ISSN 1027-5495. Functional Materials, 32, No.2 (2025), p. 259-265
doi:http://dx.doi.org/10.15407/fm32.02.259

Nanomagnetic technologies in the creation of smart porous materials

M. Riabchykov

Lutsk national technical university, Lvivska str. 75, Lutsk, Ukraine

Received November 19, 2024

The purpose of the work consists in substantiation and creation of porous materials with given parameters of size and structure of cavities. Nanocomposites based on a mixture of divalent and trivalent iron oxides are the basis for such materials. Methods of synthesis of nanocomponents are based on chemical reactions of iron sulfate and iron chloride with the addition of ammonia hydrate. Nanopowder was added to the polyurethane mixture during the formation of the foamed porous structure. The porous material was formed under the conditions of a magnetic field with induction of 5-6 mT. As a result, structures were obtained in which the pore sizes depend on the content of nanocomponents and the induction of a magnetic field. Based on the theory of elasticity, the necessary parameters of the magnetic field are determined to ensure the specified pore sizes. Application of a magnetic field with an induction of -6 to +6 mT to the finished material leads to the occurrence of hysteresis effects, resulting in final values of 1-1.5 mT. The obtained results demonstrate the possibility of adjusting the porosity parameters of the material during creation and operation.
Keywords: porous materials, magnetic technologies, nanocomponents, smart materials

Наномагнітні технології при створенні розумних пористих матеріалів. *М.Л.Рябчиков*

Мета роботи складається в обґрунтуванні і створенні пористих матеріалів з заданими параметрами розмірів і структури порожнин. Основою для подібних матеріалів виступають наноскладові на основі суміші оксидів двовалентного і тривалентного заліза. Методи синтезу наноскладових основані на хімічних реакціях сульфату заліза і хлориду заліза з додаванням гідрату аміаку. Нанопорошок додавався до поліуретанової суміші при формуванні спіненої пористої структури. Пористий матеріал утворювався в умовах магнітного поля з індукцією 5-6 мТл. В результаті були одержані структури, в яких розміри пор залежать від вмісту наноскладових і індукції магнітного поля. На основі рівнянь теорії пружності були визначені необхідні параметри магнітного поля для забезпечення заданих розмірів пор. Накладання на готовий матеріал магнітного поля з індукцією від -6 до+6 мТл призводить до гістерезисних ефектів, що реалізуються в появі остаточного 1-1.5 мТл. Одержані результати демонструють можливість регулювати параметри пористості матеріалу під час створення і експлуатації.

1.Introduction

Porous materials are widely used in various technologies and spheres of life [1]. The features of such materials determine the possibility of creating products with special properties. In particular, such materials can be used for thermal insulation, vibration insulation, and sound insulation [2]. At the same time, the structure and distribution of pores play a decisive role in the formation of thermal conductivity indicators. Filter products [3] use porous materials. The pore sizes determine the purity of the filtration and the performance of the filters [4]. The distribution of elastic deformations in such materials is also related to their structure [5].

In modern conditions of large-scale aggression, the problem of treating purulent wounds is becoming very urgent. Special porous materials establish a rational level of removal of harmful exudate from wounds [6]. It should be noted that the treatment process determines a certain intensity of exudate removal individually for each wound [7-8]. It is desirable that such porous structures additionally have medicinal or bacteriostatic properties [9].

In some cases it is possible to create porous structures with given structural parameters [10]; changing such parameters during operation requires the use of smart approaches. One of the few publications on this topic [11] provides data on the use of special aerogels in the formation of porous 3D structures.

Some approaches to the formation of such structures in humidity control devices are given in [12]. Structures of porous materials that provide special properties are described in [13-14].

The formation of structures of porous materials with given parameters in a number of cases is associated with nanotechnology [15-16]. The peculiarities of the formation of porous materials in special environments, including electromagnetic fields, are of particular interest [17-18].

Under such conditions, the use of magnetic nano-components in porous materials becomes relevant [19]. The creation of nano-components based on a mixture of divalent and trivalent iron oxides is described in [20-21]. Such materials, when exposed to a magnetic field, exhibit specific properties and can influence the structure of the mixture in which they are located [22-23]. Traditionally, magnetic nanostructures are used in purification systems, which show additional promise in creating filter structures [24].

An additional problem arises in determining the parameters of liquid penetration through such materials. Processes of liquid sorption through porous materials have been studied in a number of publications [25-26]. In this case, it is necessary to take into account nonlinear effects during the sorption of liquid in pores of different structures [27], and the possible influence of a magnetic field on this flow is noted [28]. A number of studies [29-30] provide data on the possibility of changing the geometry of porous structures under the influence of various factors. The authors of [31] prove the effects of changing geometric parameters when using magnetic nano-components. Additional three-dimensional properties of porous structures to ensure the necessary parameters are given in [32-33].

The analysis of the conducted research allows us to draw a conclusion that it is relevant to create porous structures with adjustable geometry. The potential possibility of changing the parameters of porous materials using magnetic nano-components has been revealed. Real methods of ensuring the parameters of porous materials using external regulation have not been fully studied and implemented.

The purpose of the work is to prove the possibility of real adjustment of the geometric parameters of porous materials by regulating the content of magnetic nanoparticles under electromagnetic field conditions.

2. Experimental

The technology for the production of nanocomponents consists in the synthesis of a mixture of divalent and trivalent iron based on chemical reactions in an aqueous solution of iron sulfate $FeSO_4$ and iron chloride $FeCl_3$. The synthesis takes place in a reactor at a constant temperature and with the addition of NH_4OH ammonia hydrate [34-35]. As a result of the synthesis, it is possible to obtain a nanopowder of iron oxides, which has magnetic properties.

The first method of research is electron microscopy [36]. Scanning electron microscopy is a method of imaging materials at the atomic and molecular level using electrons instead of light. Since the wavelength of electrons is much shorter than that of light, electron microscopes allow for much higher resolution images. This allows the investigation of structures inaccessible to optical microscopes, such as nanomaterials. On the other hand, this method is quite expensive and was used in this work only to ascertain the presence of nanostructures in the resulting mixture.

The main directions of research were related to digital microscopy [37]. Digital microscopy is a method of obtaining and analyzing images of objects using a microscope equipped with a digital camera. The image of the object is projected onto the digital sensor and transmitted to the screen, which allows for storage, processing and analysis of the image with high accuracy. This method is convenient for remote monitoring, research documentation, as well as for detailed analysis using software.

Unfortunately, optical methods, even digital ones, are unable to detect nano-objects. Therefore, only clusters of nano-objects can be recorded and measured. Statistical analysis of micro-sizes obtained during observation in an optical microscope allows them to be extrapolated towards nano-sizes. Thus, it is possible to use optical microscopy to predict nanoscale dimensions [38].

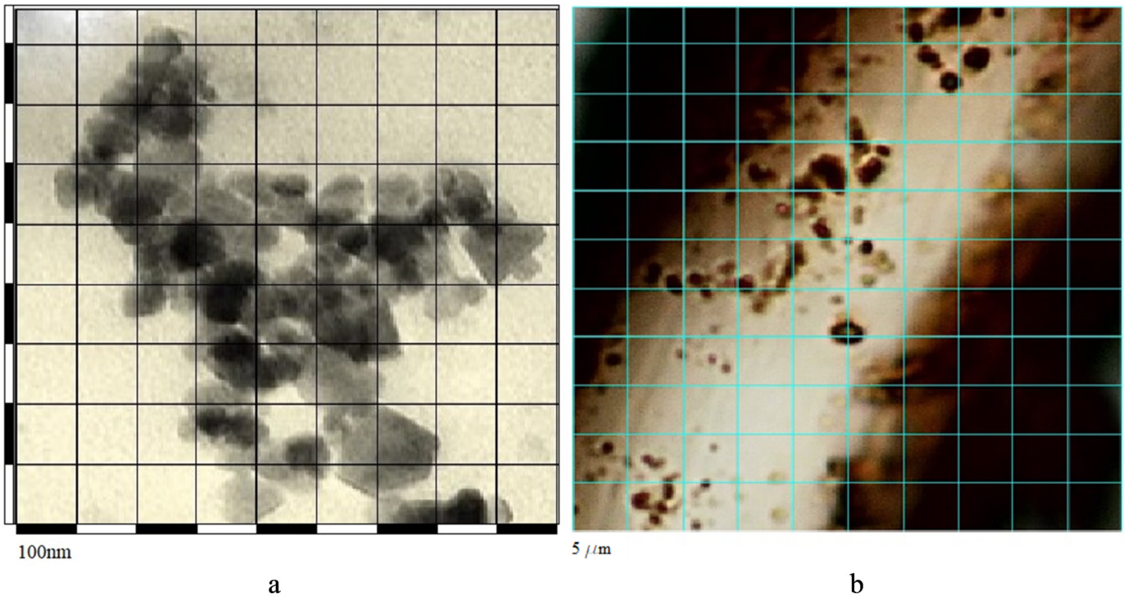

Fig.1. Image of the structures of a mixture of oxides of divalent and trivalent iron, a – nanoscale (cell size 100 nm), b – microscale (cell size 5 μm)

Magnetic technologies using direct and alternating current ring electromagnets [39] were used to create conditions for the interaction of magnetic nanoparticles with polyurethane mixtures that form foamed porous structures.

The obtained porous materials with the addition of nanocomponents based on oxides of divalent and trivalent iron acquire magnetic properties. Magnetic hysteresis is the main indicator of magnetization of the materials [40]. The magnetic properties of porous materials containing nanocomponents were studied in order to determine the final magnetic induction in the material with an increase and decrease in the magnetic induction of an external magnetic field from -6 to +6 mT.

As a result of the action of the magnetic field on the magnetic porous structure, elastic deformations occur that deform the pores. In the case of cylindrical pores, such deformations can be determined as a result of solving the Lamé problem [41]. For spherical pores, under these conditions, the corresponding equations of the theory of elasticity in spherical coordinates can be solved. It should be taken into account that for the solution of these equations of the theory of elasticity, constants for the main material are used, which determine the micromoduli of elasticity [42] in contrast to the macromoduli characteristic of the entire porous material.

3. Results and discussion

Nanocomponents obtained as a result of the synthesis were studied using electron microscopy. Fig. 1,a shows images of a structure with an average particle size of 40-60 nanometers. Particles converge into clusters that have a larger size. The structure of clusters allows them to be combined with macro-materials that have high adhesion.

Iron oxides have magnetic properties. They can be separated using a magnetic field. The separation procedure involves placing a suspension of nanoparticles in a magnetic field. The magnetic particles were attracted to the magnet, and the liquid (with impurities) was separated. The magnetic particles were washed for purification.

Magnetic polyurethane foam was produced by a chemical reaction between polyol and isocyanato with the addition of nanocomposite iron oxides. In the process, a polymer was formed with gas bubbles inside, which provide the properties of a foam-like material.

Unlike traditional technology, this process took place in a magnetic field. The reactor for the production of the material was placed in an annular electromagnetic cavity. The induction of the magnetic field was determined by the voltage of the electric current that was applied to the windings of the electromagnet. The induction of the magnetic field inside the electromagnet reached 5-6 mT. The effect of the magnetic field on the process of formation of porous

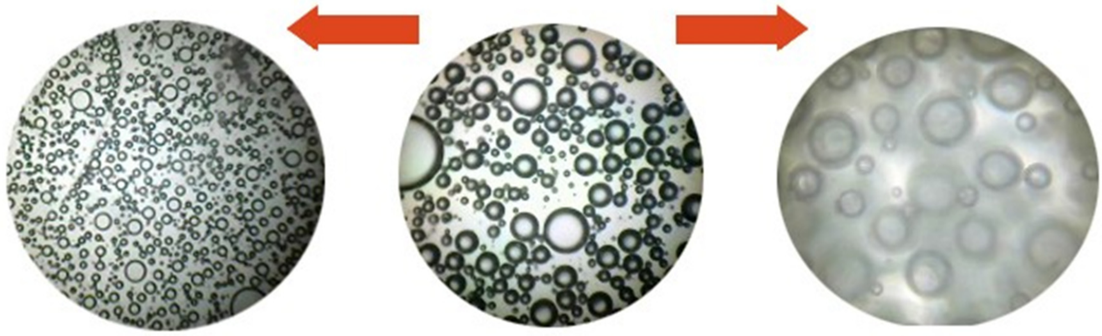

Fig.2. Change in pore sizes in a material containing magnetic nanocomponents under the action of a magnetic field

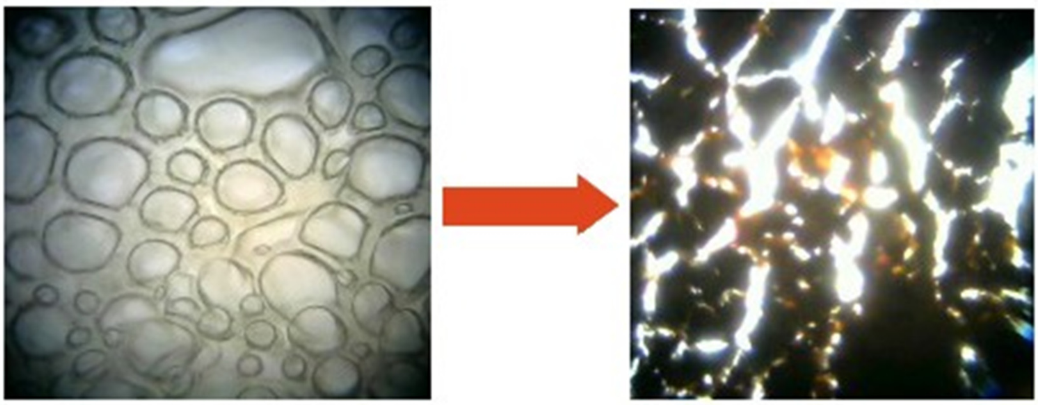

Fig.3. Transformation of closed pores into open ones when the material is filled with magnetic components

material is shown in Fig. 2. The right figure shows the result of the traditional technology of creating porous structures. The middle picture reproduces the structure of the porous material with the addition of nanocomponents. The left scheme defines the structure that is created under the action of a magnetic field. The results show a clear dependence of the pore size, their density and dispersion distribution on the magnetic field strength and the content of magnetic nanocomponents. At the same time, by creating the required level of magnetic induction, it is possible to ensure the specified average pore size with sufficient confidence.

This result determines the possibility of creating a given structure of porous materials at the manufacturing stage.

An increase in the content of nanocomposite oxides of divalent and trivalent iron under the action of a magnetic field reduces the average size of cavities with an increase in density. Studies demonstrate the presence of a critical content of nanocomponents. With this content, a qualitative change in the structure of pores is observed. Traditionally, closed pores are observed in the form of spherical or pseudospherical cavities (Fig. 3, left diagram). At a critical content of nanocomponents, the bonds are broken and the cavities merge. As a result, the pore structure becomes open. Such pores are capable of creating a capillary effect, which allows the use of materials in the direction of providing negative pressure. Similar structures are used, in particular, in medical wound dressings to remove exudate.

Thus, it can be noted that the addition of nanocomposite iron oxides under magnetic field conditions significantly affects both the pore sizes and the appearance of the porous structure as a whole. The most valuable result is that this process is regulated. That is, there is a well-defined correlation between the content of nanocomponents, the induction of a magnetic field, the size of cavities and their structure. In this sense, we can note the first level of smart technologies that provide the necessary structure at the production stage.

Under a digital microscope, a more detailed structure of the cavities with introduced iron oxide powder demonstrates the presence of clusters of magnetic components (Fig. 1,a). A statistical analysis of the sizes of visible par-

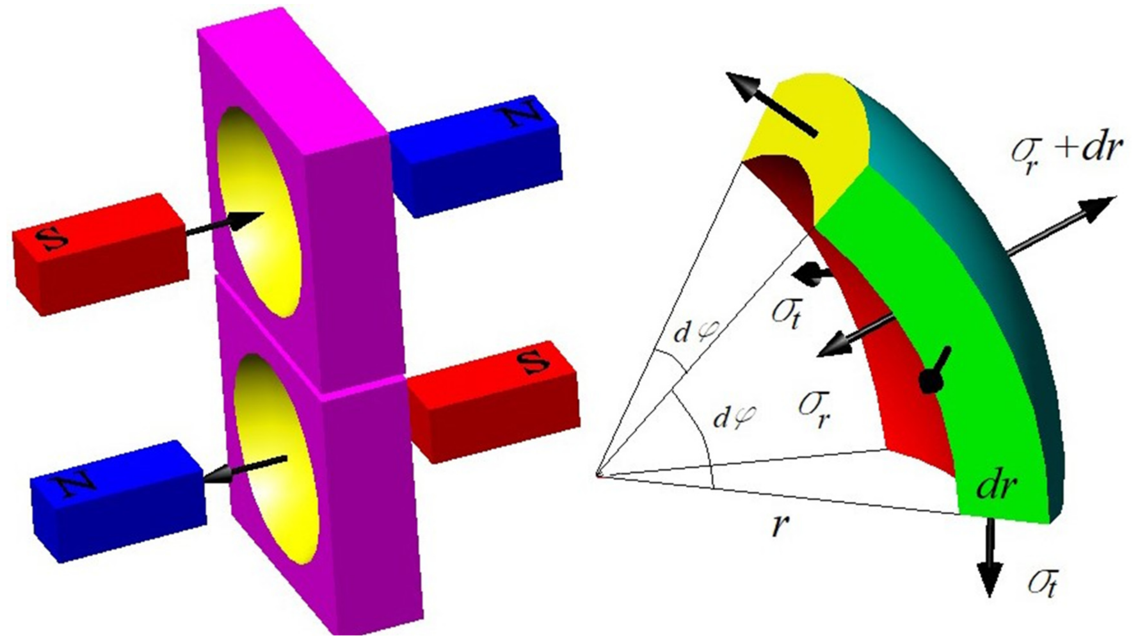

Fig 4. Load and calculated scheme of deformation of a spherical element

ticles and their clusters was carried out. Construction of the distribution polygon showed a gap at the limit of optical dimensions of 0.3-0.4 μm. Such dimensions are limited by the capabilities of optical microscopes. At the same time, the discontinuity of the distribution polygon indicates the presence of a large percentage of particles with nanosize. The real distribution of magnetic particles incorporated into the structure of materials includes micro- and nano-sizes.

This fact is confirmed by macro experiments to determine the force with which the obtained material is attracted to a magnet.

Elucidation of the mechanisms of pore formation in materials containing magnetic nanoparticles leads to the scheme shown in Fig. 4,a. Magnetic particles located on the inner surface of the cavity formed under the action of chemical reactions acquire additional internal pressure from the action of the magnetic field. Depending on the direction of the constant magnetic field, such forces can compress or stretch the cavity.

Further, it is convenient to consider the resulting diagram in spherical coordinates with the pole coinciding with the center of the cavity. We will solve the axisymmetric problem of uniform action of the magnetic field in all directions. For such a case, the calculation scheme of stresses of an elementary layer of material around a pore is presented in Fig. 4,b.

The diagram shows the stresses in the material element in the radial and tangential directions.

Based on the calculation scheme, the equilibrium equation can be written down

$$\frac{d\sigma_r}{dr} + 2\frac{\sigma_r - \sigma_t}{r} = 0 .$$

It is necessary to add deformation conditions and physical law equations to the equilibrium equation. At the same time, it is possible to obtain a differential equation for radial displacements.

$$\frac{d^2u}{dr^2} + (2+\mu)\frac{du}{rdu} - (2+\mu)\frac{u}{r^2} = 0 ,$$

μ is the Poisson ratio of the base material [39].

The solution of the equation under the action of constant pressure inside the cavity will have the form

$$u = \frac{p}{E\cdot k}\frac{1-\mu-2\mu^2}{1-\mu}\frac{a^2}{r} ,$$

where E is the modulus of elasticity of the base material, a is the radius of the cavity $a=a_0+u$, a_0 is the initial radius.

$$k = \frac{3+\mu}{2} + \sqrt{\frac{(3+\mu)^2}{4} + 2 + \mu} .$$

Given the relatively small values of the modulus of elasticity, the deformations of the cavity have a value comparable to the initial radius.

$$a = \frac{a_0}{1 - \dfrac{p}{E \cdot k} \dfrac{1 - \mu - 2\mu^2}{1 - \mu}}.$$

The results of studies of the magnetic interaction of the obtained material with a magnet demonstrate a direct proportionality between the pressure and the induction of the magnetic field

$$p = B \cdot B$$

Under these conditions, the actual size of the cavity can be determined as

$$a = \frac{a_0}{1 - \dfrac{m \cdot B}{E \cdot k} \dfrac{1 - \mu - 2\mu^2}{1 - \mu}}.$$

Analysis of the average pore sizes in the material structure based on experimental (Fig. 2) and analytical dependences allowed us to determine the dependence of the sizes on the magnetic field strength. At the same time, an external magnetic field with strength of 5-6 mT can change the pore diameter in the range of 0.8 to 1.6 from the initial one.

The indicated directions of creation of pore sizes and structures are provided by the magnetic properties of such materials. For this purpose, final magnetization was studied. The porous material containing magnetic nanocomponents was placed in the cavity of the ring electromagnet. The induction of the external magnetic field was determined by the change in the electric voltage applied to the electromagnet. The final induction of the porous magnetic material for different levels of the external field was determined as an attractive force. The hysteresis dependence of the obtained porous material is shown in Fig. 5.

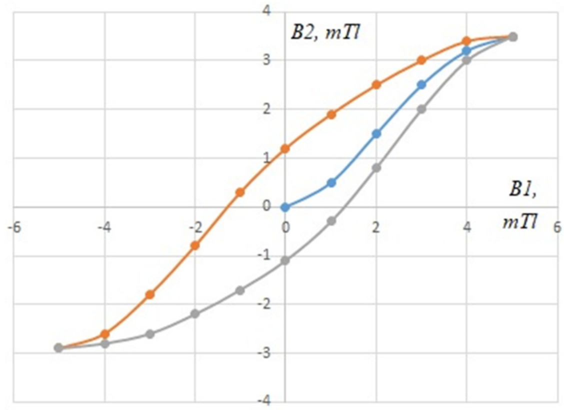

Fig.5. Hysteresis phenomenon in porous materials filled with iron oxides

In the presence of its own magnetic field, porous materials gain the ability to self-regulate. At the same time, it is possible to ensure the specified dimensions and structure of the cavities both during the production of the material and during operation.

The dependences demonstrate that when loaded with a magnetic field of 5-6 mT, the final magnetization is 1.2-1.5 mT.

The obtained results make it possible to create porous materials with a given structure, as well as smart materials that change porosity during operation under the influence of a magnetic field. In turn, this determines the given parameters of thermal conductivity, water absorption and other parameters of the material. The creation of open structures makes it possible to provide negative pressure, which determines the possibility of removing unwanted liquid according to a given law. In particular, similar tasks are relevant for wound dressings. To treat purulent wounds, certain exudate drainage regimes are required, which can be achieved by changing the size and structure of the pores.

4. Conclusions

As a result of the research, the technology of creating porous materials with the possibility of adjusting the size and structure of the pores is substantiated. Nanocomponents based on oxides of divalent and trivalent iron, added to the mixture during the production of foamed polyurethane, ensure the presence of magnetic properties.

In the process of synthesis of porous structures with the content of magnetic nanomaterials, a clear dependence of the size and distribution of pores on the powder content and magnetic field strength was discovered. A specific content of nanomagnetic components causes the appearance of open pores with adjustable size, which are able to create the effect of negative pressure.

When loaded with a magnetic field of 5-6 mT, the final magnetization of proposed material is 1.2-1.5 mT. Under the conditions of an external magnetic field, the diameter of the pores can vary from 0.8 to 1.6 from the initial one.

The results make it possible to create porous materials with a given structure, as well as a structure that can change during operation. Prospective areas of use of such materials can be filtration and medical equipment.

References

1. L.Abylgazina, I.Senkovska, S.Kaskel, *Communications Materials,* **5**, 132 (2024).
2. S.Hua, M.O. Okello, J.Zhang, *Scientific Reports,* **14**, 14277 (2024).

3. Z.Shiyun, X.Jun, X.Junxian, Z.Zhaohui, D.Qijun, C.Kefu, *Separation and Purification Technology*, **349**, 127672, (2024).
4. H.Sung-Ho, E.Kyung Jang, *Materials*, **16**, 3737 (2023).
5. O.Mikulich, In: V.Tonkonogyi, V.Ivanov, J.Trojanowska, G.Oborskyi, I. Pavlenko (eds) Advanced Manufacturing Processes IV. InterPartner 2022. Lecture Notes in Mechanical Engineering, Springer, Cham. (2023).
6. M.Riabchykov, L.Nazarchuk, O.Tkachuk, *Tekstilec*, **65**(4), 268-277 (2022).
7. F.Fan, Z.Zhihui, L.Jiwei, H.Yuesheng, C.Weichao, *Progress in Materials Science,* **146**, 101328 (2024).
8. P.Amruth, P.Akshay, M.Rosemol Jacob, J.M.Joy, S.Mathew, *International Journal of Biological Macromolecules*. **276**, Part 1, 133668 (2024).
9. M.Sharifi, S.H.Bahrami, *J. Biological Macromolecules,*, **277**, Part 2, 133666 (2024).
10. M.C.B.Cardinali, J.H.Miranda, T.B.Moraes, *Soil and Tillage Research,* **244**, 106258 (2024).
11. N.Sohrabi, H.Almasi, M.Moradi, *Food Hydrocolloids*, **156**, 110261 (2024).
12. J.Wang, W.Lin, Z.Chen, et al., *Nature Communications*, **15**, 1575 (2024).
13. O.Povstyanoy, N.Imbirovych, V.Posuvailo, O.Zabolotnyi, T.Artyukh, In: V.Tonkonogyi, V.Ivanov, J.Trojanowska, G.Oborskyi, I.Pavlenko, Advanced Manufacturing Processes IV. InterPartner 2022. Lecture Notes in Mechanical Engineering, Springer, Cham. (2023).
14. O.Povstyanoy, N.Imbirovich, R.Redko, O.Redko, P.Savaryn, In: V.Tonkonogyi, V.Ivanov, J.Trojanowska, G.Oborskyi, I.Pavlenko,. Advanced Manufacturing Processes V. InterPartner 2023. Lecture Notes in Mechanical Engineering, Springer, Cham. (2024).
15. A.Vijeata, G.R.Chaudhary, S.Chaudhary, A.A.Ibrahim, *Chemosphere*, **357**, 141935 (2024).
16. P.P.Savchuk, V.P.Kashytskyi, M.D.Melnychuk, O.L.Sadova, S.V.Myskovets, *Funct. Mater.*, **26** (3): 621-628. (2019).
17. V.I.Shvabyuk, O.A. Mikulich, *Journal of Mathematical Sciences*, **253**, 148 (2021).
18. A.Zeleňáková, V.Zeleňák, E.Beňová. *et al., Scientific Reports*, **14**, 14427 (2024).
19. W.Gu, Y.Jiang, *Materials Today Sustainability*, **27**, 100793 (2024).
20. M.Riabchykov, I.Tsykhanovska, A.Alexandrov, *J. Materials Science*, **58**(16), 7244(2023).
21. Y.Yu, X.Bu, J.Qi, Z.Zhang, J.Geng, *Applied Clay Science,* **258**, 107479 (2024).
22. W.Han, J.S.Lee, D.Lee, J.Kim, *Case Studies in Construction Materials,* **21**, e03544 (2024).
23. Y.G.Chabak, V.I.Zurnadzhy, M.A.Golinskyi, I.Petryshynets, S.P.Shymchuk, *Progress in Physics of Metals*, **23**(4), 583 (2022).
24. B.Beitzinger, P.Walther, M.Lindén, *Microporous and Mesoporous Materials*, **378**, 113247 (2024).
25. M.He, Y.Chen, G.Chen, W.Li, M.Zhang, C.Zhang, H.Zhang, X.Long, K.Tang, T.Duan, L.Zhu, *Environmental Pollution*, **357**, 124442 (2024).
26. M.Riabchykov, V.Vlasenko, S.Arabuli, *Vlakna a Textil,* **18**(2), 24 (2011)
27. A.Sumithra, R.Sivaraj, V.R.Prasad, ... S.Kuharat, B.R.Kumar. International *Journal of Modern Physics,* B, **38**(29), 2450398, (2024).
28. T.Yuan, L.Shen, D.Dini, *Acta Biomaterialia,* **173**, 123-134 (2024).
29. A.Yadav, H.Kumar, R.Sharma, R.Kumari, *Surfaces and Interfaces*, **39**, 102925 (2023).
30. M.Riabchykov, O.Tkachuk, L.Nazarchuk, A.Alexandrov, *Materials Research Express,* **10**(1),015401 (2023).
31. Y.Liu, J.Chen, W.Xu, J.Yan, *Engineering Geology*, **340**, 107666 (2024).
32. H.Tang, N.V.Nguyen, H.Nguyen-Xuan, J.Lee, *International Jou*).
33. A.T.Mohamed, R.A.Hameed, S.H.EL-Moslamy, et al., *Scientific Reports*, **14**, 6081 (2024).
34. M.Riabchykov, T.Furs, A.Alexandrov, I.Tsykhanovska, O.Hulai, V.Shemet, *J. Engineering Sciences* , **10**(2), 56-62 (2023).
35. M.Rugiel, N.Janik-Olchawa, J.Kowalczyk, K.Pomorska, M.Sitarz, E.Bik, D.Horak, M.Babic, Z.Setkowicz, J.Chwiej, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* **323**, 124888 (2024).
36. I.Y. Magda, M.S. Sayed, *Journal of Molecular Liquids*, **407**, 125284 (2024).
37. M.Riabchykov, A.Alexandrov, I.Tsykhanovska, S.Nechipor, A.Nikulina, S.Vilkov, *Vlákna a textile*, **26**(4), 47-52 (2019).
38. T.N.Ghosh, A.K.Bhunia, S.S.Pradhan*, et al,.* **35**, *Journal of Materials Science: Materials in Electronics,* 1124 (2024).
39. M.Al-Gharram, P.Uhlmann, M.Al-Hussein, *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* **684,** 133212, (2024).
40. U.A.Campos, D.E.Hall, *Thin-Walled Structures,* **138**, 199-207. (2019).
41. L. Moreno-Sanabria, T. Uhlířová, W. Pabst, M. Koller, H. Seiner, M.I. Osendi, M. Belmonte, P. Miranzo, *Journal of the European Ceramic Society,* 44, Issue 15, 116771, (2024).
42. X.Zhang, Q.Sun, X.Liang, et al., *Nature Communications*, **15**, 392 (2024).