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### PROSPECTS OF USING DLP 3D PRINTING TECHNOLOGY TO PRODUCE MEMBRANE KAOLIN MATRICES AND MEMBRANE HOLDERS

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#### Abstract

The ongoing evolution of 3D printing technologies demonstrates considerable potential for the production of porous ceramics, including ceramic matrices. These technologies enable the creation of three-dimensional structures with high complexity and precision from a variety of raw materials. This study assesses the feasibility of utilising DLP 3D printing technology to produce ceramic matrices and membrane holders for the development of ceramic membrane modules. To fabricate ceramic matrices by this method, it was proposed to use natural Ukrainian kaolin as the ceramic component in a photopolymer-based suspension. It was found that increasing the kaolin concentration (from 0-40 wt.%) in the suspension fed for 3D printing leads to an rise in viscosity, and with an increase in temperature at which the kaolin was pretreated prior to suspension preparation (0-600 °C), it decreases. The physicochemical processes occurring during kaolin heating were characterised by thermal analysis, infrared spectroscopy, and low-temperature nitrogen adsorption-desorption. The results demonstrate that heating kaolin above 450 °C triggers dehydroxylation, while heating to 640 °C leads to its transformation into metakaolinite. Consequently, the infrared bands corresponding to structural water disappear, and the specific surface area, determined using the BET model, decreases from 22.8 m<sup>2</sup>/g to 15.2 m<sup>2</sup>/g. The reduction in viscosity of the suspension with thermally treated kaolin is likely due to diminished interactions between kaolin particles and the photopolymer resin after structural water removal. Modelling and preparation for 3D printing of ceramic matrices and membrane holders were performed using Autodesk Fusion 360 and the Anycubic Photon Workshop slicing software. The results indicate that the DLP method produced structurally integral ceramic matrices and successfully printed membrane holders. Thus, DLP 3D printing technology offers significant prospects for fabricating tailored ceramic matrices and membrane holders.

Keywords: 3D printing; DLP technology; photopolymer resin; ceramic matrix; kaolin; membrane modules.

# ПЕРСПЕКТИВИ ВИКОРИСТАННЯ ТЕХНОЛОГІЇ DLP 3D ДРУКУ ДЛЯ ВИГОТОВЛЕННЯ МЕМБРАННИХ МАТРИЦЬ З КАОЛІНУ ТА МЕМБРАНОТРИМАЧІВ

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Дане дослідження присвячено встановленню перспектив використання DLP технології 3D-друку для отримання керамічних мембран та мембранотримачів з метою створення мембранних керамічних модулів на їх основі. В якості керамічної складової суспензії на основі фотополімерної смоли запропоновано використання природної української сировини – каоліну. Було встановлено, що зі збільшенням концентрації каоліну (від 0 до 40 % мас.) у суспензії, яка подається для 3D-друку, її в'язкість зростає, а зі зростанням температури, при якій каолін попередньо термічно оброблявся перед приготуванням суспензії (від 0 до 600 °С), в'язкість, навпаки, зменшується. Фізико-хімічні процеси, що відбуваються під час нагрівання каоліну, були охарактеризовані методом термічного аналізу, інфрачервоної спектроскопії та низькотемпературної адсорбції-десорбції азоту. Результати показують, що нагрівання каоліну вище 450 °С веде до дегідроксилювання, а при 640 °С відбувається його перетворення на метакаолініт. Унаслідок цього зникають ІЧ-смуги, що відповідають структурній воді, а питома поверхня, визначена за моделлю ВЕТ, зменшується з 22.8 м²/г до 15.2 м²/г. Зменшення в'язкості суспензії з термічно обробленим каоліном, ймовірно, пов'язане зі зниженням взаємодії між частинками каоліну та фотополімерною смолою після видалення структурної води. Моделювання та підготовка до 3D-друку керамічних матриць і тримачів мембран виконувалися з використанням програмного забезпечення Autodesk Fusion 360 та Anycubic Photon Workshop. Отримані результати свідчать, що метод DLP дозволив сформувати структурно цілісні керамічні матриці та успішно надрукувати тримачі мембран. Таким чином, технологія DLP 3D-друку відкриває значні перспективи для виготовлення спеціалізованих керамічних матриць і тримачів мембран.

Ключові слова: 3D-друк; технологія DLP; фотополімерна смола; керамічна матриця; каолін; мембранні модулі.

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### Introduction

The recent rise in popularity of ceramic membranes can be attributed to their physicomechanical properties, which include mechanical strength, hardness, and resistance to biofouling and corrosion [1; 2].

Additive manufacturing (AM) technologies are currently employed in a number of different industries, including construction, aerospace, automotive, thermal power, chemical, food, and medical, as well as in electronics and water treatment technologies [3]. To address a wide range of complex tasks, AM technologies employ a variety of materials, including ceramics, plastics, metals, liquids, powders, and even living cells. Despite the gradual adoption of AM technologies in the fabrication of ceramic matrix for water treatment, there is a growing interest in adapting AM processes to produce defect-free ceramic materials that can serve as reliable membranes in wastewater treatment processes [4-6].

Ceramic AM printing technologies are typically classified into two main categories: single-step and multi-step processes. In single-step processes, ceramic materials are sintered in a single stage, with examples including SLS, SLM, and DED laser technologies [7]. In contrast, multistep processes entail the formation of an initial "green body" which is then subjected to a second stage of thermal treatment. This process is employed to remove the binding material and to sinter the product. Examples of such technologies include LOM, FDC, DIW, BJ, and DLP [8-11].

In digital light processing (DLP) technology, the "green body" is formed through the photopolymerisation of a photosensitive resin [12–14]. The use of a more cost-effective UV radiation source has led to the widespread employment of DLP technology for ceramic printing, with the manufacturing of ceramic matrix being considered a particularly suitable application [15–17]. The preparation of a DLPprintable suspension requires the homogenisation and dispersion of ceramic powder within an organic liquid base, resulting in a colloidal suspension that must meet stringent requirements regarding viscosity, stability, and photosensitivity [18-20].

The work [17] identifies a number of challenges that must be addressed during the DLP printing process in order to obtain suspensions with the requisite rheological properties and an absence of residual bubbles. It has been demonstrated that the parameters of

the suspension are dependent on a number of factors, including the nature and moisture content of the ceramic components, their affinity for the resin and organic solvents, the particle size distribution of the ceramic powders, and the degree and uniformity of their homogenisation in the suspension.

Another study [21] highlights the significance of utilising ceramic materials with submicron particle sizes in DLP printing. This approach ensures the production of smoother printed layers, optimised packing of ceramic particles in the "green body", and a reduction in shrinkage following sintering. In these studies, particular attention was paid to the preliminary treatment of ceramic particles and the suspension preparation methodology, with the objective of achieving an acceptable quality outcome. The authors utilised alumina and silica powders with a low specific surface area  $(1.6 \text{ m}^2/\text{g})$  and a particle diameter of 2.5 µm, which were subjected to a two-hour vacuum drying process at 150 °C prior to use. The ratio of powder to resin was 34 vol.% : 66 vol.%. The preparation procedure entailed a two-stage mixing and homogenisation process. Initially, the mixture was stirred in a dry mixer at 300 rpm for 20 minutes. Subsequently, it was mixed in a planetary centrifugal mixer under two distinct combinations of speed and time (i.e., 1800 rpm for 2 minutes and 1200 rpm for 5 minutes).

It can be seen, therefore, that the quality of the printed material and the characteristics of the "green body" are dependent on the rheological properties of the ceramic suspension. As documented in [22], an augmentation in suspension viscosity impeded the recoating of the solidified layer with a fresh suspension, resulting in unanticipated layer thicknesses and, subsequently, ceramic defects. It is therefore essential to optimise the particle size distribution of the ceramic components, their preliminary treatment and the homogenisation procedure in order to achieve the desired rheological properties of the 3D-printing suspension, thereby improving the quality of the "green body".

The significance of the quantitative composition of the solid ceramic component within the resin and the chemical nature of the organic phase of the suspension were explored in [23]. At a low solid content (less than 40 wt.%), the suspension exhibited the requisite rheological properties for printing; however, following the cessation of polymerisation, the formation of cracks and delamination was observed in the final

Conversely, structure. an elevated ceramic powder-to-polymer ratio, essential for the structural integrity of the final product, resulted in a detrimental impact on the printability of the ceramic resin due to augmented viscosity, which the flow liquid resin. impeded the of Furthermore, it was discovered that when the suspension comprised solelv the primary components (polymer, photoinitiator, and boehmite), uncontrolled resin polymerisation occurred as a consequence of the strong light scattering effect exerted by solid particles. Nevertheless, the incorporation of the SUDAN III dye (at a mere 0.15 wt.%), functioning as a UV absorber, markedly diminished this adverse impact by regulating the light path within the liquid base. Furthermore, it was observed that the addition of propanol had a beneficial effect on maintaining the required viscosity level at a sufficiently high solid-to-polymer ratio during 3D printing.

In the context of DLP technologies, the selection of an appropriate dispersant is also a crucial factor in achieving a low viscosity while maintaining an adequate solid-to-liquid ratio in the suspension [24]. It has been demonstrated that the dispersant exerts a direct influence on interparticle interactions in UV-curable alumina suspensions, which consequently affects their rheological properties. Three distinct commercial dispersants were subjected to analysis: oleic acid (OA), an alkane-acrylic phosphate ester (PM1590), and a copolymer dispersant (BYK111). The use of BYK111 as a dispersant resulted in improved wetting of alumina powders in the photocurable resin, a reduction in viscosity (1.04 Pa·s at 30 rpm), the ability to achieve a denser packing of the alumina powders, an increase in the solid content (55 vol.%), and a slowing of particle flocculation, which facilitated better suspension flow.

A variety of metal oxide powders and clay natural materials are used as ceramic materials for the formation of ceramic matrices by traditional methods [25], which determines their choice in the formation of ceramic matrices by additive technologies. However, in the context of 3D printing of ceramic materials, there have been recent studies using kaolin as a cheap and widespread natural material [26]. The use of kaolin is usually associated with the manufacture of monolithic materials, including the creation of so-called technical ceramics: structures for construction projects, such as cavity walls; hermetic packaging for various purposes, works

of art and various accessories [27–28]. According to the literature, the use of kaolin for these ceramic products is due to its technical characteristics: good corrosion strength, resistance and good elasticity of the 3D printing slurry. For example, work [29] shows the possibility of high-precision printing of complexshaped kaolin ceramics using DLP technology. The results indicate that the ceramics were produced with a sufficiently high density  $(2.38 \text{ g/cm}^3)$  and low shrinkage (17.35 %) at a sintering temperature of 1200 °C. Nevertheless, kaolin is mostly used for additive technologies, mainly extrusion DIW methods, which help to stabilise and reduce waste from the metallurgical industry by incorporating it into printed ceramic monolithic parts for various technical purposes [30]. At the same time, there is virtually no research in the literature on the manufacture of porous kaolin-based ceramic materials bv additive technologies, including DLP, which could serve as reliable matrices for the creation of ceramic membranes. This emphasises the relevance of finding ways and methods to involve such a widespread and cheap clay material in the process of obtaining ceramic matrices by 3D printing.

In conclusion, the meticulous preparation of DLP-printable suspensions can effectively address intricate and pertinent challenges encountered in the production of ceramic materials. This is particularly crucial in the fabrication of ceramic matrix, which are subject to rigorous property specifications. As illustrated in [4], the quality of a final ceramic membrane produced through 3D printing is contingent upon the attributes of the printing suspension, which must possess a precisely defined composition to ensure the desired viscosity, photo-optical characteristics, and solid content.

The main objective of the study was to establish the prospects of using DLP 3D printing to produce ceramic matrices based on kaolin of Ukrainian origin and membrane holders.

## **Experimental part**

## Materials and methods

For the preparation of the 3D-printing suspension, High Speed Resin 2.0 (Anycubic, China; viscosity: 75-85 Pa·s) and natural Ukrainian kaolin from the Glukhovetsky deposit (Ukraine) with a particle size fraction below 54  $\mu$ m were used. Borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O) and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) were used as fin

salts to reduce the sintering temperature during the final heat treatment (sintering process).

For printing membrane holders, ABS-Like Resin V2 (Anycubic, China; viscosity: 180–200 Pa·s) was employed. All the photopolymer resins used are photosensitive within the 365–405 nm wavelength range.

The physicochemical transformations of treatment kaolin during thermal were investigated by controlled heating to 1000 °C at a heating rate of 5 °C/min using a Q-1500 derivatograph (Paulik-Paulik-Erdey system). The initial and calcined kaolin samples were examined in the infrared range of 400–4000 cm<sup>-1</sup> using а Shimadzu **IRAffinity-1S** FTIR The structural-adsorptive spectrometer. properties of the kaolin samples were studied

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using low-temperature nitrogen adsorptiondesorption on a JWGB Meso 112 porosimeter.

The 3D models of «green body» of the ceramic matrix and membrane holders were developed using Autodesk Fusion 360. The 3D printing of the «green bodies» for ceramic matrix and membrane holders was performed on an Anycubic Photon Mono M5s DLP 3D printer.

The removal of the organic component – photopolymer resin (so-called debinding process) from «green body» was carried out in a tube furnace in an inert environment (Ar) at the temperature regime shown in Figure 1a. The sintering process, as a result of which ceramic matrices are obtained, was carried out in a muffle furnace in the air environment according to the temperature regime presented in Figure 1b.



Fig. 1. Temperature regimes: (a) removal of the organic component from the «green body», (b) sintering process

The rheological properties of the kaolin-resin suspensions were assessed using a rotational viscometer VEVOR NDJ-9S (China) with spindle No. 3. Viscosity was measured at 20 °C over a range of rotational speeds. The consistency coefficient (k) was determined from the slope and intercept of log–log plots of viscosity versus rotation speed (rpm), based on the power-law model adapted to experimental conditions. All suspensions were prepared as follows. The kaolin samples were gradually added to the resin under continuous stirring using an ultrasonic bath.

#### Results and their discussion

During the first attempts to produce a suspension for 3D printing, a problem arose with native (without thermal treatment) kaolin, namely, when it was added in an amount of 20 % to the photopolymer resin, the viscosity of the suspension increased significantly, making the suspension unsuitable for printing. Therefore, it was decided to subject the native kaolin to heat

treatment. To investigate the processes occurring during heat treatment, a thermal analysis was first performed.

The resulting thermogram is presented in Figure 2.

An analysis of the curves presented in Figure 2 leads to the following conclusions: in the temperature range from ambient temperature to 450 °C, there is virtually no observed mass loss, indicating the absence of physically adsorbed and crystalline water that would be removed in this temperature interval. Beyond the inflection point (450 °C), the process of dehydroxylation begins, whereby the structural water (-OH) is rapidly lost from the aluminol surface. This is indicated by a high rate of mass loss on the TG curves and an endothermic peak on the DTA curve. Subsequently, an exothermic peak (approximately at 600 °C) occurs without mass loss, indicating the formation of disordered metakaolin ( $Al_2Si_2O_7$ ). The exothermic effect observed in the 850-960 °C range indicates the transformation of metakaolin into an as a gamma-alumina-type structure [24; 25]. aluminosilicate spinel (Si<sub>3</sub>Al<sub>4</sub>O<sub>12</sub>), also referred to



Fig. 2. Thermogram of kaolin K0 heating

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Furthermore, the impact of the treatment temperature within the 300–600 °C range on the structural-adsorptive characteristics of the natural kaolin was investigated. Thermal treatment was conducted under the specified conditions listed in Table 1 for 120 minutes in a muffle furnace under ambient conditions, followed by cooling to room temperature. The resulting samples are designated K0–K7 (Table 1).

Table 1

Thermal treatment regimes for kaolin samples								
Kaolin sample	К0	K1	K2	КЗ	K4	K5	K6	K7
Treatment T, °C	Untreated	300	350	400	450	500	550	600

To determine the removal of structural water from natural kaolin (K0) after thermal treatment at different temperatures (K1, K2, K3, K4, K5, K6), IR spectroscopy was carried out. The IR spectra of the samples obtained are shown in Figure 3. It can be seen that the kaolin is heated to 500 °C, the structural water (in the wavelength range of 3600–3700 cm<sup>-1</sup>) is completely removed. For samples K5-K7, which were thermally treated at 500–600 °C, the IR spectra show significant changes in the wavenumber range of 500–1250 cm<sup>-1</sup>, starting from K4, indicating the removal of structural water from the crystal lattice and consequently the transformation of kaolinite into metakaolinite. The IR spectroscopy results correlate with the thermogravimetric analysis data.



Fig. 3. IR spectra of kaolin samples before and after thermal treatment

For investigation of the effect of thermal treatment on the adsorptive-structural characteristics of the kaolin samples (K0, K1, K3, K5, K7), low-temperature nitrogen adsorption-desorption measurements were conducted, and the specific surface area was subsequently determined. BET method was employed to obtain the adsorption-desorption isotherms, which are presented in Figure 4.

Thermal treatment of kaolin over the range of 300-600 °C induces structural and physicochemical changes that affect its specific surface area, surface activity, and behavior in photopolymer suspensions. According to BET analysis, the specific surface area of untreated kaolin is 22.8 m<sup>2</sup>/g. Upon heating to 300 °C, this value decreases to 15.1 m<sup>2</sup>/g and remains nearly

constant for samples treated at 400, 500, and 600 °C (14.3–15.2 m<sup>2</sup>/g). This  $\sim$  33 % reduction in surface area is attributed to the collapse of the interlayer porosity, partial stacking of lamellae, and thermal densification of edge regions, consistent with observations [31-32]. While BET surface area decreases, the disordering of the crystal lattice during thermal activationparticularly at temperatures above 450 °C produces chemically active, unsaturated surface sites. These include  $Al^{3+}$  and  $Si^{4+}$  coordination defects and broken hydroxyl bridges, which increase the surface reactivity of amorphous metakaolin [31-32]. These changes have a pronounced effect on the rheological properties of kaolin-resin suspensions used in DLP 3D printing.



Fig. 4. Nitrogen adsorption-desorption isotherms of kaolin

Viscosity measurements using a rotational viscometer showed that suspension behavior is strongly dependent on kaolin pretreatment temperature and its content in the suspension (Figure 5). As can be seen, untreated kaolin (K0) led to very high suspension viscosities even at moderate loadings (e.g., k = 17.953 mPa·s at 25 wt%), making it unsuitable for printing. This is likely due to the presence of strongly hydrophilic groups and hydrogen-bonding sites, which promote interparticle bridging and hinder wetting by the acrylate resin, this behavior is attributed to the layered structure of kaolin, which leads to aggregation [33].

Kaolin treated at 300 °C (K1) yielded the lowest viscosity at higher content (>30 wt%), yet performed worse at lower concentrations. On the

other hand, kaolin treated at 600 °C (K7) exhibited markedly increased viscosity even at 25-30 wt% of kaolin (e.g., k = 59.871-113.000 mPa·s), which can be linked to the formation of highly disordered metakaolin. Among thermally treated samples, kaolin calcined at 500 °C (K5) demonstrated the lowest viscosity:  $k = 11.563 \text{ mPa} \cdot \text{s}$  at 25 wt%, and 13.456 mPa·s at 26 wt%. Therefore, kaolin calcined at 500 °C was found to be the optimal ceramic component for DLP-compatible suspensions in this system. Overall, it was established that suspensions with a consistency index exceeding 15.000 mPa·s cease to flow under the model during printing and are thus unsuitable for 3D printing.



Fig. 5. Dependence of consistency coefficient on kaolin content in resin and its calcination temperature

In addition, the consistency of kaolin suspensions with photopolymer resin was also observed visually. It was found that the thickening of the suspension was observed when using kaolin samples K0, K1, K2, K3, and K7. For samples K4, K5, and K6, a slight thickening of the suspensions was observed, as evidenced by satisfactory spreading in the printing vat. Therefore, to use kaolin as a ceramic component in the preparation of a suspension for 3D printing, it is necessary to heat it at least at 450 °C, which prevents a significant increase in the viscosity of the suspension. Then, an investigation was conducted into the photopolymerisation process, utilising a suspension prepared with the selected kaolin sample, designated as K5. Kaolin K5 was gradually introduced to the photopolymer resin (26 wt% of kaolin), with continuous mixing in an ultrasonic bath. A portion of the resulting suspension was poured into a mould (Figure 6a) and exposed to direct UV radiation (3 W, 395 nm UV lamp) for 15 minutes (Figure 6b). This led to the successful polymerization of the mixture, which will be capable of forming «green body».

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Fig. 6. Kaolin K5-photopolymer mixture: (a) before UV irradiation; (b) after UV irradiation

The stability of this suspension was also investigated. For this purpose, the suspension was placed in a test tube and visually observed for 2 days. During this period, the suspension did not delaminate, which indicates its stability and is quite sufficient for using such a suspension for 3D printing.

Next, ceramic matrix and membrane holders were modelled. 3D model of the ceramic matrix was created using the functionality of the Autodesk Fusion 360 software. Figure 7a illustrates 3D model of matrix with diameter of 25 mm and height of 2.4 mm. Following the creation of 3D model, it was prepared for 3D printing using slicing software, which generated the model supports and layer-by-layer print files. The preparation of the model for printing on the photopolymer printer was conducted using Anycubic Photon Workshop v3.1.4 software.



Fig. 7. Stages of ceramic membrane fabrication: (a) 3D CAD model; (b) «green body»; (c) sample after debinding stage in inert atmosphere; (d) sample after sintering stage at 1100 °C

The 3D printing process was initiated by importing the completed 3D model file (.stl format) into the Anycubic Photon Workshop slicer for print preparation. The suspension (26 wt% of kaolin) utilized for membrane printing comprised 125 g of photopolymer resin, 46.38 g of kaolin, 3.5 g of borax, and 3.5 g of potassium carbonate. During the 3D printing process, the photopolymer resin was polymerised under UV irradiation, with the assistance of a photoinitiator present in the resin, which facilitated the formation of a solid «green body». The resulting «green body» after printing is shown in Figure 7b. As can be seen, the obtained «green body» was printed without visible defects and with precise geometric shapes, forming a strong composite system.

The «Green body» was then subjected to thermal treatment, first in an inert atmosphere (Figure 1a), followed by treatment in air (Figure 1b), resulting in the successful formation of a kaolin-based ceramic matrix. Consequently, after the debinding and sintering processes, the printed sample retained their shape and geometric integrity (Figure 7c and 7d) without any visible cracking or warping, confirming the suitability of the kaolin-resin formulation for thermal processing. The samples obtained in this way are considered as ceramic membrane subsequent deposition matrices for of intermediate and selective layers that will

determine their transport properties. It should be noted that the obtained matrices were characterized by low mechanical strength, which requires further optimization of their composition and temperature conditions.

The subsequent stage in the creation of complete membrane modules was the modelling and printing of a membrane holder for the ceramic membrane. The methodology employed for modelling the membrane holder was identical to that used for the ceramic membrane. The membrane holders were printed using ABS-Like Resin V2 photopolymer resin, which provides enhanced stability following polymerisation. Figure 8 illustrates the designed membrane holder model and the corresponding printed sample.



Figure 8 - Membrane holder: (a) 3D model; (b) printed sample

The membrane holder was tested for leak tightness using rubber O-ring seals, and the results demonstrated complete hermeticity. Consequently, in the work, «green body» of the ceramic matrix and the membrane holder for it were successfully modeled and printed on the DLP printer. Despite the relatively low mechanical strength of the matrix, which requires additional detailed studies to optimize the composition of the matrices and their temperature treatment, a new approach to obtaining ceramic matrices and membrane holders for them can already be proposed according to the scheme shown in Figure 9.



Fig. 9. Schematic illustration of using DLP technology to create ceramic membrane modules

Therefore, it can be concluded that additive manufacturing technologies, particularly DLP, provide significant prospects for forming ceramic matrix and their respective membrane holders, including the production of custom-sized components. This capability allows the creation of membrane modules using a single technology.

#### Conclusions

The paper presents a study to explore the prospects of using DLP 3D printing technology for the fabrication of ceramic matrix and membrane holders, with the aim of developing ceramic membrane modules based on them. It also demonstrates the possibility of using kaolin as the ceramic component in the suspension for DLP printing of «green bodies» of ceramic matrix. It is shown that to use kaolin for the preparation of suspensions for 3D printing, it must first be subjected to thermal treatment.

The thermal analysis of the original kaolin showed that dehydroxylation processes occur at temperatures above 450 °C, while at 600 °C transformation to metakaolinite occurs. These dehydroxylation processes are confirmed by IR spectroscopy and low temperature nitrogen adsorption-desorption, which are in full agreement with literature data. In particular, the IR spectra show the disappearance of bands corresponding to structural water, and the specific surface area decreases from 22.8  $m^2/g$  to 15.2  $m^2/g$ .

The viscosity of kaolin-photopolymer resin suspensions was investigated as a function of kaolin content and its thermal treatment temperature, and it was found that in order to use kaolin as a ceramic component for the preparation of suspensions suitable for 3D printing, kaolin must be heat treated at least at 450 °C, but not exceeding 550 °C, due to the absence of hydroxyl groups in such kaolin. It has also been experimentally shown that when the consistency coefficient of suspensions is exceeding  $15.000 \text{ mPa} \cdot \text{s}$ , the suspension is unsuitable for 3D printing. The most suitable and rational for 3D printing was found to be the suspension containing kaolin thermally treated at 500 °C, with a content of 26 wt% in the suspension. This suspension was characterized by a consistency coefficient of 13.456 mPa·s and was such that it made it possible to obtain "green bodies" with the subsequent production of ceramic matrices without structural defects.

Autodesk Fusion 360 software and the Anycubic Photon Workshop slicer were used to model and prepare ceramic matrix and membrane holders for 3D printing. The modelled «green body» of the ceramic matrix and its holder were successfully printed, demonstrating the

#### References

- [1] Molchan, Y., Vorobyova, V., Pylypenko, I., Shtyka O., Maniecki, T., Dontsova, T. (2024). Physicochemical and antibacterial properties of ceramic membranes based on silicon carbide. *Chem. Pap.*, 78(16), 8659–8672. doi: 10.1007/s11696-024-03695-w
- [2] Kuzminchuk, A., Burmak, A., Litynska, M., Dontsova, T. (2023). New diatomaceous earth and kaolinite ceramic membranes for turbidity reduction in water. *Appl Nanosci*, *13*(7), 5335–5343. doi: 10.1007/s13204-023-02792-8
- [3] Lee, J.-Y., Tan W. S., An J., Chua C. K., Tang C. Y., Fane A.G., Chong T.H. (2016). The potential to enhance membrane module design with 3D printing technology. *Journal of Membrane Science*, 499, 480– 490. doi: 10.1016/j.memsci.2015.11.008
- [4] Abdelkader, M., Petrik, S., Nestler, D., Fijalkowski, M. (2024). Ceramics 3D Printing: A Comprehensive Overview and Applications, with Brief Insights into Industry and Market. *Ceramics*, 7, 68–85. <u>doi:</u> <u>10.3390/ceramics7010006</u>
- [5] Chen, T., Xu, P., Qiu, M., Chen, X., Zhong, Z., and Fan, Y. (2024). Construction of anti-fouling ceramic tubular membranes with corrugated inner surfaces using DLP 3D printing. *Journal of Membrane Science*, 706, 122941. doi: 10.1016/j.memsci.2024.122941
- [6] Diachenko, A.; Hutsul, K.; Dontsova, T. (2024). Prospects for Using 3d Printing to Form Ceramic Membranes: A Brief Review. Water Water Purif. Technol., Sci. Tech. News, 38(1), 14–26. doi: 10.20535/2218-930012024315361

significant potential of DLP technology for the fabrication of ceramic matrix and membrane holders, after which the ceramic matrix was obtained by debinding and sintering processes. It was found that the resulting matrix exhibited low mechanical strength, indicating the need for further detailed studies on formulation and thermal treatment conditions. Despite this, it can be concluded that this approach allows the creation of membrane modules with desired designs.

Future research will focus on optimising the formulation of the initial suspension for 3D printing of ceramic matrices and the temperature regimes of the debinding and sintering processes in order to obtain mechanically robust ceramic matrices that will serve as a support for the deposition of intermediate and selective layers to create micro- and ultrafiltration membranes.

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- [7] Xing, J., Sun, W., Rana, R. S. (2013). 3D modeling and testing of transient temperature in selective laser sintering (SLS) process. *Optik*, 124(4), 301–304. <u>doi:</u> 10.1016/j.ijleo.2011.11.064
- [8] Lakhdar, Y., Tuck, C., Binner, J., Terry, A., and Goodridge, R. (2021). Additive manufacturing of advanced ceramic materials. *Progress in Materials Science*, 116, 100736. <u>doi: 10.1016/j.pmatsci.2020.100736</u>
- [9] Chen, Z., Li, Z., Li, J., Liu, C., Lao, C., Fu, Y., Liu, C., Li, Y., Wang, P., He, Y. (2019). 3D printing of ceramics: A review. *Journal of the European Ceramic Society*, 39(4), 661–687. doi: 10.1016/j.jeurceramsoc.2018.11.013
- [10] Bai, Y., Williams, C. B. (2018). Binder jetting additive manufacturing with a particle-free metal ink as a binder precursor. *Materials & Design*, 147, 146–156. doi: 10.1016/j.matdes.2018.03.027
- [11] Hwa, L. C., Rajoo, S., Noor, A. M., Ahmad, N., Uday, M. B. (2017). Recent advances in 3D printing of porous ceramics: A review. *Current Opinion in Solid State and Materials Science*, 21(6), 323–347. <u>doi:</u> 10.1016/j.cossms.2017.08.002
- [12] Lakkala, P., Munnangi, S. R., Bandari, R., Repka, M. (2023). Additive manufacturing technologies with emphasis on stereolithography 3D printing in pharmaceutical and medical applications: A review. *International Journal of Pharmaceutics: X*(5), 100159. doi: 10.1016/j.ijpx.2023.100159
- [13] Tsolakis, I. A., Papaioannou, W., Papadopoulou, E., Dalampira, M., and Tsolakis, A. I. (2022). Comparison in

terms of accuracy between DLP and LCD printing technology for dental model printing. *Dentistry Journal*, *10*(10), 181. <u>doi: 10.3390/di10100181</u>

- [14] Roohani, I., Entezari, A., Zreiqat, H. (2023). Liquid crystal display technique (LCD) for high resolution 3D printing of triply periodic minimal surface lattices bioceramics. *Additive Manufacturing*, 74, 103720. doi: 10.1016/j.addma.2023.103720
- [15] Schmidleithner, C., and Kalaskar, D. M. (2018). Stereolithography. In 3D Printing. IntechOpen. doi: 10.5772/intechopen.78147
- [16] Ye, Y., Du, Y., Hu, T., You, J., Bao, B., Wang, Y., Wang, T. (2021). 3D Printing of Integrated Ceramic Membranes by the DLP Method. *Ind. Eng. Chem. Res.*, 60(26), 9368– 9377. doi: 10.1021/acs.iecr.1c02224
- [17] Mamatha, S., Biswas, P., Johnson, R. (2023). Digital light processing of ceramics: an overview on process, materials and challenges. *Prog Addit Manuf*, 8(5), 1083–1102. doi: 10.1007/s40964-022-00379-3
- [18] Gao, Y., Jacques Lalevée, J., Simon-Masseron, A. (2023). An Overview on 3D Printing of Structured Porous Materials and Their Applications. Advanced Materials Technologies, 8(17), 2300377. doi: 10.1002/admt.202300377
- [19] Zoumpouli, G. A., Guaraldo, T. T., Warren, Z., Mattia, D., Chew, J. (2024). Reimagining the shape of porous tubular ceramics using 3D printing. *Applied Materials Today*, 37, 102136. doi: 10.1016/j.apmt.2024.102136
- [20] Fu, Q., Ma, Y., Wang, J., Yang, Y., Wang, P., Li, S., Zhao, Y. (2024). Digital light processing of high-purity SiC ceramic membrane support modified by SiC whisker. *Ceramics International*, 50(21), Part A, 41237– 41245. doi: 10.1016/j.ceramint.2024.07.435
- [21] Gu, Q., Wang, H., Gao, W., Yu, J., and Zhou, X. (2023). Preparation of large-size alumina ceramic parts by DLP 3D printing using high-solid-loading paste and optimizing the debinding process. *Ceramics International*, 49(17), Part B, 28801–28812. doi: 10.1016/j.ceramint.2023.06.142
- [22] Santoliquido, O., Camerota, F., Rosa, A., and Ortona, A. (2021). A novel device to simply 3D print bulk green ceramic components by stereolithography employing viscous slurries. *Open Ceramics*, 5, 100089. <u>doi:</u> <u>10.1016/j.oceram.2021.100089</u>
- [23] Mastroianni, L., Russo, V., Eränen, K., Di Serio, M., Murzin, D. Y., and Salmi, T. (2024). Towards unconstrained catalyst shaping: high accuracy DLP printing of porous γ-Al2O3-based catalysts. *Catal. Sci. Technol.*, 14(5), 1336–1348. doi: 10.1039/D3CY01592K
- [24] Xu, X., Zhou, S., Wu, J., Zhang, C., and Liu, X. (2021). Inter-particle interactions of alumina powders in UVcurable suspensions for DLP stereolithography and its

effect on rheology, solid loading, and self-leveling behavior. *Journal of the European Ceramic Society*, 41(4), 2763–2774.

doi: 10.1016/j.jeurceramsoc.2020.12.004

- [25] Molchan, Y., Bohdan, L., Kyrii, S., Tymoshenko, O., Pylypenko, I., Burmak, A., Vasyliev, G., Dontsova, T. (2025). Low-cost ceramic membrane supports based on Ukrainian kaolin and saponite. *Functional Materials*, *32*(1), 87–96. <u>doi: 10.15407/fm32.01.87</u>
- [26] Sun, Q., Peng, Y., Cheng, H., Mou, Y., Chen, M. (2019). 3D printing of cavities in DPC ceramic substrates with kaolin pastes for hermetic packaging. 2019 20th International Conference on Electronic Packaging Technology (ICEPT), 1–4. doi: 10.1109/ICEPT47577.2019.9081202
- [27] Revelo, C. F., Colorado, H. A. (2019). 3D printing of kaolinite clay with small additions of lime, fly ash and talc ceramic powders. *Processing and Application of Ceramics*, 13(3), 287–299. doi: 10.2298/PAC1903287R
- [28] Revelo, C. F., Colorado, H. A. (2018). 3D printing of kaolinite clay ceramics using the direct ink writing (DIW) technique. *Ceramics International*, 44(5), 5673– 5682. doi: 10.1016/j.ceramint.2017.12.219
- [29] Hussain, M. I., Xia, M., Ren, X.-N., Ge, C., Zhao, Y., Shen, Z. (2024). High-precision printing of intricately shaped kaolin ceramics by digital light processing: Impact of solid content on microstructure and densification. *Journal of Materials Research and Technology*, 30, 2299–2310. doi: 10.1016/j.jmrt.2024.03.227
- [30] Ordoñez, E., Neves Monteiro, S., Colorado, H. A. (2022). Valorization of a hazardous waste with 3D-printing: Combination of kaolin clay and electric arc furnace dust from the steel making industry. *Materials* & Design, 217, 110617. doi: 10.1016/j.matdes.2022.110617
- [31] Serhiienko, A. O., Dontsova, T. A., Yanushevska, O. I.,
- Vorobyova, V. I., and Vasyliev, G. S. (2023). Characterization of ceramic membrane support based on Ukrainian kaolin. *Molecular Crystals and Liquid Crystals*, 752(1), 128–141. <u>doi: 10.1080/15421406.2022.2091279</u>
- [32] Vovk, O.F., Davydova, M.Y., Yanushevska, O.I., Kyrii, S.O., Linovytska, V. M., Lapinskyi, A. V., Dontsova, T. A. (2024). Antibacterial properties of ceramic membranes with TiO<sub>2</sub> selective layer. *Journal of Chemistry and Technologies*, *32*(2), 351–362. https://doi.org/10.15421/jchemtech.v32i2.298738
- [33] Xu, X., Zhou, S., Wu, J., Zhang, C., Liu, X. (2020). Interparticle interactions of alumina powders in UV-curable suspensions for DLP stereolithography and its effect on rheology, solid loading, and self-leveling behavior. *Journal of the European Ceramic Society*. doi: 10.1016/j.jeurceramsoc.2020.12.004