w rozstawie 460 cm, między nimi – dwuteowniki stalowe IPE240 w rozstawie 115 cm. Konstrukcja jest oparta na ramach stalowych HEB400 oraz słupach HEB200.

Nad zabytkowym budynkiem zaprojektowano dach dwuspadowy o nachyleniu połaci 40° w konstrukcji drewnianej. Konstrukcja dachu oparta jest na głównych ramach dwuteowych HEB400. Murłaty i jętki drewniane 14x14 cm oparte są na półce w postaci belki dwuteowej IPE270, dospawanej do ramy HEB400. Krokwie w rozstawie 93 cm. Izolacja termiczna dachu – w systemie nakrokwiowym. Izolacja w dwóch warstwach 18+12 cm SUPERROCK PREMIUM, układana pomiędzy krokwiami pomocniczymi 5x30 cm na pełnym deskowaniu. Izolację z wełny należy zabezpieczyć membraną wysokoparoprzepuszczalną. Wykończenie dachu stanowi blacha aluminiowa na rąbek stojący Magnez Matt, montowana na ruszcie z łat i kontrłat.



Rys. 31. Szczegóły
Fig. 31. Details
Źródło: opracowanie Autora.

7. Podsumowanie

Projekt budynku plombowego galerii sztuki w Białymstoku to nie tylko wyzwanie architektoniczne, ale również szansa na stworzenie przestrzeni, która będzie kształtować świadomość i wpływać na różne aspekty życia społecznego. Łącząc historyczne elementy z nowoczesnymi rozwiązaniami, galeria stanie się ważnym miejscem dla lokalnej społeczności i turystów, promując sztukę, edukację i dialog społeczny. Zaproponowane rozwiązania subtelnie integrują się z istniejącą strukturą, podkreślają jej walory. Projekt może stać się katalizatorem dalszej rewitalizacji tej części miasta.

Praca dyplomowa inżynierska. Rok obrony 2024. Promotor: dr inż. arch. Robert Misiuk.

Bibliografia

1. Bukowska W., Krawczyk J., *Karta Wenecka 1964-2014. Karta wenecka i spór o zasady postępowania konserwatorskiego*, Wydział Sztuk Pięknych Uniwersytetu Mikołaja Kopernika w Toruniu, Toruń 2015.
2. Detyna B., Matuszek J., Szołtysek J., *Praca dyplomowa inżynierska, magisterska*, Wydawnictwo Państwowe Wyższej Szkoły Zawodowej im. Angelusa Silesiusa w Wałbrzychu, Wałbrzych 2018.
3. Jagodzińska K., *Czas Muzeów w Europie Środkowej. Muzea i centra sztuki współczesnej (1989-2014)*, Międzynarodowe Centrum Kultury, Kraków 2014.
4. Kiciński A., Muzea. *Strategie i dylematy rozwoju*, Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa 2004.
5. Kłopotowska A., *Spacerem po Młynowej. W poszukiwaniu tożsamości dzielnicy,* Czasopismo techniczne z.12. Architektura z. 3-A, Wydawnictwo Politechniki Krakowskiej im. Tadeusza Kościuszki, Kraków 2012.
6. Markiewicz P., *Detale projektowe nowoczesnych technologii budowlanych*, ARCHI-PLUS, Kraków 2002.
7. Maroszek J., *Przykahałek żydowski w Białymstoku 1658-1795*, [w:] *Białystok – Mayn Heym*, (red.) D. Boćkowski, Muzeum Wojska w Białymstoku, Białystok 2002.
8. Müller-Brockmann J., *Grid Systems in Graphic Design*, Zürich 1996.
9. Neufert E., *Podręcznik do projektowania architektoniczno-budowlanego*, Arkady, Warszawa 2009.
10. Pabich M., *O kształtowaniu muzeum sztuki. Przestrzeń piękniejsza od przedmiotu*, Łódź 2004.
11. *Vademecum konserwatora zabytków. Międzynarodowe Normy Ochrony Dziedzictwa Kultury*, (red.) B. Szmygin, Polski Komitet Narodowy Międzynarodowej Rady Ochrony Zabytków ICOMOS, 2015.
12. Wróbel W., *Historia ulicy Kijowskiej. Studia z dziejów Białegostoku,* Białystok 2011.
13. Zenderowski R., *Praca magisterska. Licencjat. Krótki przewodnik po metodologii pisania i obrony pracy dyplomowej*, Wydawnictwo CeDeWu, Warszawa 2009.

Dokumenty archiwalne
(rodzaj akt., sygnatura, miejsce przechowywania, data)
14. *Ekspertyza techniczna do projektu remontu, przebudowy i zmiany sposobu użytkowania budynku dawnej fabryki przy ulicy Kijowskiej 3 w Białymstoku*, Zarząd Mienia Komunalnego w Białymstoku, Białystok 2023.
15. *Ekspertyza architektoniczno-konserwatorska drewnianego budynku mieszkalnego przy ul. Kijowskiej 1, w Białymstoku*, sygn. 9015-PWKZ, Wojewódzki Urząd Ochrony Zabytków w Białymstoku, Białystok 2010.
16. *Karta adresowa gminnej ewidencji zabytków, Dawna fabryka, ul. Kijowska 1*, Biuro Miejskiego Konserwatora Zabytków w Białymstoku, Białystok 2016.
17. *Karta ewidencyjna zabytków architektury i budownictwa, ul. Kijowska 1*, sygn. 2449, Biuro Miejskiego Konserwatora Zabytków w Białymstoku, Białystok 1989
18. Ustawa z dnia 23 lipca 2003 r. *o ochronie zabytków i opiece nad zabytkami* (Dz.U. 2003 nr 162 poz. 1568).
19. Rozporządzenie Ministra Infrastruktury z dnia 12 kwietnia 2002 r. *w sprawie warunków technicznych, jakim powinny odpowiadać budynki i ich usytuowanie* (Dz.U. 2002 nr 75 poz. 690).
20. Rozporządzenie Ministra Spraw Wewnętrznych i Administracji z dnia 7 czerwca 2010 r. *w sprawie ochrony przeciwpożarowej budynków, innych obiektów budowlanych i terenów* (Dz.U. 2010 nr 109 poz. 719).
21. Rozporządzenie Ministra Infrastruktury z dnia 03 lipca 2003 r. *w sprawie szczegółowego zakresu i formy projektu budowlanego* (Dz.U. nr 120 poz. 1133).
22. Załącznik do Uchwały Nr XLIII/618/21 Rady Miasta Białystok, z dnia 20 września 2021 r., *w sprawie zmiany miejscowego planu zagospodarowania przestrzennego części osiedli Centrum i Przydworcowe w Białymstoku (rejon ul. Młynowej i Cieszyńskiej) – etap I.*
23. https://www.rockwool.com/pl/produkty-i-rozwiazania/izolacja-dachow/dachy-skosne-i-poddasza/izolacja-nakrokwiowa-poddasza/ [dostęp: 24. 05.2024]
24. https://www.izolacje.com.pl/artykul/produkty-technologie/196182,system-renotherm-ocieplenie-od-wewnatrz [dostęp: 24.05.2024]
25. http://www.icomos-poland.org/pl/dokumenty-doktrynalne.html [dostęp: 26.05.2024]
26. https://davidchipperfield.com/projects/james-simon-galerie [dostęp: 09.06.2024]
27. https://www.youtube.com/watch?v=4Eq5xCx7-q0&t=4365s [dostęp: 09.06.2024]
28. https://www.youtube.com/watch?v=xnnOvtFe2u0&t=3375s [dostęp: 06.06.2024]
29. https://davidchipperfield.com/projects/neues-museum [dostęp: 09.06.2024]

PLOMBA MIEJSKA. PROGRAM ADAPTACJI HISTORYCZNEJ STRUKTURY W TRUDNYM KONTEKŚCIE URBANISTYCZNYM. GALERIA SZTUKI U ZBIEGU ULIC KIJOWSKIEJ I MŁYNOWEJ W BIAŁYMSTOKU

Streszczenie

Adaptacja historycznych budynków na nowe cele użytkowe staje się coraz bardziej popularna w wielu miastach na świecie. Umożliwia to zachowanie dziedzictwa kulturowego, przyczyniając się do rewitalizacji przestrzeni miejskiej, wprowadzając nowe życie w często

zaniedbane lub opuszczone struktury. Projekt zlokalizowany jest u zbiegu ulic Kijowskiej i Młynowej w Białymstoku, gdzie znajduje się budynek dawnej fabryki. Budynek ten ma bogatą historię sięgającą czasów przedwojennych i stanowi element dziedzictwa architektonicznego miasta. Podjęcie działań do rewitalizacji tego obiektu jest konieczne, ponieważ jego awaryjny stan pogarsza się z dnia na dzień. Projekt zakłada stworzenie nowoczesnej przestrzeni kultury i sztuki, która jednocześnie zachowa i wzmocni historyczny charakter zabytkowego budynku. Przewiduje się stworzenie wielofunkcyjnych przestrzeni, które będą mogły służyć różnym formom działalności kulturalnej – od wystaw i wernisaży, przez warsztaty i spotkania artystyczne, po wydarzenia edukacyjne i społeczne.

Słowa kluczowe: dziedzictwo kulturowe, adaptacja, zabytek, sztuka

URBAN INFILL. PROGRAM OF HISTORICAL STRUCTURE ADAPTATION IN AN INTENSIVELY DEVELOPING URBAN CONTEXT. ART GALLERY AT THE CORNER OF KIJOWSKA AND MŁYNOWA STREETS IN BIAŁYSTOK

Abstract

The adaptation of historical buildings for new purposes is becoming increasingly popular in many cities around the world. This approach allows for the preservation of cultural heritage while contributing to the revitalization of urban spaces, breathing new life into abandoned structure. The project is located at the intersection of Kijowska and Młynowa streets in Białystok, where a former factory building stands. This building, with a rich history dating back to pre-war times, is a significant part of the city's architectural heritage. Revitalizing this deteriorating structure is essential as its condition worsens with each passing day. The goal of the project is to create a modern space for culture and art that simultaneously preserves and enhances the historical character of the old building, contributing to the revitalization of the area and giving it new life. The plan includes creating multifunctional spaces that can accommodate various forms of cultural activities, from exhibitions and vernissages to workshops, artistic meetings, and educational and social events.

Keywords: cultural heritage, adaptation, monument, art

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CYCLODEXTRINS AS CARRIERS OF PHENOLIC COMPOUNDS IN BIOMATERIALS: SYNTHESIS, CHARACTERIZATION, AND APPLICATION

1. Cyclodextrins – structure and properties

Cyclodextrins (CDs), also known as cycloamyloses, cycloglucans, or Schardinger dextrins, are a group of naturally occurring cyclic oligosaccharides that are formed through the enzymatic degradation of starch. This process is mainly catalyzed by the enzyme cyclodextrin glucosyltransferase (CGTase), produced by microorganisms such as *Bacillus macerans*, *Klebsiella oxytoca*, *Bacillus circulans*, *Alkaliphilic bacillus* [1]. The enzymatic process occurs in several stages: first, starch is depolymerized, followed by cyclization of the degradation products, leading to the formation of various cyclodextrins forms. CDs differ in the number of α-D-glucopyranose units, which are linked by oxygen bridges (α-1,4-glycosidic). There are three main types of cyclodextrins: α-CD (six units), β-CD (seven units) and γ-CD (eight units) (Figure 1). Each type has a different size of the internal cavity, which affects its ability to form inclusion complexes with various molecules [2]. The α-CD form, with the smallest molecular cavity (4.5 Å), is limited to encapsulating small molecules. The β-CD form, commonly used due to its low production costs and more stable bonds, has a moderate cavity size (7 Å), which allows it to combine with medium-sized substances such as phenyl or heterocyclic groups. However, its disadvantage is its low solubility in water. The γ-CD form, with the largest molecular cavity (8.5 Å), has the ability to bind larger molecules such as fullerenes, or other macrocyclic compounds or steroids, but its use is limited due to high production costs [3-5].

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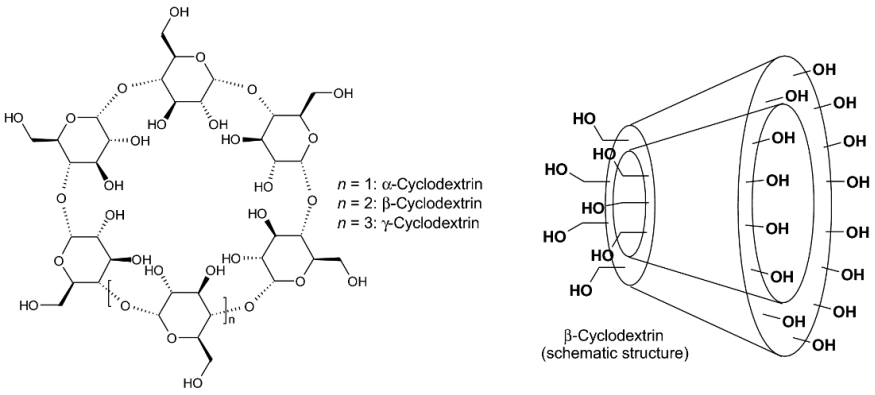

Fig. 1. Structural formulas of α-, β-, and γ-CD and a diagram of the distribution of hydroxyl groups in the β-CD molecule.

Rys. 1. Wzory strukturalne α-, β- i γ-CD oraz diagram rozkładu grup hydroksylowych w cząsteczce β-CD

Source: Hădărugă N., Bandur G.N., David I., Hădărugă D.I.: A review on thermal analyses of cyclodextrins and cyclodextrin complexes. Environmental Chemistry Letters 17, 349-373.

CDs molecules have a shape resembling a hollow torus, or truncated cone, with a hydrophobic interior and hydrophilic exterior (Figure 1). The properties of CDs are attributed to the presence of primary (C6-OH) as well as secondary hydroxyl groups (C2-OH, C3-OH) [6]. The primary hydroxyl groups, are located at the edge of the lower diameter torus, rather in the inner space of the torus, while the secondary hydroxyl groups are located in the wider part of the torus. This localization of hydroxyl groups determines the hydrophilic character of the outer surface, which in turn enhances water solubility. The inner cavity of CDs, due to its glycosidic oxygen atoms and C-H groups, exhibits hydrophobic properties, which enables them to capture a wide range of molecules and form inclusion complexes through host-guest interactions without forming covalent bonds. The structure of CDs enables them to form inclusion complexes with a wide range of molecules through various interactions, such as hydrogen bonding, dispersion forces, hydrophobic interactions, van der Waals forces, and dipole-dipole interactions. These interactions result in changes to the physicochemical properties of the complex, leading to improved solubility, stability and resistance to external factors [7, 8].

To expand the range of applications for CDs, which naturally have limited solubility in commonly used solvents and possess only one type of functional group, they are often subjected to chemical or enzymatic modifications. These modifications can significantly enhance their solubility, stability and ability to form complexes with specific compounds. Typical chemical modifications include the introduction of hydroxyl, hydroxypropyl, methyl, acetyl or sulfonic groups into the glucopyranose rings. An example of such modification is hydroxypropyl-β-cyclodextrin (HP-β-CD), which exhibits much better solubility in water compared to natural β-CD [6].

CDs are considered non-toxic substances, and their LD50 value (the dose that causes the death of 50% of test organisms) is very high and is estimated in grams per kilogram of human

body weight. For instance, the LD50 value for β-CD exceeds 3 g/kg body weight [9]. It is also worth noting that β-CD has been recognized as safe for use in food products in concentrations up to 2% and has been on the GRAS (Generally Recognized As Safe) list since 1998 [10]. CDs have a low allergenic potential and can be safely used in various forms of administration, including oral, intranasal, dermal, rectal, parenteral and ophthalmic applications. It is important to note that CDs are not absorbed in the upper gastrointestinal tract, and are completely degraded only in the colon, making their oral use safe [8].

Literature data confirm that complexation of substances with CDs leads to improved solubility, stability and resistance to environmental factors such as temperature, pH and light, as well as increased bioavailability of these compounds [11]. CDs also exhibit the ability to control the release of encapsulated substances, allowing for delayed or extended release in a controlled manner [3]. Moreover, the use of CDs as carriers can reduce the irritating or toxic effects of active substances, eliminating the need for additional excipients such as pH adjusters or organic solvents [11].

2. Phenolic Compounds – structure and properties

Phenolic compounds are secondary plant metabolites that play a key role in protecting plants from adverse environmental factors such as UV radiation, excessive water loss, extreme temperatures and microbial attacks. They are also responsible for the color and flavor of fruits, herbs and vegetables, and participate in the enzymatic browning process [12]. Chemically, phenolic compounds are characterized by the presence of at least one aromatic ring to which one or more hydroxyl groups are attached. On the basis of chemical structure, plant phenolic compounds are categorized into several main groups: flavonoids, phenolic acids (benzoic and cinnamic acid derivatives), stilbenes, lignans and tannins. Among these, flavonoids are the most diverse and numerous group, being the largest part of polyphenols found in plants. A characteristic feature of flavonoids is the presence of two benzene rings connected by a three--carbon chain or a heterocyclic ring. The specific chemical structure of phenolic compounds determines their wide range of biological properties, including anti-inflammatory, antimicrobial, antidiabetic, cardioprotective, anticancer and antioxidant activities, making them highly utilized in pharmaceutical preparations and the food industry [13].

Despite their numerous health benefits, phenolic compounds are often unstable and prone to degradation. To maintain their integrity and bioactivity, adequate protection from adverse environmental conditions is necessary. Factors such as temperature, pH and exposure to sunlight can significantly affect their properties, leading to the loss of their biological activity [11]. In addition, the low water solubility and bioavailability of these compounds can limit their effectiveness in practical applications.

To improve the stability and bioavailability of phenolic compounds, various methods, including encapsulation are employed. CDs provide an effective solution in this regard. The encapsulation technique involves trapping phenolic molecules within CD structures, which protects them from degradation and facilitates their better penetration through lipophilic membranes in the body [13]. CDs form inclusion complexes that prevent adverse interactions between polyphenols and other food or drug components [11]. Furthermore, the use of biomaterials in combination with phenolic compounds increases their stability and bioavailability, offering new opportunities for the protection and delivery of these valuable bioactive compounds.

3. Methods to prepare inclusion complexes

CDs are one of the simplest and most versatile encapsulation systems used in industry. The process of forming inclusion complexes, where guest molecules are encapsulated inside the CD structure, can be achieved through various methods (Figure 2). These methods include grinding, kneading, co-precipitation, lyophilization, spray drying, microwave radiation and many others. Each of these methods has its specific advantages and disadvantages. The choice of the optimal method depends on the characteristics of both the CDs and the encapsulated compound, as well as the desired properties of the final complex, such as stability, solubility or control of the release of the active substance [14].

The co-precipitation method is one of the most widely used, simplest, cheapest and most efficient techniques for preparing inclusion complexes. The process involves dissolving the CDs in water and then adding a solution of the guest substance dissolved in an organic solvent (e.g., ethanol, diethyl ether, benzene or chloroform), while stirring continuously. The solution is then cooled, leading to crystallization and precipitation of the complex. The final step involves washing the filtrate to remove any free guest molecules from the surface of the cyclodextrins. A major drawback of this method is the need for large quantities of organic solvents, which can be problematic on a larger scale [15].

An alternative technique is the kneading method, also known as the paste method. It involves grinding the CD with water in a mortar, then adding the guest substance and further grinding until a homogeneous mixture is obtained. This method is particularly effective for guest substances that are poorly soluble in water, as the mixture slowly dissolves during the formation of the inclusion complex. Its advantages include simplicity, no need for high temperatures, and high efficiency. The disadvantages of this method are low reproducibility for some substances and limitations in scaling up large-scale production [15, 16].

Lyophilization is an expensive method because it requires specialized equipment. This process occurs at low temperatures and involves the sublimation of water, which allows for the

formation of stable inclusion compounds. Due to the use of very low temperatures, freeze-drying is especially recommended when the components forming the complex are sensitive to high temperatures. However, this method also has its limitations, including a long processing time. The cost of freeze-drying is at least five times higher than traditional drying methods, which may make it economically unfeasible for smaller research laboratories in the long term [16].

Spray drying method is one of the oldest techniques for producing CD inclusion complexes. The process involves three main steps: i. atomization of the liquid raw material; ii. mixing and drying; iii. collection of particles. In the first stage, the liquid mixture of CDs and guest substance is atomized. After dissolving the guest substance in a saturated CD solution, parameters such as feed liquid flow rate, rotation speed, and inlet and outlet temperatures are set. The liquid is then atomized under the appropriate pressure. The atomized droplets are mixed with a stream of heated air, leading to their rapid drying. In the final stage, the dried product particles are separated from the gas stream and collected into suitable containers, resulting in a powder. The spray drying method has many advantages, including simplicity, fast drying process, and the possibility of efficient large-scale production. However, it is less suitable for substances with high volatility or thermal lability, which can degrade during the process. Additionally, this method requires specialized equipment, significant energy consumption and precise sample preparation, which can be challenging for large-scale production [17].

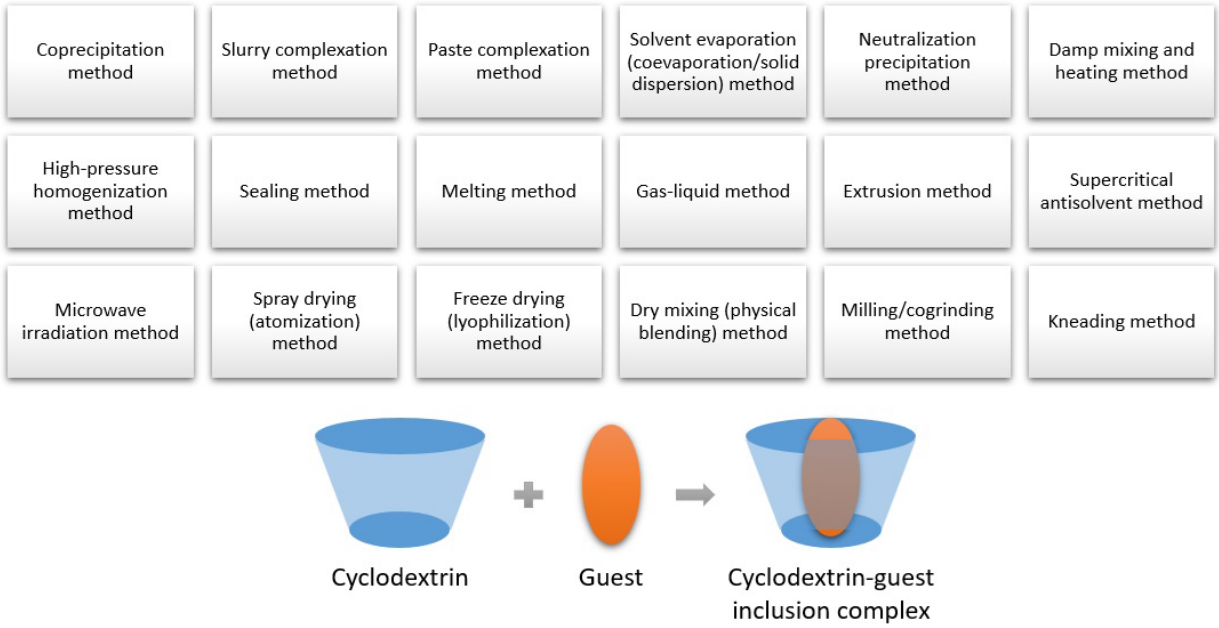

Fig. 2. Different methods involved in the complex formation with CD
Source: own elaboration.
Rys. 2. Różne metody tworzenia kompleksu z CD

4. Applications of inclusion complexes

Inclusion complexes, formed by encapsulation of bioactive substances in CDs structures, are widely used in various scientific and industrial fields due to their unique stabilizing and bioavailability-enhancing properties.

In the food industry, inclusion complexes are used to improve the thermal stability of products, delay the release of volatile substances and reduce color degradation. CDs, due to their ability to encapsulate volatile flavor compounds, increase their solubility, resistance to oxidation and stability under visible and UV light. In addition, CDs can mask unpleasant tastes and odors, hereby enhancing the sensory qualities of food products. Consequently, they are extensively used not only in the food sector but also in cosmetic products [3]. The applications of CDs in the food industry is especially crucial for protecting flavors during high-temperature processes such as sterilization and baking. CDs protect ingredients from degradation, oxidation and changes in flavor and aroma. For example, they can stabilize citral, protecting it from UV-induced cyclization. Furthermore, non-hygroscopic CDs form homogeneous complexes, which enhances water retention and simplifies the disposal of waste containing these complexes [18]. CDs are also used in food packaging, serving as antimicrobial agents. For example, estragole/β-CD nanocomposites can inhibit the growth of pathogenic microorganisms such as Staphylococcus aureus, Bacillus subtilis and Escherichia coli [3].

In cosmetology, CDs are widely used in personal care and toiletry products, primarily for controlled fragrance release and to reduce local skin irritation. Encapsulating substances with CDs enhances fragrance stability, controls the release of scents, and improves the solubility and thermal stability of essential oils, which are components of perfumes, air fresheners, and detergents [3]. CDs are also employed in dermopharmaceutical preparations and cosmetics, such as creams and lotions. Their use allows for effective control over the penetration of active ingredients through the skin and precise targeting to specific areas, providing a biocompatible system for delivering substances across the skin barrier. Additionally, methylated CDs can alter the properties of the skin barrier by interacting with skin phospholipids or cholesterol, leading to improved absorption of the active ingredient [19].

In the textile industry, CDs are used to mask unpleasant odors associated with animal--derived raw materials and to impart more attractive scents to clothing and leather products. Chemicals used in leather processing, such as formaldehyde, glutaraldehyde, chromium salts, and aluminum salts, can impart a specific odor to products, affecting consumer perception. Due to their favorable biocompatibility and low allergenicity, CDs effectively mask these undesirable smells and impart more pleasant aromas to products [3].

CDs also have extensive applications in medicine and pharmaceuticals, particularly for enhancing the bioavailability of therapeutic compounds that are water-insoluble, have unpleasant tastes, or are highly volatile. By encapsulating these compounds within CDs, their stability, solubility, and sensory acceptability are improved, thus expanding their therapeutic potential. CDs are also used to develop extended-release medications, where the complex form limits interactions with other therapeutic substances. For volatile compounds with anticancer, antibacterial, or immune-boosting properties that may be water-insoluble, have poor

bioavailability, or unpleasant tastes, CDs improve their stability, solubility, and mask undesirable flavors, increasing their potential applications. Using low-allergen CDs in complexes with these compounds allows for better stabilization and improved solubility, as well as facilitates oral administration [2, 6].

5. Summary

This review highlights the use of CDs as carriers for phenolic compounds in biomaterials, with a focus on their synthesis, characterization, and applications. The structural differences between α-, β-, and γ-CDs were analyzed, identifying β-CD as the most versatile due to its moderate cavity size and cost-effectiveness, despite its low water solubility. To overcome this limitation, numerous chemical modifications have been used, such as hydroxypropylation, resulting in HP-β-CD, which significantly increases solubility and stability in aqueous media. Various encapsulation methods for phenolic compounds, recognized for their antioxidant, antimicrobial and anti-inflammatory properties, were also evaluated. Spray drying proved to be the most suitable technique for large-scale production, providing stable inclusion complexes with enhanced thermal resistance. The successful formation of these complexes was confirmed by spectroscopic (FT-IR, NMR) and thermal (DSC, TGA) analyses, with HP-β-CD showing better performance compared to other CDs.

Applications of CD-based encapsulation span multiple industries. In the pharmaceutical industry, encapsulated phenolic compounds exhibit improved bioavailability and controlled release, enabling extended formulations and targeted drug delivery. In the food industry, CD inclusion complexes enhance the stability of bioactive compounds, protect flavors and colors from oxidation and UV degradation, and mask undesirable flavors. In cosmetics, CDs facilitate the controlled release of fragrances and active ingredients, improving product stability and reducing skin irritation. In summary, CD-based encapsulation significantly increases the solubility, stability, and functionality of phenolic compounds, expanding their industrial applications and supporting the development of advanced biomaterials with improved therapeutic and functional properties.

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Bibliography

1. Lewandowska I., Zielińska-Pisklak M., Szeleszczuk Ł., Pisklak D.M., Sobczak M.: Cyklodekstryny – zastosowanie w przemyśle farmaceutycznym. *Biuletyn Wydziału Farmaceutycznego*, 2020, p. 19-26.

2. Szejtili J.: Introduction and General Overview of Cyclodextrin Chemistry. Chemical Reviews, t. 98, nr 5, 1998, p. 1743-1753.
3. Xiao Z., Zhang Y., Niu Y., Ke Q., Kou X.: Cyclodextrins as carriers for volatile aroma compounds: A review. Carbohydrate Polymers, 269, 2021.
4. Lee J.-u., Lee S.-S., Lee S., Oh H.B.: Noncovalent Complexes of Cyclodextrin with Small Organic Molecules: Applications and Insights into Host-Guest Interactions in the Gas Phase and Condensed Phase. Molecules, 25, 2020.
5. Hădărugă N., Bandur G.N., David I., Hădărugă D.I.: A review on thermal analyses of cyclodextrins and cyclodextrin complexes. Environmental Chemistry Letters 17, 349-373.
6. Ciobanu A., Mallard I., Landy D., Brabie G., Nistor D., Fourmentin S.: Retention of aroma compounds from Mentha piperita essential oil by cyclodextrins and crosslinked cyclodextrin polymers, Food Chemistry, 138, 2013, p. 291-297.
7. Kazlauskaite J.A., Ivanauskas L., Bernatoniene J.: Cyclodextrin-Assisted Extraction Method as a Green Alternative to Increase the Isoflavone Yield from Trifolium pratensis L. Extract, Pharmaceutics, 13, 2021.
8. Górska A., Kozłowska M.: Zastosowanie cyklodekstryn w przemyśle spożywczym. Post. Techn. Przetw. Spoż., 2, 2008, 80-84.
9. Szejtli J.: The properties and potentialuses of Cyclodextrins derivatives. Journal of Inclusion Phenomena and Molecular Recognition In Chemistry 1992, 14(2): 25-36.
10. Szente L., Szejtli J.: Cyclodextrins as food ingredients, Trends in Food & Technology., 15, 2004, 137-142.
11. Pinho E., Grootved M., Soares G., Henriques M.: Cyclodextrins as encapsulation agents for plant bioactive compounds. Carbohydrate Polymers 101, 2014, p. 121-135.
12. Kosiorek A., Oszmiański J. Golański J.: Podstawy do zastosowania polifenoli roślinnych jako nutraceutyków o właściwościach przeciwpłytkowych, Postępy Fitoterapii, 2, 2013, pp. 108-117.
13. Lewandowska H., Kalinowska M., Lewnadowski W., Stępkowski T., Brzóska K.: The role of natural polyphenols in cell signaling and cytoprotection against cancer development, Journal of Nutritional Biochemistry 32, 2016, pp. 1-19.
14. Hussain, Ch. M., Kabali V. A., Shadpour M.: Antimicrobial Nanosystems : Fabrication and Development. Amsterdam: Elsevier, 2023, pp. 35-59.
15. Cid-Samamed, A.; Rakmai, J.; Mejuto, J.C.; Simal-Gandara, J.; Astray, G. Cyclodextrins inclusion complex: Preparation methods, analytical techniques and food industry applications. Food Chem., 384, 132467, 2022.
16. Patil, J.S., Kadam, D.V., Marapur, S.C., Kamalapur, M.V.: Inclusion complex system; a novel technique to improve thesolubility and bioavailability of poorly soluble drugs: a review. Int. J. Pharm. Sci. Rev. Res. 2(2), 29-34 (2010).
17. Zhou J.; Jia J.; He J.; Li J.; Cai J.: Cyclodextrin Inclusion Complexes and Their Application in Food Safety Analysis: Recent Developments and Future Prospects. Foods, 11, 3871, 2022.
18. Stojanov M., Wimmer R., Larsen K.L.: Study of the Inclusion Complexes Formed Between Cetirizine and α-, β-, and γ-Cyclodextrin and Evaluation on Their Taste-Masking Properties, Journal of Pharmaceutical Sciences, 100, 8, 2011, pp. 3177-3185.
19. Ferreira L., Mascarenhas-Melo F., Rabaça S., Mathur A., Sharma A., Giram P.S., Pawar K.D., Rahdar A., Raza F., Veiga F., Mazzola P.G., Paiva-Santos A.C.: Cyclodextrin-based dermatological formulations: Dermopharmaceutical and cosmetic applications. Colloids Surf B Biointerfaces., 221:113012, 2023.

CYCLODEXTRINS AS CARRIERS OF PHENOLIC COMPOUNDS IN BIOMATERIALS: SYNTHESIS, CHARACTERIZATION, AND APPLICATION

Abstract

Cyclodextrins (CDs; cycloamylases) are a group of macrocyclic oligosaccharides composed of α-D-glucopyranose rings linked by oxygen bridges. CDs are primarily produced through the enzymatic degradation of starch using cyclodextrin glucanotransferase (CGTase) or other enzymes from the amylase group. They can also be produced by bacteria of the genus Bacillus macerans and Klebsiella pneumoniae. Due to their unique structure, CDs can form inclusion complexes with various chemical compounds, including phenolic compounds. This ability enhances the solubility, stability, and bioavailability of these compounds, making CDs promising carriers for the development of biomaterials. In particular, the use of CDs for the transport of phenolic compounds—known for their antioxidant, anti-inflammatory, and antibacterial properties—opens new possibilities in fields such as biotechnology, medicine, food science, and environmental protection. This work focuses on the synthesis methods, characterization, and applications of cyclodextrin-based biomaterials as carriers for phenolic compounds, with a view to their extensive use in biotechnology, environmental engineering, and pharmaceuticals.

Keywords: Cyclodextrins, phenolic compounds, biomaterials

CYKLODEKSTRYNY JAKO NOŚNIKI ZWIĄZKÓW FENOLOWYCH W BIOMATERIAŁACH: SYNTEZA, CHARAKTERYSTYKA I ZASTOSOWANIE

Streszczenie

Cyklodekstryny (CDs; cykloglukopiranozy, cykloamylazy) to grupa makrocyklicznych oligosacharydów, zbudowanych z pierścieni α-D-glukopiranozy, połączonych mostkami tlenowymi. CDs są głównie otrzymywane w wyniku enzymatycznego rozkładu skrobi, przy użyciu cykloglukotransferazy (CGT-azy) lub innych enzymów z grupy amylaz. Mogą być również produkowane przez bakterie z rodzaju Bacillus macerans oraz Klebsiella Pneumonia. Dzięki swojej unikalnej strukturze, CDs mogą tworzyć kompleksy inkluzyjne z różnorodnymi związkami chemicznymi, w tym związkami fenolowymi. Zdolność ta pozwala na zwiększenie rozpuszczalności, stabilności oraz biodostępności tych związków, co czyni CDs obiecującymi nośnikami w rozwoju biomateriałów. W szczególności zastosowanie CDs do transportu

związków fenolowych, znanych ze swoich właściwości antyoksydacyjnych, przeciwzapalnych i przeciwbakteryjnych, otwiera nowe możliwości w takich dziedzinach jak biotechnologia, medycyna, nauka o żywności czy ochrona środowiska. Niniejsza praca koncentruje się na metodach syntezy, charakterystyce oraz zastosowaniu biomateriałów opartych na cyklodekstrynach jako bionośnikach związków fenolowych, z perspektywą ich szerokiego zastosowania w biotechnologii, inżynierii środowiska oraz farmacji.

Słowa kluczowe: Cyklodekstryny, związki fenolowe, biomateriały

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TECHNICAL STANDARDS AND 3D BIOPRINTING OF HYDROGELS: SYSTEMATIC ANALYSIS AND OPTIMIZATION DESIGN

1. Introduction

3D bioprinting of hydrogels represents a dynamically developing field with great potential for biomedical applications, tissue engineering, and regenerative medicine. Hydrogel became interesting in the middle of the 20th century when it began to be fully used. It is a polymer network with hydrophilic properties [1]. This network is formed by a simple reaction of one or more monomers. Interestingly, thanks to the liquid, it can swell and retain a significant amount of water in its structure without dissolving [1, 2]. These hydrophobic monomers can also tailor their properties for specific applications.

Hydrogels are increasingly important in various industries, including medicine, cosmetics, agriculture, and food, because they can absorb water, have high biocompatibility, and manage to modify physical and chemical properties. Despite their unique properties distinguishing them from traditional polymers and elastomers, there are still no norms or standards for determining their mechanical properties or printability qualifications. Currently, the mechanical properties of hydrogels are often tested using standards designed initially for polymers, elastomers, or biological materials. Norms and ISO standards for hydrogels are not primarily intended for this type of material. However, measurements may be governed by general standards that apply to polymeric materials, elastomers, or biological applications in which hydrogels are used. Although these standards can be somewhat applicable, they often must account for the unique properties of hydrogels, such as their high-water content or significant viscoelasticity, which can lead to inaccurate or inadequate results.

Although there is no specific standard yet for 3D bioprinted hydrogels, existing standards offer important guidelines for their development and testing. This article aims to identify and

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analyze existing standards that may be relevant for 3D bioprinting hydrogels and examine their applicability in practice.

In this context, it is essential to examine the standards themselves and how practitioners can effectively combine and apply them to ensure regulatory and quality requirements are met. The article will focus on an overview of the standards available through databases such as PubMed, Scopus, Web of Science, and ScienceDirect and provide a deeper analysis of their practical use in testing and developing 3D bioprinted hydrogels.

This article aims to provide an overview of existing standards that can be applied to hydrogels while identifying gaps in the current standardization environment. The study discusses various mechanical testing methods, including tensile, compressive, hardness, flexural, and rheological testing, and suggests which standards are most appropriate for hydrogels. In addition, it focuses on practical use cases of hydrogels that illustrate the challenges and needs associated with testing their mechanical properties.

While 3D bioprinted hydrogels still need a dedicated standard, several existing standards provide fundamental guidelines for their development and testing, particularly for biomedical applications. The expertise and commitment of experts and innovators like you enable the effective combination of these standards, ensuring that products meet regulatory and quality [3] requirements. This underscores the crucial role you play in this field.

This article not only points to the existing standards that can be used to measure the mechanical properties of hydrogels but also underscores the pressing need to develop new, specific hydrogel standards. These new standards will better accommodate the unique properties of hydrogels, ensuring accurate and reliable results. The study proposes a framework for developing these standards and discusses which parameters and test procedures should be prioritized. Finally, the research offers recommendations for researchers and practitioners to navigate the current regulatory environment and contribute to further developing hydrogel printability standards.

2. The current status

A few papers were identified through scientific databases when researching standards suitable for testing hydrogels in the context of 3D bioprinting. When searching for standards suitable for hydrogel testing, “EN ISO HYDROGEL” and “en AND iso AND hydrogel” were entered as keywords, PubMed (https://pubmed.ncbi.nlm.nih.gov, access 7 August 2024), Scopus (www.scopus.com, access 7 August 2024), Web of Science (www.webofscience.com, access 7 August 2024), and ScienceDirect (https://www.sciencedirect.com/, accessed 8 August 2024). Although none of these standards were created explicitly for 3D bioprinted hydrogels, many contain principles that can be adapted and implemented in this context.

The PuBMeD page contained four results that used the DIN EN ISO 10993-5 standard [4] for determining cytocompatibility for in vitro cell studies [5]; in publications [6], the DIN EN ISO 2409 standard [7] was used, based on which the amounts and sizes of the hydrogel grains were determined of the polymer according to the tape test (an adapted tape test). The degradation behavior of two hydrogels (alginate, alginate-di-aldehyde (ADA)/gelatin) based on the ISO EN 10993-14 standard [8] was determined in the publication [9]. The last publication [10] was also devoted to “iso-octane”; for this reason, it was found, even if it did not contain the use of a specific standard for hydrogel.

The Scopus page threw out eight identical documents. In publications [11], the standard EN ISO 7886 1:2018 [12] was mentioned when the hydrogel met the conditions of this standard before cross-linking. Cytocompatibility for hydrogel according to the standard DIN EN ISO 10993-5 [4] was described in the publication [13]; the same standard was also used [14] to determine the biocompatibility of an implant with hydrogel sensors. Hydrogel applied to cotton fabric [15] was tested for basis weight according to ISO 3801:1977 [16], thickness determination according to ISO 5084:1996 [17], tensile strength according to DIN EN ISO 13934-1 [18], and breathability according to HRN EN ISO 9237:2003 [19]. Biological studies [20], according to Annex C PN-EN ISO 10993-5 [4], were performed on chitosan hydrogels. Hydrogels [21] were used for the determination of water samples and evaluated according to EN ISO 17025/99 [22]. Identical publications with PuBMeD were found [6, 8].

The Web of Science page contained six results that matched the search. Five articles [5, 6, 9, 14, 15] were identical to the previous searches. The last article [23] also devoted “iso-butyl”; for this reason, it was found, even if it did not include a specific standard for hydrogel testing.

ScienceDirect found 1,425 references, so the keyword was changed to “din en iso” hydrogel “norm”. Ten references were found, but not a single publication evaluated the properties of hydrogels.

The analyzed standards mainly focus on measuring materials' strength, flexibility, and viscoelasticity. In the case of 3D bioprinted hydrogels, it is particularly important that these properties are precisely characterized, as they affect the stability and functionality of the resulting tissues. Standards from the category of biocompatibility and safety provide guidelines for evaluating cytotoxicity, immunological reactions, and other biological interactions of hydrogels with the human body. In 3D bioprinting, these materials must be not only functional but also safe for use in clinical applications. Standards related to manufacturing and quality control include requirements for sterility, consistency, and repeatability of processes. These standards are essential to ensure that every step in the production of hydrogels conforms to high standards that minimize the risk of contamination or batch-to-batch variability.

Each listed standard was subjected to a detailed analysis to determine how much it applies to 3D bioprinted hydrogels. It was found that while existing standards provide useful basic frameworks, they often require modification and adaptation to account for the specifics of 3D bioprinting, such as the need for precise material layering or the integration of multiple cell types into a single structure.

An important finding is also the need to create new, specific standards for 3D bioprinting, which would better reflect the complexity and innovative nature of this technology. Until then, it is imperative that professionals working in this field use existing standards creatively, adapting and combining them to achieve the desired results in accordance with regulatory and safety requirements.

3. Material and methods

Research and development of the Standard (Norm) workflow design for the printability of hydrogel materials intended for 3D bioprinting. The first step is to determine the draft title: "Optimalization of the Standard for the Printability of Hydrogel Materials intended for 3D Bioprinting".

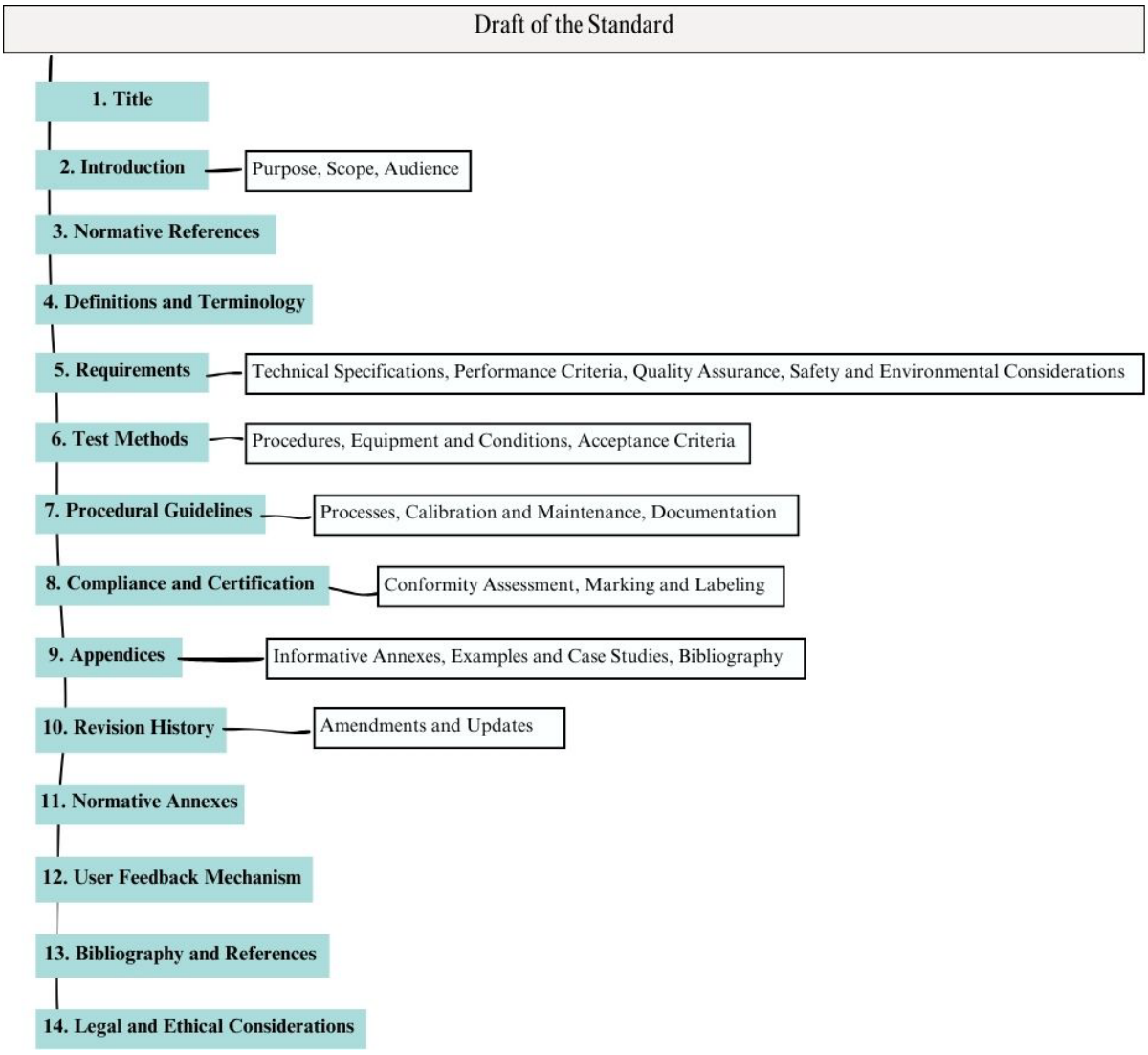

Fig. 1. Workflow Design of the General Standard (Norm) [24, 25, 26, 27, 28, 29, 30]
Rys. 1. Projekt przepływu pracy normy ogólnej (Normy) [24, 25, 26, 27, 28, 29, 30]

4. Introduction

The purpose of this draft standard is to outline simple options for evaluating the printability of hydrogel materials, ability to maintain structural integrity and options for analyzing the similarity and fidelity of the shape of the printed construct. This document defines specifications and test methods for evaluating the printability of hydrogel materials intended for 3D bioprinting. The printability of hydrogels is a crucial factor [31, 32, 33] in ensuring their functionality and accuracy in the production of tissues, implants and other biomedical applications. The workflow is intended for researchers and users of hydrogels in bioprinting.

5. Normative References

The draft of the standard is mainly based on additive manufacturing standards. It uses the ISO/ASTM 52900 standard [24] for fundamental principles and terminology. However, this standard does not cover hydrogels. ASTM F2912-11 [25] covers the characterization of hydrogels. It serves as a standard guide for defining, classifying, and describing hydrogels used in tissue engineering medical products, including those used in 3D bioprinting. This standard discusses aspects related to mechanical properties, swelling, and degradation. When using hydrogel bioprinting for tissue engineering and regenerative medicine, adhere to the instructions regarding the chemical and physical properties of the materials used in medical devices and their biological evaluation as per ISO/TS 10993-19 [26]. For 3D bioprinting, it is important to use the ISO 10993 series standard [28] for the biocompatibility of materials, such as hydrogels, to meet regulatory requirements for medical applications. Another necessary standard is ISO/TS 21560:2021 [29], the wording of which is Tissue Engineering Medical Products (TEMP). This norm is a process standard for evaluating absorbable scaffold materials used in TEMP. When utilizing cells in bioprinting, adhering to the guidelines for cell and gene therapies [30] is crucial.

6. Definitions and Terminology

Hydrogels are cross-linked, three-dimensional networks of hydrophilic polymers that can retain large quantities of water or biological fluids [34]. They can absorb several hundred times their dry weight. This high-water content imparts a soft and elastic nature to hydrogels, closely replicating the physical properties of natural tissues. Because of these characteristics, hydrogels resemble natural tissues [35] and are widely used in biomedical fields such as drug delivery, wound healing, and tissue engineering [35, 36, 37].

Hydrogels are categorized into Natural, Synthetic, and Hybrid Hydrogels [38]. Natural hydrogels, such as alginate, collagen, gelatin, chitosan, and hyaluronic acid, exhibit biocompatible and biodegradable properties. They play a crucial role in tissue engineering by promoting cell attachment and proliferation. However, it's important to note that they often require chemical modifications to improve their mechanical strength and degradation rates, which can be challenging. On the other hand, synthetic hydrogels like Polyethylene glycol [39, 40] (PEG), polyacrylamide, and polyvinyl alcohol (PVA) offer adjustable mechanical and physical properties through controlled synthesis and cross-linking. They can be customized to degrade at specific rates and are commonly used in drug delivery systems.

3D bioprinting is a additive manufacturing process that entails the layer-by-layer deposition of bio-inks (material mixed with cells and grow factors) or biomaterials (hydrogels without cells). The objective is to produce intricate, three-dimensional structures that imitate the architecture and function of natural tissues and organs. The primary purpose of 3D or 4D bioprinting is to create tissue-like constructs for medical applications such as tissue engineering, regenerative medicine, and drug testing [41, 42]. Hydrogels are materials capable of being printed into specific shapes while maintaining the viability and functionality of cells. This process involves sequentially depositing bioinks to create complex 3D structures based on digital models. 3D bioprinting is utilized in the development of tissue scaffolds, organs-on-a-chip, and even complete organ models for research and transplantation [43, 44].

7. Requirements

The Technical Specifications of Hydrogels for Bioprinting relate to the rheological properties of the material, which affect its printability and, therefore, the passage of the material through the nozzle, cross-linking, biocompatibility [45], degradation, and mechanical properties [46] and porosity [47]. Considering that the hydrogel is printable at a viscosity range of 10-1000 mPa·s [48], it is necessary to choose the type of cross-linking adequately. In many cases, a combination of different types is necessary, such as physical, chemical, enzymatic, or with the help of photoinitiators and UV light [49]. The ability of the material to maintain the planned shape after printing depends on the mentioned processes [50]. Degradation processes depend on the considered application [51].

The performance criteria of the hydrogel consist of the degree of durability [52] in resisting external and internal forces and maintaining adequate physicochemical properties during the entire work process, which creates the intended construct. Furthermore, it is the effectiveness of the hydrogel in mimicking the biological environment effectively [53]. Accuracy is the criteria of the print in conformance with the STL model [54] and, last but not least, biocompatibility and biodegradability [55]. Determining the degree of biocompatibility will

determine the eventual possibility of an unwanted immune reaction of the organism and cell proliferation. The biodegradability criterion will determine the limit of safe decomposition of the print.

Safety and environmental impacts are determined. This point must include material sheets, hydrogel preparation and bioprinting protocols, safety standards, environmental impact assessments, and storage requirements [56]. This part of the specifications establishes criteria for protecting human health [57] and the environment during the production, use, and disposal of materials and products [58]. For example, when determining biocompatibility, the material is tested for cytotoxicity, genotoxicity, hemocompatibility, and long-term safety [59]. Testing is done to detect the presence of harmful substances throughout the work process and after application in a clinical environment.

8. Test Methods

This section of the technical standard includes detailed information on procedural steps to ensure test consistency and repeatability [60], as well as information on the equipment used [61], testing conditions [62], and acceptance criteria used to evaluate the quality [63] and performance of hydrogels in the context of 3D bioprinting.

Mechanical evaluation of hydrogels is important for evaluating the physical properties of hydrogels and the suitability of the hydrogel for a specific application. Important methods for mechanical testing of hydrogels include tensile testing, compressive strength testing, hardness testing, flexural testing, rheological testing, penetration testing, and adhesion testing.

9. Tensile Testing

The purpose of tensile testing is to measure the maximum strength and elasticity of the hydrogel [64, 65, 66]. The hydrogel sample is placed between the jaws, which gradually move away from each other until rupture occurs. The data are used to create a stress-strain diagram. With this measurement, we obtain the value of tensile strength, modulus of elasticity and maximum elongation. We can perform tensile strength testing according to general European standards, which are intended for the evaluation of the mechanical properties of polymers and gel materials EN ISO 527-1 – Plastics – Determination of mechanical tensile properties [67], EN ISO 37 – Rubber, vulcanized or thermoplastic – Determination of strength in traction and other physical properties during traction [68].

General measurement procedure:

- Sample preparation – they must be made according to specific dimensions and shapes (dogbone or rectangular strips).
- Assembly of the sample – the sample is fixed in the jaws of the machine.
- Load application – the machine applies a scalding force to the clamp at a constant pull speed until it breaks.
- Data recording – stresses and deformations of the sample are measured during the test.
- Calculation of properties – determination of the strength in the sting, elongation at break, modulus of elasticity and other mechanical properties.

10. Compression Testing

The purpose of compression testing is to determine the hydrogel's ability to resist compressive forces [64, 69, 70]. The hydrogel sample is compressed between two plates and the change in its length is recorded. The result of the measurement is the modulus of elasticity, compressive strength and maximum deformation capacity. We can perform compressive strength testing according to general European standards, which are intended for evaluating the mechanical properties of polymers and similar materials – EN ISO 604 – Plastics – Determination of compressive strength [71], compressive modulus and other mechanical properties under compression, EN ISO 3386-1 Polymeric materials, cellular flexible – Determination of stress-strain characteristics in compression Part 1: Low-density materials [72].

General measurement procedure:

- Sample preparation – creation of standardized samples (for example, cylinders or blocks) according to the dimensions in the standard.
- Assembly of the sample – the sample is fixed in the pressure device between two parallel plates.
- Load application – the machine applies compressive force to the clamp at a controlled speed until its deformation or rupture.
- Data recording – measurement of the force and corresponding deformation of the clamp during the test.
- Calculation of properties – determination of tensile strength and modulus of elasticity in compression.

11. Hardness Testing

Determination of surface hardness is the task of hardness testing [66, 73]. The tip of the durometer in the shape of a cone or needle is pressed into the surface of the tested material. A hardness tester – Shore durometer – is used to measure the hydrogel's resistance to indentation. The hardness value is given according to the Shore A or Shore D scale. This testing is simple, fast and accurate. Surface hardness testing for hydrogels can be performed according to European standards that focus on testing soft materials – EN ISO 868 – Plastics and ebonite – Determination of hardness according to Shore A and D [74]. In publications [73], the surface resistance of cured films was estimated using depth profiles penetration as a function of normal force according to ASTM D 7187 [75].

General measurement procedure:

- Preparation of the sample – it must be flat, clean and without surface defects. The minimum thickness depends on the durometer.
- Application of the device – the machine is pressed against the surface of the sample at a specified pressure and speed.
- Value reading – after the taught time (usually 3 seconds), the hardness value is read on the durometer.

12. Flexural Testing

The task of flexural testing is to measure the hydrogel's ability to withstand bending forces. A hydrogel sample is placed between two supports and subjected to a bending load at the center until rupture [76, 77]. The result of the measurement is the flexural strength and modulus of elasticity when bending. One possible standard for bending testing is EN ISO 178 – Plastics – Determination of bending properties [78], which is focused on polymeric materials and elastomers. For the measurement of hydrogels, it is necessary to maintain suitable environmental conditions – temperature and humidity, to ensure natural hydration and mechanical properties. In addition to the mentioned standard, the American standard ASTM D790 [79] can be used – Standard method for testing the bending properties of plastics and eclectic insulating materials.

General measurement procedure:

- Preparation of the sample – it must be straight, rectangular and thick enough to allow proper measurement.
- Mounting the specimen – the specimen is placed on two support points, while the load is applied in the center of the specimen.

- Load application – using the machine, the load gradually increases until the sample cracks or deforms.
- Data recording – force and bending deformation measurements are recorded throughout the test.

13. Rheological Testing

Rheological tests [73] evaluate the viscoelastic properties of hydrogels and their behavior under different types of mechanical loading. A rheometer is used to apply an oscillating or rotational load and measure the response of a material. The output of the measurement is the storage modulus (G′), the loss modulus (G′′), and the viscosity of the hydrogel [70]. Hydrogels can be tested using the standard EN ISO 3219 – Rheology – Determination of rheological properties in shear mode using rotary rheometers [80]. Also, according to EN ISO 6721-1 – Plastics – Determination of dynamic-mechanical properties [81]. In publications [82], the British national standard EN/DIN EN 14770 [83] – Bitumen and bituminous binders – Determination of complex shear modulus and phase angle – Dynamic Shear Rheometer (DSR) was used.

General measurement procedure:

- Sample preparation – the hydrogel sample must be homogeneous and prepared according to the specification of the standard to ensure the accuracy and repeatability of the measurement.
- Setting the rheometer – a rotary rheometer or a dynamic-mechanical analyzer is used, depending on the type of measurement.
- Load application – the sample is subjected to a controlled shear or oscillating load.
- Data recording – data on the material's resistance to deformation and its rheological behavior are recorded and analyzed.

14. Puncture Testing

The purpose of puncture testing is to obtain the resistance value of the hydrogel against the penetration by a sharp object [84]. The punch is pushed into the surface of the material at a controlled force and speed. The result of the measurement is the force required to break through and the deformation energy. Penetration testing can be performed according to the European standard for mechanical testing of elastomers and soft plastics – EN ISO 527-1 – Plastics – Determination of tensile mechanical properties [67]. An alternative or additional

standard if the hydrogel has rubber-like properties is EN ISO 37 – Rubber, vulcanized or thermoplastic – Determination of tensile strength and other physical tensile properties [68]. According to the regulations of ASTM F1342-91 [85] and ASTM F2054-07 [86], the puncture resistance and burst resistance of composites were measured at 50 and 100 mm/min, respectively [87].

General measurement procedure:

- Sample preparation – samples must be made according to specific dimensions and shapes (e.g. dogbone or rectangular strips).
- Assembly of the sample – the sample is fixed in the jaws of the pulling machine.
- Load application – the loading machine applies tensile force to the sample at a constant tensile speed until rupture.
- Data recording – the stresses and strains of the sample are measured throughout the test, usually displayed on a stress-strain diagram.
- Calculation of properties – determination of tensile strength, elongation at break, modulus of elasticity and other mechanical properties.

15. Adhesion Testing

Adhesion testing is the determination of the adhesion properties of the hydrogel to other materials. Adhesive tests such as the “peel test” or “lap shear test” are used, where the force required to separate the hydrogel from the substrate is measured. The adhesion strength and the energy required for peeling are measured [88, 89]. We can perform adhesion testing according to several European standards that deal with the assessment of the adhesive properties of materials – EN 1464 – Adhesives – Determination of the tensile shear strength of rigid substrates [90], EN 12004 – Adhesives for cladding and floor elements [91] – which can also be applied to testing hydrogels used for gluing or fixing biomaterials. EN ISO 4624 [92] – Coating substances – Tear adhesion test and EN ISO 2409 [93] – Coating substances – Grid test. A recent theory indicates that both the energy dissipated during loading and the release of the stored elastic energy corresponding to crack propagation contribute to the hydrogel coating's toughness and adhesion [94].

General measurement procedure:

- Sample preparation – the hydrogel is applied to the test substrate and allowed to harden or dry as specified.
- Assembly of the sample – the sample is placed in the test device, where the substrates are fixed and prepared for testing.

- Application of force – a pulling force is gradually applied until the separation of the hydrogel from the substrate occurs.
- Data recording – the maximum force required for separation is measured and the adhesion strength is calculated.

16. Procedural Guidelines

This part discusses specific guidelines for all processes related to the production and test cycle [95], as well as calibration and maintenance [96], as well as documentation for tracking and ensuring quality and safety [97]. Compliance and certification include all relevant legal and certification requirements for placing the product on the market or for its use in a specific application. Furthermore, there are international regulations and compliance with international standards. Specific procedures that lead to compliance with the following regulations must be specified. Proper certification documentation must be maintained to include information on quality controls, compliance monitoring and maintenance, and audit reports [98, 99, 100, 101, 102]. Appendices is space for uploading detailed statistical analysis, extensive tabular data, images, recipes, protocols, specifications of laboratory equipment, procedural algorithms, or program codes. Legal and ethical documents can also be uploaded here. Revision history is focused on tracking and recording all changes in the project and classifies the versions. It records the data chronologically and describes the changes and the identification of the change in question, the reason for the revision, and the approval of the change. Normative Annexes contains detailed technical specifications, test methods, reference standards, references, instructions, and specific safety and environmental requirements.

17. Results

The Design of Experiments (DoE) for optimization of the hydrogel printability standard results from assessing the printability of hydrogel materials for 3D bioprinting. The study shows the effects of different printing parameters on the quality and performance of printed hydrogel structures. This analysis aims to identify the settings that ensure consistent and quality bioprinting results through this DoE (see Figure 2). The first step involves describing the factors and levels, where there are options for selecting the type of hydrogel material, experimental printing parameters, and replication. The primary factors include the type of hydrogel composition, consistency, and preparation method, such as hydration and mixing, to ensure uniformity. The standard recipe comprises primary polymer, clean water (deionized, distilled, or ultrapure water), additives, and modifiers. Preparation methods of solutions include sterilization, mixing, storage, and reactivation.

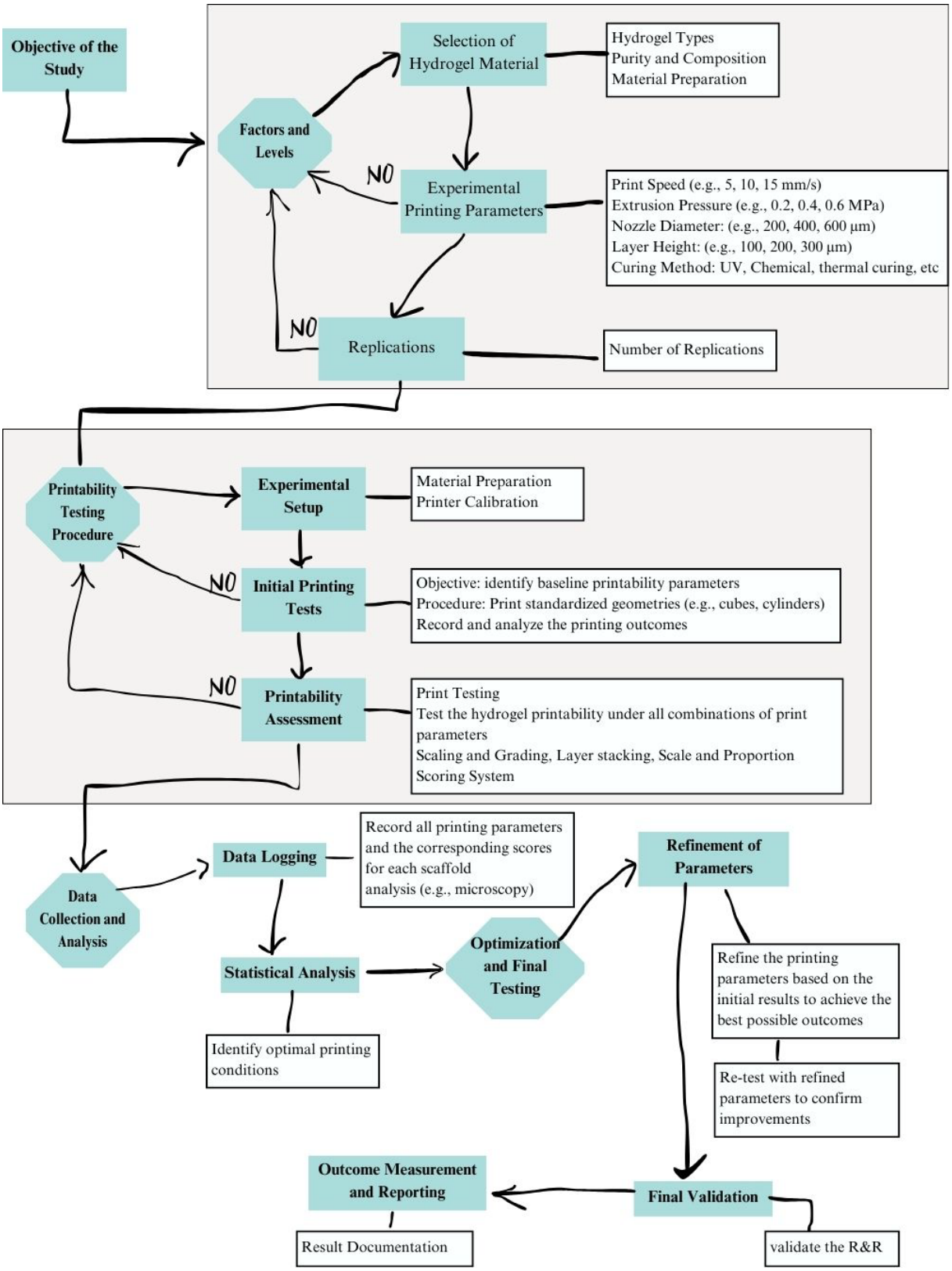

Fig. 2. Design of Experiment (DoE) for Hydrogel Printability Study
Rys. 2. Projekt eksperymentu (DoE) do badania drukowalności hydrożelu

The next step is to determine the experimental printing parameters. Ensuring that all hydrogel-filled cartridges are stored and activated similarly is essential. A centrifuge is useful for removing air bubbles (degassing). Thermoreversible hydrogels should change from a gel state to a liquid state according to the experimentally determined head and bed temperature, which must be maintained during the entire printing period. The same rule applies to hydrogels that are not thermoreversible and do not react to heat, but their cross-linking occurs due to a change in pH, the presence of ions, or the help of a photo initiator and UV light; the cross--linking agent must always be the same and fed in the same way, and the speed, concentration intensity, pressure and time of action of the cross-linking agent must be the same for each printing process. For the purpose of accurate evaluation, it is crucial to consistently produce identical shape (3D model) for printing.

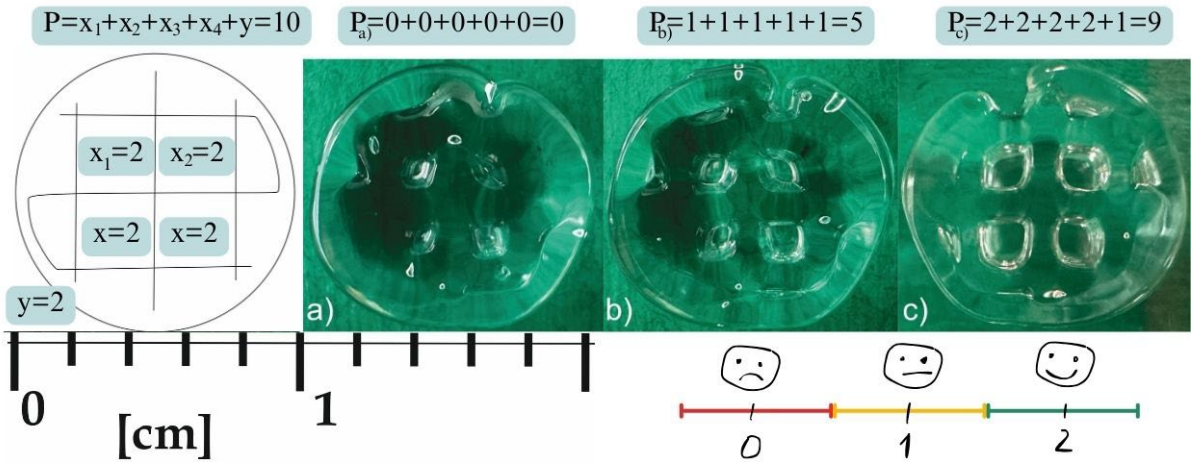

Fig. 3. Printability evaluation of printouts, Top view
Rys. 3. Ocena drukowalności wydruków, widok z góry

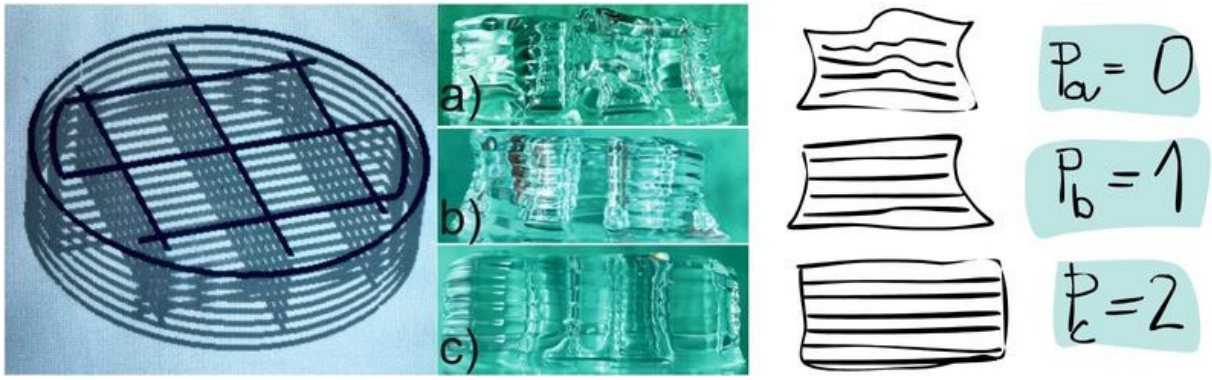

Fig. 4. Printability evaluation of printouts, Side view
Rys. 4. Ocena drukowalności wydruków, widok z boku

Printability Assessment involves analyzing the printing outcomes, focusing on filament consistency, shape retention, and layer adhesion under all combinations of print parameters, and recording the fidelity and structural integrity of the printed constructs. Each printed scaffold

must be assessed in the Top View (Figure 3) and Side View (Figure 4) to identify layer alignment and the uniformity of layer deposition. Shape accuracy, consistent layer spacing, and adhesion is also important. A scoring system is used to evaluate the printing quality. For this study, a scoring system was used for each view (0-2 scale) where 0 indicates poor quality and 2 means excellent quality. Described criteria defined each score to ensure consistent grading. Following this, the data collection and analysis are crucial for a detailed analysis of the printed constructs using standard imaging techniques and data logging. Variance analysis (parametric and non-parametric ANOVA) determines the significance of factors and their interactions to identify optimal printing conditions that maximize print quality. The final steps involve optimization, refinement of parameters, and validation through additional tests to ensure repeatability and reliability of the results.

For process validation, it is essential to determine the number of replications. A minimum of three repetitions for each combination of factors is required to ensure statistical reliability. The Printability Testing Procedure involves preparing hydrogel for selected material types. A calibrated 3D bioprinter must be used across all experiments. After the initial printing tests, baseline printability parameters were identified by printing standardized geometries using the selected printing parameters.

18. Discussion

A primary limitation is the inherent variability in hydrogel formulations, making establishing universal standards challenging. Hydrogels are highly customizable, with different formulations tailored to specific applications, such as tissue scaffolding or drug delivery. This variability makes it difficult to create a one-size-fits-all standard that can encompass all potential uses of hydrogels in bioprinting. Due to this variability, it is difficult to achieve consistent results across different laboratories or even within the same lab over time. This inconsistency can lead to reproducibility issues, which are significant concerns in both research and clinical settings.

Existing standards often do not account for the full range of mechanical properties that hydrogels can exhibit. For instance, the mechanical strength, elasticity, and degradation rates of hydrogels can vary widely depending on their composition and cross-linking density. Current standards may not adequately address these variations, potentially resulting in mismatches between the intended and actual performance of the printed structures.

One of the main problems when applying existing standards to hydrogels is their need for these materials' specific mechanical and rheological properties. For example, standards targeting traditional polymers or other biomaterials often assume higher strength or stiffness properties that hydrogels do not possess. This leads to incorrect calibration of the instruments and interpretation of the results, which can affect the quality of the created 3D structures. In the

case of a study [103] focused on creating 3D structures from hydrogels for tissue engineering, it was found that the application of standards intended for harder biomaterials led to mechanical deformations of the printed structures. Incorrect parameters for determining the viscosity and rheological properties caused the hydrogels to not maintain the desired structure after printing.

The standards for evaluating the biocompatibility and bioactivity of hydrogels are often insufficient, particularly when considering the complex interactions between cells and the hydrogel matrix. Existing guidelines may not fully capture the nuances of how different cell types respond to various hydrogel formulations, which is crucial for applications in tissue engineering. Standards such as ISO 10993 [8] for the biological evaluation of medical products can be applied, but these are primarily concerned with the overall biocompatibility of the material and not specifically with its behavior in 3D printing.

The standardization process is further complicated by the interdisciplinary nature of 3D bioprinting, which involves materials science, biology, and engineering. Each discipline has its own set of standards and metrics, making it difficult to create integrated guidelines that are universally accepted. Incorrect setting of standards can lead to failure of functionality of hydrogel structures in clinical applications. For example, if hydrogels are used as drug carriers, standards that do not take into account their degradation rate or drug release capability may cause the drug to not be released in the correct manner, compromising patient safety. In one study, it was found that standardized degradation tests used for other types of biomaterials were not suitable for hydrogels, leading to an incorrect estimate of the stability of the hydrogel carrier for antibiotics [104]. This misjudgment could have led to rapid breakdown of the hydrogel in the body, reducing the effectiveness of the treatment and increasing the risk of developing resistant bacteria.

As 3D bioprinting technology continues to rapidly evolve, current standards quickly become outdated. This rapid evolution outpaces the development of new standards, leaving a gap between the capabilities of the technology and the guidelines that govern its use. In some cases, standards have not been sufficiently updated to reflect advances in materials research. This has caused problems in getting new hydrogel materials approved by regulatory authorities, which has slowed their introduction to the market. One case occurred in 2018 when there was an incident where a manufacturer of a new hydrogel for surgical applications was unable to obtain approval from a regulatory body because there were no clear standards that the material would meet [105]. As a result, clinical trials were postponed and the time needed for this product to be available on the market was extended, which could have a negative impact on patients who could benefit from this innovation.

There is no separate norm or standard for hydrogel in bioprinting. One of the critical aspects in the printability of hydrogels is their viscosity, flexibility, and ability to maintain shape after printing. Although there are standards for testing rheological properties (eg ASTM D2196 for viscosity of liquids [112]), these standards are not specifically designed for hydrogels used in bioprinting, where the material requirements are much more stringent. The biodegradation properties of the hydrogel can be tested according to EN ISO 10993-4:2017 [113] and ISO

109993-14:2001 [114], as in the publication [90]. Testing the mechanical properties of hydrogels would be possible with the help of standards designed for plastic and rubber. Based on the above-mentioned possibilities of using standardized standards, a clear table was created for testing the mechanical properties of hydrogels.

Tabela 1

Overview of norms and standards suitable for mechanical testing of hydrogels

Measurement name	Norm	Why is it suitable for hydrogel?
Tensile Testing	EN ISO 527-1:2019 Plastics – Determination of tensile properties Part 1: General principles [67]	Hydrogels, which are a mixture of polymers, have mechanical properties similar to elastomers and soft plastics.
	EN ISO 37:2024 Rubber, vulcanized or thermoplastic – Determination of tensile stress-strain properties [68]	The standard is intended for elastomers, it can be intended for hydrogel, which has rubber-like properties.
Compression Testing	EN ISO 604:2002 Plastics – Determination of compressive properties [71]	Suitable for hydrogels that have a similar polymer structure to plastics.
	EN ISO 3386-1:1986 Polymeric materials, cellular flexible – Determination of stress-strain characteristics in compression Part 1: Low-density materials [72]	Suitable for hydrogel with higher material strength.
Hardness Testing	EN ISO 868:2003 Plastics and ebonite – Determination of indentation hardness by means of a durometer (Shore hardness) [74]	For hydrogels, which are a mixture of polymers and have similar properties to soft plastics and elastomers. The hydrogel must be sufficiently thick and homogeneous to be measured without deforming the base or surface.
Flexural Testing	EN ISO 178:2019 Plastics – Determination of flexural properties [78]	For hydrogels that do not have specific thickness and sample preparation requirements, deformations and inaccuracies during testing must be avoided.
Rheological Testing	EN ISO 3219-2:2021 Rheology Part 2: General principles of rotational and oscillatory rheometry [115]	Suitable for hydrogels which behave as viscoelastic materials.
	EN ISO 6721-1:2019 Plastics – Determination of dynamic mechanical properties Part 1: General principles [81]	Suitable for hydrogels that exhibit viscoelastic behavior. Viscoelastic properties are measured using dynamic mechanical analyzers (DMA).

Measurement name	Norm	Why is it suitable for hydrogel?
Puncture Testing	EN ISO 527-1:2019 Plastics – Determination of tensile properties Part 1: General principles [67]	For hydrogels that have mechanical properties similar to elastomers and soft plastics.
	EN ISO 37:2024 Rubber, vulcanized or thermoplastic – Determination of tensile stress-strain properties [68]	For hydrogels that have rubber-like properties.
Adhesion Testing	EN 1464:2022 Adhesives – Determination of peel resistance of adhesive bonds – Floating roller method [90]	The standard specifies a method for determining the adhesion strength of adhesives on rigid substrates using a tensile shear test.
	EN 12004-2:2018 Adhesives for ceramic tiles Part 2: Test methods [91]	Evaluation of the adhesive properties of adhesives can also be applied to testing hydrogels used for gluing or fixing biomaterials.
	EN ISO 4624:2023 Paints and varnishes – Pull-off test for adhesion [92]	Suitable for evaluating the adhesion of hydrogels to different substrates.
	EN ISO 2409:2020 Paints and varnishes – Cross-cut test [28]	The methodology can be applied to hydrogel adhesion testing.

Source: own elaboration.

The mentioned methods enable a comprehensive evaluation of the mechanical properties of hydrogels and provide the data necessary for their optimization. Modifications may be necessary when testing hydrogels due to their properties such as high-water content and viscoelasticity. The importance of mechanical measurements is to ensure that the hydrogel has consistent and predictable properties, which is important when using it in a biomedical application.

We can also test hydrogels using microscopic techniques. These techniques allow detailed analysis of the structure, morphology and distribution of components in the hydrogel. They provide information about the size and location of pores. Other testing options include chemical analysis, swelling and degradation testing, electrical and electrochemical testing, permeability testing, thermal analysis, and biological testing.

One critical aspect of hydrogels' printability is their viscosity, flexibility, and ability to maintain shape after printing. Although there are standards for testing rheological properties (e.g., ASTM D2196 [112] for the viscosity of liquids), these standards are not specifically designed for hydrogels used in bioprinting, where the material requirements are much more stringent.

Studies [79] discuss the critical parameters of bioink printability, emphasizing the importance of rheological properties and the balance between mechanical integrity and biological functionality. The study underscores the need for hydrogels to maintain structure

during and after printing while supporting cell viability. Research [32] delves into using hydrogels for 4D bioprinting, focusing on how the ability to print is affected by the material's response to stimuli after printing. It offers valuable insights into the essential requirements for preserving structural integrity during the dynamic transformations inherent in 4D bioprinting. Some research [33] outlines how various rheological parameters of hydrogels affect their printability in 3D bioprinting. The authors demonstrate that optimal printability is achieved by carefully tuning material composition to balance viscosity, gelation speed, and mechanical properties. The study [91] focuses on optimizing the parameters of 3D printing of hydrogels in order to achieve high accuracy and consistency. The authors discuss the need for standardization of these parameters, which could contribute to the development of standards for the printability of hydrogels. One study [92] presents a 3D printing process known as FRESH (Freeform Reversible Embedding of Suspended Hydrogels), which allows printing of more complex hydrogel structures. The authors discuss the properties of hydrogels required for successful printing and potential parameters for standardization. A study [93] investigating the rheological properties of hydrogels as a key factor for 3D printing is also interesting for this research. In it, the authors propose a methodology for evaluating the printability of hydrogels. The results can be used as a basis for creating standards that specify optimal rheological properties for printing hydrogels. Of note is research [94] that focuses on printing cell-containing hydrogels and discusses criteria for successful printing, including factors that could be included in standards for printability. A significant development is the study [95] where the authors propose standards for measuring the viscosity and other rheological properties of hydrogels, which are critical for 3D printing. The study offers recommendations that can serve as a basis for formal standards.

The increasing interest in using bioprinting for clinical purposes has prompted scientific teams and standardization organizations like ASTM, ISO, and the FDA to collaborate on establishing comprehensive standards for 3D bioprinting with hydrogels. The challenge lies in keeping up with the rapid advancements in additive manufacturing technologies, specific materials, and their various combinations and applications.

19. Conclusions

Currently, there are no specific standards for the printability of hydrogels, which represents a significant gap in the field of standardization for 3D bioprinting. Developing such standards is essential to ensure hydrogel products' reliability, safety, and efficacy in various applications, especially in tissue engineering and regenerative medicine. The current standards for hydrogel formulations and their applications have limitations. There is a need for the development of more comprehensive and adaptable standards that can address these limitations. These standards should include detailed testing protocols for mechanical and biological properties and

be flexible enough to keep up with the rapidly advancing field of 3D bioprinting. Collaboration across disciplines and continuous updates to existing guidelines will be crucial in overcoming these challenges and ensuring the reliable use of hydrogels in bioprinting applications. This study identifies critical gaps in current standards and emphasizes the need for future improvements to support the growing field of 3D bioprinting. In this work, we tried to recommend standards suitable for testing hydrogels' mechanical properties. Although not intended directly for the hydrogel, they can be applied for tensile testing, compression testing, hardness testing, flexural testing, rheological testing, puncture testing, and adhesion testing. The document contains all findings, including images, data tables, and statistical analyses. It is a summary of the optimal parameters and their corresponding results.

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Bibliography

1. Ahmed E.M.: Hydrogel: Preparation, characterization, and applications: A review. J Adv Res. 2015 Mar; 6(2):105-21. 2013.
2. Padhi J.R.: Preparation and Characterization of Novel Gelatin and Carrageenan Based Hydrogels for Topical Delivery. Thesis submitted to National Institute of Technology, Rourkela. 2015.
3. Quality Control Technician Job Description - Manufacturing. [Online], Jobdescription.org, https://jobdescription.org/job-descriptions/quality-control-technician-job-description-manufacturing [date: 06.08.2024].
4. ISO 10993-5:2009, Biological evaluation of medical devices – Part 5: Tests for in vitro cytotoxicity.
5. Vasquez J.M., Idrees A., Carmagnola I., Sigen A., McMahon S., Marlinghaus L., Ciardelli G., Greiser U., Tai H., Wang W., Salber J., Chiono V.: In situ Forming Hyperbranched PEG--Thiolated Hyaluronic Acid Hydrogels With Honey-Mimetic Antibacterial Properties. Front Bioeng Biotechnol., 2021.
6. Stieghorst J., Doll T.: Dispersed Hydrogel Actuator for Modiolar Hugging Cochlear Implant Electrode Arrays. IEEE Trans Biomed Eng., 2016.
7. ISO 2409:2020, Paints and varnishes – Cross-cut test.
8. ISO 10993-14:2001, Biological evaluation of medical devices – Part 14: Identification and quantification of degradation products from ceramics.
9. Seidenstuecker M., Schmeichel T., Ritschl L., Vinke J., Schilling P., Schmal H., Bernstein A.: Mechanical Properties of the Composite Material consisting of β-TCP and Alginate-Di--Aldehyde-Gelatin Hydrogel and Its Degradation Behavior. Materials (Basel), 2021.

10. Okura N.S., Sabi G.J., Crivellenti M.C., Gomes R.A.B., Fernandez-Lafuente R., Mendes A.A.: Improved immobilization of lipase from Thermomyces lanuginosus on a new chitosan-based heterofunctional support: Mixed ion exchange plus hydrophobic interactions. Int J Biol Macromol., 2020.
11. Niosi I., Trucco D., Vannozzi L., Farè S., Ricotti L.: Injectable gelatin-based photocurable fiber-reinforced hydrogel for the treatment of osteochondral defects. Convegno Nazionale di Bioingegneria, 2023.
12. ISO 7886-1:2017, Sterile hypodermic syringes for single use – Part 1: Syringes for manual use.
13. Vasquez J.M., Idrees A., Carmagnola I., Sigen A., McMahon S., Marlinghaus L., Ciardelli G., Greiser U., Tai H., Wang W., Salber J., Chiono V.: In situ Forming Hyperbranched PEG – Thiolated Hyaluronic Acid Hydrogels With Honey-Mimetic Antibacterial Properties. Frontiers in Bioengineering and Biotechnology, 9, 2021.
14. Jorsch C., Schmidt U., Ulkoski D., Scholz C., Guenther M., Gerlach G.: Implantable biomedical sensor array with biocompatible hermetic encapsulation. Journal of Sensors and Sensor Systems, 5 (2), 2016, pp. 229-235.
15. Flinčec Grgac S., Katović A., Katović D.: Method of preparing stable composites of a Cu-aluminosilicate microporous compound and cellulose material and their characterization. Cellulose, 22 (3), 2015, pp. 1813-1827.
16. ISO 3801:1977, Textiles – Woven fabrics – Determination of mass per unit length and mass per unit area.
17. ISO 5084:1996, Textiles – Determination of thickness of textiles and textile products.
18. ISO 13934-1:2013, Textiles — Tensile properties of fabrics – Part 1: Determination of maximum force and elongation at maximum force using the strip method.
19. HRN EN ISO 9237:2003, Textiles – Determination of the permeability of fabrics to air, Hrvatski normativni document.
20. Modrzejewska Z., Paluch D., Skwarczyńska A: Biological properties of thermosensitive chitosan gels conditioning in water. Progress on Chemistry and Application of Chitin and its Derivatives, 20, 2015, pp. 204-212.
21. Bekiari V., Avramidis P.: Data quality in water analysis: validation of combustion-infrared and combustion-chemiluminescence methods for the simultaneous determination of Total Organic Carbon (TOC) and Total Nitrogen (TN). International Journal of Environmental Analytical Chemistry, 2013.
22. ISO/IEC 17025:1999, General requirements for the competence of testing and calibration laboratories.
23. Obata Y., Sato H., Li Ch. J., Takayama K., Higashiyama K., Nagai T., Isowa K.: Effect of synthesized cyclohexanol derivatives using l-menthol as a lead compound on the percutaneous absorption of ketoprofen. International Journal of Pharmaceutics, Volume 198, Issue 2, Pages 191-200, 2000.
24. ISO/ASTM 52900:2015, Additive Manufacturing – General Principles – Terminology.
25. ASTM F2912-11:2011, Standard Guide for Characterization of Hydrogels for Tissue--Engineered Medical Products.
26. ASTM F3091/F3091M-14:2014, Standard Specification for Powder Bed Fusion of Plastic Materials.
27. ISO/TS 10993-19:2020 Biological Evaluation of Medical Devices – Part 19: Physico--Chemical, Morphological, and Topographical Characterization of Materials.

28. ISO 10993-1:2018, Biological Evaluation of Medical Devices – Part 1: Evaluation and Testing within a Risk Management Process.
29. ISO/TS 21560:2021, Tissue-Engineered Medical Products (TEMPs) – Process Standard for the Assessment of Absorbable Scaffold Materials Used in TEMPs.
30. United States Pharmacopeia (USP), "USP Chapter <1046> Cell and Gene Therapy Products", United States Pharmacopeia Convention, Rockville, MD.
31. Gungor-Ozkerim P.S., Inci I., Zhang Y.S., Khademhosseini A., Dokmeci M.R.: Bioinks for 3D Bioprinting: An Overview. Biomaterials Science, 6(5), 915-946. 2018.
32. Mouser V.H.M., Melchels F.P.W., Visser J., Dhert W.J.A., Gawlitta D., Malda J.: Yield Stress Determines Bioprintability of Hydrogels Based on GelMA and Matrigel. Biomaterials Science, 8(9), 4176-4185. 2020.
33. Ouyang L., Yao R., Zhao Y., Sun W.: Effect of Bioink Properties on Printability and Cell Viability for 3D Bioplotting of Embryonic Stem Cells. Biofabrication, 8(3), 2016.
34. Zandraa O., Asabuwa Ngwabebhoh F., Patwa R., Nguyen H.T., Motiei M., Saha N., Sáha T., Sáha P.: Development of dual crosslinked mumio-based hydrogel dressing for wound healing application: Physico-chemistry and antimicrobial activity, 2021.
35. Aytaç, Z.: Electrospinning of biocompatible polymeric nanofibers functionalized with cyclodextrin inclusion complex. A Thesis submitted to the materials science and nanotechnology, Bilkent university, 2012.
36. Mishra A., Ghosal A., Ravi R., Singh N.: Biomedical Application of Hydrogels and Their Importance. CRC Press EBooks. 2020.
37. Bachs-Herrera A., et al.: Melt Electrospinning of Polymers: Blends, Nanocomposites, Additives and Applications. Applied Sciences, vol. 11, no. 4, 2021.
38. Recent advances in engineering hydrogels for niche biomimicking and hematopoietic stem cell culturing. [Online] Frontiers, https://www.frontiersin.org/articles/10.3389/fbioe.2022.1049965/full [date: 08.08.2024].
39. Marks S.: 3D printing of chitosan-based scaffolds for wound healing. University of Wollongong, 2019.
40. Almeida D., Küppers F., Gusmão A., Manjua A.C., Ferreira C., Portugal C.A.M., Silva J.C., Sanjuán-Alberte P., Ferreira F.C.: Design of Magnetic κ-Carrageenan-Collagen Bioinks for 3D Bioprinting. Research Square. Research Square, 2024.
41. Mandrycky C., Wang Z., Kim K., Kim D.H.: 3D Bioprinting for Engineering Complex Tissues. Biotechnology Advances, 34(4), 422-434, 2016.
42. Murphy S.V., Atala A.: 3D Bioprinting of Tissues and Organs. Nature Biotechnology, 32(8), 773-785, 2014.
43. Miao S., Castro N., Nowicki M., Xia L., Cui H., Zhou X., Zhang L.G.: 4D Printing Smart Biomedical Scaffolds with Novel Soybean Oil Epoxidized Acrylate. Scientific Reports, 7(1), 1-12, 2017.
44. Chimene D., Lennox K.K., Kaunas R.R., Gaharwar A.K.: Advanced Bioinks for 3D Printing: A Materials Science Perspective. Annals of Biomedical Engineering, 48(7), 1836-1850, 2020.
45. Li J., Mooney D.J.: Designing hydrogels for controlled drug delivery. Nature Reviews Materials, 1(12), 1-17, 2016.
46. Billiet T., Vandenhaute M., Schelfhout J., Van Vlierberghe S., Dubruel P.: A review of trends and methods for designing hydrogels for tissue engineering. Biomaterials, 33(26), 6020-6041, 2012.

47. Bertassoni L.E., Cardoso J.C., Manoharan V., Cristino A.L.: Direct-write bioprinting of cell-laden methacrylated gelatin hydrogels. Lab on a Chip, 14(13), 2202-2211, 2014.
48. Wüst S., Müller R., Hofmann S.: Controlled positioning of cells in biomaterials – Approaches towards 3D tissue printing. Biofabrication, 6(1), 2014.
49. Gopinathan J., Noh I.: Recent trends in bioinks for 3D printing. Biomaterials Research, 22(11), 1-15, 2018.
50. Nguyen D., Häfeli U.O., Yeung B., Purzner T., Butcher E.C.: Advanced hydrogel systems for 3D printing. Advanced Healthcare Materials, 6(17), 2017.
51. Guvendiren M., Burdick J.A.: Stem cell response to spatially and temporally defined dynamic hydrogels. Nature Communications, 3, 792, 2012.
52. Jang J., Park J.Y., Gao G., Cho D.W.: 3D printing of hydrogel-based biomimetic vascular constructs for in vitro modeling. Biofabrication, 10(3), 2018.
53. Lee A., Hudson A.R., Shiwarski D.J., Tashman J.W., Hinton T.J., Yerneni S., Bliley J.M., Campbell P.G., Feinberg A.W.: 3D bioprinting of collagen to rebuild components of the human heart. Science, 365(6452), 482-487, 2019.
54. Murphy S.V., Atala A.: 3D bioprinting of tissues and organs. Nature Biotechnology, 32(8), 773-785, 2014.
55. Lin H., Zhang D., Alexander P.G., Yang G., Tan J., Cheng A.W.M., Tuan R.S.: Application of visible light-based projection stereolithography for live cell-scaffold fabrication with designed architecture. Biomaterials, 34(2), 331-339, 2014.
56. ISO 10993-1:2009, Biological evaluation of medical devices – Part 1: Evaluation and testing within a risk management process.
57. Fthenakis V., Kim H.C.: Life cycle uses of water in U.S. electricity generation. Renewable and Sustainable Energy Reviews, 14(7), 2039-2048, 2010.
58. Siracusa V., Rocculi P., Romani S., Dalla Rosa M.: Biodegradable polymers for food packaging: a review. Trends in Food Science & Technology, 19(12), 634-643, 2018.
59. Williams D.F.: On the mechanisms of biocompatibility. Biomaterials, 29(20), 2941-953, 2008.
60. ASTM F2900-11:2019, Standard Guide for Characterization of Hydrogels Used in Regenerative Medicine.
61. ISO 527-2:2012, Plastics – Determination of tensile properties – Part 2: Test conditions for moulding and extrusion plastics.
62. ISO 10993-12:2021, Biological evaluation of medical devices – Part 12: Sample preparation and reference materials.
63. ASTM F2819-18, Standard Test Methods for Evaluation of the Durability of Bonded Joints in Plastic and Metal Orthopaedic Implants.
64. Devara V.K., Mamilla R.S.: Synthesis and characterization of SiO2 nanoparticles reinforced 3D printable gelatin/PVA/guar gum/ hydroxypropyl methylcellulose-based biocomposite hydrogel, Industrial Crops and Products, Volume 218, 2024.
65. Li G., Cheng J., Haiwang W., Tianxiao M., Jian Q.: Design and construction of high strength double network hydrogel with flow-induced orientation, Journal of Colloid and Interface Science, Volume 672, Pages 497-511, 2024.
66. Bialik-Wąs K., Kulawik-Pióro A., Sienkiewicz A., Łętocha A., Osińska J., Malarz K., Mrozek-Wilczkiewicz A., Barczewski M., Lanoue A., Giglioli-Guivarc'h N., Miastkowska M.: Design and development of multibiocomponent hybrid alginate hydrogels and lipid

nanodispersion as new materials for medical and cosmetic applications. International Journal of Biological Macromolecules, 134405, 2024.
67. EN ISO 527-1:2019, Plastics – Determination of tensile properties – Part 1: General principles.
68. EN ISO 37:2017, Rubber, vulcanized or thermoplastic – Determination of strength in traction and other physical properties during traction.
69. Noriyuki I., Satoshi K., Masahisa W., Shigeru D.: Poroelasticity of cellulose hydrogel, Journal of the Taiwan Institute of Chemical Engineers, Volume 92, 2018.
70. Raheem H.M., Bay B., Rochefort S.: Viscoelastic properties of a novel hydrogel/foam composites for nucleus pulposus replacement. SN Appl. Sci. 1, 2019.
71. EN ISO 604:2002, Plastics – Determination of compressive strength, compressive modulus and other mechanical properties under compression.
72. ISO 3386-1:1986/AMD 1:2010 – Polymeric materials, cellular flexible – Determination of stress-strain characteristics in compression – Part 1: Low-density materials – Amendment 1.
73. Park J., Kim N., Jung K.I., Yoon S., Noh S.M., Bang J., Jung H.W.: Effect of Silica Nanoparticles Blocked with Epoxy Groups on the Crosslinking and Surface Properties of PEG Hydrogel Films. Polymers. 2021.
74. EN ISO 868:2003, Plastics and ebonite – Determination of hardness according to Shore A and D.
75. ASTM D7187-10, Standard Test Method for Measuring Mechanistic Aspects of Scratch/Mar Behavior of Paint Coatings by Nanoscratching.
76. Durst Ch. A., Cuchiara M.P., Mansfield E.G., West J.L., Grande-Allen K.J.: Flexural characterization of cell encapsulated PEGDA hydrogels with applications for tissue engineered heart valves, Acta Biomaterialia, Volume 7, Issue 6, 2011.
77. Xu D., Harvey T., Begiristain E., Domínguez C., Sánchez-Abella L., Browne M., Cook R.B.: Measuring the elastic modulus of soft biomaterials using nanoindentation, Journal of the Mechanical Behavior of Biomedical Materials, Volume 133, 2022.
78. EN ISO 178:2019, Plastics – Determination of bending properties.
79. ASTM D790, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials.
80. EN ISO 3219:1993, Rheology – Determination of rheological properties in shear mode using rotary rheometers.
81. ISO 6721-1:2019, Plastics – Determination of dynamic mechanical properties – Part 1: General principles.
82. Fitzpatrick D.P., Kealey C., Brady D., Gately N.: Adapted sterilisation for the production of thermoresponsive hydrogels for downstream wound healing applications, Polymer Testing, Volume 132, 2024.
83. EN/DIN EN 14770:2012, Bitumen and bituminous binders - Determination of complex shear modulus and phase angle – Dynamic Shear Rheometer (DSR).
84. Liu J., Jiang Z., Hu N., Zhang Q., Li Y., Zhong D., Wang P.: Fluctuation of puncture force in medical needle puncture of soft solids, Polymer Testing, Volume 128, 2023, 108218, ISSN 0142-9418, https://doi.org/10.1016/j.polymertesting.2023.108218.
85. ASTM F1342-91:1996, Standard Test Method for Protective Clothing Material Resistance to Puncture.
86. ASTM F2054-07:2012, Standard Test Method for Burst Testing of Flexible Package Seals Using Internal Air Pressurization Within Restraining Plates.

87. Lin J.H., Han X., Zhang X.Y., et al.: Construction of high-toughness and self-healing gel-matrix/aramid fabric soft composites with high-performance puncture resistance. Polym Adv Technol. 2024.
88. Liu J., Hu N., Xie Y., Wang P., Chen J., Kan Q.: Polyacrylic Acid Hydrogel Coating for Underwater Adhesion: Preparation and Characterization. Gels. 2023.
89. Li Q., Wang L., Liu Q., Hong W., Yang C.: Fatigue Damage–Resistant Physical Hydrogel Adhesion, Frontiers in Robotics and AI, 8, 2021.
90. EN 1464:2022 Adhesives – Determination of peel resistance of adhesive bonds – Floating roller method.
91. EN 12004-2:2018, Adhesives for ceramic tiles – Part 2: Test methods.
92. EN ISO 4624:2023 Paints and varnishes – Pull-off test for adhesion.
93. EN ISO 2409:2020, Coating substances – Grid test.
94. Liu J., Qu S., Suo Z., Yang W.: Functional hydrogel coatings, National Science Review, Volume 8, Issue 2, February 2021.
95. ASTM E2905-19, Standard Practice for Examination of Mill and Kiln Girth Gear Teeth.
96. ISO 17025:2017, General requirements for the competence of testing and calibration laboratories.
97. ISO 13485:2016, Medical devices – Quality management systems – Requirements for regulatory purposes.
98. ISO 10993-1:2018, Biological Evaluation of Medical Devices – Part 1: Evaluation and Testing within a Risk Management Process.
99. ISO 13485:2016, Medical Devices – Quality Management Systems – Requirements for Regulatory Purposes.
100. U.S. Food and Drug Administration (FDA). Guidance for Industry: Preparation of IDEs for Early Feasibility Medical Device Clinical Studies, Including First in Human (FIH) Studies. U.S. Department of Health and Human Services, Food and Drug Administration, 2013.
101. ASTM F2900-11:2019, Standard Guide for Characterization of Hydrogels Used in Regenerative Medicine.
102. REACH Regulation (EC) No 1907/2006. Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). European Chemicals Agency, 2006.
103. Smith R.B., et al.: 3D Bioprinting of Hydrogels: The Impact of Existing Polymer Standards on Structural Integrity. Biofabrication, vol. 13, no. 3, 2020.
104. Jones L.A., et al.: Degradation Challenges in Hydrogel Drug Carriers: Implications for Clinical Use. Journal of Biomedical Materials Research, vol. 112, no. 2, 2021.
105. Williams M.J.: Regulatory Challenges in the Approval of New Hydrogel-Based Medical Devices. Regulatory Affairs Journal, vol. 25, no. 5, 2018.
106. Egle K., Dohle E., Hoffmann V., Salma I., Al-Maawi S., Ghanaati S., Dubnika A.: Fucoidan/chitosan hydrogels as carrier for sustained delivery of platelet-rich fibrin containing bioactive molecules, International Journal of Biological Macromolecules, Volume 262, Part 1, 2024.
107. Mouser, Vivian H.M., et al.: Development of a Structured Process for the Selection of Hydrogels for Regenerative Medicine Applications. Advanced Healthcare Materials, vol. 6, no. 7, 2017.

108. Hinton Thomas J., et al.: Three-Dimensional Printing of Complex Biological Structures by Freeform Reversible Embedding of Suspended Hydrogels. Science Advances, vol. 1, no. 9, 2015.
109. Ouyang Liang, et al.: The Impact of Bioink Properties on Printability and Cell Viability for 3D Bioprinting of Soft Materials. Biofabrication, vol. 8, no. 3, 2016.
110. Cui Xiaofeng, Thomas Boland: Human Microvasculature Fabrication Using Thermal Inkjet Printing Technology. Biomaterials, vol. 30, no. 31, 2009.
111. Nguyen D., et al.: Revealing the Design Principles of High-Resolution 3D Printed Microfibrillar Scaffolds. Advanced Materials, vol. 29, no. 19, 2017.
112. ASTM D2196, Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational Viscometer.
113. ISO 10993-4:2017, Biological evaluation of medical devices – Part 4: Selection of tests for interactions with blood.
114. ISO 10993-14:2001, Biological evaluation of medical devices – Part 14: Identification and quantification of degradation products from ceramics.
115. EN ISO 3219 -2:2021 Rheology – Part 2: General principles of rotational and oscillatory rheometry.

TECHNICAL STANDARDS AND 3D BIOPRINTING OF HYDROGELS: SYSTEMATIC ANALYSIS AND OPTIMIZATION DESIGN

Abstract

3D bioprinting of hydrogels represents a significant advance in many fields from tissue and biomedical engineering, regenerative medicine, pharmacy and many other fields. In the near future, it is expected to fulfill the needs of transplantology and handle the creation of complex tissue structures and entire organs. But for now, he faces many questions. Additive manufacturing technologies are advancing rapidly, but material for bioprinting is still an unexplored area. There are many ways to create and access print material. The printability of the hydrogel and the resulting properties of the print are influenced by the chemical composition, concentration of the solutions, the preparation process itself, printing parameters, cross-linking, time and storage. Since there are no specific standards for this innovative process, it is possible to use existing standards focused on mechanical properties, biocompatibility, sterility and quality of hydrogel production. This study systematically analyzes relevant standards identified through the scientific databases PubMed, Scopus, Web of Science and ScienceDirect, focusing on their applicability and the need for modifications for the specific requirements of 3D bioprinting. The results suggest that, while useful, current standards often require adaptation to account for the specifics of this technology. The study points to the need for the development of new standards that would better reflect the complexity and innovations

in the field of 3D bioprinting, thereby ensuring higher quality and safety of bioprinted materials. The aim of the study is to create a list of applicable norms and also a proposal for optimizing the printability of hydrogels.

Keywords: 3D bioprinting, hydrogel, technical standards, printability, regulatory requirements

STANDARDY TECHNICZNE I BIODRUK 3D HYDROŻELI: ANALIZA SYSTEMATYCZNA I PROJEKTOWANIE OPTYMALIZACJI

Streszczenie

Biodruk 3D hydrożeli stanowi znaczący postęp w wielu dziedzinach, od inżynierii tkankowej i biomedycznej, medycyny regeneracyjnej, farmacji i wielu innych dziedzin. W najbliższej przyszłości ma spełniać potrzeby transplantologii i zajmować się tworzeniem skomplikowanych struktur tkankowych i całych narządów. Ale na razie stoi przed wieloma pytaniami. Technologie wytwarzania przyrostowego szybko się rozwijają, ale materiały do biodruku to wciąż niezbadany obszar. Istnieje wiele sposobów tworzenia materiałów drukowanych i uzyskiwania do nich dostępu. Na drukowność hydrożelu i wynikające z niego właściwości druku ma wpływ skład chemiczny, stężenie roztworów, sam proces przygotowania, parametry druku, usieciowanie, czas i przechowywanie. Ponieważ nie ma konkretnych standardów dla tego innowacyjnego procesu, możliwe jest wykorzystanie istniejących standardów skupiających się na właściwościach mechanicznych, biokompatybilności, sterylności i jakości produkcji hydrożeli. W niniejszym badaniu systematycznie analizowano odpowiednie standardy zidentyfikowane w naukowych bazach danych PubMed, Scopus, Web of Science i ScienceDirect, koncentrując się na ich stosowalności i potrzebie modyfikacji pod kątem specyficznych wymagań biodruku 3D. Wyniki sugerują, że choć obecne standardy są przydatne, często wymagają adaptacji w celu uwzględnienia specyfiki tej technologii. W badaniu wskazano na potrzebę opracowania nowych standardów, które lepiej oddałyby złożoność i innowacje w obszarze biodruku 3D, zapewniając tym samym wyższą jakość i bezpieczeństwo materiałów biodrukowanych. Celem pracy jest stworzenie wykazu obowiązujących norm, a także propozycji optymalizacji drukowalności hydrożeli.

Słowa kluczowe: biodruk 3D, hydrożel, standardy techniczne, drukowalność, wymagania regulacyjne

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HERBICIDES DERIVED FROM PICOLINIC ACID – STRUCTURE, MECHANISM OF ACTION, ENVIRONMENTAL FATE

1. Introduction

According to FAO (Food and Agriculture Organization of the United Nations) total use of pesticides in agriculture doubled since 1990, and in 2021 was 3,5 million tons of active ingredient (Fig. 1), of which 49% were herbicides [1]. This means that only in 2021, over 1,7 million tons of herbicides have found their way into the environment. The popularity ofherbicides is caused by their ability to control the growth of variety of weeds that may decrease levels of crop productivity and safety. Herbicides are commonly used in different sectors of agriculture, including crops, horticulture, floristry and forestry production. The widespread use of those substances is rising concern due to potential risks they can cause, either through direct or indirect influence they can have on various ecosystems [2].

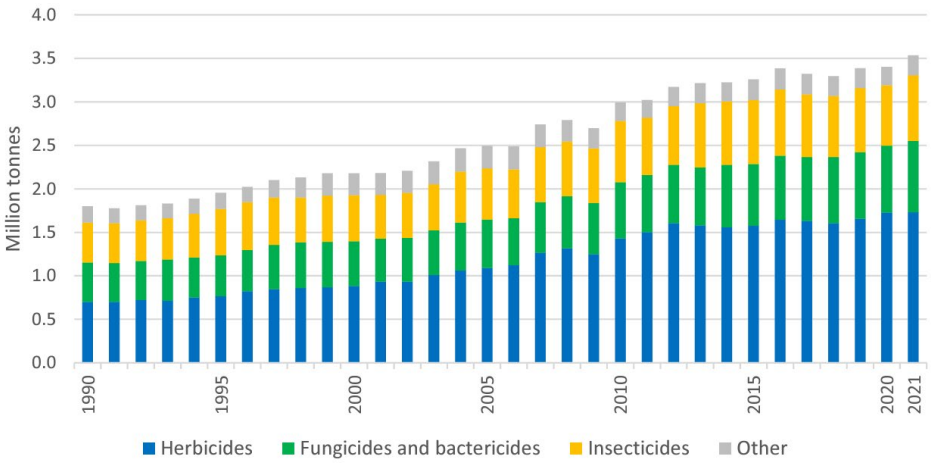

Fig. 1. Global pesticide use by category
Rys. 1. Globalne zużycie pestycydów według kategorii
Source: FAO. 2023. Pesticides use and trade, 1990–2021. FAOSTAT Analytical Briefs Series No. 70. Rome.

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One of the classes of synthetic herbicides are picolinate compounds – derivatives of picolinic acid belonging to the group of auxin mimics [3, 4].

2. Structure of herbicides derived from picolinic acid

There are seven herbicides that can be classified as derivatives of picolinic acid (Fig. 2.) [4]. As seen in the Fig. 2., all of the herbicides from this group possess an aromatic ring with nitrogen atom substituting for one of the carbon atoms. Another common features are chlorine/and fluorine atoms connected to the pyridine ring and presence of a carboxyl group attached to the pyridine ring (with the exception of triclopyr and fluroxypyr where it is not connected directly). It seems that for a molecule to mimic auxin activity there has to be a strong negative charge on its carboxylic acid group, positioned at a defined distance from a weaker positive charge on an aromatic ring [5, 6].

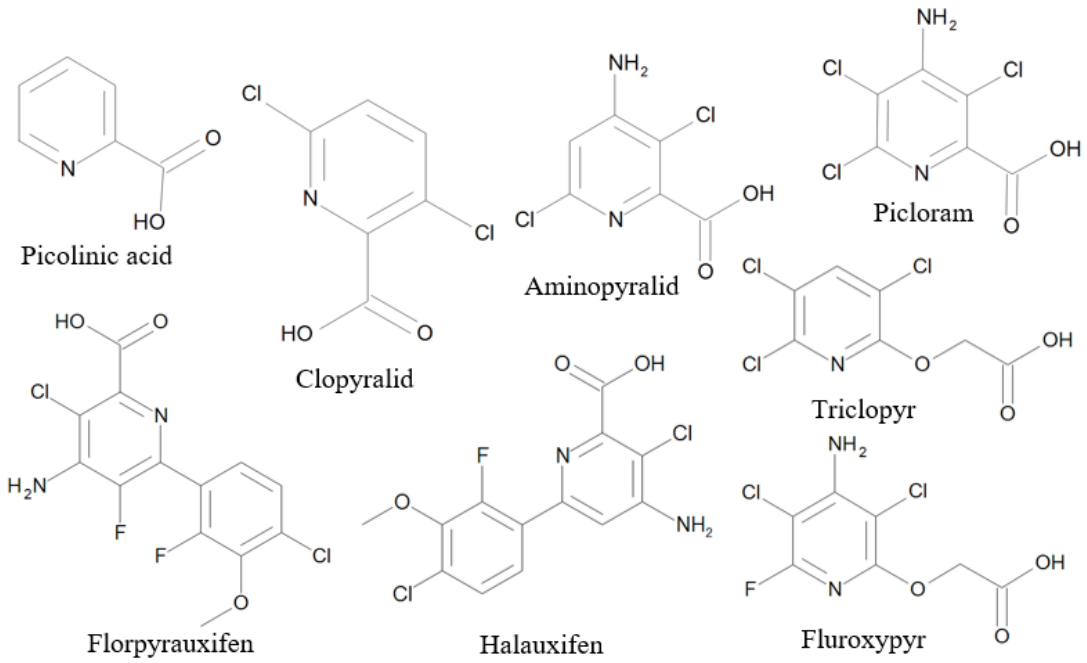

Fig. 2. Structures of herbicides derived from picolinic acid
Rys. 2. Struktury herbicydów pochodzących od kwasu pikolinowego

3. Auxin mimicking herbicides and their mechanism of action

HRAC (Herbicide Resistance Action Committee) classifies herbicides based on their modes of action into three main groups: affecting light activation of ROS (reactive oxygen species),

affecting cellular metabolism and affecting cell division and growth. Compounds affecting cell division and growth include: inhibitors of microtubule assembly, inhibitors of microtubule organization, auxin mimics (Fig. 3.), uncouplers and auxin transport inhibitors. All herbicides derived prom picolinic acid belong to the group of auxin mimics [4].

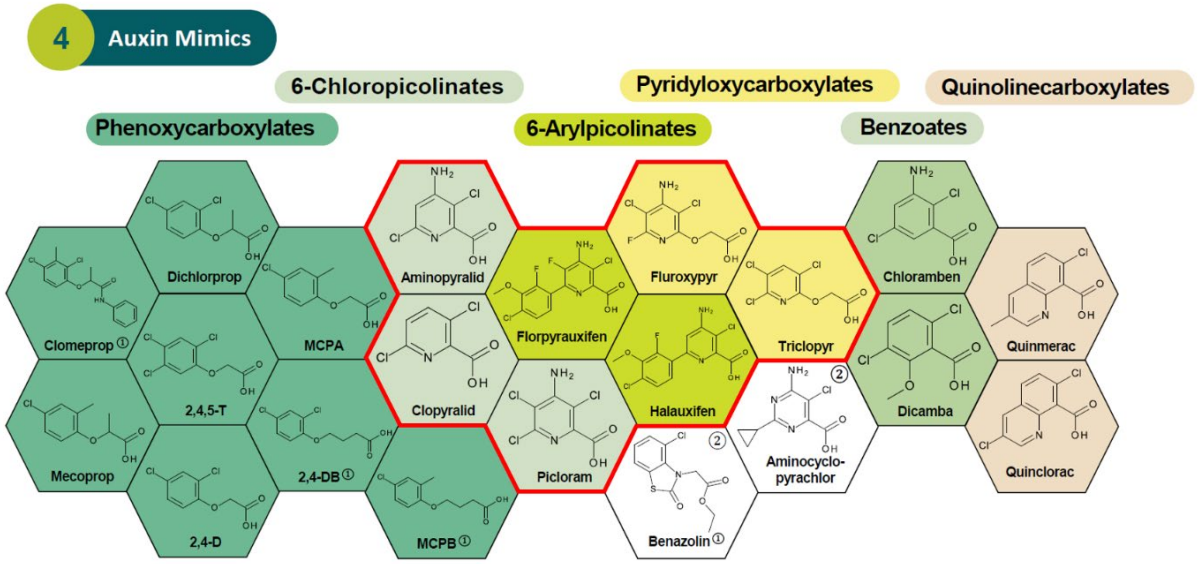

Fig. 3. Auxinic herbicides according to Herbicide Resistance Action Committee with highlighted herbicides derived from picolinic acid.
Rys. 3. Herbicydy auksynowe według Herbicide Resistance Action Committee z wyróżnionymi herbicydami pochodnymi kwasu pikolinowego.
Source: HRAC Global Herbicide Mode of Action Classification 2024 [4].

Auxin herbicides are the third (after acetolactate synthase inhibitors and glyphosate) most used group of herbicides in the world [7, 8]. They are used mostly against broadleaf weeds in cereal and grass crops [6, 7, 8, 9].

Auxin mimicking herbicides, or otherwise referred to as synthetic auxins, mimic indole-3-acetic acid (IAA) [7, 10]. IAA is a main plant hormone classified as auxin [6, 11], and because of that those terms are sometimes used synonymously [11]. The other auxins are: phenylacetic acid, indole-3-butyric acid and 4-chloroindole-3-acetic acid [5, 12] (Fig. 4). It seems that for a molecule to mimic auxin activity there has to be a strong negative charge on its carboxylic acid group, positioned at a defined distance from a weaker positive charge on an aromatic ring [5, 6].

IAA is responsible for regulating various aspects of plant development, including cell growth, division and differentiation, leaf initiation, root formation, senescence and tropism [5, 6, 10, 11, 13, 14]. Whereas listed processes are stimulated at low auxin concentration, too high concentration leads to their disturbance and results in death of a plant [5].

Plants possess mechanisms of auxin response allowing them to keep auxin concentration at a proper level [5]. Receptors such as Transport Inhibitor Response 1 (TIR1) recognize auxins

and bind them. After that Auxin/Indole-3-acetic acid (Aux/IAA) proteins bind over the top and as a consequence are modified and then proteolyzed. Their absence trigger Auxin Response Factors (ARF) that regulate expression of auxin-regulating genes resulting in activation of responses related to auxin action [8, 10].

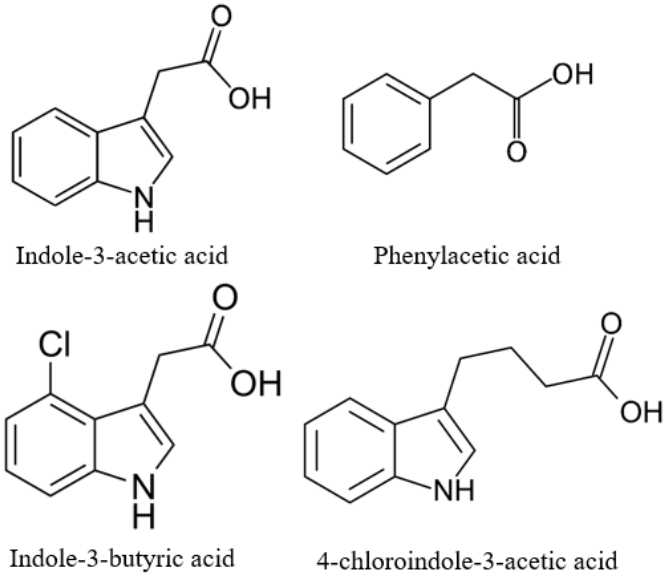

Fig. 4. Structures of auxins: indole-3-acetic acid, phenylacetic acid, indole-3-butyric acid and 4-chloroindole-3-acetic acid.

Rys. 4. Struktury auksyn: kwasu indolilo-3-octowego, kwasu fenylooctowego, kwasu indolilomasłowego i kwasu 4-chloroindolilo-3-octowego.

Synthetic auxin herbicides overload natural auxin-response mechanisms causing “auxin overdose” – effect that can be result of too high concentration of IAA resulting in plant death [5], [6]. They bind to TIR1 receptors and deregulate expression of auxin-regulating genes [10]. According a new model presented by McCauley et al. (2020) the main reasons of plant death due to auxin herbicides are inhibition of photosynthetic processes and accumulation of abscisic acid (ABA) caused by increased expression of NCED gene [15]. Mechanism and mode of action of auxin herbicides and IAA is shown in Fig. 5.

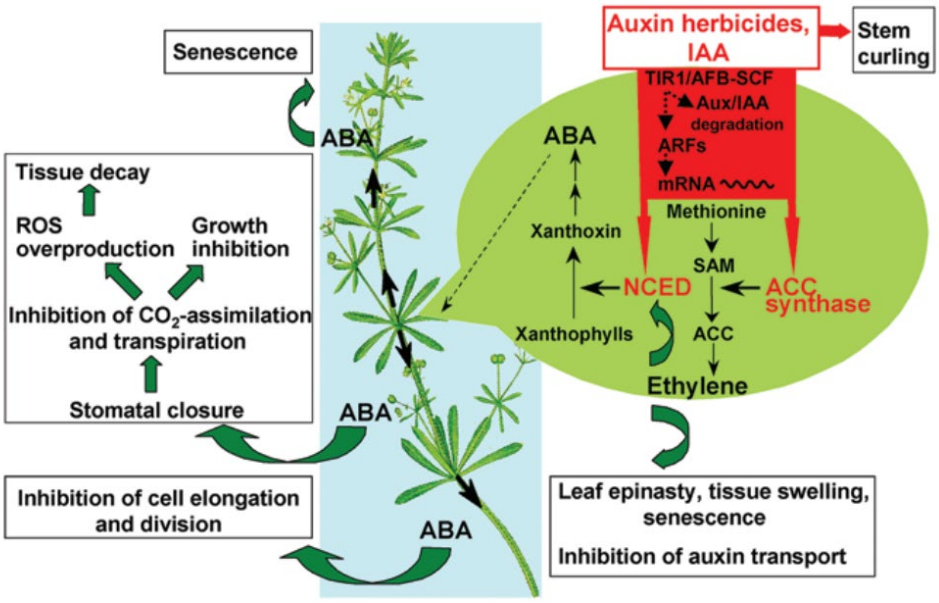

Fig. 5. Mechanism and mode of action of auxin herbicides and Indole-3-Acetic Acid (IAA) in Dicot Plants, Illustrated for Cleavers (Galium aparine). Auxin herbicides are detected by F-box proteins, including Transport Inhibitor Response 1 (TIR1) and homolog auxin signalling F-box proteins (AFB). Auxin binding to these receptors leads to the degradation of Aux/IAA repressor proteins via the Skp1-cullin-F-box (SCF) ubiquitin-protein ligase complex. This degradation releases auxin response factors (ARFs), which activate auxin-responsive genes. In shoot tissue, with involvement of S-adenosylmethionine (SAM), this activation notably upregulates genes for ethylene and abscisic acid (ABA) biosynthesis, such as 1-aminocyclopropane-1-carboxylic acid (ACC) synthase and NCED. Increased ethylene level causes leaf epinasty, tissue swelling, and local inhibition of auxin transport, leading to stem curling. Ethylene also enhances NCED activity, boosting ABA production, which then induces stomatal closure, reduces transpiration, and triggers reactive oxygen species (ROS) production. ABA, in combination with ethylene, inhibits cell division, promotes foliar senescence, and damages chloroplasts and vascular tissues. These effects result in growth inhibition, tissue desiccation, decay, and ultimately plant death [16].

Rys. 5. Mechanizm działania herbicydów auksynowych i kwasu indolilo-3-octowego (IAA) w roślinach dwuliściennych, zilustrowany na przykładzie przytulii czepnej (Galium aparine). Herbicydy auksynowe są wykrywane przez białka F-box, w tym Transport Inhibitor Response 1 (TIR1) oraz homologiczne białka F-box sygnałowe auksyn (AFB). Wiązanie auksyny z tymi receptorami prowadzi do degradacji białek represorowych Aux/IAA za pośrednictwem kompleksu ligazy ubikwitynowo-białkowej Skp1-cullin-F-box (SCF). Degradacja ta uwalnia czynniki odpowiedzi na auksyny (ARF), które aktywują geny odpowiedzi na auksyny. W tkankach pędu, z udziałem S-adenozylometioniny (SAM), aktywacja ta znacząco zwiększa ekspresję genów odpowiedzialnych za biosyntezę etylenu i kwasu abscysynowego (ABA), takich jak syntaza kwasu 1-aminocyklopropano-1-karboksylowego (ACC) oraz NCED. Zwiększony poziom etylenu powoduje epinastię liści, pęcznienie tkanek i lokalne zahamowanie transportu auksyn, co prowadzi do skręcania łodyg. Etylen zwiększa także aktywność NCED, co podnosi produkcję ABA, która następnie indukuje zamykanie aparatów szparkowych, zmniejsza transpirację i wywołuje produkcję reaktywnych form tlenu (ROS). ABA, w połączeniu z etylenem, hamuje podział komórek, przyspiesza starzenie liści oraz uszkadza chloroplasty i tkanki naczyniowe. Te efekty prowadzą do zahamowania wzrostu, wysychania tkanek, ich rozkładu, a ostatecznie do śmierci rośliny [16].

Source: Grossmann K. (2007) Auxin Herbicide Action, Plant Signaling & Behavior, 2:5, 421-423.

Grossmann (2010) described different phased of plant death caused by auxin herbicides. In the first phase – stimulation – activation of metabolic processes is followed by aberrant growth (which is manifested by stem curling, leaf epinasty and tissue swelling) and accumulation of ABA. In the next stage, there is a noticeable slowdown in the growth of both roots and stems accompanied by an enhanced pigmentation of green leaves. Simultaneously, the closure of stomata results in decreased transpiration, carbon assimilation, and starch formation, while also leading to an excessive production of reactive oxygen species. The third phase is defined by chloroplast damage and progressive chlorosis. At the same time the breakdown of membrane and vascular system integrity results in wilting, necrosis and plant death [6].

4. Environmental fate of picolinic acid herbicides

Having fulfilled its function of controlling unwanted organisms, herbicides should undergo degradation to simple substances [17], without leaving residues in the harvested crop, or at least leaving lower residues than the statutory maximum residue limits [18]. Persistence of herbicide active substances in soil depends on many factors [17, 19] that can be divided into three groups: soil factors, climatic conditions, and herbicidal properties [19] (Fig. 6.).

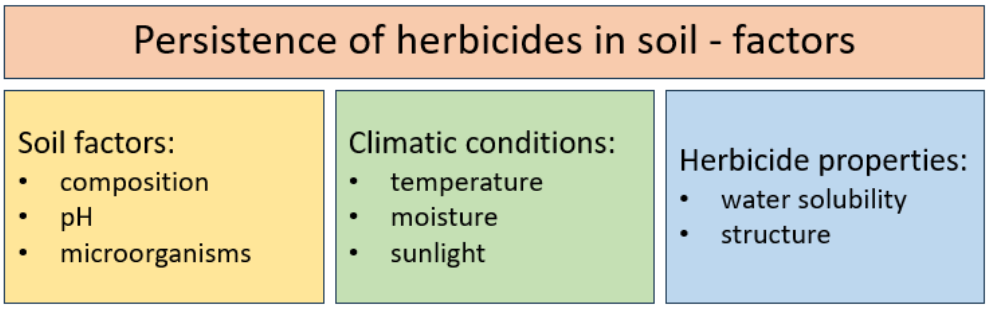

Fig. 6. Persistence of herbicides in soil – factors
Rys. 6. Trwałość herbicydów w glebie – czynniki wpływające
Source: Based on: Curran W. (2016) Persistence of herbicides in soil, Crops & Soils, 16-21.

Because persistence of herbicides is dependent on a lot of factors, it is difficult to clearly establish their environmental fate. Clopyralid being the most commonly used herbicides from picolinic acid derivatives group is also best studied one. It seems that regarding clopyralid, warm, moist soils with high microbial activity tend to break down clopyralid relatively quickly, while in sterile, dry, cold, or waterlogged soils, the herbicide can persist for several months or even years [20]. In study from 2022, Tandon and Singh [21] found half-life of clopyralid in soil to be approximately 13 days. This is considered a relatively short period, with the soil characteristics (low in organic carbon content and loamy with good aeration) being cited as the

primary factor influencing this result [21]. Another study [22] proved half-life of clopyralid to be 71,5 and 23,9 days for pasture (shaded) and bare ground (shaded) respectively. Those values change dramatically in unshaded conditions to 5,0 days for pasture and 12,9 days for bare ground [22]. When studied in laboratory trials simulating typical composting situations, clopyralid residues degraded at a rate consistent with a 30-day half-life [23]. Kucharski and Kalitkowska (2016) state that [17] presence of heavy metals (Zn, Cu) in soil may slow down clopyralid degradation. According to study from 2019 [24] clopyralid and picloram have ones of the highest leachability to groundwater and picolinic acid derived herbicides have been detected in groundwater on multiple occasions [25, 26, 27].

5. Summary

Since 1990, global pesticide use has doubled, reaching 3.5 million tons in 2021, with herbicides accounting for 49% of that total. Herbicides are widely used due to their effectiveness in controlling weeds, which enhances crop productivity. However, their widespread application raises environmental concerns. Picolinic acid-derived herbicides, a class of synthetic auxin mimics, have the ability to mimic plant hormones, disrupting natural auxin-response mechanisms and causing plant death. These herbicides contain a pyridine ring in their chemical structure, which is critical for their activity. Their mode of action involves overloading the plant's auxin-response system, which leads to aberrant growth and eventual plant death. Picolinic acid herbicides, especially clopyralid, tend to be persistent in the environment. Their degradation rates differ depending on soil properties and climate. In biologically active soils, clopyralid can degrade quickly, with a half-life as short as 13 days, while in sterile, cold, or waterlogged soils, it may persist for months or even years. Studies have found half-lives ranging from 5 to 71 days under different conditions. Picolinic acid-derived herbicides have high leachability and have been detected in groundwater, raising concerns about their long-term environmental impact.

Bibliografia

1. Pesticides use and trade 1990-2021, Jul. 2023. DOI: 10.4060/cc6958en.
2. E. Wołejko, U. Wydro, J.I. Odziejewicz, A. Koronkiewicz, A. Jabłońska-Trypuć, “Biomonitoring of Soil Contaminated with Herbicides”, Water (Basel), vol. 14, no. 10, p. 1534, May 2022, DOI: 10.3390/w14101534.
3. T. Feng et al., “Design, Synthesis, Herbicidal Activity, and Structure – Activity Relationship Study of Novel 6-(5-Aryl-Substituted-1-Pyrazolyl)-2-Picolinic Acid as Potential Herbicides”, Molecules, vol. 28, no. 3, p. 1431, Feb. 2023, DOI: 10.3390/molecules28031431.

4. HRAC (Herbicide Resistance Action Committee), “Global Herbicide Mode of Action Classification 2024”, https://hracglobal.com/tools/2024-hrac-global-herbicide-moa-classification.
5. C.-L. Do-Thanh, J.J. Vargas, J.W. Thomas, G.R. Armel, M.D. Best, “Design, Synthesis, and Evaluation of Novel Auxin Mimic Herbicides”, J Agric Food Chem, vol. 64, no. 18, pp. 3533-3537, May 2016, DOI: 10.1021/acs.jafc.6b00675.
6. K. Grossmann, “Auxin herbicides: current status of mechanism and mode of action”, Pest Manag Sci, vol. 66, no. 2, pp. 113-120, Feb. 2010, DOI: 10.1002/ps.1860.
7. R. Busi et al., “Weed resistance to synthetic auxin herbicides”, Pest Manag Sci, vol. 74, no. 10, pp. 2265-2276, Oct. 2018, DOI: 10.1002/ps.4823.
8. J. Prusinska, V. Uzunova, P. Schmitzer, M. Weimer, J. Bell, R.M. Napier, “The differential binding and biological efficacy of auxin herbicides”, Pest Manag Sci, vol. 79, no. 4, pp. 1305-1315, Apr. 2023, DOI: 10.1002/ps.7294.
9. J. Xu, X. Liu, R. Napier, L. Dong, J. Li, “Mode of Action of a Novel Synthetic Auxin Herbicide Halauxifen-Methyl”, Agronomy, vol. 12, no. 7, p. 1659, Jul. 2022, DOI: 10.3390/agronomy12071659.
10. O.E. Todd et al., “Synthetic auxin herbicides: finding the lock and key to weed resistance”, Plant Science, vol. 300, p. 110631, Nov. 2020, DOI: 10.1016/j.plantsci.2020.110631.
11. S.-F. Fu, J.-Y. Wei, H.-W. Chen, Y.-Y. Liu, H.-Y. Lu, J.-Y. Chou, “Indole-3-acetic acid: A widespread physiological code in interactions of fungi with other organisms”, Plant Signal Behav, vol. 10, no. 8, p. e1048052, Aug. 2015, DOI: 10.1080/15592324. 2015.1048052.
12. S. Simon, J. Petrášek, “Why plants need more than one type of auxin”, Plant Science, vol. 180, no. 3, pp. 454-460, Mar. 2011, DOI: 10.1016/j.plantsci.2010.12.007.
13. Y. Mano, K. Nemoto, “The pathway of auxin biosynthesis in plants”, J Exp Bot, vol. 63, no. 8, pp. 2853-2872, May 2012, DOI: 10.1093/jxb/ers091.
14. M. Zhang et al., “Melatonin and Indole-3-Acetic Acid Synergistically Regulate Plant Growth and Stress Resistance”, Cells, vol. 11, no. 20, p. 3250, Oct. 2022, DOI: 10.3390/cells11203250.
15. C.L. McCauley, S.A.M. McAdam, K. Bhide, J. Thimmapuram, J.A. Banks, B.G. Young, “Transcriptomics in Erigeron canadensis reveals rapid photosynthetic and hormonal responses to auxin herbicide application”, J Exp Bot, vol. 71, no. 12, pp. 3701-3709, Jun. 2020, DOI: 10.1093/jxb/eraa124.
16. K. Grossmann, “Auxin Herbicide Action”, Plant Signal Behav, vol. 2, no. 5, pp. 421-423, Sep. 2007, DOI: 10.4161/psb.2.5.4417.
17. M. Kucharski, O. Kalitowska, “CLOPYRALID DISSIPATION IN THE SOIL CONTAMINATED WITH HEAVY METALS”, Journal of Ecological Engineering, vol. 16, pp. 38-42, 2015, DOI: 10.12911/22998993/584.
18. E. Szpyrka, S. Walorczyk, “Dissipation kinetics of fluquinconazole and pyrimethanil residues in apples intended for baby food production”, Food Chem, vol. 141, no. 4, pp. 3525-3530, Dec. 2013, DOI: 10.1016/j.foodchem.2013.06.055.
19. W.S. Curran, “Persistence of herbicides in soil”, Crops & Soils, vol. 49, no. 5, pp. 16-21, Sep. 2016, DOI: 10.2134/cs2016-49-0504.
20. A.J. Pik, E. Peake, M.T. Strosher, G.W. Hodgson, “Fate of 3,6-dichloropicolinic acid in soils”, J Agric Food Chem, vol. 25, no. 5, pp. 1054-1061, May 1977, DOI: 10.1021/jf60213a011.
21. S. Tandon, A. Singh, “Residue Behavior of Clopyralid Herbicide in Soil and Sugar Beet Crop under Subtropical Field Conditions”, J Food Prot, vol. 85, no. 5, pp. 735-739, May 2022, DOI: 10.4315/JFP-21-355.

22. R. Ahmad, T.K. James, A. Rahman, P.T. Holland, “Dissipation of the Herbicide Clopyralid in an Allophanic Soil: Laboratory and Field Studies”, Journal of Environmental Science and Health, Part B, vol. 38, no. 6, pp. 683-695, Dec. 2003, DOI: 10.1081/PFC-120025553.
23. W.F. Brinton, “Presence, fate, and effects of clopyralid and other anthropogenic residues in green waste composting”, in Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Battelle Press, Columbus, OH, May 2004.
24. A.E. Akay Demir, F.B. Dilek, U. Yetis, “A new screening index for pesticides leachability to groundwater”, J Environ Manage, vol. 231, pp. 1193-1202, Feb. 2019, DOI: 10.1016/j.jenvman.2018.11.007.
25. D.J. Lapworth et al., “Pesticides in groundwater: some observations on temporal and spatial trends”, Water and Environment Journal, vol. 20, no. 2, pp. 55-64, Jun. 2006, DOI: 10.1111/j.1747-6593.2005.00007.x.
26. S. Munira, A. Farenhorst, K. Sapkota, D. Nilsson, C. Sheedy, “Auxin Herbicides and Pesticide Mixtures in Groundwater of a Canadian Prairie Province”, J Environ Qual, vol. 47, no. 6, pp. 1462-1467, Nov. 2018, DOI: 10.2134/jeq2018.05.0202.
27. A.J. Mwakalesi, I.D. Potter, “Removal of picloram herbicide from an aqueous environment using polymer inclusion membranes”, J Environ Chem Eng, vol. 8, no. 5, p. 103936, Oct. 2020, DOI: 10.1016/j.jece.2020.103936.

HERBICIDES DERIVED FROM PICOLINIC ACID – STRUCTURE, MECHANISM OF ACTION, ENVIRONMENTAL FATE

Abstract

Picolinic acid-derived herbicides, including clopyralid, aminopyralid, triclopyr, picloram, halauxifen, florpyrauxifen, and fluroxypyr, are characterized by the presence of a pyridine ring in their chemical structure. This feature is believed to play a key role in their ability to mimic natural plant hormones, specifically auxins. By overloading the plant's auxin-response mechanisms, these herbicides induce an 'auxin overdose,' ultimately leading to plant death. The environmental fate of picolinic acid herbicides depends on various factors, making it difficult to determine their exact half-life. However, they tend to persist in the soil and can even leach into groundwater.

Keywords: herbicides, structure, environmental fate, mode of action

HERBICYDY POCHODNE KWASU PIKOLINOWEGO – STRUKTURA, MECHANIZM DZIAŁANIA, LOSY W ŚRODOWISKU

Streszczenie

Herbicydy pochodne kwasu pikolinowego (chlopyralid, aminopyralid, triklopyr, pikloram, halauksyfen, florpyrauksifen, fluroksypyr), charakteryzują się obecnością pierścienia pirydynowego w swojej strukturze chemicznej. Uważa się, że element ten odgrywa kluczową rolę w ich zdolności do naśladowania naturalnych hormonów roślinnych – auksyn. Poprzez przeciążenie mechanizmów odpowiedzi na auksyny, herbicydy te wywołują „przedawkowanie auksyn", co ostatecznie prowadzi do śmierci rośliny. Losy w środowisku herbicydów kwasu pikolinowego zależne są od wielu czynników, dlatego trudno określić ich dokładny okres półtrwania, jednak mają tendencję do utrzymywania się w glebie, a nawet przenikania do wód gruntowych.

Słowa kluczowe: herbicydy, struktura, losy w środowisku, mechanizm działania

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DESIGN OF A HAND AND FOREARM REHABILITATION ORTHOSIS FOR SUBJECTS WITH IMPAIRED MANIPULATIVE ABILITY

1. Introduction

Intensive rehabilitation of motor functions is crucial for patients with reduced or lost grip strength. This is particularly important for tetraplegic patients, those who have suffered a stroke, and patients with spinal cord injuries. It has been proven that this type of rehabilitation not only improves hand grip function but also contributes to neurological recovery in the brain, which is beneficial for the patient's return to active daily life. The rehabilitation process involves actively or passively gripping and moving standardized objects. If there is insufficient strength in the upper limb, a rehabilitation assistant assists the patient in performing specific tasks. [1, 2]

1.1. Physiotherapy

Grip physiotherapy is a specialized form of physiotherapy aimed at restoring and improving the grip and movement function of the hands after injury, illness, or surgery. This type of therapy is commonly used for patients with hand, wrist, elbow, or shoulder injuries, as well as patients who have limited hand movement due to neurological problems such as stroke or spinal cord injury. Grip physiotherapy has several benefits: it helps restore hand control and coordination, reduces hand and joint pain, improves mobility, reduces the risk of complications, and improves their quality of life by helping them return to daily activities [3]. Exercises with a soft ball are an effective way of physical grip therapy. Using a soft ball reduces the risk of injury and provides patients with safety during exercise. For example, pressing a ball helps with

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hand muscle recovery, improves blood circulation, and helps strengthen the lumbar spine, which is especially important for people with spinal cord injuries because it helps prevent muscle atrophy. In addition, exercises with a soft ball help to improve the coordination and accuracy of grasping movements, as patients can perform different movements with different degrees of difficulty (Fig. 1). [4]

Fig. 1. Grip exercises with a soft ball. [5]
Rys. 1. Ćwiczenia chwytne z miękką piłką. [5]

Finger physiotherapy and the development of fine motor skills also deserve special attention because the ability to grasp an object is significantly affected by finger control. This training includes any movement or attempt to move the fingers, preferably in a pr ecise manner. For example, as shown in Fig. 2A, the patient may try to touch the thumb with each finger. However, such exercises require a certain degree of fine motor coordination and may not be feasible for patients with a severe hand manipulation disorder. Combining the bandage with finger flexion exercises is also beneficial for patients as it reduces swelling, pain or discomfort and improves motor development. The bandages themselves can have different stiffness and elasticity and are selected individually for the patient according to his movement abilities, needs and causes of the disease, to ensure the most effective use (Fig. 2B). [6, 7]

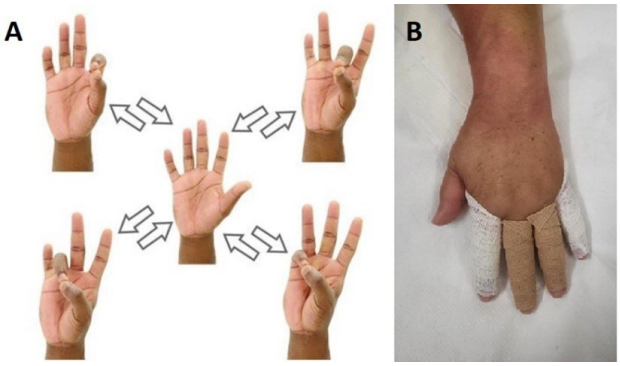

Fig. 2. Precise movements for the development of finger motor skills (A) and using different bandages on the fingers (B). [6, 7]
Rys. 2. Precyzyjne ruchy rozwijające sprawność motoryczną palców (A) i stosowanie różnych bandaży na palcach (B). [6, 7]

Common active hand movements are also used in daily physiotherapy and are completely safe for the patient [4, 6]. These exercises are aimed at restoring mobility, increasing range of motion, strength, and control in the wrist. Active wrist exercises can include a variety of movements such as flexion, extension, abduction and adduction of the wrist, pronation, and supination (Fig. 3). These movements can be performed at different intensities and in different planes, allowing patients to adapt the exercises to their needs and abilities. It can also be practiced with support on a table or stabilization surface.

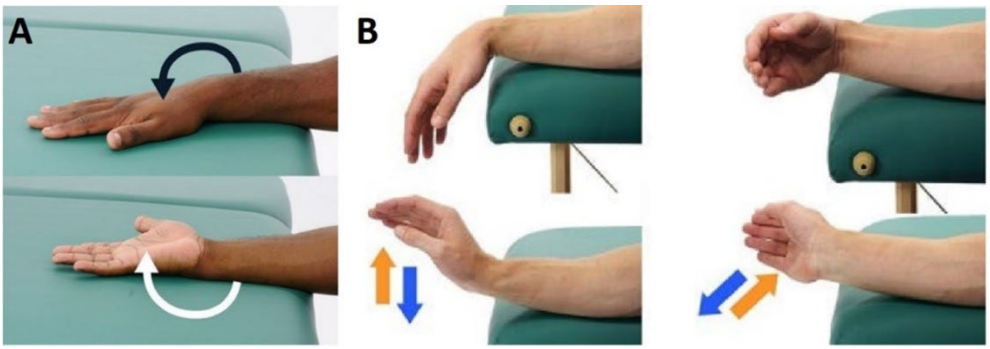

Fig. 3. Active movements in the wrist: (A) pronation and supination, (B) flexion and extension. [6]
Rys. 3. Aktywne ruchy nadgarstka: (A) pronacja i supinacja, (B) zgięcie i wyprost. [6]

Exercises with light weight help restore grip function and muscle strength of the upper limb (Fig. 4) [8]. During such training, the patient practices the grip movement as well as the mobility and control of the wrist. If it is difficult to move the hand while holding an object, it is possible to start with training to hold it statically in the hand.

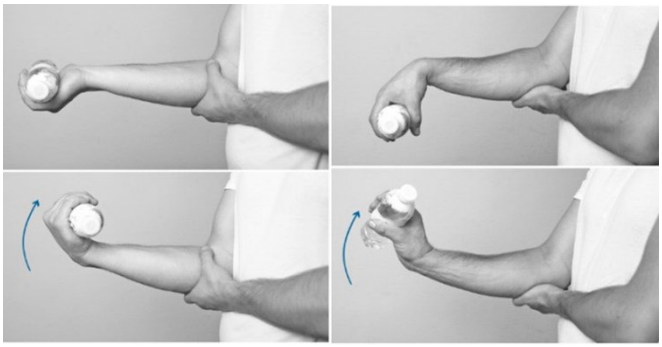

Fig. 4. Exercises with light weight. [8]
Rys. 4. Ćwiczenia z lekkim ciężarem. [8]

To eliminate the need for an assistant during the rehabilitation process and enhance the effectiveness process itself, special rehabilitative mechatronic orthoses have been developed to aid in the rehabilitation of hand motor functions. These devices, developed in scientific institutions worldwide, have been tested on patients with no or insufficient upper limb strength for gripping and have had a positive impact on overall health.

1.2. Robotic therapy

Robotic Therapy (RT) provides repeatable and intensive training and can improve the effectiveness of conventional therapy or physical therapy by providing treatment in a more precise, consistent, and detailed manner. RT uses robots and computer systems to improve mobility, strength, and control of the upper limb in people with impaired manipulative abilities. An example of RT is a recent study in which a group of tetraplegic patients used combined upper limb RT using the ArmeoPower device (Hocoma Inc., Volketswil, Switzerland), which trains the entire upper limb including the shoulder, elbow, and wrist, and the Amadeo device (Tyromotion Inc., Graz, Austria), which trains the hand. Training was performed in order from proximal to distal: ArmeoPower 20 minutes and Amadeo 20 minutes. ArmeoPower (Fig. 5) can support or assist the patient in movement by widening or narrowing the ROM (Range of Motion) according to the patient's therapeutic goals. This robotic device contains 21 games that can be divided according to therapeutic goals and joints. Each game can be adjusted in terms of difficulty (3 steps), progress time (2-5 min) and degree of hand support (0-100%). [9, 10].

Fig. 5. Training of the proximal upper limb with ArmeoPower [10]
Rys. 5. Trening proksymalnej części kończyny górnej z ArmeoPower [10]

Amadeo is a device that can rehabilitate fingers and hands of patients with distal upper limb dysfunction (Fig. 6). The Amadeo device moves the patient's fingers according to a pattern defined by the software. The treatment program includes continuous passive movement (CPM), CPM plus, assistive therapy, motor skills and memory. CPM provides training in “simultaneous thumb and finger movements” and “crossed thumb and finger movements”. In CPM plus, as an extended version of CPM, biofeedback is additionally offered. Biofeedback was offered by expressing the recorded finger force during flexion and extension exercises in the form of a smile, helping to motivate the patient to focus on their movements. In assistive therapy, the robotic device helps the patient complete flexion and extension actions until the side of the finger the patient is moving stops moving. Other Amadeo applications provide finger flexion

and extension training. In RT, the therapist chooses different programs with individual settings to train specific areas in which patients previously had problems with, or to strengthen weak muscles of the upper limb. [9, 10].

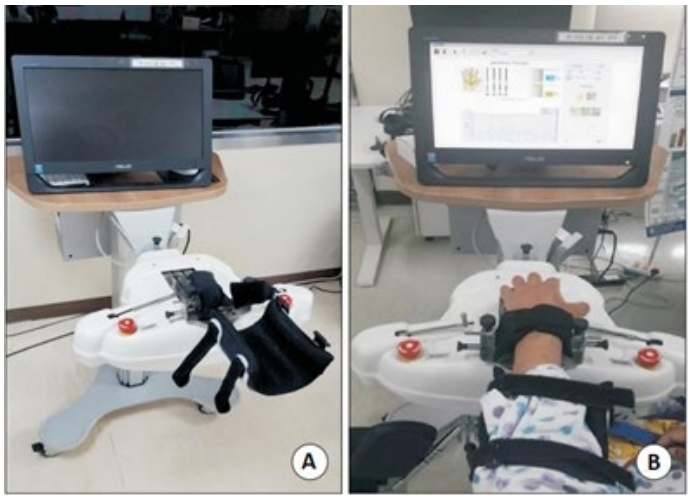

Fig. 6. Amadeo device (A), and hand and forearm training with Amadeo (B) [10]
Rys. 6. Urządzenie Amadeo (A) oraz trening dłoni i przedramienia z użyciem Amadeo (B) [10]

Studies have shown good results of the effectiveness of RT in patients with stroke or spinal cord injury, because of which patients lose the ability to control the upper limb [9, 11]. RT improves muscle strength and motor kinematics of the hand and wrist and is effective in rehabilitating the entire upper limb as well as the grip strength. This therapy is suitable for patients with a high degree of muscle damage, provides simple work for the rehabilitation assistant with the patient and is an interesting rehabilitation process thanks to the use of computer games, or virtual reality and biofeedback, which improve the patient's psychological state, which increases the patient’s treatment motivation.

1.3. Electrical muscle stimulation

The Functional Electrical Stimulation (FES) system is a four-channel surface stimulation device consisting of a software, portable stimulator with a programmed smart card, and self--adhesive muscle stimulation electrodes. FES therapy has been successfully used in patients with paralysis due to stroke or spinal cord injury [12]. Therapeutic exercises consist of task--oriented unilateral movements of the affected upper limb using electromyographic (EMG) impulses to reach, grasp and laterally lift cylindrical objects to different heights, depending on the improvement of the patient's dexterity and ROM (Fig. 7). During each exercise and the entire rehabilitation period, therapists can provide patients with a little movement support if needed [13].

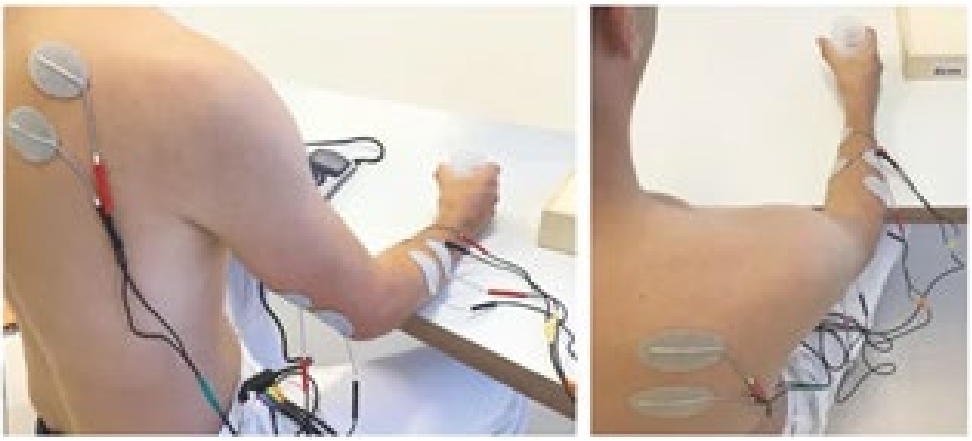

Fig. 7. Electrode placement for 4-channel EMG pulses during movements such as reaching, grasping, and laterally lifting cylindrical objects to different heights [12]
Rys. 7. Rozmieszczenie elektrod dla 4-kanałowych impulsów EMG podczas ruchów takich jak sięganie, chwytanie i boczne podnoszenie cylindrycznych przedmiotów na różne wysokości [12]

FES therapy allows people with limited or complete absence of voluntary movement in the wrist and fingers to perform simple tasks with muscle stimulation, and after completing a rehabilitation course, patients can voluntarily perform FES-trained activities on their own. However, this technology has some limitations. Limb muscles to be treated with FES must be accessible for placement of stimulation electrodes. There should not be considerable damage to the lower motor neurons or nerve roots in the stimulated muscle. In addition, the patient must have the cognitive ability to follow instructions and actively participate in the therapy process. The patient must not have any contraindications for the use of FES, such as metal implants at the stimulation site, a pacemaker, an open wound or a rash around electrode placement. [13]

In general, electrical muscle stimulation rehabilitation helps restore and strengthen weak or atrophied muscles after injury or illness, improves blood flow to tissues, which contributes to faster recovery and reduced inflammation, and can help increase sensitivity and sensation in affected areas, making it easier to perform movements and improve hand control. Electrostimulation of muscles can also be used as a supplement to other rehabilitation methods, which contributes to a faster and more effective recovery of the motor functions of the upper limb. [12, 13]

1.4. Mechatronic upper limb orthoses

Mechatronic orthoses are a valuable tool in hand rehabilitation for people with damaged or lost muscle strength. They significantly improve the physical therapy process for patients who are unable to perform training on their own and simplify training with a rehabilitation assistant. In general, mechatronic orthoses can be divided into two main groups:

1. static-progressive orthoses – allow passive movement of the body segment,

2. dynamic orthoses – ensure active movement of the body segment based on the energy source.

1.4.1. Static-progressive orthoses

The goal of the static-progressive orthosis is to gradually increase the ROM of the given body segment. This type of orthosis provides constant pressure or flexion/extension to the farthest point the joint can move. Once the tissues (joint, muscles, tendons, ligaments) have adapted to the position and flexion/extension no longer continues, the brace is adjusted to increase traction. This is repeated until the desired ROM is achieved. One of them is a static--progressive orthosis for the hand and wrist, which performs based on a developed assistive device in the shape of a shark's fin [14]. This device was developed using additive manufacturing and functions as a static progressive hand rehabilitation orthosis. Factors such as cost, weight, volume, stability of the hand, material, as well as tolerance and compliance of the device were considered during the development process. Such an orthosis has several applications, but primarily for people with contractures, it can be used to extend the wrist joint. As shown in Fig. 8A, the rehabilitation orthosis is attached to the body segment on the dorsal side of the forearm, and then the palm is extended by attaching the tape to the device. To ensure a stable progressive traction force, the tape is fixed to the highest position of the rehabilitation device, since the wrist joint extension angle will be limited from the beginning. When the condition improves, the tape is moved and fixed lower to provide sufficient torque and increase the tensile force. This application can increase the ROM of the wrist extension. Similarly, if this device is fixed on the volar side of the forearm, it can be used to increase flexion ROM of the wrist (Fig. 8B).

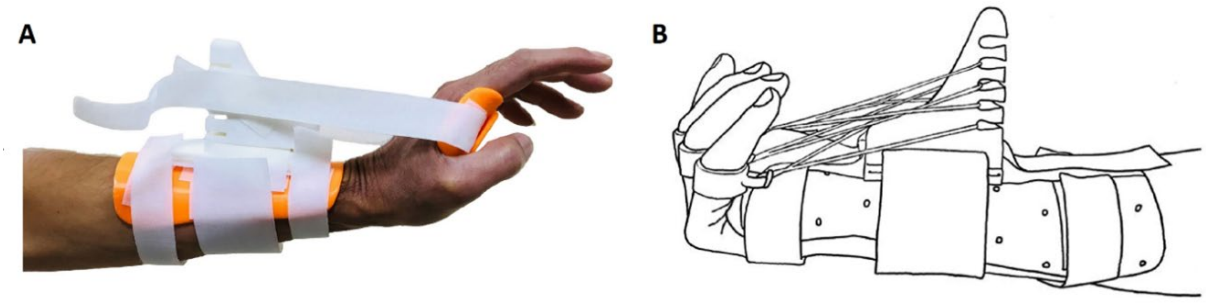

Fig. 8. Use of a radiocarpal joint extraction device in a patient with a fracture of the distal radius (A), and the use of the device for the metacarpal phalanx joint stretching (B) [14]

Rys. 8. Zastosowanie urządzenia do ekstrakcji stawu promieniowo-nadgarstkowego u pacjenta ze złamaniem dalszego końca kości promieniowej (A) oraz zastosowanie urządzenia do rozciągania stawu paliczka śródręcznego (B) [14]

The use of this device is universal, as patients who have problems controlling their own hand can have the basic position of the wrist joint in both hyperflexion and hyperextension. Hand rehabilitation is performed while wearing the device using a constant, progressive force that keeps the wrist in reverse flexion from the base position without the brace, keeping the muscles in constant mild tension, but in such a way that the patient does not feel pain. Such braces can also be used on fingers and thumbs for the same purpose.

Another example of a static-progressive orthosis is a splint (Fig. 9), which aims to reduce hand spasticity in patients with chronic stroke and to help manage spasticity during the motor recovery phase by constant flexion/extension. The splint is light weight, easy to manufacture, easy to operate and inexpensive. Stroke patients can also use it to wear at home as an additional training program that complements their rehabilitation in the hospital. The idea behind the development of this splint is to use a pulley as a drive and a fishing line as a connection between the static bases and the moving parts. This concept was inspired by the fishing mechanism that allows the reel to turn on the fishing line. The splint was manufactured using the FDM (Fused Deposition Modelling) method, and the ABS (Acrylonitrile Butadiene Styrene) polymer was chosen due to its high tensile strength and ductility compared to the material PLA (Polylactic Acid) polymer. [15]

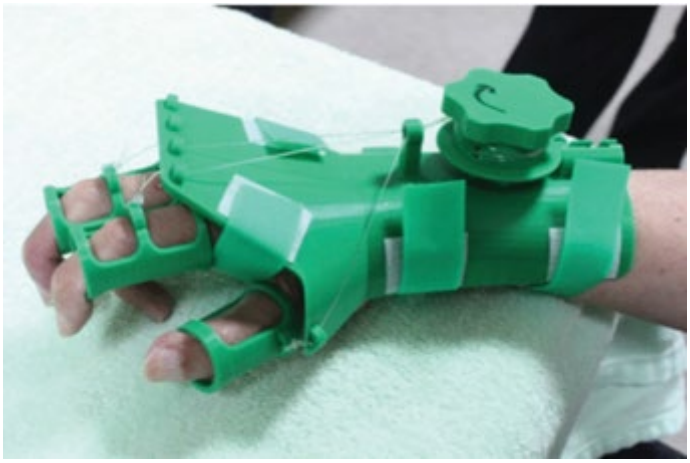

Fig. 9. Rehabilitation orthosis based on the pulley rotation design [15]
Rys. 9. Orteza rehabilitacyjna oparta na konstrukcji rotacji bloczka [15]

With this orthosis, it is possible to train diverse types of grips using all fingers, however, it focuses on the extension of three fingers (thumb, index, and middle finger), as their function is used most often in daily activities. When designing the tool, common patterns of small grip forms were used in which the finger and thumb are involved, such as key, scribe and pincer grip. Patients' hands usually try to clench into fists and the fingers curl inward due to spasticity, so this brace is designed to support the hand and fingers in an open position and gradually

reduce muscle tone. Users can spread their fingers and open their hands using a single-handed (non-injured side) rotating pulley design. In addition, they can use it in daily life [15].

1.4.2. Dynamic orthoses

Dynamic orthoses ensure active movement of a body segment based on an energy source. They can be driven by an electric motor and controlled by electromyographic (EMG) signals generated by the movement of undamaged muscles and sensed by sensors attached to them. This method helps control the orthosis on a fixed segment of the body using healthy muscles. An example of a dynamic hand and wrist orthosis is a 3D printed myoelectric hand orthosis for patients with lost upper limb muscle strength who are unable to perform individual movements independently (Fig. 10) [16]. SolidWorks software was used to create a 3D model of the orthosis, and it was produced on a FDM type 3D printer from PLA polymer material. The developed orthosis consists of 3 parts: forearm bracelet, hand orthosis and finger rings. The forearm brace consists of 2 parts, the dorsal and volar forearm splint. The dorsal forearm splint has a linear motor (L12-30F-4®, IR Robot Co., Ltd., Korea) that can generate a force of 30 N with a stroke length of 41 mm to control wrist extension. The volar forearm splint stabilizes the wrist joint and is connected to the dorsal forearm splint with a Velcro strap so that it can be adjusted to the subject's forearm. The wrist part wraps around the hand and is connected to the linear motor. When the motor is activated, the wrist is pulled toward the forearm, moving the wrist into extension. Rings are placed on the thumb, index, and middle fingers, and the palmar side of each ring is connected to the volar splint with a nylon thread. Guide channels were added on the volar side of each ring and arm brace to guide the nylon thread along the fingers to the volar forearm splint. When the wrist is moved into extension by the linear motor, the nylon thread is stretched, which strengthens the grip. Wrist extension results in simultaneous flexion of the interphalangeal and metacarpophalangeal joints of each finger, including the thumb. When the object is placed in the palm or between the fingers, the user can grasp it by activating the linear motor. This is the key mechanism of the orthosis that allows the device to be used by more people, including patients with a high degree of spinal cord injury who cannot control their wrist. The developed myoelectric orthosis is controlled by an electroencephalogram recorded in the muscles of the user's upper limb. A total of three sEMG (surface electromyography) electrodes are required for its operation: two are placed either on the ipsilateral biceps or on the upper trapezius muscle, depending on the subjects' comfort. The third, grounding electrode, is placed on the shoulder of the dominant hand [16].

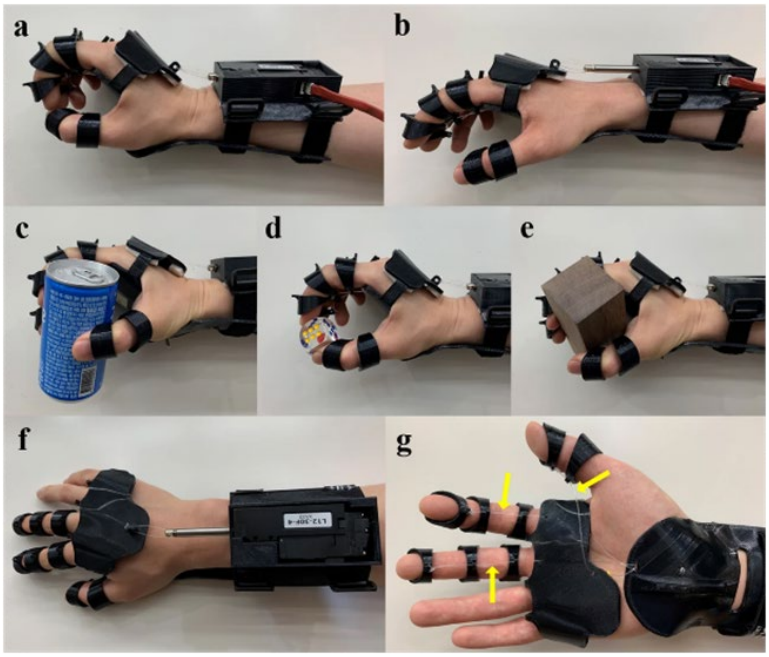

Fig. 10. Every movement of the 3D printed orthosis: (a) the linear motor is activated by sEMG signals, the wrist is extended into extension, executing a grip, (b) as the motor returns to its neutral position, the extended wrist and tension on the nylon thread are released and the hand returns to neutral, (c-e) the use of the orthosis for soda can, a cube, and a block of wood grasping, (f) top view of the orthosis, (g) bottom view of the orthosis, where arrows point to the nylon thread that connects the orthosis ring of each finger and the volar splint of the forearm [16]

Rys. 10. Każdy ruch ortezy drukowanej w 3D: (a) silnik liniowy jest aktywowany przez sygnały sEMG, nadgarstek jest rozciągany do wyprostu, wykonując chwyt, (b) gdy silnik powraca do pozycji neutralnej, rozciągnięty nadgarstek i napięcie na nici nylonowej zostają zwolnione, a ręka wraca do pozycji neutralnej, (c-e) użycie ortezy do chwytania puszki po napoju, kostki i klocka z drewna, (f) widok ortezy z góry, (g) widok ortezy z dołu, gdzie strzałki wskazują na nici nylonowe, które łączą pierścień ortezy każdego palca i szynę dłoniową przedramienia [16]

Another example of a mechatronic dynamic orthosis is a recently developed rehabilitation device, which consists of a hybrid system that performs active control of mobilization during articulation or assisted movement of the upper limb using electrical stimulation, as well as online characterization of EMG signals captured in the trapezius and deltoid muscles [17]. The constructed device was equipped with electronic devices as an all-wheel drive robot and was controlled in a decentralized manner using a set of state feedback algorithms (proportional derivative). The tested device (Fig. 11A) is intended for all joints of the upper limb: shoulder, elbow, wrist, and fingers. It consists of a shoulder supporting exoskeleton, a sleeve with FES electrodes and a hand orthosis (Fig. 11B). However, the patient can wear this orthosis without external mechanical support, depending on his needs and the degree of damage to the upper limb. The orthosis was made on a 3D printer from PLA material. The mechanical construction of the orthosis consists of four segments corresponding to the hand, forearm, shoulder, and shoulder support. The design also allows for length adjustment for the forearm area. [17].

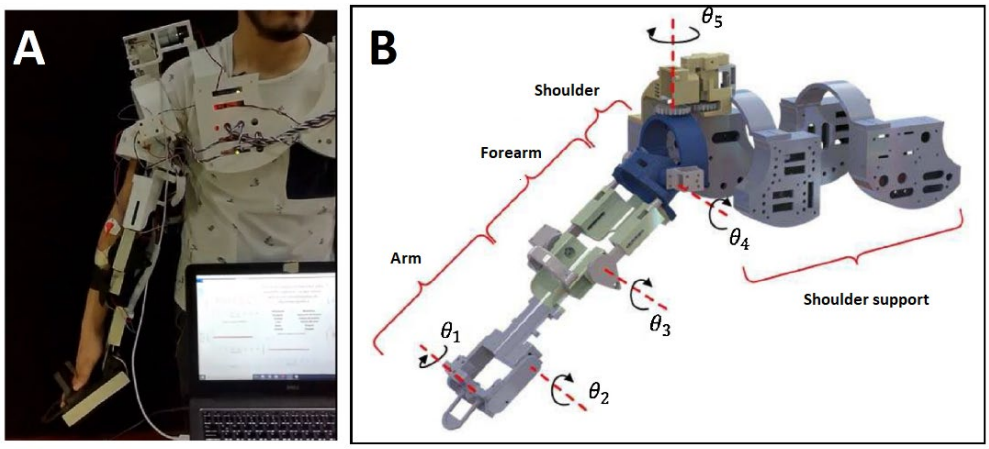

Fig. 11. (A) Device testing, (B) Mechanical construction of the orthosis [17]
Rys. 11. (A) Testowanie urządzenia, (B) Konstrukcja mechaniczna ortezy [17]

This active orthotic device assists in the rehabilitation of the upper limb by implementing a FES device triggered by an artificial neural network signal classifier [17]. This function offers a new alternative to the use of long-term hand rehabilitation. However, some functional movements of the upper limb can only be executed by a sequence of basic movements using the proposed system.

1.5. Exoskeletons

An exoskeleton is an electromechanical system that provides a person with additional strength or functional support to perform various limb actions. It can have different designs and purposes, but the basic idea is to help a person increase strength, endurance or perform a certain type of movement [18]. Exoskeletons are often used in medicine to rehabilitate patients with musculoskeletal disorders. The need for upper limb exoskeletons for therapy and assistance in daily life is highly dependent on the target group [19]. In adults, they have been assessed for different patient groups, such as spinal cord injury, muscular dystrophy or stroke. In the case of a child, it could be cerebral palsy. There are also general requirements for all target groups, which include criteria such as ease of use, ergonomic design, intuitive control, as well as design criteria such as required functions, ROM and kinematics, maximum closing force, duration of closing movement and weight [20]. An example of an upper limb exoskeleton is the children's exoskeleton PEXO for the hand and wrist, which is modified from the full-scale RELab tenoexo wearable exoskeleton (Fig. 12), intended for adults with functional disability of the hand due to neuromotor disorders. Therapy with this exoskeleton aims at supporting the use of the affected hand by training functional skills using intensive interventions based on goals and task-oriented activities, such as grasp therapy with assistive devices (e.g. cutlery, keys and writing aids). The

RELab tenoexo exoskeleton for adults can assist the user in the power, precision and lateral grips required to grasp many objects used on daily life basis [21]. It is completely wearable and can exert up to 5N of force on your fingertips, which is enough to grip a full 500ml water bottle. It can be intuitively controlled via forearm muscle EMG using the Myo armband (Thalmic Labs, Ontario, Canada) and its battery lasts for just over 1,000 grasp cycles, covering one hour of therapy. RELab tenoexo consists of a handheld module that attaches to the hand and a backpack that contains electronics, motors, and a battery. The backpack and handheld module are connected by a cable transmission system and can be fastened with a clip. In the hand module, three degrees of freedom enable forceful, precise, and lateral grasping: combined controlled flexion/extension of the index finger to little finger, individual flexion/extension of the thumb and manual opposition/reposition of the thumb. In the backpack, two DC motors drive the flexion/extension of the fingers and thumb. The motors are powered by a power supply and apply force at two pre-defined levels, either to close or to open. Force levels can be adjusted before opening or closing using a manual controller located on a small integrated control board. To switch between opening and closing the hand exoskeleton, either the Myo armband (via Bluetooth connection) or any TTL-trigger connected via standard audio connectors supplied in the backpack can be used. [20, 21]

Fig. 12. Exoskeleton RELab tenoexo [21]
Rys. 12. Egzoszkielet RELab tenoexo [21]

The PEXO children's exoskeleton, shown in Fig. 13, has the same features as the RELab tenoexo exoskeleton, with the difference that the size of the hand module and its design for children have been modified to resemble a crocodile, because the attractive appearance, as well as intuitive control with visual feedback linked to muscle activation, they should keep the user motivated during training in the clinic or at home and help improve residual hand function. The PEXO device can be attached to the hand in two ways depending on the functionality and therapeutic needs as well as the user's preferences. The first method, with straps for each finger

and wrist, which leaves the hand mostly open and provides sensory feedback when grasping objects. The second approach uses a Velcro glove that makes it easier to put on but completely encloses the hand. With the PEXO, the patient can grasp different objects such as cones, balls and cubes of varied sizes and weights and release them in various places. While the PEXO device helps with grasping movements, the occupational therapist guides the patient's hand when necessary. PEXO actively supports flexion, extension only when necessary and helps the thumb to be in an oppositional position. When EMG is used as a trigger, PEXO has the potential to improve physiological control. Despite disadvantages, such as greater complexity and increased weight of the backpack, PEXO can provide a complementary approach that not only supports targeted training or continuous passive movement therapy, but also assists with activities of daily living. [21]

Fig. 13. Grip therapy with physical exercises using the PEXO exoskeleton [21]
Rys. 13. Terapia chwytem z ćwiczeniami fizycznymi z wykorzystaniem egzoszkieletu PEXO [21]

Currently, few mechatronic orthoses are used in practice due to their complex design, operation, and high manufacturing costs. Therefore, it is necessary to design and produce a low--cost mechatronic rehabilitative orthosis with simple operation and customizable design. The aim of this research was to develop this device using CAx (Computer Aided Technologies) systems such as 3D scanning, CAD (Computer Aided Design) modelling and additive manufacturing.

2. Methods

The designed hand and forearm rehabilitation orthosis (Fig. 14) for people with impaired manipulative abilities consists of two parts:

1. finger orthoses,
2. orthosis for forearm and thumb.

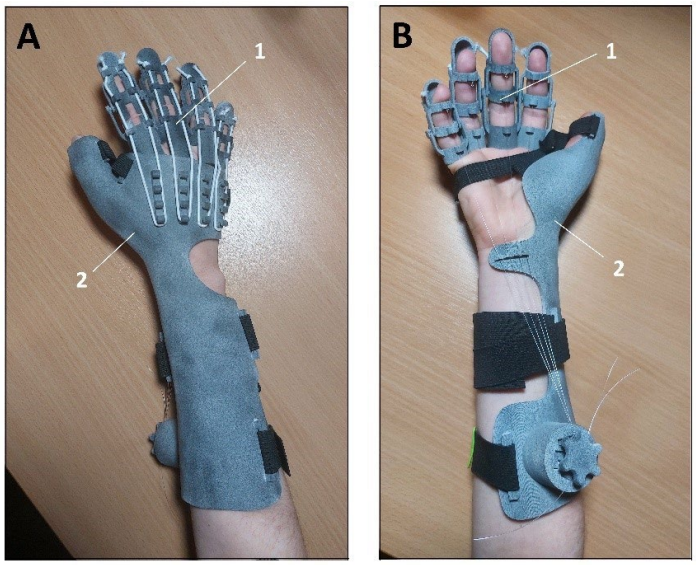

Fig. 14. The proposed rehabilitation orthosis design: (A) View of the orthosis from the dorsal side, (B) View of the orthosis from the palmar side. 1 – orthosis for the fingers, 2 – orthosis for the forearm and thumb.

Rys. 14. Proponowany projekt ortezy rehabilitacyjnej: (A) Widok ortezy od strony grzbietowej, (B) Widok ortezy od strony dłoniowej. 1 – orteza na palce, 2 – orteza na przedramię i kciuk

The forearm brace was designed in Meshmixer CAD software (Autodesk, San Francisco, USA) based on an STL (Standard Triangle Language) model from a 3D scan of the hand and forearm. The finger orthoses were designed in Solidworks CAD software based on manual measurements of parameters such as finger joint circumferences and finger length. The reason is the difficulty of accurately scanning each finger separately, and it is very difficult for patients with affected muscles of the upper limb.

2.1. 3D scanning

Scanning was performed using an ArtecEva (Artec 3D, Luxembourg, Luxembourg) handheld optical 3D scanner. The scanning process focuses on the dorsal side of the hand and thumb, but the entire forearm must also be captured because all sides of the forearm engage in the formation of the body of the orthosis. The goal of the proposed orthosis for a person with impaired manipulative ability is to ensure the execution of a grip. By design, only the fingers will move, so the thumb will be fixed in the starting position for the power grip. Therefore, it

should be in slight opposition to the fingers during scanning, with the wrist is in 5-10° extension (Fig. 15A). The upper limb was scanned in 90-degree flexion with the elbow resting on the table. Also, the hand was in 90° pronation from the basic anatomical position (Fig. 15B).

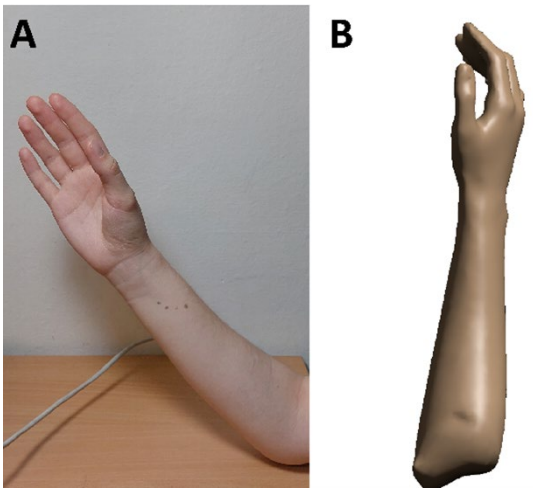

Fig. 15. (A) Position of the thumb, hand and forearm during the scan, (B) Resulting STL model of the hand and forearm from the scan, opened in Meshmixer software.
Rys. 15. (A) Position of the thumb, hand and forearm during the scan, (B) Resulting STL model of the hand and forearm from the scan, opened in Meshmixer software

A person with a disability of the muscles of the upper limbs is not able to extend and hold his hand independently, so during the scanning process, it is necessary for the patient's hand and forearm to be held by an assistant, as shown in Fig. 16. The assistant holds the hand and forearm of the scanned person in a way that with one hand he supports the proximal end of the forearm and the elbow, and with the other hand he supports the thumb and fingers in the desired position while the other person scans (Fig. 16). This method of scanning is suitable for the presented orthosis because, the palmar side of the hand is not used for the orthosis modelling. [25].

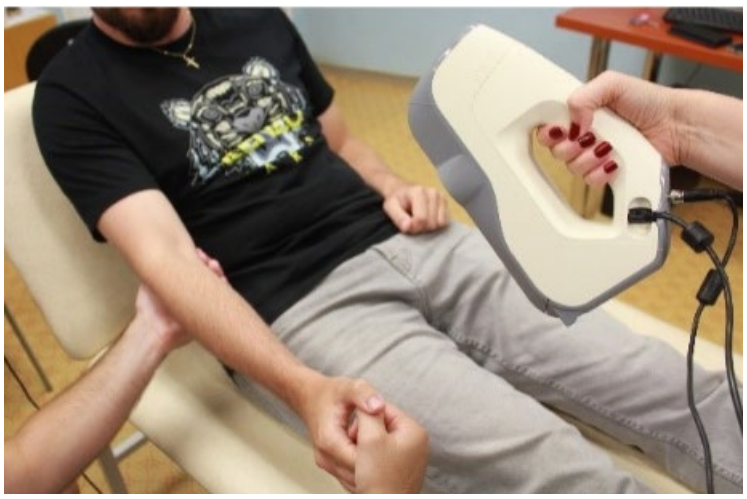

Fig. 16. Scanning of the hand and forearm using an assistant [25]
Rys. 16. Skanowanie dłoni i przedramienia z wykorzystaniem asystenta [25]

2.2. Finger orthoses design

The basis of the orthosis are three rings, placed on each of the joints of the finger directly in front of the corresponding joint (Fig. 17A). These rings are connected to each other by joints on the medial and lateral sides, so they do not dislocate on the finger, while bending in the finger joints is still possible (Fig. 17B). To prevent the orthosis from dislocating from its position when the finger is extended, the distal (end) ring was modelled with a cap rounded to the shape of the tip of the finger. The cap will be open on the palmar (bottom) side so that the surface of the objects is in direct contact with the fingertip (Fig.17C). Specific limiters were designed on the dorsal (upper) side in front and back to prevent hyperextension when pulling the fingers into extension using flexible threads (Fig. 17C, D).

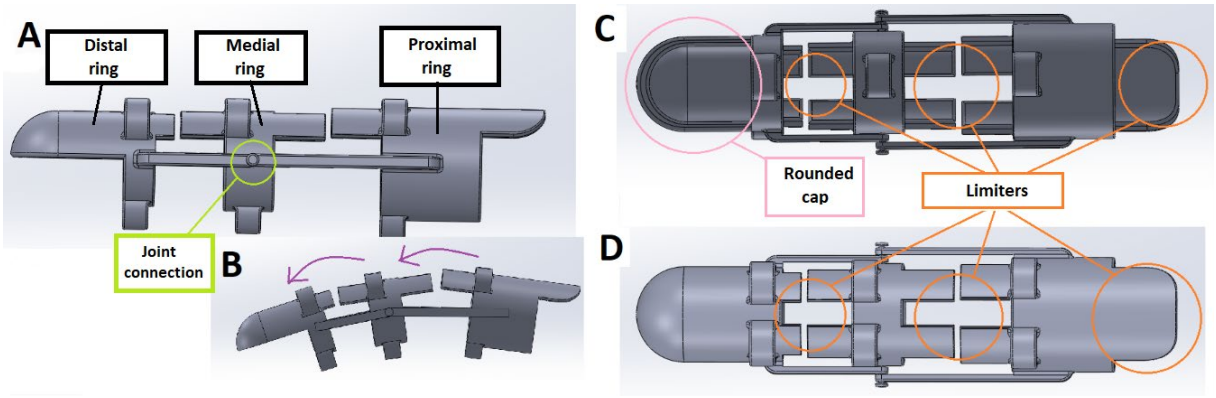

Fig. 17. (A) Lateral view of orthosis, (B) direction of bending (flexion), (C) bottom view, (D) top view
Rys. 17. (A) Widok boczny ortezy, (B) kierunek zgięcia (fleksja), (C) widok od dołu, (D) widok od góry

There are holes for the rigid and flexible threads on each of the rings. The dorsal (upper) flexible threads will perform the extension and will be connected in the form of a loop to the ridge on the dorsal part of the arm brace. On the palmar side, the rings have an opening for the guidance of a rigid thread, which is fixed on the distal ring and by pulling it will bring the finger into flexion (Fig. 18A). The mechanism of the joint is as follows: the distal and proximal rings are connected to the medial ring by means of two rods that are attached to them, but they can rotate about a small pin that protrudes from the medial ring, which allows the movement of the individual components relative to each other in one plane. The pin is extruded at the end to prevent rods from accidentally falling out of the pin axis (Fig. 18B).

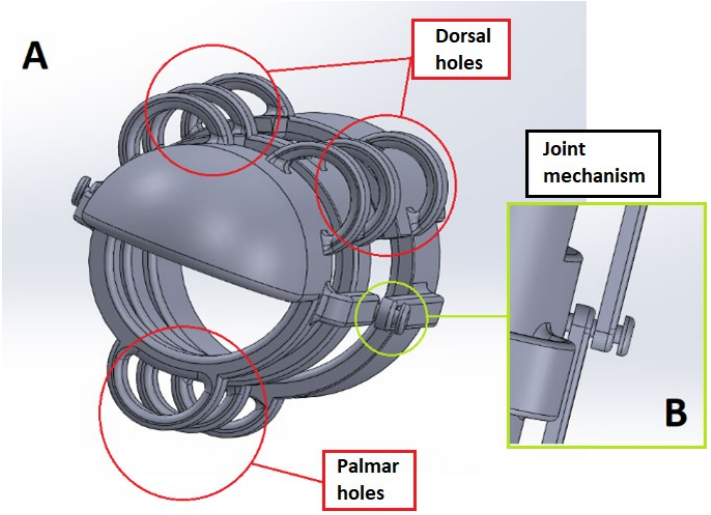

Fig. 18. (A) Illustration of ring holes, (B) joint articulation mechanism
Rys. 18. (A) Ilustracja otworów pierścieniowych, (B) mechanizm artykulacji stawu

2.3. Hand and forearm orthosis design

The construction of the orthosis is specially designed to allow the assistant to easily put the orthosis on a patient with affected muscles of the upper limbs. Instead of forcing the hand into a tubular orthosis, this design allows it to be fitted to the segment using elastic straps that are secured with a Velcro. To place the straps, clips were attached to the orthosis construction (Fig. 19).

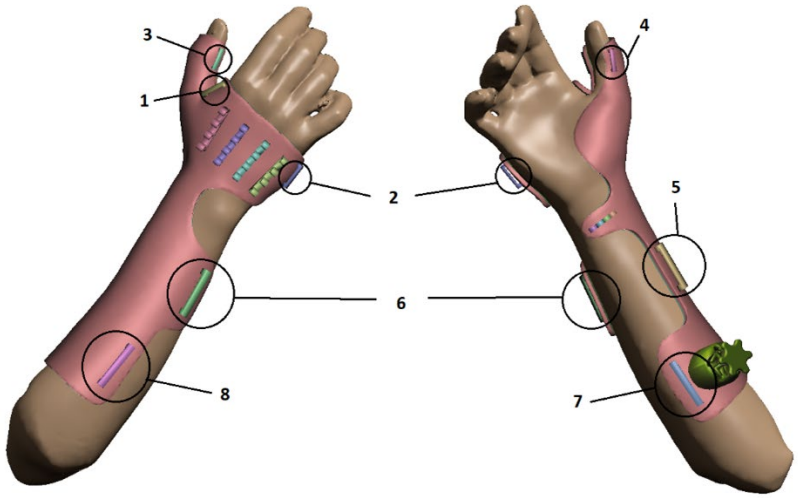

Fig. 19. Numbering of clips on the orthosis. A strap on the palmar side of the palm will pass through clips 1-2, a smaller strap will pass through clips 3-4, catching the thumb and keeping it in slight opposition. Wider straps pass through clips 5-6 and 7-8 and secure the brace on the forearm
Rys. 19. Numeracja klipsów na ortezie. Pasek na dłoniowej stronie dłoni przechodzi przez klipsy 1-2, mniejszy pasek przechodzi przez klipsy 3-4, chwytając kciuk i utrzymując go w lekkim opozycji. Szersze paski przechodzą przez klipsy 5-6 i 7-8 i zabezpieczają ortezę na przedramieniu

On the dorsal side of the orthosis there are four ridges to which flexible threads from finger orthoses are attached. Each ridge has four protrusions (degrees of fixation) – in the position of full extension of the fingers, the threads will be fixed on the most distal one of them. During flexion, the dorsal flexible threads can be extended, but if this is not enough, they can be fixed to the more proximal ridge (Fig. 20A). On the volar (inner) side of the forearm, the orthosis has four holes through which the dorsal rigid threads will pass, which will pull the fingers in flexion during the grip movement (Fig. 20B). The proximal end of the threads will be connected to a specially designed flexion control mechanism that is also located on the volar side of the forearm orthosis segment. When the rehabilitation assistant rotates the mechanism, the rigid threads tighten and pull the finger orthoses into flexion (Fig. 20C).

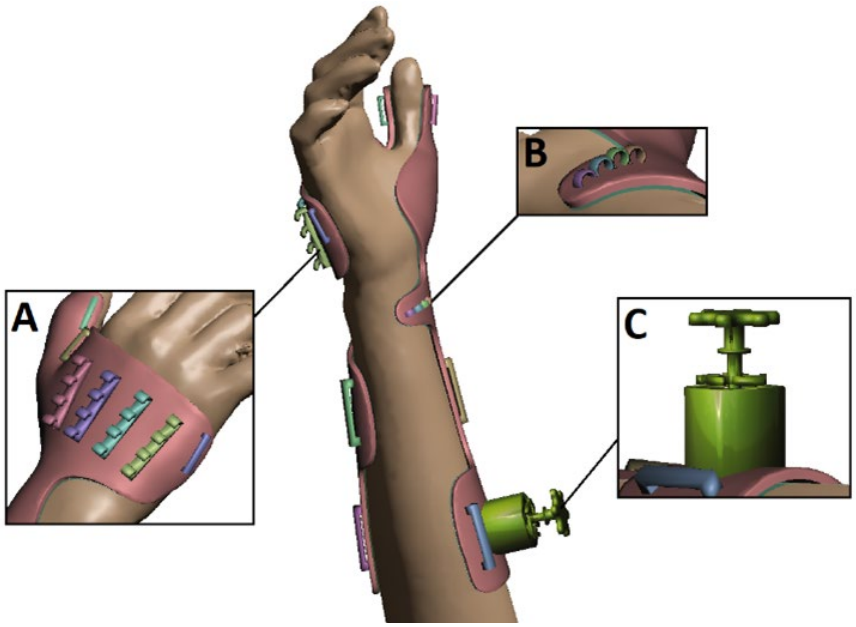

Fig. 20. Elements of the forearm orthosis mechanism: (A) ridges for attachment of flexible extension control threads, (B) holes for dorsal rigid threads, (C) finger flexion mechanism

Rys. 20. Elementy mechanizmu ortezy przedramienia: (A) grzbiety do mocowania elastycznych nici sterujących wyprostem, (B) otwory na sztywne nici grzbietowe, (C) mechanizm zginania palców

2.4. Finger flexion mechanism

In the open position, the mechanism can rotate and wind the rigid threads around itself (Fig. 21A). The threads pass through a small hole under the handle of the mechanism and are tied into a knot on the opposite side. A ring is created under this hole, which ensures that the threads are wound only on the upper shaft and do not slide. At the end of the thin shaft there is an attachment that prevents the handle of the mechanism from jumping out of the base. The main principle of the mechanism is its blades, which fit into grooves of the same shape (Fig. 21A, section A-A). When the rehabilitation assistant has wound the threads sufficiently,

the mechanism is closed by inserting the blades into the grooves (Fig. 21B). Limiters are placed to fix the tension of the rigid threads inside the opening for the blades: when the mechanism tries to unwind back under the influence of the flexible dorsal threads, which will constantly pull the fingers into extension, the blades will hit the limiters inside, which will not allow them to unwind further (Fig. 21B, section A-A). The mechanism will also not be able to open, because in the stopped position the contour of the blades does not coincide with the contour of the grooves (Fig. 21B, section B-B). Such a mechanism makes it possible to freely stretch the rigid threads and fix them in any position.

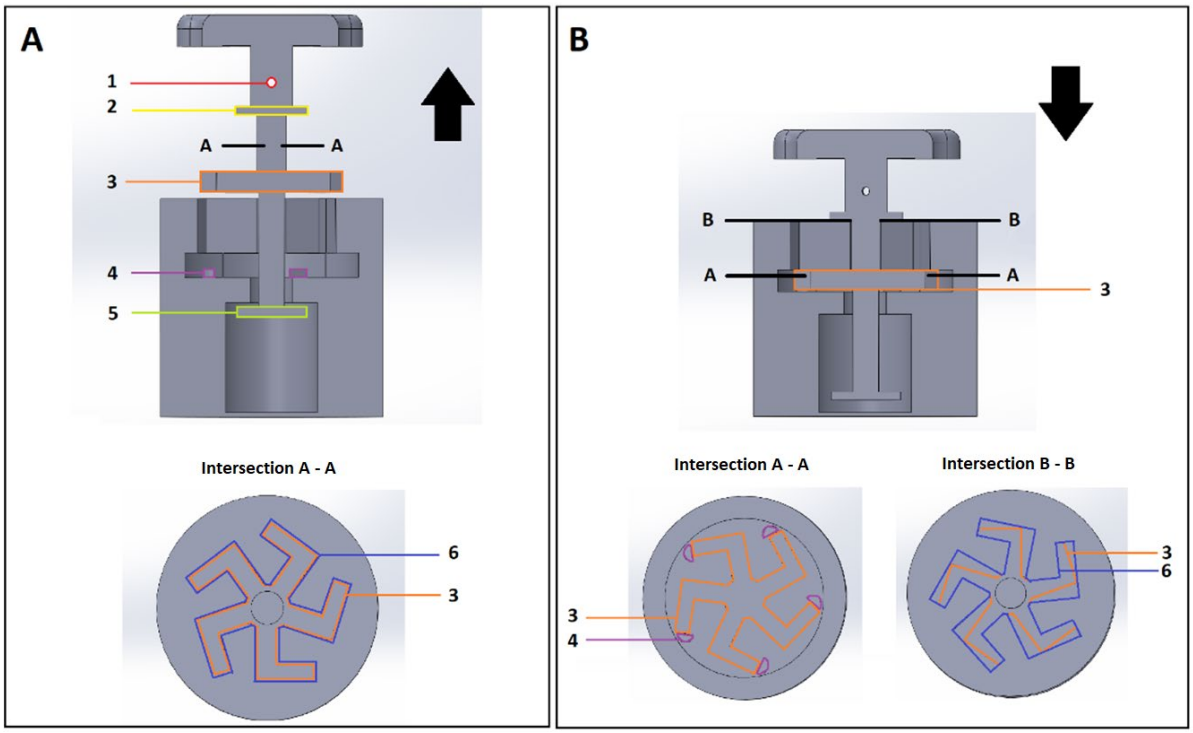

Fig. 21. Illustration of the finger flexion control mechanism: (A) the open position, (B) the closed position. 1 – hole for fixing rigid threads, 2 – limiting ring, 3 – blades, 4 – limiters, 5 – attachment to prevent the handle from jumping out, 6 – grooves

Rys. 21. Ilustracja mechanizmu sterowania zginaniem palców: (A) pozycja otwarta, (B) pozycja zamknięta. 1 – otwór do mocowania sztywnych nici, 2 – pierścień ograniczający, 3 – ostrza, 4 – ograniczniki, 5 – mocowanie zapobiegające wyskakiwaniu rączki, 6 – rowki

2.5. Additive manufacturing

The HP MJF 5200 (Hewlett-Packard, California, USA) 3D printer, which uses PA12 (Hewlett-Packard, California, USA) polyamide material, was chosen for the manufacturing of the prototype. MJF (Multi Jet Fusion) is an innovative 3D printing technique developed by Hewlett-Packard (HP) which uses a powder delivery system, ink jets and infrared energy source. MJF uses a system of infrared lamps as an energy source to melt the desired area, which is penetrated with a melting substance that can absorb infrared energy. The MJF printer uses

a series of 30 ink jets (which can release up to 350 million drops per second at maximum print resolution) that layer various liquid agents onto the print surface [22]. The printing process involves depositing a thin layer of powder polymer material onto a build platform, followed by the selective application of a fusing agent in the areas where the powder particles are to be joined, and the addition of a detailing agent to the outline of the pattern. The melting agent is selectively applied to the top layer of the polymer powder of the part being formed to increase the absorption of heat by irradiation of the desired part of the material. It contains solvents and surfactants that contribute to the expected moisturizing and thermal properties. A layer of powder moistened with a melting agent is combined under the influence of an infrared energy source to form a part. A second chemical, a detailing agent, is injected at the boundary of the layer contours to create a barrier for heat absorption and transfer outside the molten zone. The detailing agent prevents the phenomenon of coalescence leakage, i.e. the coalescence of liquid droplets in another liquid, thereby improving the resolution and accuracy of details. When printing large parts, the release agent is also poured into certain areas of the large parts to partially prevent excessive heat build-up. [23].

5. Results

The first prototypes (Fig. 22) diameters of the rings were chosen correctly, where the wall thickness of 2 mm is optimal in terms of strength and thinness, and thus comfortable of wearing on all fingers. It was also necessary to increase the width of the lateral bars that fit through the holes, so they were widened from 1 mm to 5 mm. To improve the strength of the joint, the thickness of the lateral bars was also increased from 1 mm to 1,8 mm. The joint mechanism on the prototype broke, which was caused by small gaps between the elements of the joint model, for example, the distance between the rods on the pin were 0,2 mm, which was insufficient. Leftover polyamide powder got stuck in these gaps, because of which the elements of the joint mechanism stuck together, and when trying to get the remaining powder out and flexing the finger with the brace, the joint broke. When designing a finger brace, the main task is to make it as narrow as possible so that the braces do not rub against each other when worn. It was because of this effort to reduce the width that there were problems with the gaps in the first printing. Also, in Fig. 22A it is possible to see how the distal joint bars protrude too much, while the proximal ones are pressed into the rings. This placement of the rods is not suitable when using the entire orthosis, as the distal joint rods will bump into each other, so this issue was also addressed in the second prototype design.

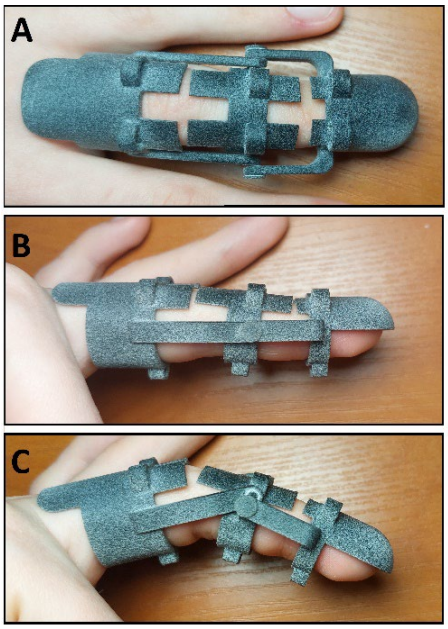

Fig. 22. The first finger rings prototype (A) from the dorsal view, from the lateral view in extension (B) and in flexion(C)

Rys. 22. Pierwszy prototyp pierścieni palcowych (A) z widoku grzbietowego, z widoku bocznego w wyproście (B) i w zgięciu (C)

In the second prototype (Fig. 23), the joint bars were swapped with each other, so that none of them protrudes significantly more than the other and are at the same level. To ensure successful printing, the gaps between the elements of the joint mechanism were increased from 0,2 to 0,4 mm, which had almost no effect on the width of the orthosis and allowed to successfully print a fully functional finger orthosis. It was also decided to slightly lengthen the most proximal limiter, as the previous length was insufficient to adequately prevent hyperextension of the finger. The second prototype is the last of the finger orthosis prototypes and is the final version of the middle finger orthosis. Considering all the errors from the previous print and the parameters of the final prototype, orthoses for the other fingers were designed.

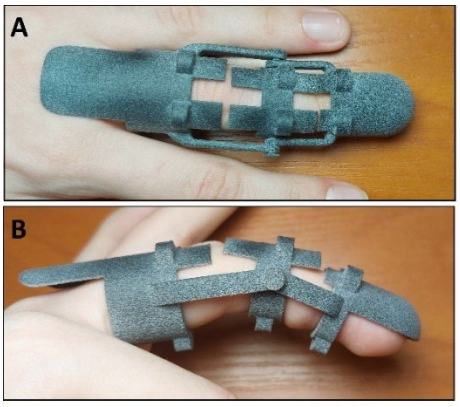

Fig. 23. The second finger rings prototype from the dorsal view (A), and from the lateral view in flexion (B)

Rys. 23. Prototyp pierścienia drugiego palca w widoku grzbietowym (A) i w widoku bocznym w zgięciu (B)

To test the functionality of the finger flexion control mechanism, a model of the mechanism was first manufactured separately (Fig. 24A, B). The diameter of the base of the mechanism was chosen to be 35 mm. The mechanism itself was printed in the open (unlocked) position to prevent the blades and grooves from sticking together due to the joining of the polyamide powder in the small gap between them. The first print of the finger flexion control mechanism turned out to be fully functional, with only one obstacle: due to clogged polyamide powder in the cavity of the base, the mechanism could not be closed at first, but it was only necessary to remove the remaining unjointed powder that remained inside the model. After the successful first prototype was printed, the entire forearm brace was printed along with a model of the finger flexion control mechanism (Fig. 24C).

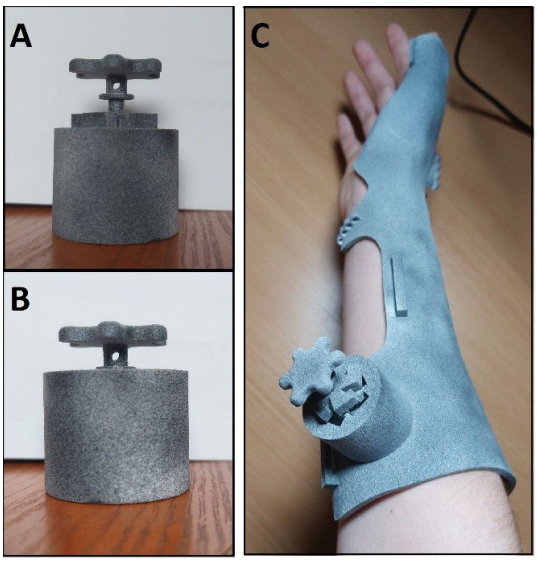

Fig. 24. The finger flexion control mechanism prototype in the open position (A), in the closed position (B), and attached to the forearm brace (C)
Rys. 24. Prototyp mechanizmu sterowania zgięciem palca w pozycji otwartej (A), w pozycji zamkniętej (B) i przymocowany do ortezy przedramienia (C)

4. Discussion

From a practical point of view, scanning the body surface using 3D scanners is a suitable method for designing orthotic devices because it is non-contact, faster, more detailed and more comfortable for the patient compared to the traditional method of data collection [24]. 3D modelling of orthoses and their subsequent 3D printing is an ideal technology to produce low--cost individual orthotic aids, especially upper limb orthoses. The advantages that this technology offers allow for greater creativity and personalization, while also providing room for new possibilities for control mechanisms in terms of movement efficiency [25].

Creating a 3D model of an orthosis in CAD software based on a positive obtained from a 3D scan of a certain body segment is a simple and effective way of developing an orthosis with the possibility of simple correction of the orthosis construction if necessary. The scanning process itself was quick and an accurate positive of the hand and forearm was obtained, on which the orthosis could then be designed in the CAD software and adjusted as desired. The only downside to using portable 3D scanners that it needs must be connected to a suitable computer using a cable, which limits the distance between the computer and the scanned object and limits the freedom of movement of the person scanning the subject.

The orthosis developed in this work was originally planned to be printed using SLS (Selective Laser Sintering) technology. The first two prototypes of the finger orthosis were printed on a SLS type 3D printer EOS P 396 (EOS Group, Hamburg, Germany), which uses two 70W CO2 lasers, which allows fast and accurate printing of all elements of the orthosis. This printer has a build area of 150 litres and prints at a speed of up to 5,6 litres per hour, which means that parts are printed quickly. During printing, the input energy is effectively homogenized, resulting in consistent mechanical properties and dimensional accuracy of the entire orthosis. Overlapping laser zones also ensure smooth production without visible edges. However, after attempting to print a third prototype on an HP MJF 5200 3D printer, which also uses PA12, it was decided to print the entire orthosis with this technology for several reasons. Firstly, the surface roughness of the part is minimized when printed with MJF, so the surface of the orthosis was smoother to the touch, and secondly, the white polyamide powder turns grey due to the use of an infrared lamp, which will make the printed orthosis look less dirty when it´s actively used.

The developed orthosis is not intended for permanent home use and is only an aid for the rehabilitation of the affected upper limb. In grasp therapy, the patient would have to practice grasping movements and try to grasp different objects, but even if the patient could grasp an object in his hand, he/she would not be able to grasp objects with a hard, smooth surface, such as a glass cup, because the holes at the bottom would interfere for nylon ropes. Therefore, this orthosis is more suitable for training with soft objects, such as an elastic ball or plasticine. This problem could be solved by making the lower holes inside the walls of the rings, but this would require an increase in their thickness, which would significantly affect the width of the finger brace, and thus the comfort. The developed rehabilitation orthosis does not use a power source and for its functionality it uses a specially developed mechanism that will be controlled by the patient's rehabilitation assistant.

5. Conclusion

Based on the need of people affected by the manipulative ability of the upper limbs to use auxiliary orthoses during rehabilitation to improve the results of physiotherapy, the comfort of the patient and the assistant during work, the concept of developing individual hand and forearm orthoses for the given patients was investigated. The developed rehabilitation orthosis was created using the CAD/CAM method, specifically 3D scanning, CAD modelling and subsequent additive manufacturing. The CAD/CAM method was chosen because it provides the possibility of constant corrections and changes in the design, allows to precisely reproduce the patient's anatomical segments and consider his/her individual needs. Each component of the final orthosis was made on a 3D printer of the MJF type from polyamide polymer material, only the threads for controlling the orthosis flexion mechanism and the elastic and Velcro straps must be added manually.

Future research includes optimalization of the rehabilitation orthosis design, application of surface EMG sensors and electric step motor mechanism for the finger flexion control, and practical testing of the orthosis on a patient with affected manipulative ability of the upper limb.

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Bibliography

1. Harvey L.A., Glinsky J.V., Chu J.: Early and intensive motor training to enhance neurological recovery in people with spinal cord injury: trial protocol, t. 6, nr 11 (2023), DOI: 10.1038/s41393-023-00908-z.
2. Kabir R., Sunny M.S.H., Ahmed H.U., Rahmati M.: Hand Rehabilitation Devices: A Comprehensive Systematic Review, t. 13, nr 7 (2022), DOI: 10.3390/mi13071033.
3. Negahban H., Aval S.B., Moradi A., Kachooei A.R.: Effectiveness of physiotherapy plus acupuncture compared with physiotherapy alone on pain, disability and grip strength in people with carpal tunnel syndrome: A randomized clinical trial., t. 35 (2023), DOI: 10.1016/j.jbmt.2023.04.033.
4. Kowalczewski J., Chong S.L., Galea M.P., Prochazka A.: In-home tele-rehabilitation improves tetraplegic hand function, t. 25, nr 5 (2011), DOI: 10.1177/1545968310394869.
5. Theraband hand exerciser – Antistresový Posilovač Ruky, (2023), https://www.gymsport.sk/produkt/theraband-hand-exerciser-antistresovy-posilovac-ruky-original-usa-farba-stupen-zlta-stupen-2/.
6. Hand exercises for spinal cord injury: How to improve function, (2022), https://www.flintrehab.com/hand-exercises-for-spinal-cord-injury/.

7. Santandrea S., Benassi M., Tedeschi R.: Comparison of short-stretch bandage and long-stretch bandage for post-traumatic hand edema, t. 111 (2023), DOI: 10.1016/j.ijscr.2023.108854.
8. Exercises after a wrist fracture, (2024), https://baldinelli.ua/ua/articles/uprazhnenija-posle-pereloma-zapjastja.
9. Jung J.H., Lee H.J., Cho D.Y.: Effects of Combined Upper Limb Robotic Therapy in Patients with Tetraplegic Spinal Cord Injury, t. 43, nr 4 (2019), DOI: 10.5535/ARM.2019.43.4.445.
10. Qassim H.M., Wan Hasan W.Z., A Review on Upper Limb Rehabilitation Robots, t. 10, nr 19 (2020), DOI: 10.3390/APP10196976.
11. Keller U., Schölch S., Albisser U.: Robot-assisted arm assessments in spinal cord injured patients: a consideration of concept study, t. 10 nr 5 (2015), DOI: 10.1371/JOURNAL.PONE.0126948.
12. Schick T., Kolm D., Leitner A.: Efficacy of Four-Channel Functional Electrical Stimulation on Moderate Arm Paresis in Subacute Stroke Patients – Results from a Randomized Controlled Trial, t. 10, nr 4 (2022), DOI: 10.3390/healthcare10040704.
13. Kapadia N., Moineau B., Moineau B., Popovic M.R.: Functional Electrical Stimulation Therapy for Retraining Reaching and Grasping After Spinal Cord Injury and Stroke., t. 14 (2020), DOI: 10.3389/FNINS.2020.00718.
14. Huang L.Y., Wang T.H., Wang T.H.: Printing a static progressive orthosis for hand rehabilitation, t. 84, nr 8 (2021), DOI: 10.1097/JCMA.0000000000000568.
15. Yang Y.-S., Emzain Z.F., Huang S.-C.: Biomechanical Evaluation of Dynamic Splint Based on Pulley Rotation Design for Management of Hand Spasticity, t. 29 (2021), DOI: 10.1109/TNSRE.2021.3068453.
16. Yoo H.-J., Lee S., Kim J.-H.: Development of 3D-printed myoelectric hand orthosis for patients with spinal cord injury, t. 16, nr 1 (2019), DOI: 10.1186/S12984-019-0633-6.
17. Medina F., Perez K., Cruz-Ortiz D.: Control of a hybrid upper-limb orthosis device based on a data-driven artificial neural network classifier of electromyography signals, t. 68 (2021), DOI: 10.1016/J.BSPC.2021.102624.
18. Gull M.A., Bai S., Bak T.: A review on design of upper limb exoskeletons, t. 9, nr 1 (2020), DOI: 10.3390/ROBOTICS9010016.
19. Boser Q.A., Dawson M.R.W., Schofield J.S.: Defining the design requirements for an assistive powered hand exoskeleton: A pilot explorative interview study and case series, t. 45, nr 2 (2021), DOI: 10.1177/0309364620963943.
20. Haider F., Kadhim D.A., Hussein J.S.: A comparative review of upper limb exoskeletons for rehabilitation, (2024), DOI: 10.1063/5.0205039.
21. Bützer T.: PEXO-A pediatric whole hand exoskeleton for grasping assistance in task--oriented training, (2019).
22. Tagliaferri V., Trovalusci F., Guarino S., Venettacci S., Environmental and Economic Analysis of FDM, SLS and MJF Additive Manufacturing Technologies, t. 12, nr 24 (2019), DOI: 10.3390/MA12244161.
23. Kim H., Zhao Y., Zhao L., Process-level modeling and simulation for HP's Multi Jet Fusion 3D printing technology, [w:] IEEE 2016.
24. Štefanovič B., Ondrejová B., Lucia B.: Comparison of Optical Handheld 3D Scanners Suitable for Prosthetic and Orthotic Applications, (2022), DOI: 10.15221/22.06.
25. Belvoncikova D., Bednarčíková L., Michalíková M.: Development of Mechanism for Finger Prosthesis, t. 24, nr 4 (2020), DOI: 10.21496/AMS.2020.028.

DESIGN OF A HAND AND FOREARM REHABILITATION ORTHOSIS FOR SUBJECTS WITH IMPAIRED MANIPULATIVE ABILITY

Abstract

This work presents the design and development of a hand and forearm rehabilitation orthosis aimed at improving motor function in patients with impaired manipulative ability due to conditions such as tetraplegia, stroke, and spinal cord injuries. The orthosis is intended to support intensive rehabilitation, which is crucial for restoring grip strength and enhancing neurological recovery. Various physiotherapeutic approaches, including grip exercises, robotic therapy, and electrical muscle stimulation, are explored in conjunction with the orthosis. The work also discusses the role of mechatronic devices, such as static-progressive and dynamic orthoses, in facilitating rehabilitation without the need for constant assistance. The innovative design incorporates elements such as 3D printing and myoelectric control to provide customizable and effective solutions for enhancing upper limb function. Preliminary results indicate that the orthosis should significantly contribute to the rehabilitation process, offering improved patient outcomes and greater independence in daily activities.

Key words: rehabilitation, orthosis, 3D scanning, CAD modelling, additive manufacturing

PROJEKT ORTEZY REHABILITACYJNEJ DŁONI I PRZEDRAMIENIA DLA OSÓB Z UPOŚLEDZONĄ ZDOLNOŚCIĄ MANIPULACYJNĄ

Streszczenie

Niniejsza praca przedstawia projekt i rozwój ortezy rehabilitacyjnej dłoni i przedramienia mającej na celu poprawę funkcji motorycznych u pacjentów z upośledzoną zdolnością manipulacyjną z powodu takich schorzeń jak tetraplegia, udar i urazy rdzenia kręgowego. Orteza ma wspierać intensywną rehabilitację, która jest kluczowa dla przywrócenia siły chwytu i poprawy neurologicznej regeneracji. Różne podejścia fizjoterapeutyczne, w tym ćwiczenia chwytu, terapia robotyczna i elektryczna stymulacja mięśni, są badane w powiązaniu z ortezą. Praca omawia również rolę urządzeń mechatronicznych, takich jak ortezy statyczno-progresywne i dynamiczne, w ułatwianiu rehabilitacji bez konieczności stałej pomocy. Innowacyjny projekt obejmuje elementy takie jak drukowanie 3D i sterowanie mioelektryczne, aby zapewnić dostosowywalne i skuteczne rozwiązania w celu poprawy funkcji kończyn górnych. Wstępne wyniki wskazują, że orteza powinna znacząco przyczynić się do procesu rehabilitacji, oferując pacjentom lepsze wyniki leczenia i większą niezależność w codziennych czynnościach.

Słowa kluczowe: rehabilitacja, orteza, skanowanie 3D, modelowanie CAD, produkcja addytywna

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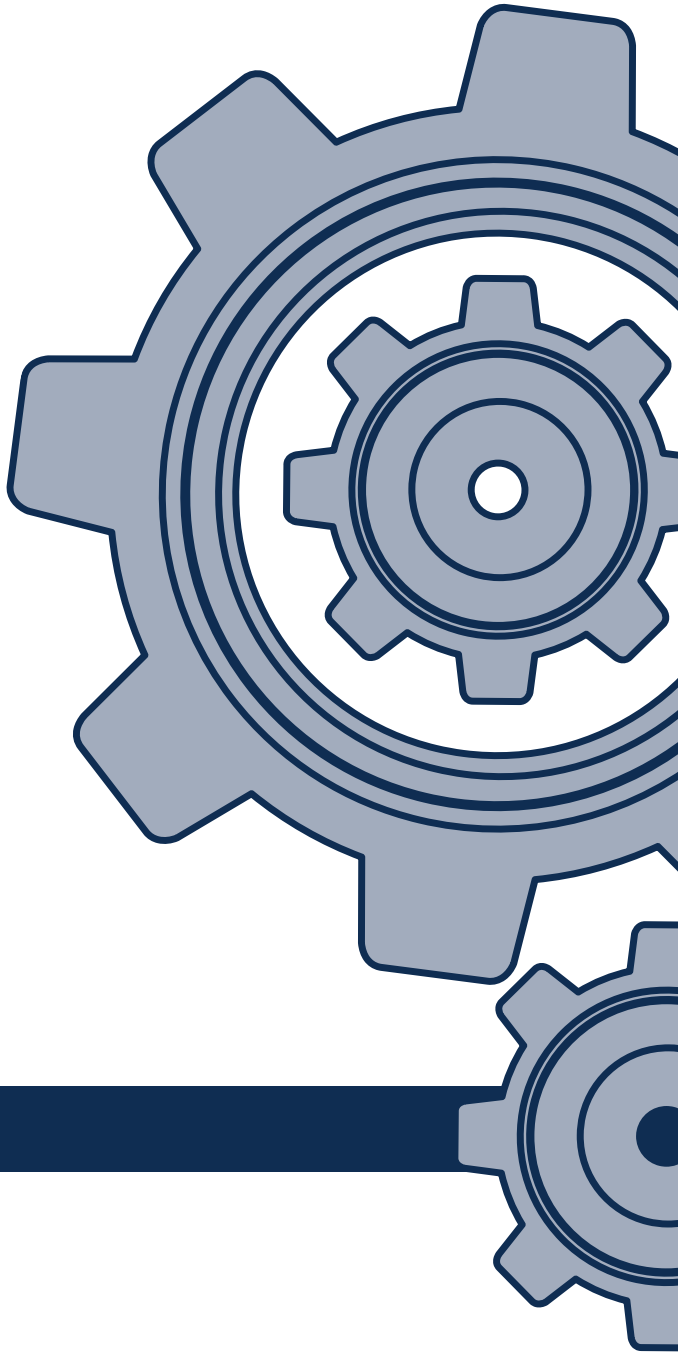

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