

JOURNAL OF CASTING & MATERIALS ENGINEERING



AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY FACULTY OF FOUNDRY ENGINEERING



AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY PRESS KRAKOW 2021

Head of Publishing of AGH University of Science and Technology Press Jan Sas

Editorial Board of Journal of Casting & Materials Engineering:

Editor-in-Chief

Beata Grabowska, AGH University of Science and Technology, Poland

Vice-Editor in Chief

Karolina Kaczmarska AGH University of Science and Technology, Poland

Co-editors

Giuliano Angella, National Research Council of Italy, Institute ICMATE, Italy Artur Bobrowski, AGH University of Science and Technology, Poland Peter Futas, Technical University of Kosice, Slovakia Daniel Gurgul, AGH University of Science and Technology, Poland Bożena Tyliszczak, Cracow University of Technology, Poland

Language Editor Aeddan Shaw

<u>Technical Editor</u> Agnieszka Rusinek

Cover Designer Małgorzata Biel

The articles published in the Journal of Casting & Materials Engineering have been given a favorable opinion by the rewievers designated by the Editorial Board.

www:

https://journals.agh.edu.pl/jcme/

© Wydawnictwa AGH, Krakow 2021



AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY PRESS

KRAKOW 2021

Wydawnictwa AGH (AGH University of Science and Technology Press) al. A. Mickiewicza 30, 30-059 Kraków tel. 12 617 32 28, 12 638 40 38 e-mail: redakcja@wydawnictwoagh.pl http://www.wydawnictwa.agh.edu.pl

Contents

A Study of The Properties of Forming Mixtures Containing Polystyrene Wastes 1 Magdalena Głąb, Sonia Kudłacik-Kramarczyk, Anna Drabczyk, Beata Grabowska, Bożena Tyliszczak	
Magdalena Głąb, Sonia Kudłacik-Kramarczyk, Anna Drabczyk, Beata Grabowska, Bożena Tyliszczak	.4
Deuta Grabowska, Dozena Tynszezak	
Physicochemical Investigations of Hydrogels Containing Gold Nanoparticles Designed for Biomedical Use 2	20
Katarzyna Major-Gabryś, Sabina Puzio, Agata Bryłka, Jadwiga Kamińska	
The Influence of Various Matrixes on the Strength Properties of Moulding Sands with Thermally Hardened Hydrated Sodium Silicate	
for the Ablation Casting Process 3	31

A STUDY OF THE PROPERTIES OF FORMING MIXTURES CONTAINING POLYSTYRENE WASTES

Olena Dan^{a*}, Larysa Trofimova^b

^a The John Paul II Catholic University of Lublin, Department of Environmental Engineering, ul. Ofiar Katynia 8b, 37-450 Stalowa Wola, Poland ^b The State Higher Education Institution "Pryazovskyi State Technical University", Department of Theory of Metallurgical Processes and Foundry Engineering, vul. Universytets'ka 7, Mariupol 87555, Ukraine *e-mail: olena.dan@kul.pl

© 2021 Authors. This is an open access publication, which can be used, distributed and reproduced in any medium according to the Creative Commons CC-BY 4.0 License requiring that the original work has been properly cited.

Received: 21 March 2021/Accepted: 11 May 2021/ Published online: 9 June 2021 This article is published with open access at AGH University of Science and Technology Press

Abstract

Expanded polystyrene is widely used as a material for packaging, in modern construction as a heat and sound insulation layer, in thermal insulation systems for buildings, as well as tanks and pipelines. It is additionally used in foundry engineering for the production of models which are gasified during the production of castings from ferrous and non-ferrous alloys under the contact with liquid metal. The use of expanded polystyrene products is associated with waste generation, both in production and in consumption. About 40–50 kg/person of polystyrene waste is generated per year. The peculiarity of polymeric wastes is their resistance to aggressive environments. They do not rot and the destruction processes in natural conditions proceed rather slowly, with the formation of harmful substances that poison the environment. Therefore, the problem of the processing of waste from polymeric materials is of great importance, not only from the standpoint of environmental protection, but also due to the fact that in conditions of a shortage of polymer raw materials, this waste becomes a powerful raw material resource. This article describes the prospects for recycling expanded polystyrene wastes in foundry engineering. In this work, the properties of molding and core sands containing a combined binder, consisting of a solution of expanded polystyrene wastes in turpentine and clay were investigated, and their main characteristics (weight during stretching and crumbling) were determined. Molding and core mixtures, which contain only a binder in the form of a solution of expanded polystyrene in turpentine, have a crude strength of not more than 0.01 MPa. The introduction of a mixture of clay in the amount of 2–3% allows a crude strength of the mixture of up to 0.05 MPa to be obtained. After drying, the investigated mixtures containing a solution of expanded polystyrene wastes and clay have a tensile strength of up to 2.1 MPa. Mixtures into which a solution of polystyrene wastes and clay was introduced have an insignificant gas capacity and satisfactory gas permeability.

Keywords:

waste, solution, polystyrene, turpentine, strength limit, sprinkling, residual strength

1. INTRODUCTION

The use of products made of polymeric materials is inextricably linked with the generation of wastes, both in the field of production and in the field of consumption. The peculiarity of polymer waste is their resistance to aggressive environments. Such materials simply do not rot. The processes of their destruction in natural conditions are quite slow, with the formation of harmful substances that poison the environment. In 2016, the global production of polystyrene and expanded polystyrene (EPS) was around 14.7 and 6.6 million metric tons per annum [1].

The problem of processing and recycling polymeric waste is currently of great importance, not only from the standpoint of environmental protection but also due to the fact that in conditions of shortage of polymeric raw materials, such wastes become a powerful raw material resource.

The properties of sand-clay molding mixtures containing a solution of polystyrene waste in turpentine as a component are the object of the study. The aim of this study is to improve the properties of sand-clay molding and core mixtures by using a solution of EPS in turpentine as a binder.

2. USE OF EXPANDED POLYSTYRENE AND THE FORMATION OF ITS WASTE

EPS can be found in many areas of modern life. EPS is widely used as a material for food packaging and storage. This fact emphasizes the hygienic properties of EPS, the properties of which do not change over time. EPS packaging often contains meat, fish, frozen or fresh vegetables, and beverages. Almost all packaging for household electronics is currently made of EPS. It is widely used in modern construction as a heat and sound insulation layer in systems of warming of houses and other buildings, and also capacitive devices and pipelines [2–5]. EPS is also used in foundry engineering to obtain models under gasification in contact with liquid metal in the production of castings from ferrous and nonferrous alloys [6–10]. Up to 10% of raw materials goes to waste during the production of gasified models by the method of thermoplotter cutting of polystyrene block [11].

3. RE-USING OF EPS WASTE

EPS packaging accounts for 40% of all household waste and does not decompose. Therefore, the use of such packaging is associated with the generation of waste totaling approximately 40–50 kg/year per person [11]. EPS wastes do not decompose during deposition in landfills and cause great damage to the soil. An alternative method is incineration. However, compounds are released during combustion which cause acid rain and is detrimental to the environment. Ash is also formed during combustion which is easily sprayed with air over a large area. Such ash causes great harm when inhaled, leading to pulmonary poisoning and irritation.

Generally, re-using, mechanical recycling, chemical recycling, and energy recovery have been the four main options conventionally-used for the reclamation and recycling of plastics. EPS contains more than 98% of air, making its recycling uneconomical and inexpedient [12].

These are the following priority areas for the re-use of EPS waste [13–17]:

- · polystyrene coating for waterproofing,
- · protective and decorative polystyrene coverings,
- polystyrene coatings for pottery,
- paints and varnishes for painting,
- thermocompaction of polystyrene waste,
- · composite materials with expanded polystyrene matrix,
- binder component for molding and rod mixtures.

It should be noted that molding and rod mixtures based on the binder have easy knockout and high strength [18–23]. EPS wastes are mainly used in foundry engineering as a component for molding and core mixtures in the form of solutions at the metallurgical enterprises of Ukraine and nearby countries.

The preparation of solutions of EPS in organic solvents is due to a multiple decrease in the initial volume of expanded polystyrene and a significant increase in the volume of the solution compared to the volume of the solvent. Therefore, the preparation of polystyrene solutions is a convenient way to compact it. The most commonly used solvent for polystyrene wastes is gum turpentine [24]. Turpentine dissolves polystyrene wastes well and has low volatility.

As a result of a number of studies [20–23], the technology of EPS recycling was created. It is possible to make modern, low-toxic binding materials for the production of sand molding and core mixes, and also coverings of molds using EPS wastes. It makes it possible to improve and develop new, more efficient and cost-effective metal casting processes. In addition, the use of EPS wastes is of great environmental importance, as it is about reducing the amount of such wastes in landfills [25–29].

If the low volatility of gum turpentine is a positive factor from the point of view of the requirements of sanitary working conditions, it is negative from the perspective that there is a technological need to ensure the accelerated hardening of forms and cores, since this demands the compulsory removal of any solvent from mix. There are a number of ways to remove the liquid composition from the mixture, including vacuuming and blowing the mixture with dry heated air. The temperature exposure during drying in ovens is the most affordable method [26–28]. Analyzing the use of an EPS solution as a binder for molding and core mixtures, a number of problems can be identified that are associated with the implementation of this scheme into production.

The most significant problem is technical. The use of binder in a "pure" form provides a raw strength of mixtures of no more than 0.01 MPa. It is known that if the strength of mixtures in the raw state is very low – less than 0.01 MPa, it requires the use of additional special equipment-drivers, equipment necessary to move the manufactured product to the driver, subsequent transportation and heat treatment to obtain the required technological strength, which increases the cost of production as well as lengthening the technological cycle of manufacturing casting. The solution to this problem may be the application of a combined binder containing additional liquid glass or clay to the EPS solution [27–30].

4. MATERIALS AND METHODS

In this study, research was carried out by dissolving EPS waste PSBS-25 in turpentine (Technical Specification No. 24.3-30959 201-001-2004). The choice of PSBS-25 samples is justified by the fact that it is used in the manufacture of models for Lost Foam technology by means of thermoplotter cutting. PSPB-25 is the most common type of expanded polystyrene due to its low density, and therefore a low ash residue after combustion and low carburization of steel. 30% of the used polystyrene foam is scraped off. Therefore, disposal of polystyrene foam wastes is an urgent problem. Dissolving them with turpentine is a regulated and environmentally friendly process. Turpentine vapors are environmentally neutral, unlike nitro solvents.

The quartz sand grade K2 was used as a grain base for the preparation of mixtures. A clay from deposit of Chasiv Yar was used as a binder in the form of a dry powder.

The mixture was prepared in a paddle mixer. First, the dry components were mixed for 5 minutes, and then a solution of foam plastic in turpentine was added and mixed for 10 minutes.

Standard test samples were made using the 2M030 laboratory device for the production of standard samples of foundry mixture. Drying of the samples was performed in a chamber dryer model for 1 hour at a temperature of 150°C.

Compression and tensile tests were performed on standard samples on a universal model device 5070A. Determination

of gas permeability was carried out using the accelerated method DSTU 29234.11-91 by passing room temperature air through a standard sample of the test material on the model device 042-M. The gas-forming capacity of the mixture was determined in accordance with GOST 23409.12-78 – "Molding and rod mixtures. Method for determining gas solubility".

Scattering was determined on standard samples according to DSTU 23409.9-78: in 10 minutes after preparation of mixtures and production of samples, in an hour, in 3 hours and after 24 hours. Residual strength was determined by heat shock in the temperature range 150–800°C.

The hygroscopicity of the samples was determined according to GOST 23409.10-78.

5. RESULTS AND DISCUSSION

5.1. Dissolution of EPS in turpentine

It is known from the literature [17–20] that the best strength properties of foundry mixtures are given by 38–40% solution of EPS in turpentine.

Preparation of such a solution from EPS waste in turpentine showed the first positive result of the study on their utilization, namely that there is a sharp decrease in the volume of waste.

Figure 1 shows the volume of 40 grams of EPS waste and the volume of the solution obtained after dissolution to obtain the desired 40% concentration (ingredients ratio EPS/turpentine = 40 g/60 g).



Fig. 1. The volume of 40 grams of EPS waste: a) before dissolution; b) after dissolution

5.2. Investigation of the properties of molding mixtures containing EPS wastes and clay as a binder

In this study, the possibility was investigated of obtaining molding of a sufficient raw strength by introducing small additives of molding clay mixtures with a binder solution of EPS waste in turpentine.

In the preparation of mixtures, 1.5, 2.0 and 3.0% clay was administered. Figure 2 shows the effect of clay content on the raw compressive strength, and Figure 3 on the dry tensile strength of mixtures.

From the figures it is visible that the introduction of clay in the investigated mix allows us to obtain a crude durability of more than 0,01 MPa. So, the possibility of manipulation of cores without additional technological operations and special equipment is provided. Increasing the clay content from 1.5% to 3.0% leads to an increase in the raw compressive strength of the samples from 0.01 MPa to 0.05 MPa. At the same time, the tensile strength of dry samples increases insignificantly from 2.07 MPa to 2.10 MPa.



Fig. 2. Influence of clay content on crude compressive strength of mixtures



Fig. 3. Influence of clay content on the dry tensile strength of the mixture

Measurement of the gas capacity of the studied mixtures of 2% clay showed their insignificant gas evolution (10 cm³/g), and gas permeability (275 units). The hygroscopicity of these mixtures was 0.14%, which makes it possible after storage to keep the rods and molds for a long time without compromising their properties.

The obtained results were compared with the available literature data [20] on the strength of the mixture with different compositions. It was found that the strength of the mixture with an EPS waste binder is at the level of existing analogues with resins, and exceeds them in terms of manufacturability and harmful effects on the environment. Residual strength was determined on samples of a mixture containing 3% clay, after heating to 150, 200, 250, 300 and 400°C. The test results of the samples under compression are shown in Figure 4.



Fig. 4. Residual strength of samples after heating

The compressive strength of this mixture after exposure to 150°C for 1 hour exceeds 3 MPa.

The curve in Figure 4 shows that the investigated mixture begins to lose strength intensively at 250°C ($\sigma = 0.3$ MPa). Presumably this is due to the thermal destruction of the polystyrene film that binds the grains of sand. After heating to 300°C, the mixture significantly loses strength ($\sigma = 0.08$ MPa), and after heating to 400°C, the samples were destroyed in the furnace.

5.3. Investigation of the effect of small impurities of EPS solution in turpentine on the properties of standard sand-clay mixtures

The study was performed on a sand-clay mixture containing 10% clay as a binder. Additionally, a 40% solution of EPS in turpentine was introduced into the mixture (this corresponded to 0.4% in terms of polystyrene). Samples of the control mixture that did not contain polystyrene were examined at the same time. The bulkiness and residual strength (which characterizes the knockout) of mixtures were investigated.

The bulk (surface strength) characterizes the ability of a mold or rod to maintain its configuration under the influence of a jet of liquid metal, as well as other forces that occur, for example, during transportation or assembly of the mold. One way to reduce the scattering is to increase the clay content in the mixture. The inevitable consequence of increasing the clay content in the mixture is a deterioration of its knockout and pliability, which is undesirable.

The aim of this stage of the study was to use small impurities of a solution of expanded polystyrene in turpentine to obtain a sand-clay mixture with high scattering rates and low residual strength. Figure 5 in semi-logarithmic coordinates shows a graph of the change in the scattering of the control and experimental mixture over time. During the experiments, it was observed that the samples from the test mixture had a scatter less than the control in all cases.



Fig. 5. Changes in the scattering of the control (1) and experimental (2) mixture over time τ

The figure shows that after exposure for 1 hour, the scattering of both mixtures increases slightly, after 3 hours decreases significantly and, after 24 hours, grows again.

Figure 6 shows the dependence of the residual strength of the test mixture in comparison with the control from the heating temperature of the samples.



Fig. 6. Residual strength of samples from the control (1) and experimental (2) mixtures

Figure 6 shows that the mixture has greater tensile strength than the control in the initial state of the test. That is, the admixture of expanded polystyrene solution acts as a strengthening component.

It was found that at heating temperatures < 600°C, the test specimens also had a residual strength greater by 15–20%

than the control ones. This is most likely due to the incomplete destruction of the polystyrene molecules. The completion of this process at a higher temperatures ($600-800^{\circ}$ C) provided a decrease in the compressive strength of the experimental samples in comparison with the control by 10-12% (Fig. 6), so the mixture of these samples had better knockout. Analysis of Figure 6 shows that a small amount of EPS waste acts as a strengthening and softening component of the sand-clay mixture.

6. CONCLUSIONS

A large amount of waste is generated under the production and consumption of expanded polystyrene. Possessing chemical inertness, this waste accumulates in the environment and harms it. Expanded polystyrene wastes can be used as a raw material for the production of waterproofing, protective and decorative coatings for wood and pottery, paints and varnishes for painting, the basis of composite materials, a binder component for molding and core mixtures in foundry production.

Based on the research, it was found that:

- 1. Molding and core mixtures containing only a binder in the form of an EPS solution in turpentine, have a raw strength of not more than 0.01 MPa.
- The introduction of clay into the mixture in the amount of 2.0–3.0% allows us to obtain a crude strength of the mixture of up to 0.05 MPa.
- 3. After drying, the test mixtures, in which a solution of EPS waste and clay was introduced, have a tensile strength from 2.07 MPa to 2.10 MPa.
- 4. Mixtures with the EPS waste solution and clay have insignificant gas capacity and satisfactory gas permeability.
- 5. The study of the effect of small impurities of the EPS solution in turpentine on the properties of sand-clay mixtures have revealed that the studied mixtures (in comparison with the control) have less scattering and residual strength.

REFERENCES

- [1] Uttaravalli A.N., Dinda S. & Gidla B.R. (2020). Scientific and Engineering Aspects of Recycling and Reuse of Expanded Polystyrene Waste for Various Potential Applications: A Review. *Process Safety and Environmental Protection*, 137, 140–148. Doi: https://doi.org.10.1016/j.psep.2020.02.023.
- [2] Ramli Sulong N.H., Mustapa S.A.S. & Abdul Rashid M.K. (2019). Application of expanded polystyrene (EPS) in buildings and constructions: A review. *Journal of Applied Polymer Science*, 136, 47529. Doi: https://doi.org.10.1002/app.47529.
- [3] Khlyestova O.A. & Dubovkina M.Yu. (2016). Enerhoefektyvnisť vykorystannya teploizolyatsiynykh materialiv dlya uteplennya zhytlovykh budynkiv. Marketynhovi komunikatsiyi ta lohistyka u sferi tekhnolohiy enerhozberezhennya v Ukrayini ta sviti: Mizhnar. naukovo-prakt. konf.: 9.11.2016. Dnipro, Dnipro: Dnipropetrov. nats. un-t im. O. Honchara, 20–23 [Хлєстова О.А., Дубовкіна М.Ю. (2016). Енергоефективність використання теплоізоляційних матеріалів для утеплення житлових будинків. Маркетингові комунікації та логістика у сфері технологій енергозбереження в Україні та світі: Міжнар. науково-практ. конф.: 9.11.2016. Дніпро Дніпро: Дніпропетров. нац. ун-т ім. О. Гончара, 20–23].

- [4] Savkin Yu.V. (2012). Rossiyskiy rynok penopolistirola: zadachi, dostizheniya, perspektivy. Stroiteľnyne materialy, 1, 1–3 [Савкин Ю.В. (2012). Российский рынок пенополистирола: задачи, достижения, перспективы. Строительные материалы, 1, 1–3].
- [5] Shulyak V.S., Rybakov S.A. & Grigoryan K.A. (2001). Proizvodstvo otlivok po gazifitsiruyemym modelyam. Moskva: MGIU [Шуляк В.С., Рыбаков С.А., Григорян К.А. (2001). Производство отливок по газифицируемым моделям. Москва: МГИУ].
- [6] Оzerov V.A., Shulyak V.S. & Plotnikov G.A. (1970). Lit'ye po modelyam iz penopolistirola. Moskva: Mashinostroyeniye [Озеров В.А., Шуляк В.С., Плотников Г.А. (1970). Литье по моделям из пенополистирола. Москва: Машиностроение].
- [7] Stepanov Yu.A. & Grishin D.S. (1976). Lit'ye po gazifitsiruyemym modelyam. Moscow: Mashinostroenie [Степанов Ю.А., Гришин Д.С. (1976). Литье по газифицируемым моделям. Москва: Машиностроение].
- [8] Chudnovskiy A.R. (1970). Lit'ye po modelyam iz penoplasta. Moskva: Khimiya [Чудновский А.Р. (1970). Литье по моделям из пенопласта. Москва: Химия].
- [9] Kirpichenkov V.P. (1971). Tekhnologicheskiy protsess lit'ya po gazifitsiruyemym modelyam. Moskva: NIIMASH [Кирпиченков В.П. (1971). Технологический процесс литья по газифицируемым моделям. Москва: НИИМАШ].
- [10] Dan LA, Trofimova LA. & Velichko A.A. (2009). Analiz vozmozhnosti primeneniya termoplottera dlya izgotovleniya gazifitsiruyemykh liteynykh modeley. Vestnik Priazovskogo Gosudarstvennogo Tekhnicheskogo Universiteta, 19, 84–86 [Дан Л.А., Трофимова Л.А., Величко А.А. (2009). Анализ возможности применения термоплоттера для изготовления газифицируемых литейных моделей. Вестник Приазовского Государственного Технического Университета, 19, 84–86].
- [11] Penopolistirol i yestestvennaya sreda. Fakty [Пенополистирол и естественная среда. Факты]. Retrieved from http://stroika. biz.ua/articles/350/ [3.05.2021].
- [12] Rajaeifar M.A., Abdi R. & Tabatabaei M. (2017). Expanded polystyrene waste application for improving biodiesel environmental performance parameters from life cycle assessment point of view. *Renewable and Sustainable Energy Reviews*, 74, 278–298. Doi: https://doi.org.10.1016/j.rser.2017.02.032.
- [13] Ponomareva V.T., Likhacheva N.N. & Tkachik Z.A. (2002). Ispol'zovaniye plastmassovykh otkhodov za rubezhom. *Plasticheskiye massy*, 5, 44–48 [Пономарева В.Т., Лихачева Н.Н., Ткачик З.А. (2002). Использование пластмассовых отходов за рубежом. *Пластические массы*, 5, 44–48].
- [14] Shtarke L. (1987). Ispol'zovaniye promyshlennykh ibytovykh otkhodov plastmass. Leningrad: Khimiya [Штарке Л. (1987). Использование промышленных и бытовых отходов пластмасс. Ленинград: Химия].
- [15] Pirs D. & Uolter I. (1981). Ispol'zovaniye vtorichnykh resursov: ekonomicheskiye aspekty. Moskva: Ekonomika [Пирс Д., Уолтер И. (1981). Использование вторичных ресурсов: экономические аспекты. Москва: Экономика].
- [16] Hocking M.B. (1991). Paper Versus Polystyrene: A Complex Choice. Science. 251, 504–505. Doi: https://doi.org.10.1126. science.251.4993.504.
- [17] Dan L.A., Oleynik I.M. & Trofimova L.A. (2013). Svoystva zashchitnykh pokrytiy na osnove otkhodov penopolistirola. Vestnik Priazovskogo Gosudarstvennogo Tekhnicheskogo Universiteta, 27, 110–115 [Дан Л.А., Олейник И.М., Трофимова Л.А. (2013). Свойства защитных покрытий на основе отходов пенополистирола. Вестник Приазовского Государственного Технического Университета, 27, 110–115].
- [18] Doroshenko V.S. (2014). Novyye napravleniya pererabotki otkhodov penopolistirola. *Ekologiya predpriyatiya*, 1, 68–78 [Дорошенко В.С. (2014). Новые направления переработки отходов пенополистирола. Экология предприятия, 1, 68–78].
- [19] Shinskiy O.I., Doroshenko V.S. & Stryuchenko A.A. (2008). Polucheniye svyazuyushchikh materialov dlya formovochnykh i sterzhnevykh peschanykh smesey iz otkhodov penopolistirola. *Metall i lit'ye Ukrainy*, 3–4, 57–61 [Шинский О.И., Дорошенко В.С., Стрюченко А.А. (2008). Получение связующих материалов для формовочных и стержневых песчаных смесей из отходов пенополистирола. *Металл и литье Украины*, 3–4, 57–61].

- [20] Shinskiy O.I., Ladareva Yu.Yu. & Mairko T.A. (2007). Novyy svyazuyushchiy material na osnove otkhodov penopolistirola. *Protsessy lit'ya*, 4, 58–60 [Шинский О.И., Ладарева Ю.Ю., Маирко Т.А. (2007). Новый связующий материал на основе отходов пенополистирола. *Процессы литья*, 4, 58–60].
- [21] Stryuchenko A.A., Ladareva Yu.Yu. & Mairko T.A. (2005). Novyye metody utilizatsii bytovykh i promyshlennykh otkhodov penopolistirola. Tezisy dokladov mezhdunarodnogo nauchno--tekhnicheskogo kongressa: Ekonomicheskiy puť k vysokokachestvennomu liťyu: 2005. Kiyev [Стрюченко А.А., Ладарева Ю.Ю., Маирко А.А. (2005). Новые методы утилизации бытовых и промышленных отходов пенополистирола. Тезисы докладов международного научно-технического конгресса: Экономический путь к высококачественному литью: 2005. Киев].
- [22] Stryuchenko A.A., Ladareva Yu.Yu. & Mairko T.A. (2005). Formovochnyye i sterzhnevyye smesi na polistirol'nom svyazuyushchem. Tezisy dokladov mezhdunarodnogo nauchno--tekhnicheskogo kongressa: Ekonomicheskiy puť k vysokokachestvennomuliťyu: 2005. Kiyev [Стрюченко А.А., Ладарева Ю.Ю., Маирко А.А. (2005). Формовочные и стержневые смеси на полистирольном связующем. Тезисы докладов международного научно-технического конгресса: Экономический путь к высококачественному литью: 2005. Киев].
- [23] Shinskiy O.I., Stryuchenko A.A. & Doroshenko V.S. (2009). Polucheniye svyazuyushchikh iz otkhodov penopolistirola dlya liteynykh form i strezhney i izucheniye ryada kharakteristik etikh protsessov. Protsessy lit'ya, 1, 48–52 [Шинский О.И., Стрюченко А.А., Дорошенко В.С. (2009). Получение связующих из отходов пенополистирола для литейных форм и стрежней и изучение ряда характеристик этих процессов. Процессы литья, 1, 48–52].
- [24] Shinsky O.I., Terlikovsky E.V. & Stryuchenko A.A. (2005). UA Patent No. 9003. Kyiv, Ukrainian Patent Office.
- [25] Dan L.O., Trofimova L.A., Shevchenko S.V., Shvarts V.L & Dan O.L. (2013). UA Patent No. 102624. Kyiv, Ukrainian Patent Office.

- [26] Dan L.A., Trofimova L.A., Reva I.A. & Dan Ye.L. (2014). Svoystva smesey so svyazuyushchim, soderzhashchim otkhody penopolistirola i glinu. *Liteynoye proizvodstvo*, 4, 24–26 [Дан Л.А., Трофимова Л.А., Рева И.А., Дан Е.Л. (2014). Свойства смесей со связующим, содержащим отходы пенополистирола и глину. Литейное производство, 4, 24–26].
- [27] Dan LA. & Trofimova L.A. (2014). Osypayemost' i vybivayemost' peschano-glinistykh smesey soderzhashchikh małyye dobavki rastvora penopolistirola. Universitetskaya nauka – 2014: Mezhdunarodnaya nauchno-tekhn. konf.: 20–22 maya. Mariupol'. Mariupol': PGTU, 130–131 [Дан Л.А., Трофимова Л.А. (2014). Осыпаемостъ и выбиваемостъ песчано-глинистых смесей содержащих малые добавки раствора пенополистирола. Университетская наука – 2014: Международная научно-техн. конф.: 20–22 мая. Мариуполь. (сс. 130-131). Мариуполь: ПГТУ].
- [28] Dan L.A. & Trofimova L.A. (2014). Vliyanie malyh dobavok rastvora penopolistirola v skipidare na osypaemost' i vybivaemost' peschano-glinistyh smesej. Novi materiali i tekhnologiï v mashinobuduvanni: materiali VI Mizhnar. naukovo-tekhnich. konf: May 20 – May 21. Kyiv. (pp. 32–33). Kyiv: National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute" [Дан Л.А., Трофимова Л.А. (2014). Влияние малых добавок раствора пенополистирола в скипидаре на осыпаемость и выбиваемость песчано-глинистых смесей. Нові матеріали і технології в машинобудуванні: матеріали VI Міжнар. науково-техніч. конф.: 20 – 21 мая. Киев. (сс. 32–33). Киев: НТУ КІІІ].
- [29] Shinskiy O.I., Ladareva Yu.Yu. & Rybitskiy A.I. (2010). Razrabotka svyazuyushchego materiala dlya liteynogo proizvodstva putem pererabotki otkhodov penopolistirola. *Protsessy lit'ya*, 4, 56–59 [Шинский О.И., Ладарева Ю.Ю., Рыбицкий А.И. (2010). Разработка связующего материала для литейного производства путем переработки отходов пенополистирола. *Процессы литья*, 4, 56–59].
- [30] Ponomarenko O., Yevtushenko N. & Lysenko T. (2019). A New Technology for Producing the Polystyrene Foam Molds Including Implants at Foundry Industry. *Advances in Design, Simulation and Manufacturing*, II, 430–437. Doi:10.1007/978-3-030-22365-6_43.

Physicochemical Investigations of Hydrogels Containing Gold Nanoparticles Designed for Biomedical Use

Magdalena Głąb^{a*}, Sonia Kudłacik-Kramarczyk^a, Anna Drabczyk^a, Beata Grabowska^b, Bożena Tyliszczak^a

^a Cracow University of Technology, Faculty of Materials Engineering and Physics, Department of Materials Science, 37 Jana Pawła II Av., 31-864 Krakow, Poland

^b AGH University of Science and Technology, Faculty of Foundry Engineering, 23 Reymonta St., 30-059 Krakow, Poland **e-mail: magdalena.glab@doktorant.pk.edu.pl*

© 2021 Authors. This is an open access publication, which can be used, distributed and reproduced in any medium according to the Creative Commons CC-BY 4.0 License requiring that the original work has been properly cited.

Received: 23 February 2021/Accepted: 23 June 2021/ Published online: 2 July 2021 This article is published with open access at AGH University of Science and Technology Press

Abstract

Currently, many investigations are being performed to develop dressing materials with a positive effect on the wound healing process. In general, innovative dressings should ensure wound exudate absorption, constitute an external barrier limiting the possibility of wound contamination and, importantly, also provide therapeutic properties. This work is focused on obtaining materials with potential use as dressings for treatment of difficult-to-heal wounds. The synthesis methodology of acrylic hydrogels modified with selected modifiers, i.e. arabic gum, nanogold, bee pollen and chamomile extract, was developed. Next, the sorption properties of the materials were determined as well as their behavior during the incubation in fluids imitating the environment of the human body. Additionally, the impact of such an incubation on their structure was evaluated by FT-IR spectroscopy. It was proved that the modifiers affected the sorption properties of hydrogels, i.e. samples with additives showed even approx. 2.5-fold lower swelling ability. In turn, incubation of hydrogels in simulated body fluids did not cause any rapid changes in pH, which may indicate the biocompatibility of the tested materials with the tested fluids. Thus, it may be concluded that the developed materials show great application potential for biomedical purposes and may be subjected to more advanced studies such as cytotoxicity assessments towards selected cell lines.

Keywords:

acrylic hydrogels, gold nanoparticles, sorption properties, incubation studies, FT-IR analysis

4. INTRODUCTION

In recent years, the application of hydrogels in various fields including medicine and related areas has been growing rapidly [1]. These materials are also widely used in agriculture [2], environmental protection [3] or cosmetology [4]. Growing interest in these polymers result from their unique properties including great water absorption capacity, flexibility, or the possibility of their modification with various active substances which may be further release to the application site [5]. Importantly, both hydrogels based on natural materials such as chitosan [6], gelatin [7] or arabic gum [8] and synthetic ones, i.e. poly(vinyl alcohol) [9] or acrylic acid [10] are widely applied.

Hydrogels based on acrylic acid are widely considered for application e.g. in controlled drug delivery systems [11], as wound dressings [12], in tissue engineering [13] or as biosensors [14]. For example, Mohamad et al. described hydrogels based on acrylic acid and bacterial cellulose obtained via electron beam irradiation. They performed measurements as well as an analysis of the sorption properties of obtained materials. An interesting aspect of the research was the evaluation of the cytotoxicity of the prepared hydrogels toward L929 cell lines and in vivo experiments using Sprague Dawley rats. It was proved that the hydrogels did not exhibit cytotoxic activity. Furthermore, the application of hydrogels promoted more effective wound healing via the accelerated proliferation of fibroblasts compared to the control group [15]. Other investigations on the acrylic hydrogels have been conducted by Staneva et al. who modified these materials with cotton fabric and silver nanoparticles. Their studies aimed at determining the antibacterial activity of the composites prepared against Escherichia coli and Acinetobacter johnsonii and allowed them to demonstrate the antibacterial properties of the developed systems [16]. In turn, Kumar et al. proposed the hydrogels based on acrylic acid and tamarind kernel polysaccharides for application in regenerative medicinal treatment of the skeletal system. They proved that the presence of the hydrogels accelerated the differentiation, mineralization and the expression of various osteogenic genes in Saos-2 cell lines which in the case of the bone injuries treatment may provide more effective osteogenesis process [17].

As mentioned previously, a significant feature of hydrogels is their potential modification with various materials that, in turn, increase the spectrum of their potential application [18]. Particularly important modifying agents are natural ones such as e.g. plant extracts [19]. However, substances of synthetic origin such as e.g. metallic nanoparticles are also widely applied [20]. For example, Park et al. developed alginate hydrogels modified with low molecular weight hyaluronate with potential use in cartilage regeneration. They proved that such hydrogels may successfully regulate the chondrogenic differentiation which contributes to the increase in the effectiveness of the cartilage regeneration [21]. Next, Derkach et al. conducted studies on determining the impact of anionic polysaccharide (k-carrageenan) on the gelling process of gelatin-based hydrogels. They proved that the increase in the concentration of k-carrageenan accelerated the mentioned process at the same time leading to the significant increase in the viscoelastic parameters of modified hydrogels [22]. In turn, the main purpose of the research of Makvandi et al. was to develop thermosensitive hydrogels based on hyaluronic acid and modified with corn silk and silver nanoparticles. Due to the good biocompatibility and antibacterial activity of these hydrogels, they have been determined as promising materials with great application potential for wound healing [23]. Next, Li et al. have developed hydrogels based on poly(ethylene glycol) and modified with gold nanoparticles (which acted as a radiosensitizer) and anticancer drug (doxorubicin). The drug release profiles in vitro and in vivo have been determined. Results of the skin safety investigations as well as the histologic observations of organs and the body weight changes indicated the biocompatibility of the developed materials. Furthermore, the inhibition of the growth and the proliferation of cancer cells has been observed which is a promising result in terms of the application of such materials in cancer treatment [24]. In turn, Ragab et al. developed an active multicomponent hydrogel for the treatment of chronic wounds. Such material has been synthesized using a methacrylated chitosan as a base and Punica granatum peel extract and ethyl acetate fraction as modifiers [25]. Moreover, the modification of hydrogel materials was also the research subject of Gallo et al. [26], Rask et al. [27] and Pankongadisak and Suwangton [28].

The main purpose of the investigations was to obtain and characterize the multicomponent hydrogel materials based on acrylic acid and arabic gum and modified additionally with gold nanoparticles, bee pollen and chamomile extract. Natural modifiers (bee pollen and chamomile extract) were selected due to their antibacterial and antioxidative properties beneficial for wound healing process [29, 30]. In turn, gold nanoparticles showing the large specific surface may constitute effective carriers for the selective and targeted delivery of active substances [31]. Additionally, they also increase drug stability [32]. Importantly, in appropriate concentrations these nanomaterials are biocompatible while at the same time maintaining antibacterial properties, a particularly important factor in the case of the application of such modified hydrogels as dressing materials [33, 34]. Due to the potential application of these polymers for biomedical purposes, incubation investigations have been performed to evaluate their behavior in liquids simulating environments occurring in the human body. Additionally, the sorption properties of the obtained hydrogels have also been verified in these environments. After the incubation studies, the impact of such an immersion on the chemical structure of hydrogels has been evaluated via Fourier transform infrared (FT-IR) spectroscopy. The studies performed also included the characterization of gold nanoparticles which were used as modifiers of hydrogel matrix. Their size was determined via dynamic light scattering (DLS) wherein their optical properties were evaluated via UV-Vis spectrophotometry.

2. EXPERIMENTAL PART

2.1. Materials

Potassium hydroxide (pure, p.a.), diacrylate poly(ethylene glycol) (crosslinking agent, PEGDA 700, average $M_n = 700$ g/mol; d = 1.120 g/mL), 2-hydroxy-2-methylpropiophenone (photoinitiator, d = 1.077 g/mL), arabic gum (pure, p.a., powder) were bought in Avantor Performance Materials Poland S.A. Acrylic acid (99%, anhydrous, contains 200 ppm hydroquinone monomethyl ether as inhibitor) was supplied by Merck. The bee pollen and chamomile were purchased in Herbapol (Lublin, Poland). Gold nanoparticles were obtained according to the procedure described in [35].

2.2. Synthesis of hydrogels

In order to obtain hydrogel materials, the first step was to neutralize 13.5 mL of acrylic acid with 15 mL of 40% KOH solution. Due to the exothermic character of this reaction, the process was performed in a cooling medium (tap water). After cooling to room temperature, arabic gum, an adequate amount of the selected modifier (chamomile extract or bee pollen suspension), a crosslinking agent (PEGDA 700) and a photoinitiator (2-hydroxy-2-methylpropiophenone) were added to the mixture. Such prepared reaction mixtures were subsequently treated with UV radiation for 3 min (as a source of radiation, an EMITA VP-60 lamp was used, power: 180 W, λ = 320 nm). A row of syntheses was conducted using various amounts of selected modifiers. Compositions of the hydrogels obtained are presented in Table 1 (hydrogels modified with bee pollen and gold nanoparticles) and in Table 2 (materials with chamomile extract and gold nanoparticles).

After the synthesis, the prepared hydrogels were dried at room temperature and subjected to studies aimed at characterizing their physicochemical properties. The experiments performed included incubation studies determining the behavior of obtained materials in liquids simulating environments occurring in the human body. Furthermore, the sorption properties of hydrogels were also evaluated. Additionally, gold nanoparticles used as one of the modifying agents were characterized using dynamic light scattering (DLS) and UV-Vis spectrophotometry.

Series	Acrylic acid [mL]	KOH [mL]	Crosslinking agent [mL]	Photoinitiator [mL]	Arabic gum [g]	Bee pollen* [v/v]	Gold nanoparticles suspension [mL]						
							0						
T						10	- -						
1						20							
						30							
	13.5 15.0	15.0	15.0	13.5 15.0 0.03 0.	0.03	0.03	0.03	0.03	0.03	0.13	5	0	
						10	-						
II						20	5						
						30	-						
* bee polle	en suspension – pre	pared via intr	oducing 1 g of this s	ubstance into 100	mL of distilled wa	ater							

Compositions of hydrogels modified	with bee pollen and gold nanoparticles
------------------------------------	--

 Table 2

 Compositions of hydrogels modified with chamomile extract and gold nanoparticles

Series	Acrylic acid [mL]	KOH [mL]	Crosslinking agent [mL]	Photoinitiator [mL]	Arabic gum [g]	Chamomile extract** [v/v]	Gold nanoparticles suspension [mL]
						0	_
Ш						10	_
111						20	-
					_	30	
	13.5	15.0	0.03	0.13	5	0	_
IV					-	10	5
						20	
						30	

** chamomile extract – prepared via introducing 1 g of this substance into 100 mL of distilled water (water temperature 96°C, brewing time 10 min)

2.3. Characteristic of gold nanoparticles using the DLS technique

The size of gold nanoparticles was determined via the dynamic light scattering (DLS) technique. The measurement was performed for gold nanoparticles suspension before its introduction into the polymer matrix and using Zetasizer Nano ZS Malvern. The analysis was conducted at room temperature. In order to characterize the gold nanoparticles more precisely, the optical properties of their suspension were determined via UV-Vis spectrophotometry. The study was carried out using a Thermo Scientific Evolution 220 (the measurement range: 350–700 nm) and also at room temperature.

2.4. Investigation on the sorption properties

One of the basic analysis performed for hydrogel materials is the analysis of their sorption ability. This is particularly important in terms of their potential application as wound dressings, one of the most essential features of which is a capacity for wound exudate absorption. The sorption properties of hydrogels was evaluated using 2% citric acid, Ringer liquid (liquid isotonic to the human blood), SBF (simulated body fluid, isotonic to the human blood plasma), Tyrode solution (isotonic to the interstitial fluid), Hank solution (buffer used in the cell culture media to maintain optimal physiological pH) and distilled water (used as a reference liquid). The study was conducted for all obtained hydrogels. For this purpose, hydrogel samples were introduced into the sterile vessels containing 50 mL of the tested solution. After 1 h samples were separated from the liquids, excess water was removed using a paper towel and weighed again. The sorption capacity of the materials was defined using swelling ratios α [g/g] which were determined using the following Equation (1):

$$\alpha = \frac{(m - m_0)}{m_0} \tag{1}$$

where:

- α swelling ratio [g/g],
- *m* mass of a swollen hydrogel [g],
- m_{o} mass of a dry hydrogel (before swelling) [g].

Table 1

2.5. Investigations on the behavior of hydrogel in simulated body fluids

In order to determine the behavior of obtained hydrogels in liquids simulating environments occurring in the human body incubation studies have been performed. Studies were conducted in SBF, artificial saliva and Ringer liquid. Approx. 1 g hydrogel samples were introduced into sterile vessels containing 50 mL of the liquid. Next, solutions with immersed samples were incubated at 37°C. During a fourweek incubation period, the pH values of the solutions were measured and pH changes were also checked for the tested liquids without the immersed hydrogels (such liquids were treated as reference liquids).

2.6. Analysis of the chemical structure of hydrogels via Fourier transform infrared (FT-IR) spectroscopy

To determine potential changes in the structure of hydrogels caused by immersion in the simulated body fluids, FT-IR analysis was performed. The study was conducted for hydrogels containing 10% and 30% of the additive both before and after the incubation in Ringer liquid, SBF and artificial saliva. For this purpose, a Spectrum 65 (Perkin Elmer) spectrophotometer equipped with an attenuated total reflectance (ATR) attachment with a diamond/ZnSe crystal was used. FT-IR spectra were recorded within the range: 4000–600 cm⁻¹ (32 scans, resolution 4.0 cm⁻¹) at room temperature.

3. RESULTS AND DISCUSSION

3.1. Characteristic of gold nanoparticles

In the research, the size of the particles obtained was verified using DLS technique wherein their optical properties were determined via UV-Vis spectrophotometry. Results of the performed investigations are shown below in Figure 1.

According to the literature reports, the term "nanoparticles" refers to the particles with at least one dimension ranging from 1 nm to 100 nm [36]. Based on the DLS analysis performed it was observed that the tested suspension contained particles having a size of approx. 30 nm. Thus it may be concluded that the particle suspension used a modifying agent of the polymer matrix contain nanoparticles. Importantly, the narrow particle size distribution was shown to indicate that the suspension with an uniform particle size and probably without the agglomerates of particles was introduced into the reaction mixture.

Figure 1b shows the results of UV-vis spectrophotometric analysis. Suspension of gold nanoparticles is characterized by an intense ruby color which is caused by the surface plasmon resonance (SPR). This, in turn, is a result of the collective oscillations of free conduction electrons caused by the electromagnetic field [37–39]. Thus the presence of gold nanoparticles in a tested suspension may be confirmed via confirmed UV-Vis spectrophotometry wherein the SPR absorption peak characteristic for nanogold occurs within the wavelength range 515–570 nm [40]. What is more, the position of the absorption band is strictly related to such factors as e.g. the size and the shape of the particles, their interactions with the medium in which they are suspended or the refractive index. Thus it is assumed that a single SPR band in the absorption spectra indicates the presence of spherical nanoparticles while in the case of anisotropic nanoparticles two or more SPR bands depending on their shape are observed [37, 41]. In the case of the tested suspension, maximum absorbance observed on the UV-Vis spectra was at approx. 515 nm which proves the presence of gold nanoparticles in tested medium. The maximum absorbance characteristic for gold nanoparticles in the similar range was also reported by Ngo et al. [42], Duan et al. [43] and Amendola and Meneghetti [44]. Next, due to the presence of a single absorption band on the UV-Vis spectrum obtained, it may also be concluded that spherical-shape nanoparticles occur in the analyzed suspension.



Fig. 1. Results of DLS analysis (a) and UV-Vis spectrum of gold nanoparticles suspension (b)

3.2. Investigations on the sorption properties of hydrogels

Considering the potential applications of the developed materials in biomedical fields such as pharmacy, an essential aspect of the research was to determine the sorption ability of the obtained hydrogels. Swelling properties are particularly important in the case of the use of such materials as dressings, where one of the major tasks is to absorb the wound exudate, or in drug delivery systems where swelling of the material proceeds in parallel to the release of the active substance present in the polymer matrix. Characteristics of the sorption of prepared materials in selected liquids is presented in Figure 2.

The swelling of hydrogel materials is due to the hydration of hydrophilic functional groups present in the structure of these polymers. Diffusion of water or other fluids is based on the migration of this fluid into pre-existing or dynamically forming spaces between polymer chains. After the introduction of the hydrogel matrix into the tested liquid, processes of dissociation and solvation of functional groups present in the polymer structure take place. As a result of the electrostatic interactions, the repulsion of similar ones (with the same charge) is observed, which in turn leads to the formation of free spaces between polymer chains and finally to the loosening of the polymer structure. As a result, water molecules easily penetrate such spaces [45, 46].

Considering the results of the performed investigations, it was proven that the highest swelling ratios were calculated for hydrogels immersed in distilled water. On the other hand, samples tested in SBF, Hank solution and Tyrode solution showed significantly lower swelling ability. This phenomenon may be caused by the presence of such ions as Ca²⁺, Mg²⁺ or Na⁺ in these solutions which may affect the crosslinking density of the hydrogel matrix. For example, due to the presence of divalent ions, i.e. Ca²⁺ and Mg²⁺, additional crosslinks between polymer chains in the polymer structure may be formed. As a result, an increase in the crosslinking density of such polymer followed by the limitation of free spaces available for absorbed liquid takes place. The presence of Na⁺ ions may also reduce the sorption capacity of hydrogel materials. When the hydrogel swells in a medium containing sodium ions, the ion exchange including the hydrogen ions formed as a result of dissociation of functional groups occurring in the polymer structure and the sodium ions from absorbed liquids may take place. Such neutralization, in turn, may reduce the hydrophilic character of the carboxyl group leading finally to the lower swelling properties of such a structure. These conclusions are consistent with the conclusions of studies concerning the impact of various ions on the swelling process performed by Zhu et al. [47].

Low values of the swelling ratios were also calculated for samples swelling in 2% citric acid solution. The low swelling ability of hydrogels in low pH solutions is related to the high concentration of hydrogen ions in the presence of which the protonation of carboxylic anions may occur. As a result, the main anion - anion repulsive forces are eliminated. This, in turn, leads to the reduction in the formation of free spaces between polymer chains and, finally, to the reduction in the swelling capacity of such material. Similar results were presented by Al-Anbakey et al. who also observed that hydrogel materials placed in low pH solutions exhibited low sorption capacity [48]. Thus, it was proved that sorption properties of hydrogels depend on the type of fluid in which such a study is performed.

The presence of various modifying agents in the hydrogel matrix may also affect sorption properties. In the case of all the tested samples, the highest swelling ratios were observed for unmodified hydrogels. As the modifier content increased, swelling ratios decreased, e.g. $\alpha = 17.69$ g/g for samples containing 10% bee pollen and $\alpha = 8.38$ g/g for a sample containing 30% bee pollen (swelling ratios in distilled water).



Fig. 2. Results of the swelling studies of obtained hydrogels: a) series I (modified with bee pollen); b) series II (modified with bee pollen and gold nanoparticles); c) series III (modified with chamomile extract); d) series IV (modified with chamomile extract and gold nanoparticles)

The greatest decrease in the swelling was observed in the case of samples tested in distilled water. Higher sorption properties of unmodified hydrogels may stem from the fact that more free spaces occur in the matrix of these polymers compared to the matrix of modified materials in which spaces between polymer chains are partially filled by modifiers. Thus, the modifying agents significantly limit the space which might be filled by the absorbed liquid. Therefore, the reduction in the swelling capacity of such materials is observed. Moreover, additives such as bee pollen or chamomile contain a number of chemical compounds, including those with aromatic rings. These structures cause the so-called steric effect which may also limit the penetration of fluids between polymers. In the case of the presence of gold nanoparticles, any significant changes in swelling properties of the materials modified additionally with these additives was not noticed. Only in the case of hydrogels containing both chamomile extract and gold nanoparticles was an increase in the swelling ratios observed. This is probably a result of the release of some amounts of the modifying agents into the tested liquid and thus forming free spaces previously occupied by the modifiers which may be filled with absorbed liquid.

3.3. Results of the investigations on the behavior of hydrogels in simulated body fluids

Incubation studies were aimed at determining the behavior of the obtained hydrogels in liquids simulating environments occurring in the human body. These investigations are particularly important in terms of the potential application of the developed materials for biomedical purposes. The behavior of hydrogels presented as pH changes in the course of their four-week incubation in selected liquids is presented below in Figures 3–5.

In the case of all hydrogels immersed in various types of fluids, an analogous course of the curves presenting pH changes was observed. Firstly, i.e. after the first week of the immersion, a drop in pH value in all tested environments was reported. Such a pH decrease may be due to the interactions that probably occurred between the dry hydrogel sample and the incubation medium. It is also likely that such a change in pH may be a result of the beginning of the degradation of the immersed samples.

At the beginning of the immersion, the tested liquid penetrates the interior of the material and a dry hydrogel begins to swell. Next, the elution of unreacted or non-crosslinked reagents present in the polymer matrix probably takes place.

Additionally, during the first days of the immersion liquid penetrating the material, being incubated causes the elution of the additives, i.e. bee pollen or chamomile extract. All these processes may contribute to the pH changes observed at the beginning of the investigation. In the next weeks of pH measurements, stabilization of the pH values may be observed. Any changes in pH values were not observed and its constant value maintained over the next days of the study which may indicate the buffering properties of the hydrogels.

Slight greater changes in pH may be noticed in the case of modified hydrogels. In the case of samples with various modifying agents, a slightly larger pH decrease was observed compared to this change reported for unmodified materials.



Fig. 3. pH changes measured during the incubation of hydrogels in Ringer liquid: a) series I (modified with bee pollen); b) series II (modified with bee pollen and gold nanoparticles); c) series III (modified with chamomile extract); d) series IV (modified with chamomile extract) and gold nanoparticles); c) series III (modified with chamomile extract); d) series IV (modified with chamomile extract) and gold nanoparticles); c) series III (modified with chamomile extract); d) series IV (modified with chamom



Fig. 4. pH changes measured during the incubation of hydrogels in SBF: a) series I (modified with bee pollen); b) series II (modified with bee pollen and gold nanoparticles); c) series III (modified with chamomile extract); d) series IV (modified with chamomile extract and gold nanoparticles)



Fig. 5. pH changes measured during the incubation of hydrogels in artificial saliva: a) series I (modified with bee pollen); b) series II (modified with bee pollen and gold nanoparticles); c) series III (modified with chamomile extract); d) series IV (modified with chamomile extract and gold nanoparticles)

26

This probably results from the release of the modifying substance from the polymer matrix which, in turn, may be caused by the interactions of the hydrogel sample with the incubation liquid. The release of both bee pollen and chamomile extract may cause greater changes in pH of tested liquids due to the presence of various chemical compounds such as e.g. organic acids or different enzymes in these additives which may contribute to the additional acidification of the environment. Nonetheless, these changes are only observable during the first week of the incubation. During the next week of the study, the pH of the solutions stabilizes and the lack of any further changes may indicate the biocompatibility of the analyzed materials with respect to the applied liquids.

3.4. Results of Fourier transform infrared (FT-IR) spectroscopy

Results of the spectroscopic analyses performed to verify the impact of the incubation of hydrogels in simulated physiological liquids on their chemical structure are shown in Figures 6 and 7. Based on the literature data, absorption bands observed on the above-presented FT-IR spectra were assigned to the adequate functional groups presented in Table 3.

A broad band of relatively high intensity observed within the range of 3700–3300 cm⁻¹ may be assigned to the –OH groups resulting probably from the presence of water molecules in the structure of the analyzed hydrogels. Among the absorption bands characteristic for acrylic hydrogels, bands in the following ranges may be observed: 3000–2900 cm⁻¹ (stretching vibrations of –CH₂ groups), 1740–1650 cm⁻¹ (stretching vibrations of -C=O groups) and 1580-1520 cm⁻¹ (stretching vibrations of -OH groups). Due to the possibility of the overlapping of bands deriving from groups characteristic for both polymer matrix and the compounds occurring in modifiers, it is difficult to clearly assign absorption bands visible on obtained FT-IR spectra for particular components. For example, an absorption band corresponding to the stretching vibrations of the carbonyl groups may derive both from -C=O bonds present in the hydrogel matrix and the conjugated esters from luteolin present in chamomile extract [49] or to phenolic compounds derived from bee pollen [50]. Furthermore, due to the numerous amino acids occurring in the compositions of the modifying agents, absorption bands within the range 1650–1500 cm⁻¹ may be assigned to the amino groups while the absorption band at 1360–1000 cm⁻¹ may be assigned to the stretching vibrations of C-N groups. Next, band visible within the 1050-1000 cm⁻¹ range corresponds to the stretching vibrations of -CO groups and is characteristic for polysaccharides (included in the composition of modifying agents).

Analyzing the FT-IR spectra of samples before and after the incubation in simulated body fluids, it is important to determine the changes in the intensity of the absorption bands. The decrease in the intensity of particular bands or their complete disappearance may indicate changes occurring in the immersed material such as e.g. the degradation of incubated polymers or the release of the modifying agents present in the polymer matrix. The greatest changes in the intensity of particular bands have been marked in above-presented FT-IR spectra via the black frame.



Fig. 6. FT-IR spectra of hydrogels containing: a) before incubation; b) Ringer incubation; c) SBF incubation; d) artificial saliva incubation; 1) 10% bee pollen; 2) 30% bee pollen; 3) 10% bee pollen and gold nanoparticles; 4) 30% bee pollen and gold nanoparticles



Fig. 7. FT-IR spectra of hydrogels containing: a) before incubation; b) Ringer incubation; c) SBF incubation; d) artificial saliva incubation; 1) 10% chamomile extract; 2) 30% chamomile extract; 3) 10% chamomile extract and gold nanoparticles; 4) 30% chamomile extract and gold nanoparticles

 Table 3

 Vibrations observed on FT-IR spectra and corresponding functional groups

Wavelength range [cm ⁻¹]	Functional group	Type of vibration
3700-3300	ОН	stretching
3000-2900	CH_2	stretching
1740-1650	C=0	stretching
1650-1500	N–H	deformation
1580-1520	СООН	stretching
1360-1000	C–N	stretching
1050-1000	С-О	stretching

The changes concern the absorption bands which may be attributed to the vibrations of groups characteristic for compounds present in the compositions of modifiers applied. Thus, it may be concluded that the decrease in the intensity of these bands indicates the release of certain amounts of the modifiers to the incubation medium. These conclusions are consistent with the results of pH changes observed during the incubation studies which indicated the acidification of the incubation environment. Considering different incubation fluids, the highest changes in the intensity of observed bands were observed in SBF and, importantly, in this solution the greatest pH decrease was reported during the incubation period. Therefore, it may be concluded that in this incubation medium the greatest amount of the additive is released or that the degradation occurs most intensively.

4. CONCLUSIONS

Based on the results presented above, the following conclusions and observations were formulated:

- The DLS analysis showed that the suspension introduced into the hydrogel matrix contained gold particles having a size of approx. 30 nm and so gold nanoparticles. Moreover, the occurrence of a single narrow peak on UV-Vis spectrum indicates that a suspension with particles of a uniform size was used.
- The highest swelling capacity was shown by hydrogel materials in distilled water. Ions such as Ca²⁺, Na⁺ or Mg²⁺ in absorbed liquids reduce the sorption properties of hydrogels which results from the formation of additional crosslinks between these ions and hydrophilic functional groups present in polymer chains of the hydrogel network.
- Modified hydrogels showed a lower sorption capacity than unmodified ones. This may result from the fact that additives present in the matrix fill the spaces between the polymer chains thus limiting the space available for liquids.
- Incubation of tested hydrogels in simulated body fluids did not cause any rapid changes in their pH, which may indicate the biocompatibility of materials with the fluids used.
- During spectroscopic analysis, changes in intensity of selected absorption bands on FT-IR spectra of samples before and after the incubation were observed. This probably resulted from the partial degradation of the materials being incubated or from the release of modifiers present in the polymer matrix into the incubation medium.

- The analyses did not show any significant influence of the addition of nano-gold on the sorption properties of hydrogels or on the course of their incubation process. However, the introduction of this additive into the polymer matrix is important because of the antibacterial effect of gold nanoparticles, which is beneficial due to the potential use of these materials as dressings.
- The presence of additives in the polymer matrix affects selected physicochemical properties of these materials. It was proved that selected additives, i.e. bee pollen or chamomile, reduce the sorption capacity of hydrogels. However, due to their therapeutic effect, such a modification allows materials to be designed with new properties which may be beneficial in terms of their use as dressing materials.

The research work was carried out within the SMART-MAT Functional Materials Science Club at the Faculty of Materials Engineering and Physics of the Cracow University of Technology.

REFERENCES

- Mahinroosta M., Jomeh Farsangi Z., Allahverdi A. & Shakoori Z. (2018). Hydrogels as intelligent materials: A brief review of synthesis, properties and applications. *Materials Today Chemistry*, 8, 42–55. Doi: https://doi.org/10.1016/j.mtchem.2018.02.004.
- [2] Kim S., Iyer G., Nadarajah A., Frantz J.M. & Spongberg A.L. (2010). Polyacrylamide Hydrogel Properties for Horticultural Applications. *International Journal of Polymer Analysis and Characterization*, 15(5), 307–318. Doi: https://doi.org/10.1080/ 1023666X.2010.493271.
- [3] Thakur S., Sharma B., Verma A., Chaudhary J., Tamulevicius S. & Thakur V.K. (2018). Recent approaches in guar gum hydrogel synthesis for water purification. *International Journal of Polymer Analysis and Characterization*, 23, 621–632. Doi: https:// doi.org/10.1080/1023666X.2018.1488661.
- [4] Zagórska-Dziok M. & Sobczak M. (2020). Hydrogel-Based Active Substance Release Systems for Cosmetology and Dermatology Application: A Review. *Pharmaceutics*, 12(5), 396. Doi: https:// doi.org/10.3390/pharmaceutics12050396.
- [5] Ahsan A., Tian W., Farooq M.A. & Khan D.H. (2020). An overview of hydrogels and their role in transdermal drug delivery. *International Journal of Polymeric Materials and Polymeric Biomaterials*, 70(8). Doi: https://doi.org/10.1080/00914037.2020.174 0989.
- [6] Varaprasad K., Narayana Reddy N., Mithil Kumar N., Vimala K., Ravindra S. & Mohana Raju K. (2010). Poly(acrylamide-chitosan) Hydrogels: Interaction with Surfactants. *International Journal of Polymeric Materials and Polymeric Biomaterials*, 59(12), 981–993. Doi: https://doi.org/10.1080/00914037.2 010.504147.
- [7] Liu Y, Weng R, Wang W, Wei X, Li J, Chen X, Liu Y, Lu F & Li Y. (2020). Tunable physical and mechanical properties of gelatin hydrogel after transglutaminase crosslinking on two gelatin types. *International Journal of Biological Macromolecules*, 162, 405–413. Doi: https://doi.org/10.1016/ j.ijbiomac.2020.06.185.
- [8] Ahmad S., Ahmad M., Manzoor K., Purwar R. & Ikram S. (2019). A review on latest innovations in natural gums based hydrogels: Preparations & applications. *International Journal of Biological Macromolecules*, 136, 870–890. Doi: https://doi. org/10.1016/j.ijbiomac.2019.06.113.
- [9] Kumar A. & Han S.S. (2017). PVA-based hydrogels for tissue engineering: A review. *International Journal of Polymeric Materials* and Polymeric Biomaterials, 66(4), 159–182. Doi: https://doi. org/10.1080/00914037.2016.1190930.
- https://journals.agh.edu.pl/jcme

- [10] Drabczyk A., Kudłacik-Kramarczyk S., Tyliszczak B., Rudnicka K., Urbaniak M., Michlewska S., Królczyk J.B., Gajda P. & Pielichowski K. (2020). Measurement methodology toward determination of structure-property relationships in acrylic hydrogels with starch and nanogold designed for biomedical applications. *Measurement*, 156, 107608. Doi: https://doi. org/10.1016/j.measurement.2020.107608.
- [11] Deepa G., Thulasidasan A.K., Anto R.J., Pillai J.J. & Kumar G.S. (2012). Cross-linked acrylic hydrogel for the controlled delivery of hydrophobic drugs in cancer therapy. *International Journal of Nanomedicine*, 7, 4077–4088. Doi: https://doi. org/10.2147/IJN.S30149.
- [12] Sennakesavan G., Mostakhdemin M., Dkhar L.K., Seyfoddin A. & Fatihhi S.J. (2020). Acrylic acid/acrylamide based hydrogels and its properties – A review. *Polymer Degradation* and Stability, 180, 109308. Doi: https://doi.org/10.1016/ j.polymdegradstab.2020.109308.
- [13] Arnold M.P., Daniels A.U., Ronken S., García H.A., Friederich N.F., Kurokawa T., Gong J.P. & Wirz P. (2011). Acrylamide Polymer Double-Network Hydrogels: Candidate Cartilage Repair Materials with Cartilage-Like Dynamic Stiffness and Attractive Surgery-Related Attachment Mechanics. *Cartilage*, 2, 374–383. Doi: https://doi.org/10.1177/1947603511402320.
- [14] Sandu T., Sarbu A., Constantin F., Vulpe S. & Iovu H. (2012). Acrylic Hydrogels-Based Biocomposites: Synthesis and Characterization. *Journal of Applied Polymer Science*, 127(5), 4061–4071. Doi: https://doi.org/10.1002/app.37992.
- [15] Mohamad N., Mohd Amina M.C.I., Pandeya M., Ahmada N. & Rajab N.F. (2014). Bacterial cellulose/acrylic acid hydrogel synthesized via electron beam irradiation: Accelerated burn wound healing in an animal model. *Carbohydrate Polymers*, 114, 312–320. Doi: https://doi.org/10.1016/j.carbpol.2014. 08.025.
- [16] Staneva D., Vasileva-Tonkova E. & Grabchev I. (2017). Preparation, characterization, and antibacterial activity of composite material: Cotton fabric/hydrogel/silver nanoparticles. International Journal of Polymer Analysis and Characterization, 22(2), 104–111. Doi: https://doi.org/10.1080/102366 6X.2016.1249220.
- [17] Kumar S., Majhi R. K., Sanyasi S., Goswami C. & Goswami L. (2018). Acrylic acid grafted tamarind kernel polysaccharide-based hydrogel for bone tissue engineering in absence of any osteo-inducing factors. *Connective Tissue Research*, 59(sup1), 111–121. Doi: https://doi.org/10.1080/03008207. 2018.1442444.
- [18] Tyliszczak B., Kudłacik-Kramarczyk S., Drabczyk A., Bogucki R., Olejnik E., Kinasiewicz J. & Głąb M. (2018). Hydrogels containing caffeine and based on Beetosan® – proecological chitosan – preparation, characterization, and in vitro cytotoxicity. *International Journal of Polymeric Materials and Polymeric Biomaterials*, 68(15), 931–935. Doi: https://doi.org/10.1080/0091 4037.2018.1525537.
- [19] Jayaramudu T., Varaprasad K., Raghavendra G.M., Sadiku E.R. & Mohana Raju K. (2017). Green synthesis of tea Ag nanocomposite hydrogels via mint leaf extraction for effective antibacterial activity. *Journal of Biomaterials Science, Polymer Edition*, 28(14), 1588–1602.
- [20] Tan H.-L, Teow S.-Y. & Pushpamalar J. (2019). Application of Metal Nanoparticle–Hydrogel Composites in Tissue Regeneration. *Bioengineering*, 6(1), 17.
- [21] Park H., Lee H., An H. & Lee K.Y. (2017). Alginate hydrogels modified with low molecular weight hyaluronate for cartilage regeneration. *Carbohydrate Polymers*, 162, 100–107. Doi: https://doi.org/10.1016/j.carbpol.2017.01.045.
- [22] Derkach S.R., Ilyin S.O., Maklakova A.A., Kulichikhin V.G. & Malkin A.Y. (2015). The rheology of gelatin hydrogels modified by κ-carrageenan. *LWT – Food Science and Technology*, 63(1), 612–619. Doi: https://doi.org/10.1016/j.lwt.2015.03.024.
- [23] Makvandi P, Ali G.W., Sala F.D., Abdel-Fattah W.I. & Borzacchiello A. (2019). Biosynthesis and characterization of antibacterial thermosensitive hydrogels based on corn silk extract, hyaluronic acid and nanosilver for potential wound healing. *Carbohydrate Polymers*, 223, 115023. Doi: https:// doi.org/10.1016/j.carbpol.2019.115023.

- [24] Li T., Zhang M., Wang J., Wang T., Yao Y., Zhang X., Zhang C. & Zhang N. (2016).Thermosensitive Hydrogel Co-loaded with Gold Nanoparticles and Doxorubicin for Effective Chemoradiotherapy. *AAPS Journal*, 18, 146–155. Doi: https://doi. org/10.1208/s12248-015-9828-3.
- [25] Ragab T.I.M., Nada A.A., Ali E.A., Shalaby A.S.G., Soliman A.A.F., Emam M. & El Raey M.A. (2019). Soft hydrogel based on modified chitosan containing *P. granatum* peel extract and its nano-forms: Multiparticulate study on chronic wounds treatment. *International Journal of Biological Macromolecules*, 135, 407–421. Doi: https://doi.org/10.1016/j.ijbiomac.2019.05.156.
- [26] Gallo E., Diaferia C., Di Gregorio E., Morelli G., Gianolio E. & Accardo A. (2020). Peptide-Based Soft Hydrogels Modified with Gadolinium Complexes as MRI Contrast Agents. *Pharmaceuticals*, 13(2), 19. Doi: https://doi.org/10.3390/ph13020019.
- [27] Rask F., Mihic A., Reis L., Dallabrida S.M., Ismail N.S., Sider K., Simmons C.A., Rupnick M.A., Weisel R.D., Li R.K. & Radisic M. (2010). Hydrogels modified with QHREDGS peptide support cardiomyocyte survival in vitro and after sub-cutaneous implantation. *Soft Matter*, 6, 5089–5099. Doi: https://doi.org /10.1039/C0SM00362J.
- [28] Pankongadisak P. & Suwantong O. (2019). Enhanced properties of injectable chitosan-based thermogelling hydrogels by silk fibroin and longan seed extract for bone tissue engineering. *International Journal of Biological Macromolecules*, 138, 412–424. Doi: https://doi.org/10.1016/j.ijbiomac.2019.07.100.
- [29] Sotiropoulou N.S., Megremi S.F. & Tarantilis P. (2020). Evaluation of Antioxidant Activity, Toxicity, and Phenolic Profile of Aqueous Extracts of Chamomile (*Matricaria chamomilla L.*) and Sage (*Salvia offcinalis L.*) Prepared at Different Temperatures. *Applied Sciences*, 10(7), 2270. Doi: https://doi.org/10.3390/app-10072270.
- [30] Kurek-Górecka A., Górecki M., Rzepecka-Stojko A., Balwierz R. & Stojko J. (2020). Bee Products in Dermatology and Skin Care. *Molecules*, 25(3), 556. Doi: https://doi.org/10.3390/molecules-25030556.
- [31] Kong F.Y., Zhang J.W., Li R.F., Wang Z.X. Wang W.J. & Wang W. (2017). Unique Roles of Gold Nanoparticles in Drug Delivery, Targeting and Imaging Applications. *Molecules*, 22(9), 1445. Doi: https://doi.org/10.3390/molecules22091445.
- [32] Yafout M., Ousaid A., Khayati Y. & Otmani I.S. (2021). Gold nanoparticles as a drug delivery system for standard chemotherapeutics: A new lead for targeted pharmacological cancer treatments. *Science African*, 11, e00685. Doi: https://doi. org/10.1016/j.sciaf.2020.e00685.
- [33] Topsakal A., Midha S., Yuca E., Tukay A., Sasmazel H.T., Kalaskar D.M. & Gunduz O. (2021). Study on the cytocompatibility, mechanical and antimicrobial properties of 3D printed composite scaffolds based on PVA/ Gold nanoparticles (AuNP)/ Ampicillin (AMP) for bone tissue engineering. *Materials Today Communications*, 28, 102458. Doi: https://doi.org/10.1016/ j.mtcomm.2021.102458.
- [34] Abdulazeem L., Jasim S.A. & Rajab W.J. (2021). Anti-bacterial activity of gold nanoparticles against two type of antibiotic resistance pathogenic bacteria in Al-Hilla city. *Materials Today: Proceedings*. Doi: https://doi.org/10.1016/j.matpr.2021.05.234.
- [35] Tyliszczak B., Drabczyk A., Kudłacik-Kramarczyk S. & Sobczak-Kupiec A. (2018). Synthesis, characterization, and in vitro cytotoxicity of chitosan hydrogels containing nanogold. *International Journal of Polymeric Materials and Polymeric Biomaterials*, 68(4), 175–182. Doi: https://doi.org/10.1080/00914037.2018. 1429438.
- [36] Vargas-Estrada L., Torres-Arellano S., Longoria A., Arias D.M., Okoye P.U. & Sebastian PJ. (2020). Role of nanoparticles on microalgal cultivation: A review. *Fuel*, 280, 118598. Doi: https:// doi.org/10.1016/j.fuel.2020.118598

- [37] Srinath B.S. & Ravishankar Rai V. (2014). Biosynthesis of highly monodispersed, spherical gold nanoparticles of size 4–10 nm from spent cultures of *Klebsiella pneumoniae*. *3 Biotech*, 5, 671–676. Doi: https://doi.org/10.1007/s13205-014-0265-2.
- [38] Liang A., Liu Q., Wen G. & Jiang Z. (2012). The surface-plasmon-resonance effect of nanogold/silver and its analytical applications. *Trends in Analytical Chemistry*, 37, 32–47. Doi: https://doi.org/10.1016/j.trac.2012.03.015.
- [39] Huang X. & El-Sayed M.A. (2010). Gold nanoparticles: Optical properties and implementations in cancer diagnosis and photothermal therapy. *Journal of Advanced Research*, 1, 13–28. Doi: https://doi.org/10.1016/j.jare.2010.02.002.
- [40] Albusta N., Alarabi D., Alsoud S.A., Keogh M., Akhtar S. & Henari F. (2018). Detection of Glucose using Gold Nanoparticles Prepared by Green Synthesis. *International Journal of Engineering & Scientific Research*, 6(10), 1–10.
- [41] Kar P.K., Murmu S., Saha S., Tandon V. & Acharya K. (2014). Anthelminitic Efficacy of Gold Nanoparticles Derived from a Phytopathogenic Fungus, *Nigrospora oryzae. PLoS ONE*, 9(1), e84693. Doi: https://doi.org/10.1371/journal.pone.0084693.
- [42] Ngo V.K.T., Nguyen H.P.U., Huynh T.P., Tran N.N.P., Lam Q.V. & Huynh T.D. (2015). Preparation of gold nanoparticles by microwave heating and application of spectroscopy to study conjugate of gold nanoparticles with antibody *E. coli* 0157:H7. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 6(3), 035015.
- [43] Duan L., Yefu W., Li S.S., Zhixiang W. & Zhai J. (2005). Rapid and simultaneous detection of human hepatitis B virus and hepatitis C virus antibodies based on a protein chip assay using nano-gold immunological amplification and silver staining method. *BMC Infectious Diseases*, 5(53). Doi: https://doi. org/10.1186/1471-2334-5-53.
- [44] Amendola V. & Meneghetti M. (2009). Size Evaluation of Gold Nanoparticles by UV-vis Spectroscopy. *Journal of Physical Chemistry*, 113(11), 4277–4285. Doi: https://doi.org/10.1021/ jp8082425.
- [45] Zhan Y., Fu W., Xing Y., Ma X. & Chen C. (2021). Advances in versatile anti-swelling polymer hydrogels. *Materials Science and Engineering: C*, 127, 112208. Doi: https://doi.org/10.1016/ j.msec.2021.112208.
- [46] Richbourg N. & Peppas N.A. (2020). The swollen polymer network hypothesis: Quantitativemodels of hydrogel swelling, stiffness, and solute transport. *Progress in Polymer Science*, 105, 101243. Doi: https://doi.org/10.1016/j.progpolymsci.2020.101243.
- [47] Zhu Q., Barney C.W. & Kendra A.E. (2015). Effect of ionic crosslinking on the swelling and mechanical response of model superabsorbent polymer hydrogels for internally cured concrete. *Materials and Structures*, 48, 2261–2276. Doi: https://doi. org/10.1617/s11527-014-0308-5.
- [48] Al-Anbakey A.M.S. (2014). Effect of pH on swelling properties of commercial polyacrylic acid hydrogel bead. *Journal of Atoms* and Molecules, 4(1), 656–665.
- [49] Parlinska-Wojtan M., Kus-Liskiewicz M., Depciuch J. & Sadik O. (2016). Green synthesis and antibacterial effects of aqueous colloidal solutions of silver nanoparticles using chamomile terpenoids as a combined reducing and capping agent. *Bioprocess and Biosystems Engineering*, 39, 1213–1223. Doi: https://doi. org/10.1007/s00449-016-1599-4.
- [50] Anjos O., Santos A.J.A., Dias T. & Estevinho L.M. (2017). Application of FTIR-ATR spectroscopy on the bee pollen characterization. *Journal of Apicultural Research*, 56(3), 210–218. Doi: https://doi.org/10.1080/00218839.2017.1289657.

The Influence of Various Matrixes on the Strength Properties of Moulding Sands with Thermally Hardened Hydrated Sodium Silicate for the Ablation Casting Process

Katarzyna Major-Gabryś^{a*}, Sabina Puzio^a, Agata Bryłka^a, Jadwiga Kamińska^b

^aAGH University of Science and Technology, Faculty of Foundry Engineering, Department of Moulding Materials, Mould Technology and Foundry of Non-ferrous Metals, Mickiewicza 30, 30-059 Krakow, Poland ^bLukasiewicz Research Network – Krakow Institute of Technology, Zakopianska 73, 30-418 Krakow, Poland **e-mail: katmg@agh.edu.pl*

© 2021 Authors. This is an open access publication, which can be used, distributed and reproduced in any medium according to the Creative Commons CC-BY 4.0 License requiring that the original work has been properly cited.

Receive 5 May 2021/Accepted: 23 June 2021/ Published online: 5 July 2021 This article is published with open access at AGH University of Science and Technology Press

Abstract

The essence of ablation casting technology consists in pouring castings into single-use moulds made from the mixture of sand and a water-soluble binder. After pouring the mould with liquid metal yet while the casting is still solidifying, the mould destruction (washing out, erosion) takes place using a stream of cooling medium, which in this case is water. This paper focuses on the selection of moulding sands with hydrated sodium silicate for moulds used in ablation casting. The research is based on the use of water glass 145 and 150 as binders. As part of the research, loose moulding mixtures based on two silica sands from different sand mines with different content of binders were prepared. The review of literature data and the results of own studies have shown that moulding sand with hydrated sodium silicate hardened by dehydration is characterized by sufficient strength properties to be used in the ablation casting process. Our own research also confirmed the possibility of using these sand mixtures in terms of both casting surface quality and sand reclamation. The results presented in this paper prove that both sand grains and types of binder tested may be used as components in moulding sands devoted to ablation casting.

Keywords:

innovative foundry technologies and materials, moulding sand, ablation casting, water glass, thermal curing

1. INTRODUCTION

Ablation casting is a term taken probably from the Latin ablatio meaning removal or ablutio which means washing. The essence of ablation casting technology consists in pouring castings in single-use moulds made from a mixture of sand and a water-soluble binder. After pouring the mould with liquid metal, while the casting is still solidifying, it is destroyed (washed out, erased). It takes place using a stream of cooling medium, which in this case is water. China is considered to be the precursor of ablation casting technology [1]. A piece of rope or cord was coated with clay which was fired and washed out, and a mould obtained in this way was filled with liquid metal. This technique was used to produce dish handles from around 1600 BC (Fig. 1).



Fig. 1. Examples of the use of ablation in ancient China [1]

In 2006, Alotech patented a casting station using the ablation casting method. The process of ablation casting consists of the following steps (1) make a mould of aggregates bonded with a water-soluble binder such as sodium silicate, (2) fill the mould cavity with a molten metal, (3) wait for a required delay between the mould filling and the start of ablation, and (4) start ablation of the mould [2]. Figure 2 shows an example of the ablation casting process proposed by Alotech [3]. The molten metal poured into the cavity of the sand moulds which are located on a belt conveyor and are moved horizontally to the water jets, is firstly cooled in the sand mould. As the mould travels toward the water jets, mould ablation starts from the edge of the mould, reaches the distal end of the solidifying casting, and moves progressively toward the feeder of the casting shown in Figure 2a, until the casting is solidified (Fig. 2b). The sand mould is broken down under high water pressure [2-8].

a)

b)



Fig. 2. View of the ablation casting process of a steering knuckle proposed by Alotech (a) with a solidified casting (b) [7]

Ablation casting technology offers advantages such as:

- The mould is destroyed with a stream of liquid medium during the casting solidification process, which eliminates the additional operation of knocking out from the mould and considerably reduces the dust pollution in a foundry plant.
- Some components of the moulding sand can be reclaimed.
- There is no air gap between the mould and the top layer of the cooled casting, which limits the heat flow to the outside. This enables solidification under the conditions of unprecedentedly large temperature gradients and high solidification rates. The mechanical properties of castings made using the ablation casting technology are reported to be superior to that made using low-pressure permanent mould (LPPM) casting process [2, 8].

- Controlled, directional cooling, achieved in this technology, favours the elimination of shrinkage porosity.
- The economic factor of the process is making high-quality castings in compact, single-use moulds as compared to high-tech permanent-mould technologies.
- The ecological factor associated with the use of an inorganic water-soluble binder.

The effect of ablation casting on solidification characteristics, microstructure formation, and mechanical properties of the casts have also been described in several publications [2, 9-12].

2. RESEARCH

The moulding sand used in the modified ablation casting process should be characterized by a durability that allows the transfer of the hydrostatic pressure of the liquid metal while being susceptible to the destructive effect of the cooling medium [13]. The use of hydrated sodium silicate as a binder for ablation casting technology is therefore justified. The inorganic binder is water-soluble and environmentally friendly. The ecological nature of the binder currently makes it the object of numerous studies [14], while modern processes using hydrated sodium silicate are increasingly used in foundry practice.

Figure 3 shows the modified ablation casting process steps elaborated in the Lukasiewicz Research Network – Krakow Institute of Technology. A patent application for the technology has been filed [15] In previous studies, the authors proposed the use of moulding sands with a Cordis binder [16] produced by the Hüttenes-Albertus Company. It was a new-generation inorganic binder based on hydrated sodium silicate. Its hardening occurred under the effect of high temperature. In that technology, a loose inorganic Anorgit additive [16] was also used as an agent which prevents burn-on defects and improves the durability of cores, mitigating the adverse effect of humidity present in the environment [16].



Fig. 3. Modified ablation casting process steps; Lukasiewicz Research Network – Krakow Institute of Technology [17]

Previous works [17] included preliminary semi-industrial tests were carried out on the use of moulding sand with water glass 145 in the manufacture of moulds for ablation casting. The potential to use these sand mixtures has been confirmed in terms of both casting surface quality and sand reclamation.

3. EXPERIMENTAL PROCEDURE

As part of our own research, we proposed using moulding sands with hydrated sodium silicate thermally cured by dehydration as a material for the moulds in ablation casting. The main advantage of the dehydration process is the achievement of high strength properties, much higher than in the case of chemical hardening, combined with the absence of harmful products of the chemical reaction of hardening.

The mechanism of thermal curing of hydrated sodium silicate consists in its dehydration. It has been found that in the temperature range from 20°C to about 70°C, free water is removed, while in the temperature range from about 115°C to about 140°C, the removal of bound water occurs [18–20].

As a result of the thermal curing of sodium water glass, a structure composed of precipitated, amorphous, monolithic silicate shells is formed. The inverted reactions produce a gel (physical hardening) [18].

The aim of this paper was the comparison of the influence of different sand matrixes and different binder types on the strength properties of moulding sands. Moulding sands based on following sand matrixes were used:

- 1K silica sand from the Grudzen Las Company with a main fraction of 0.20/0.40/0.315,
- silica sand from the Sibelco Poland Company; classified according to the Polish standard PN-85/H-11001 as medium; with the value of the main fraction of 84%, which determines the sand as homogeneous.

As a binder, the inorganic water glass 145 and water glass 150 were used in an amount of 1.0, 1.5 and 2.0 parts by weight. Chosen properties of binders are shown in Table 1.

Table 1Chosen properties of water glass 145 and water glass 150 [21, 22]

Property / unit	Water glass 145 binder	Water glass 150 binder	
form	water solution	water solution	
physical condition	liquid	liquid	
colour	colourless	colourless	
smell	odourless	odourless	
$Na_{2}0 + SiO_{2}$ (min), %	39	40	
Na ₂ 0/SiO ₂ (molar module)	2.4-2.6	1.9–2.1	
density (in temp. 20°C), g/cm ³	1.45-1.48	1.50-1.53	
viscosity (in temp. 20°C)	1	1	

Moulding sands were prepared in a laboratory ribbon mixer, type LMR-2. The sand was mixed with the additive for 60 seconds, then the binder was introduced and the whole was mixed for another 150 seconds.

From the moulding sands, standard specimens were prepared for bending strength tests. Specimens were made in a universal LUT shooter. They were cured at 160°C for 30, 60, 90 and 120 seconds. The time and pressure of shooting were the same for all the specimens and amounted to 2 seconds and 0.5 MPa, respectively.

Measurements of the moulding sand bending strength were carried out on an LRu-2 type apparatus in accordance with guidelines given in the PN-83/H-11073 standard.

The moulding sands' properties were tested in both a hot state (directly after the removal from shooting machine) and a cold state (after 1 hour of curing at ambient temperature).

4. RESULTS AND DISCUSSION

Figures 4–7 show the obtained results of bending strength tests of moulding sands with water glass.



Fig. 4. The influence of R145 binder amount on bending strength properties of moulding sand based on Grudzen Las sand matrix and hardened in 160°C [23]



Fig. 5. The influence of R150 binder amount on bending strength properties of moulding sand based on Grudzen Las sand matrix and hardened in 160°C [23]



Fig. 6. The influence of R145 binder amount on bending strength properties of moulding sand based on Sibelco sand matrix and hardened in 160°C [23]



Fig. 7. The influence of R150 binder amount on bending strength properties of moulding sand based on Sibelco sand matrix and hardened in 160° C [23]

In the case of the use of the Grudzen Las sand matrix to prepare moulding sands with hydrated sodium silicate, the obtained test results for two types of binder, R145 and R150, were similar. Moulding sands with a content of 1.0 p.p.w. tested "hot" are characterized by strength of approx. 0.55 MPa when hardened for 30 s and approx. 0.90 MPa when hardened for 120 s. Moulding sands with a content of 1.5 p.p.w. tested "hot" have a strength of approx. 0.7 MPa when hardened for 30 s and approx. 1.4 MPa when hardened for 120 s. Moulding sands with a content of 2.0 p.p.w. tested "hot" have a strength of approx. 0.8 MPa when hardened for 30 s and approx. 1.87 MPa when hardened for 120 s. Moulding sands with a content of 1.0 p.p.w. tested in the "cold" state have a strength of approx. 2.0 MPa, regardless of the hardening time. Moulding sands with a content of 1.5 p.p.w. tested in the "cold" state have a strength of approx. 2.7 MPa, and here no influence of hardening time on the strength of the moulding sands was observed. Moulding sands with a content of 2.0 p.p.w. tested in the "cold" state are characterized by a strength of approx. 3.3 MPa and there was no effect of hardening time on the strength of the moulding sands.

In the case of the Sibelco Poland sand matrix used to prepare moulding sands with hydrated sodium silicate, the obtained test results for the two types of binder, R145 and R150, were different. The moulding sands containing the R150 binder are characterized by strength properties similar to those of the moulding sands based on Grudzen Las sand matrix. In the case of composition with R145 binder, their strength in the entire tested range is lower by an average of 30%. Strength values similar to other compositions are obtained by the moulding sand based on Sibelco Poland matrix with R145 binder, tested in cold state, with binder content of 1.5 and 2.0 p.p.w. hardened in 60, 90 and 120 s. In the case of all tested moulding sands, curing for 30 seconds are characterized by the lowest strength properties in the hot state.

5. CONCLUSIONS

The analysis of literature data and our own research allow for the formulation of the following conclusions:

- The use of moulding sands with hydrated sodium silicate as a binder for ablation casting moulds is fully justified.
- From the ablation casting point of view, the most suitable sands with hydrated sodium silicate are physically hardened sands, which include thermal curing (warm-box) by dehydration.
- The results of tests obtained for Grudzen Las sand matrix to prepare moulding sands with hydrated sodium silicate with two types of binder, R145 and R150, are similar.
- The results of tests obtained for Sibelco Poland sand matrix to prepare moulding sands with hydrated sodium silicate with two types of binder, R145 and R150, are different. The results of tests obtained for the Sibelco Poland sand matrix to prepare moulding sands with hydrated sodium silicate with two types of binder, R145 and R150, are similar and are characterized by strength properties similar to those of the moulding sands based on the Grudzen Las sand matrix. In the case of compositions with R145 binder, their strength properties in the entire tested range are lower by an average of 30%.
- The best strength properties are obtained by moulding sands containing 2 p.p.w. of binders examined in a "cold" state in the case of both tested sand matrixes.
- The research presented in this paper is a part of a wider ranging study which will be continued both in the context of the selection of moulding sands and the evaluation of the properties of the castings obtained by means of ablation casting technology.

Acknowledgement

The research was financed by AGH Research Project No. 16.16.170.654.

REFERENCES

- Derui T. & Haiping L. (2011). The ancient Chinese casting techniques. 69th WFC Paper 2010. *China Foundry*, 8(1), 127–136.
- [2] Han Q. (2021). Ablation casting: solidification characteristics, microstructure formation, and mechanical properties. *International Journal of Metalcasting*. Doi: https://doi.org/10.1007/ s40962-020-00544-w.
- [3] Grassi J.R. & Campbell J. (2006). Solidification microstructure of aggregatemolded shaped castings, patent US 2008/0041499 A1, United States Patent Application Publication.
- [4] Weiss D., Grassi J., Schultz B. & Rohatgi P. (2011). Ablation of Hybrid Metal Matrix Composite, *Transactions of the American Foundry Society*, 119, 35–41.
- [5] Grassi J., Campbell J., Hartlieb M. & Major F. (2009). The Ablation Casting Process. *Materials Science Forum*, 618–619, 591–594.
- [6] Weiss D., Schultz B. & Rohatgi P. (2012). Discovering Ablation: An emerging technology known as ablation can achieve fine microstructure and better mechanical properties in casting alloys. *Metal Casting Design & Purchasing*, January/February, 36–39.
- [7] Weiss D., Grassi J., Schultz B. & Rohatgi P. (2011). Testing the Limits of Ablation. *Modern Casting*, December, 26–29.
- [8] Dudek P., Fajkiel A., Reguła T. & Bochenek J. (2014). Badania nad technologią odlewania ablacyjnego stopów aluminium [Research on ablation casting technology for aluminium alloys]. *Prace Instytutu Odlewnictwa*, 54(2), 23–35.
- [9] Grassi J., Campbell J., Hartlieb M. & Major F. (2008). Ablation Casting. In: Yin W. & Das S.K., Aluminium Alloys: Fabrication, Characterization and Applications. The Minerals, Metals & Materials Society, Warrendale, 73–77.
- [10] Bohlooli V., Shabani-Mahalli M. & Boutorabi S.M.A. (2013). Effect of Ablation Casting on Microstructure and Casting Properties of A356 Aluminium Casting Alloy. *Acta Metallurgica Sinica (English Letters)*, 26(1), 85–91. Doi: https://doi.org/10.1007/s40195-012-0092-6.

- [11] Taghipouriana M., Mohammadaliha M., Boutorabi S.M. & Mirdamadi S.H. (2016). The effect of waterjet beginning time on the microstructure and mechanical properties of A356 aluminum alloy during the ablation casting process. *Journal of Materials Processing Technology*, 238, 89–95.
- [12] Williams T.J., Galles D. & Beckermann Ch. (2013). Translating Water Spray Cooling of a Steel Bar Sand Casting. In: Proceedings of the 67th SFSA Technical and Operating Conference. Paper No. 5.4. Steel Founders' Society of America, Chicago.
- [13] Izdebska-Szanda I., Angrecki M. & Palma A. (2015). Dobór technologii formy dla zmodyfikowanej metody ablacyjnego odlewania [Choice of mould-making technology for the modified ablation casting process]. Prace Instytutu Odlewnictwa, 55(2), 55–66.
- [14] Major-Gabryś K. (2016). Odlewnicze masy formierskie i rdzeniowe przyjazne dla środowiska. Gliwice: Wydawnictwo Archives of Foundry Engineering, Komisja Odlewnictwa PAN Katowice.
- [15] Kamińska J., Hosadyna-Kondracka M., Puzio S. & Major-Gabryś K. (2020). Jednorazowa forma odlewnicza, opis zgłoszeniowy wynalazku, PL 429888 A1. *Biuletyn Urzędu Patentowego*, 24, 16. Available on http://patenty.bg.agh.edu.pl/pelneteksty/PL429888A1.pdf.
- [16] Hosadyna-Kondracka M., Major-Gabryś K., Kamińska J., Grabarczyk A. & Angrecki M. (2018). Moulding Sand with Inorganic Cordis Binder for Ablation Casting. *Archives of Foundry Engineering*, 18(4), 110–115.
- [17] Major-Gabryś K., Hosadyna-Kondracka M., Puzio S., Kamińska J., Angrecki M. (2020). The influence of the modified ablation casting on casts properties produced in microwave hardened moulds with hydrated sodium silicate binder. *Archives of Metallurgy and Materials*, 65(1), 497–502.
- [18] Baliński A. (2000). Wybrane zagadnienia technologii mas formierskich ze spoiwami nieorganicznymi. Struktura uwodnionego krzemianu sodu i jej wpływ na wiązanie mas formierskich. Wydawnictwo Instytutu Odlewnictwa, Kraków.
- [19] CIATF Comission 1.6, Alkali Silica Binder, 1982–1985, Düsseldorf, Germany.
- [20] Różycka D., Stechman M., Wilkosz B. & Baliński A. (2000). Szkło wodne jako spoiwo w odlewnictwie. Cz. II. Struktura. *Chemik*, 53(8), 215–219.
- [21] Z.Ch. Rudniki S.A. (2016). Offer specification of the product: No. 14/7.
- [22] Z.Ch. Rudniki S.A. (2017). Offer specification of the products: Sodium silicate R150.
- [23] Bryłka A. (2019). Dobór mas formierskich na formy do ablacyjnego odlewania stopów Al. AGH, Kraków [Master thesis].